
Electronic spectroscopy and structure of gas-phase molecular ions

MICHAEL STRAFFORD SCHOLZ

ORCID: 0000-0003-3290-2722

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To my family.

Abstract

This thesis describes investigations of gas-phase molecular cations — protonated azobenzenes, ruthenium sulfoxide coordination complexes, and the ferrocenium and tropylium cations — using electronic action spectroscopy. Protonated azobenzenes and ruthenium sulfoxide complexes are prototypical molecular photoswitches, which reversibly change isomeric form in response to light, and are building blocks of light-activated molecular machines. The ferrocenium cation is, along with its reduced form ferrocene, a common redox standard and an archetypal organometallic complex. Tropylium is a 6π -aromatic molecule with rare sevenfold symmetry and is involved in the combustion of aromatic hydrocarbons. The electronic spectra of these molecular cations, recorded by measuring photoisomerisation or photodissociation yields as a function of wavelength, provide insight into their electronic and molecular structures.

Action spectra of the protonated azobenzene and 4-aminoazobenzene cations are obtained by measuring the *trans*-to-*cis* photoisomerisation yield over the 350–600 nm range. One band corresponding to the $S_1 \leftarrow S_0 \pi\pi^*$ transition is observed for each species with maxima at 435 and 525 nm for protonated azobenzene and 4-aminoazobenzene, respectively. The transitions are assigned based on density functional theory and coupled cluster calculations. The experimental and computational results indicate that photoisomerisation occurs following $\pi\pi^*$ excitation in protonated azobenzenes and that the lowest-energy $\pi\pi^*$ transitions are significantly red-shifted compared to their neutral azobenzene counterparts.

Ruthenium bis-sulfoxide bipyridyl coordination complexes undergo linkage photoisomerisation, where the binding modes of two sulfoxide groups in a chelating ligand change from S- to O-bound following electronic excitation. Photoisomerisation is observed over the 295–515 nm range following excitation of distinct metal-to-ligand charge transfer and ligand-centred $\pi\pi^*$ transitions. Concerted isomerisation of both sulfoxide groups from S- to O-bound following single-photon absorption is the predominant gas-phase pathway, whereas sequential isomerisation of each sulfoxide group, requiring two photons of two different wavelengths, is the only process observed in solution. Comparison of the gas-phase results with time-resolved experiments in solution suggest the apparent change in dynamics upon solvation is caused by rapid quenching of vibrational energy in the electronically-excited state associated with isomerisation.

Electronic spectra of the ferrocenium cation, $\text{Fe}(\text{C}_5\text{H}_5)_2^+$, are measured over the 560–640 nm range through photodissociation of its weakly-bound complexes with neon and argon. Band systems with origin transitions at 15830 cm^{-1} and 15809 cm^{-1} for the neon and argon complexes, respectively, are assigned to the $\tilde{\text{B}}^2\text{E}'_1 \leftarrow \tilde{\text{X}}^2\text{E}'_2$ ligand-to-metal charge transfer transition, on the basis of multireference electronic structure calculations. The dominant vibrational progression corresponds to the totally-symmetric ligand-metal-ligand stretching mode ν_4 with a spacing of $\sim 285\text{ cm}^{-1}$. Several non-Franck-Condon bands likely arise from a weak Jahn-Teller effect or from spin-orbit coupling. The vibronic bands measured for the neon complexes are sharp, whereas those for the argon complexes are broad and show substructure.

Vibronic coupling in the $\text{S}_1\ ^1\text{E}'_3$ state of the tropylium cation, C_7H_7^+ , is characterised using density functional theory, coupled cluster, and multiconfigurational self-consistent field electronic structure calculations. The weak, forbidden $\tilde{\text{A}}^1\text{E}'_3 \leftarrow \tilde{\text{X}}^1\text{A}'_1$ transition, recorded over the 250–285 nm range through photodissociation of tropylium-argon complexes, is found to gain intensity through Herzberg-Teller coupling to the bright $\tilde{\text{B}}^1\text{E}'_1$ state mediated by vibrational modes with e'_2 and e'_3 symmetries. A weak Jahn-Teller effect occurs in the $\tilde{\text{A}}^1\text{E}'_3$ state associated with the ν_7 (e'_1) mode, although its influence on the electronic spectrum is predicted to be small.

The spectroscopic investigations of these molecular cations lay the foundations for further exploration of their photoisomerisation dynamics and vibronic interactions. Time-resolved experiments should complement the photoisomerisation action spectra by following the excited-state dynamics of these photoswitches in real time. The vibrationally-resolved spectra of ferrocenium and tropylium should provide starting points for high-resolution spectroscopic investigations of these cations. The reported spectra should serve as benchmarks for accurate electronic structure theories, which may help to guide future experiments.

Declaration

This is to certify that:

- (i) the thesis comprises only my original work towards the PhD except where indicated in the Preface,
- (ii) due acknowledgement has been made in the text to all other material used,
- (iii) the thesis is less than 100,000 words in length, exclusive of tables, maps, bibliographies and appendices.

Michael S. Scholz

Preface

The research contained within this thesis has been or will be published as articles in peer-reviewed journals and presented at conferences, symposia, and workshops. A list of publications and presentations is provided below.

Two chapters are reproductions of published, peer-reviewed journal articles, with the publication details and copyright information listed at the beginning of each chapter. The figure and table labels were adjusted to reflect their positions within the full thesis. The supplementary information for each article has been assembled as a separate chapter. PDF reproductions of the published articles are included as an appendix at the end of the thesis with permission from the publishers.

The following collaborators and colleagues are gratefully acknowledged for providing chemical samples, experimental assistance, and computational support:

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Peer-reviewed publications

The work presented in this thesis has been published in the following peer-reviewed journal articles:

1. Scholz, M. S., Bull, J. N., Coughlan, N. J. A., Carrascosa, E., Adamson, B. D., Bieske, E. J. Photoisomerization of protonated azobenzenes in the gas phase. *J. Phys. Chem. A* **2017**, *121* (34), 6413–6419.
2. Scholz, M. S., Bull, J. N., Carrascosa, E., Kosgei, G. K., Rack, J. J., Bieske, E. J. Linkage photoisomerization of an isolated ruthenium sulfoxide complex: sequential versus concerted rearrangement. *Inorg. Chem.* **2018**, *57* (9), 5701–5706.

The following publications were contributed to during my candidature, but are not discussed in this thesis:

1. Coughlan, N. J. A., Scholz, M. S., Trevitt, A. J., Hansen, C. S., Adamson, B. D., Bieske, E. J. Photo and collision induced isomerization of a cyclic retinal derivative: an ion mobility study. *J. Am. Soc. Mass. Spectrom.* **2016**, *27*, 1483.
2. Bull, J. N., Scholz, M. S., Coughlan, N. J. A., Kawai, A., Bieske, E. J. Monitoring isomerization of molecules in solution using ion mobility mass spectrometry. *Anal. Chem.* **2017**, *88* (24), 11978–11981.
3. Georgiou, D. C., Haghighatbin, M. A., Hogan, C. F., Scholz, M. S., Bull, J. N., Bieske, E. J., Wilson, D. J., Dutton, J. L. A strong *cis*-effect in an imidazole-imidazolium-substituted alkene. *Angew. Chem. Int. Ed.* **2017**, *56* (29), 8473–8480.
4. Bull, J. N., Scholz, M. S., Coughlan, N. J. A., Bieske, E. J. Isomerization of an intramolecularly hydrogen-bonded photoswitch: protonated azobis(2-imidazole). *Phys. Chem. Chem. Phys.* **2017**, *19*, 12776–12783.
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6. Lim, S. F., Harris, B. L., Khairallah, G. N., Bieske, E. J., Maître, P., da Silva, G., Adamson, B. D., Scholz, M. S., Coughlan, N. J. A., O’Hair, R. A. J., Rathjen, M., Stares, D., White, J. M. Seleniranium ions undergo π -ligand exchange via an associative mechanism in the gas phase. *J. Org. Chem.* **2017**, *82* (12), 6289–6297.
7. Bull, J. N., Scholz, M. S., Carrascosa, E., Bieske, E. J. From *E* to *Z* and back again: reversible photoisomerization of an isolated charge-tagged azobenzene. *Phys. Chem. Chem. Phys.* **2018**, *20*, 509–513.

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8. Bull, J. N., Carrascosa, E., Mallo, N., Scholz, M. S., da Silva, G., Beves, J. E., Bieske, E. J. Photoswitching an isolated donor-acceptor Stenhouse adduct. *J. Phys. Chem. Lett.* **2018**, *9* (3), 665–671.
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 11. Bull, J. N., Buntine, J. T., Scholz, M. S., Carrascosa, E., Bieske, E. J. Photodetachment and photoreactions of substituted naphthalene anions in a tandem ion mobility spectrometer. *Faraday Discuss.* **2019**, *217*, 34–46.
 12. Bull, J. N., da Silva, G., Scholz, M. S., Carrascosa, E., Bieske, E. J. Photoinitiated intramolecular proton transfer in deprotonated *para*-coumaric acid. *J. Phys. Chem. A* **2019**, *123* (20), 4419–4430.
 13. Muller, G., Catani, K. J., Scholz, M. S., Jacovella, U., Bartlett, N. I., Bieske, E. J. Electronic spectra of diacetylene cations (HC_4H^+) tagged with Ar and N_2 . *J. Phys. Chem. A* **2019**, *123* (33), 7228–7236.
 14. Bull, J. N., Scholz, M. S., Carrascosa, E., Kristiansson, M. K., Eklund, G., Punnakayathil, N., de Ruette, N., Zettergren, H., Schmidt, H. T., Cederquist, H., Stockett, M. H. Ultraslow radiative cooling of C_n^- ($n = 3\text{--}5$). *J. Chem. Phys.* **2019**, *151* (11), 114304.
 15. Ma, H. Z., McKay, A., Mravak, A., Scholz, M. S., White, J. M., Multer, R. J., Bieske, E. J., Bonačić-Koutecký, V., O’Hair, R. A. J. Structural characterisation and gas-phase studies of the $[\text{Ag}_{10}\text{H}_8\text{L}_6]^{2+}$ nanocluster dication. *Nanoscale*, **2019**, *11*, 22880–22889.
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6. “Using ion mobility-mass spectrometry to probe molecular photoisomerization”, Experimental Quantum Biophysics seminar, 2018, Aarhus University.
7. “Gas-phase photoisomerisation in a ruthenium sulfoxide complex”, University of Melbourne–Tohoku University Chemistry workshop, 2018, University of Melbourne.

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2. “Gas-phase photoisomerization in a ruthenium sulfoxide photoswitch”, Australia and New Zealand Society for Mass Spectrometry 26 Conference, 2017, Flinders University.
3. “Photoisomerization action spectroscopy of a ruthenium sulfoxide complex”, 2nd International Mass Spectrometry Conference, 2018, Florence.
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Chapter 1

Introduction

This thesis describes spectroscopic investigations into the interplay of electronic structure and nuclear geometry in molecular cations. The species described within include protonated azobenzene cations, ruthenium sulfoxide coordination complexes, and the ferrocenium and tropylium cations. The azobenzenes and ruthenium complexes are prototypical molecular photoswitches which change shape and properties in response to light. The ferrocenium and tropylium cations are molecules which play fundamental roles in redox chemistry and hydrocarbon combustion, respectively. The experimental work was performed using gas-phase action spectroscopy employing custom-built tandem mass spectrometers and was supported by electronic structure calculations.

The aim of this thesis is to use electronic spectroscopy to study the electronic and molecular structures of isolated cationic chromophores. Through studying the cations in the gas phase, complications from solvation and other forms of intermolecular interaction are removed, simplifying interpretation and understanding of the experimental and computational results. Comparison of information gathered in the gas and condensed phases enables a bottom-up understanding of the role played by solvation in complex systems.

This chapter introduces the families of molecules described within this thesis, starting with photoswitching molecular machines and moving on to the ferrocenium and tropylium cations. Brief backgrounds and the current state of research are presented for each study with an emphasis on the role that electronic spectroscopy has played in previous investigations. The introduction concludes with a brief review of the gas-phase spectroscopy of molecular ions, the associated challenges with its implementation, and the chemical insights it can provide, along with a brief overview of the gas-phase action spectroscopies employed to study the molecular cations.

1.1 Molecular photoswitches

The first molecules described within this thesis are protonated azobenzenes and ruthenium sulfoxide coordination complexes. These compounds are molecular photoswitches, a class of molecular machines that change form in response to light.^{1–5} Molecular switches including photoswitches can respond to a range of stimuli including light, pH, temperature, and electric fields,^{6,7} and are a building block of machinery on the molecular scale, proposed for use as motors and engines.^{8,9} These nanoscale machines can be powered by light or through redox chemistry,^{10–12} with the latter process analogous to combustion of fuel or metabolism of glucose.¹³ Light-powered switches play a key role in the field of photopharmacology, where the aim is to control biological processes with light.¹⁴ Examples of photopharmacological processes facilitated by molecular photoswitches include localisation of antibiotic activity, opening and closing of ion channels, and cytotoxic photosensitiser activation in chemotherapy.^{15,16} Other efforts have targeted solar energy storage with photoswitches,^{17–19} with light inducing a transformation to a long-lived metastable state higher in energy from which the energy can be later released as heat.

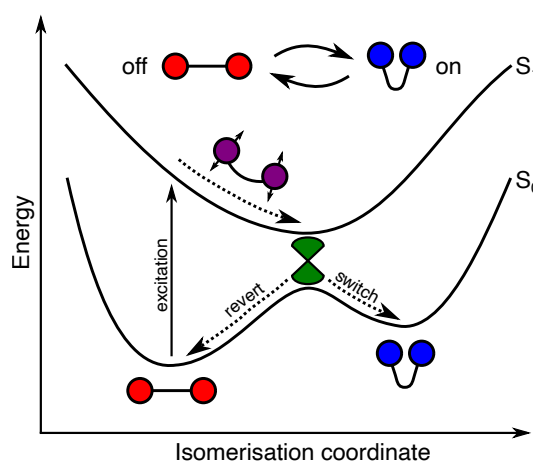


Figure 1.1: Example isomerisation mechanism in a simple photoswitch. The “off” form (red) absorbs a photon and is electronically excited to its S_1 state (purple). The molecular geometry rearranges to reach the S_1 minimum energy point, which lies near a conical intersection (green) with the ground S_0 state. The displacement vectors indicate coherent vibrational motion, which may drive passage through the conical intersection. Upon reaching the intersection with a geometry intermediate between the “off” and “on” form, the population is transferred rapidly back to the ground electronic state. The probability of reversion to reform the “off” isomer compared to switching to the “on” form (blue) is governed by wavepacket dynamics. The “on” form lies higher in energy than the “off” form. The “on” form can decay thermally or photochemically, depending on the reverse barrier height and excited-state surface shape, respectively.

The structural change of a photoswitch in response to light generally results in a change in colour called photochromism, reflecting a shift in its optical spectrum.⁵ Light of a second colour can be used to revert the switch back to the original form. However, if the absorption spectra of the two forms overlap, exposure to light absorbed by both forms leads to formation of a photostationary state, an equilibrium governed by the relative oscillator strengths and

isomerisation quantum yields at that wavelength. The photoisomerisation quantum yield depends on the topology of the ground- and excited-state potential surfaces and the coupling between them. The hypothetical two-state photoswitching system illustrated in Figure 1.1 demonstrates isomerisation through a conical intersection between the ground- and excited-state surfaces. The intersection occurs in the proximity of the ground-state barrier between the “on” and “off” forms. The quantum yield of isomerisation depends on the dynamics of passage through the conical intersection.²⁰ The reversion barrier height and relative stabilities of the “on” and “off” forms will determine the thermal lifetime of the activated photoswitch. When the activated forms of these switches are thermally stable, their photochromism is called “P-type” because they only photochemically revert. If the triggered switch is unstable and thermally reverts over time, it is called “T-type”.²¹ For solar energy storage, P-type photoswitches are required because thermal losses would reduce storage capability, whereas for biological applications either P- or T-type molecules may be preferred depending on the application. The oscillator strength, isomerisation quantum yield, and thermal lifetime represent major optimisation targets in the rational design of useful photoswitching molecules.^{22,23}

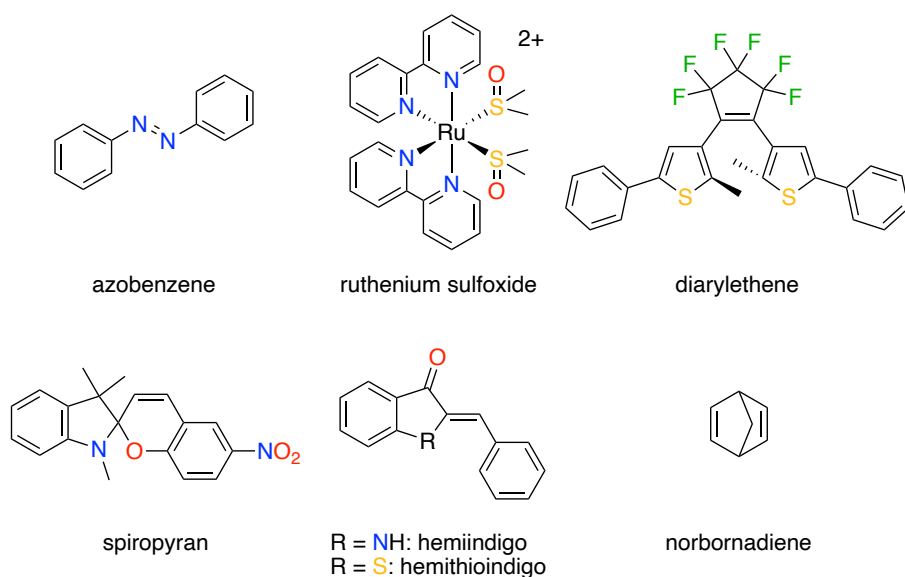


Figure 1.2: Backbone structures for representative families of molecular photoswitches. Spectroscopic studies on azobenzene- and ruthenium sulfoxide-based switches, which undergo *trans/cis* and linkage isomerisation, respectively, are described within Chapters 3 and 4. Other examples of popular photoswitching molecules include diarylethenes and spiropyrans (ring-opening/closing), hemi(thio)indigos (*trans/cis*), and norbornadienes (electrocyclisation/cycloreversion).

This thesis describes spectroscopic investigations of two types of molecular photoswitches: azobenzenes and ruthenium sulfoxides, illustrated in Figure 1.2. These represent two members of a range of versatile molecular photoswitches that have been developed for photopharmacological and energy-storage purposes, including diarylethenes,^{24,25} spiropyrans,^{26,27} hemiindigos and hemithioindigos,^{28–30} and norbornadienes.¹⁸ Azobenzenes are T-type switches and are the most

popular trigger for light-activated medicines.³¹ The ruthenium sulfoxide complexes are molecules with T- and P-type characteristics which reversibly store photonic energy after electronic excitation through linkage isomerisation to give a metastable complex.³² The following subsections provide a brief literature review and describe motivations for the use of electronic spectroscopy to help understand their photoisomerisation dynamics.

1.1.1 Azobenzenes and azonium cations

Azobenzenes are the prototypical photochromic molecules, that undergo reversible *trans/cis* isomerisation upon exposure to light, with a corresponding change in colour.^{33–35} Their photoisomerisation is rapid, complete within hundreds of fs,^{36,37} and efficient, with typical quantum yields exceeding 10%.^{34,38} Despite the apparent simplicity of the azobenzene molecule, its precise isomerisation mechanism has been the focus of numerous studies over the last century.^{35–37,39–43} Isomerisation can occur after excitation to the S_1 ($n\pi^*$, 420 nm) or S_{2+} ($\pi\pi^*$, <350 nm) states. However, the quantum yield for *trans*-to-*cis* isomerisation is roughly twice as large after excitation to S_1 than to higher states.^{34,37,38} This apparent breakdown of Kasha’s rule has been attributed, on the basis of combined experimental and theoretical ultrafast spectroscopies, to efficient deactivation of $\pi\pi^*$ excited states through a conical intersection at a planar geometry, which recovers the *trans* S_0 electronic ground state without torsion around the azo N=N bond.^{43,44} Internal conversion and vibrational energy redistribution can induce torsion after $\pi\pi^*$ excitation, following which the *cis* isomer can be formed through the so-called “inversion-assisted torsion” channel illustrated in Figure 1.3.

The efficient photoisomerisation of azobenzenes, combined with their easy functionalisation, has made them workhorse molecular photoswitches.^{31,35,45,46} Azo-based dyes, a close relative of azobenzenes, are in wide use in industry with well-known synthetic routes to target specific photochemical properties,⁴⁷ so that synthetic principles are readily transferred to modification of photoswitching azobenzenes.⁴⁶ Functionalised azobenzenes are among the most popular photoswitches for applications in biological contexts.³¹ A major challenge toward useful photoswitchable molecular machines is activation using visible light,^{48–50} preferably within the so-called “bio-optical window”, the wavelength range over which the human body is most transparent.⁵¹ Azobenzene compounds that isomerise upon exposure to red and near-infrared light have been reported, and are generally produced through extensive modification to add electron-donating and electron-withdrawing groups to minimise the highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) gap.^{51–53}

Perhaps the simplest way to red-shift absorption of azobenzene-based photoswitches is through protonation of the azo group.^{52,54–56} Protonation red-shifts the lowest electronic transition while changing its character to $\pi\pi^*$ with a corresponding increase in oscillator strength. The shift in absorption spectrum in response to (de-)protonation unpins the role of many azo dyes,

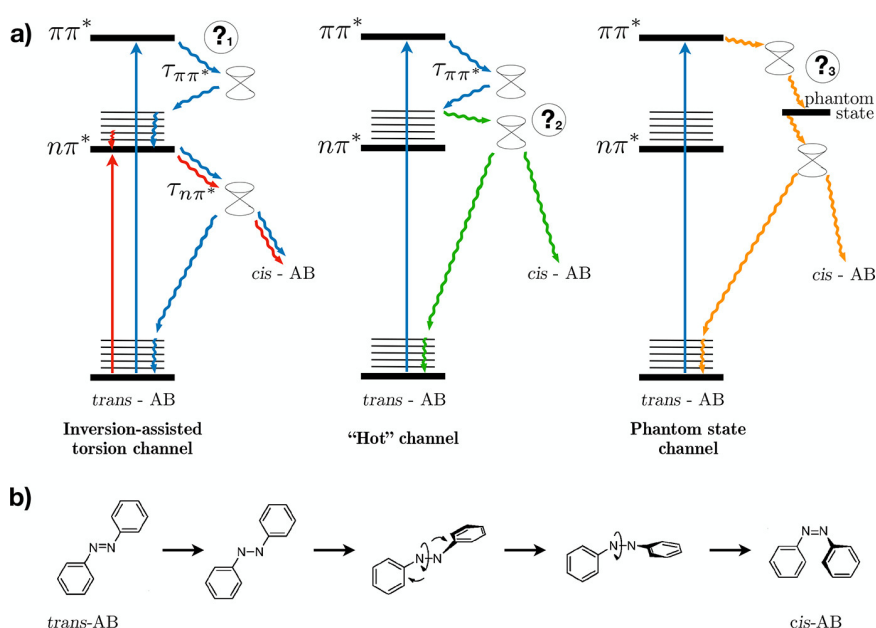


Figure 1.3: a) Proposed mechanisms for azobenzene isomerisation following S_1 $n\pi^*$ (red) or S_2 $\pi\pi^*$ excitation (blue). Alternative decay channels through conical intersections above the S_1 vibrationless level or *via* a dark state are sketched in green and yellow, respectively. b) Schematic illustration of chemical structure changes following the inversion-assisted torsion isomerisation pathway. Adapted with permission from Nenov *et al.*⁴³ Copyright 2018 American Chemical Society.

such as methyl yellow (*para*-aminoazobenzene), as pH indicators. Strongly basic azobenzenes are required to achieve high degrees of protonation under physiological conditions, where the pH is approximately 7.⁵⁵ Substitution at the *ortho* positions (relative to the azo bond) with hydrogen bond acceptors, such as methoxy groups, strongly stabilises protonation of the azo group.⁵² Addition of amine groups to the *para* positions increases the red-shift further and allows conjugation to biomolecules through amide linkages. These azonium ions, such as the one shown in Figure 1.4, have been used to control localised release of pharmaceutical compounds from biomimetic cages following targeted irradiation with near-infrared light.⁵⁷

Presently azonium ions only comprise a small fraction of photopharmacological active units. Rather, neutral azobenzenes are by far the most common, due to the detailed information available on the influence of substitution and functionalisation on isomerisation activity.¹⁶ Little is known about the isomerisation dynamics of even the simplest azonium ion, protonated azobenzene. Gas-phase photodissociation spectra of protonated azobenzene and protonated *para*-dimethylaminoazobenzene suggest that torsion of the azo N=N bond occurs upon $\pi\pi^*$ excitation, implying the S_1 state might have a twisted minimum-energy geometry.⁵⁸ The spectra are rather broad with little vibrational structure, possibly due to congestion by hot bands and overlaid progressions associated with the low frequency torsional mode, which might not be entirely cooled at 40 K, or caused by a short lifetime of the S_1 state before passage through a

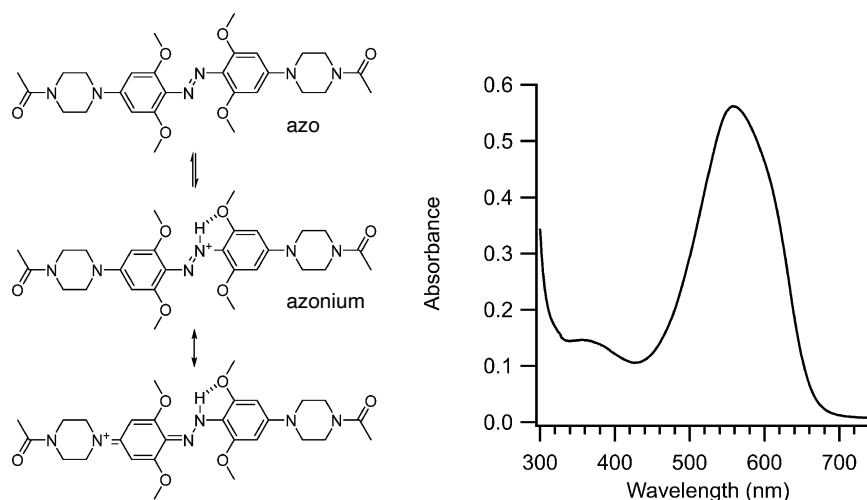


Figure 1.4: Protonation of an azobenzene to yield an azonium cation. The *ortho* methoxy groups act as hydrogen bond acceptors, stabilising the protonated ion. The azonium species has a strongly red-shifted absorption spectrum compared to the neutral azo compound, with the lowest $\pi\pi^*$ transition peaking around 560 nm and extending to 660 nm. Adapted with permission from Dong *et al.*⁵² Copyright 2015 American Chemical Society.

conical intersection to recover the S_0 ground state.

1.1.2 Ruthenium sulfoxide photoswitches

Inorganic photoswitches based on coordination complexes offer increased tunability of their photochromic response compared to organic molecules through the freedom of ligand substitution — essentially the same functionalisation techniques as in organic photoswitches can be applied to each of the coordinating ligands. Additionally, the chromophore need not be the same as the isomerising unit, as is usually the case in organic photoswitches, because energy transfer can occur between the metal centre and the ligands. However, while silver halide salts are perhaps the prototypical photochromic material, famous for their use in photographic emulsions,⁵⁹ discrete photochromic coordination complexes are relatively uncommon, compared to photoswitches derived from predominantly organic molecules. The coordination complex in which photochromism was first observed is pentaamminonitrocobalt(III) chloride, which undergoes thermally-reversible nitro-nitroso linkage isomerisation after irradiation.^{60–63} Reversible change in binding modes has been observed in a range of ligands, including dinitrogen (N_2),⁶⁴ sulfur dioxide (SO_2),⁶⁵ and nitrosyl (NO).⁶³ Intra-ligand isomerisation, where photochromism originates from a photo-induced intramolecular reaction within a ligand, is a field of active research, and its relevance towards making functional light-responsive materials has been reviewed extensively.^{66–68}

Chromophore complexes with ruthenium(II) bound to polypyridyl ligands are among the most studied coordination complexes,⁷⁰ due to their optical and photoredox properties.^{71,72} The

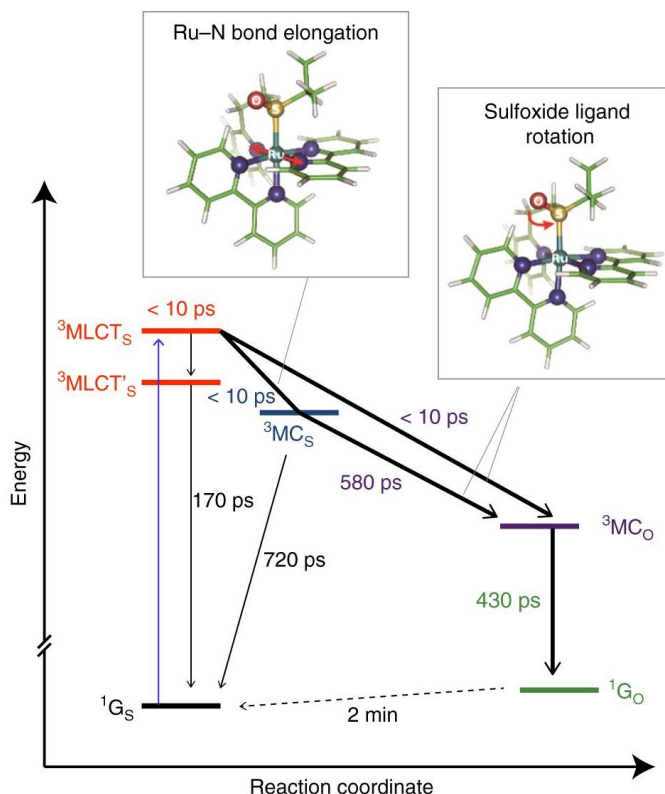


Figure 1.5: Photoisomerisation kinetics in a ruthenium sulfoxide complex, measured using picosecond transient X-ray absorption spectroscopy. After excitation by the actinic laser pulse, rapid intersystem crossing (ISC) yields a triplet metal-to-ligand charge transfer (MLCT) state. The triplet population either decays through a lower-energy MLCT state to the singlet ground state, or is transferred to MC (metal centered, dd^*) states. The MC state formation is accompanied by Ru–N bond elongation due to the antibonding character of the d^* orbitals. Rearrangement of the sulfoxide ligand from S- to O-bound can occur directly from the metal-to-ligand charge transfer (MLCT) state (faster) or through the MC state (slower). Adapted from Cordones *et al.*⁶⁹ under the CC BY 4.0 licence.

occupied d -orbitals on the Ru(II) centre lie reasonably close in energy to the π^* orbitals on the pyridyl-derived ligands, such that intramolecular charge transfer transitions typically lie within the visible region of the optical spectrum. Metal-to-ligand charge transfer (MLCT) is typically followed by intersystem crossing (ISC) to a triplet state, which is complete within hundreds of femtoseconds with a quantum yield near unity.^{73,74} The triplet state is relatively long-lived and can be exploited to induce redox chemistry or for charge separation in photovoltaic cells.^{75–79} Alternatively, the long lifetime of the triplet states allows for nuclear rearrangement to occur before intersystem crossing (ISC) to the singlet manifold quenches the excited state.

Ruthenium sulfoxide photoswitches utilise this long-lived triplet state to effect efficient linkage isomerisation, where the binding mode of a sulfoxide ligand reversibly switches between sulfur- and oxygen-bound.³² The $[\text{Ru}(\text{bpy})_2(\text{dmsO})_2]^{2+}$ complex, where bpy and dmsO are 2,2'-bipyridine and dimethyl sulfoxide, respectively, is a prototypical member of this class of

photoswitch.⁸⁰ Due to ruthenium's position in the middle of the transition metals, it possesses roughly equal affinities for both hard (oxygen) and soft (sulfur) ligands. The lowest energy geometry has both dmsoligands bound to Ru *via* the sulfur atoms; the O-bound geometries lie slightly higher in energy. Switching between S- and O-binding modes is triggered by oxidation of Ru(II) or reduction of Ru(III).⁸¹ The redox processes can be triggered either electrochemically or photochemically; the former process requires an external potential, while the latter involves intramolecular electron transfer, either from Ru(II) to a closed-shell pyridyl ligand or from an open-shell pyridyl radical to Ru(III).⁷³ The photochemical isomerisation process is schematically depicted in Figure 1.5. Photoisomerisation occurs on a triplet surface with a mixture of MLCT and localised metal centered (MC) or dd^* characters. The singlet ground state is recovered from the triplet state through ISC, with the rate depending on the strength of nonadiabatic coupling between the states.^{82,83}

The required energy to induce isomerisation, the associated timescale of ground-state recovery, which correlates with efficiency of the process, and the character of the isomerising state are tunable through ligand substitution. The MLCT state energy can be adjusted through functionalisation of the polypyridyl ligands, as the gap between the Ru(II) d -orbitals and the π^* ligand orbitals determines the transition energy.⁸⁴ Introducing electron-withdrawing groups or enlarging the aromatic groups on the ligands will reduce the π^* orbital energies, red-shifting the MLCT transition. The timescale of ISC to return to the singlet ground state varies widely between species, ranging from a few picoseconds up to microseconds.⁸⁵ Rapid recovery increases the quantum yield of isomerisation, whereas slow surface crossing implies competition from radiative decay, reducing isomerisation efficiency. Finally, the character of the triplet surface on which isomerisation proceeds can be mixed and strongly multiconfigurational.⁸⁶ Nonadiabatic and vibronic couplings, which mix the diabatic surfaces and drive the ultrafast dynamics, depend on the energy gaps between the states.⁸⁷ The dynamics will therefore be sensitive to even subtle shifts in vibronic energy levels caused by ligand modification.

1.1.3 Electronic spectroscopy of photoswitches

Electronic spectroscopy is the natural technique of choice for studying the protonated azobenzene and ruthenium sulfoxide molecular switches, due to the changes in optical properties between the different isomeric forms. Stationary absorption spectroscopy has long played a role for studying photoswitching molecules,⁸⁸ and is particularly powerful when the different forms have distinct electronic spectra. The appearance of isosbestic points in the spectrum upon irradiation indicates the presence of multiple forms of the photoswitch, allowing deconvolution into individual contributions from each constituent isomer.⁸⁹ Conversely, the presence of multiple isomers in a sample with similar optical spectra renders interpretation difficult due to the closely overlapping transitions.^{90,91} If the thermal equilibrium is such that two or more forms of a

photoswitch are always present and the electronic spectra overlap significantly, the observed induced photochemistry will involve contributions from all states of the photoswitch present in the sample. Continued irradiation with a wavelength of light absorbed by two or more isomers can lead to formation of a photostationary state, with the populations of each isomer governed by relative oscillator strengths, isomerisation quantum yields, and thermal kinetics. Moreover, the probe light in a static absorption measurement can induce photoisomerisation in the sample and lead to a change in the sample composition over the timescale of the experiment, although this can be avoided by flowing fresh sample through the spectroscopic cell.^{69,92}

One approach to unlocking mechanistic detail of photoisomerisation is time-resolved spectroscopy, allowing one to study the isomerisation process in real time, uncovering information about the excited-state potential energy surfaces which is unavailable through static spectroscopy. A range of time-resolved spectroscopic techniques have been applied to study photochemistry since the advent of flash photolysis to investigate chemical kinetics.^{93–95} The most generally applicable technique is transient absorption spectroscopy, which probes the change in absorption of light as a function of time, and which has been extensively used to study azobenzenes and ruthenium sulfoxide complexes.^{36,43,85,96} Alternatively, fluorescence upconversion spectroscopy in combination with transient absorption provides another avenue, such as in the investigation of the isomerisation mechanism in the S_2 state of the weakly-fluorescent azobenzene (quantum yield of fluorescence below 10^{-5}).^{97,98}

Both static and transient optical spectroscopy of molecular switches, either through absorption or emission, are generally performed in solution, where the choice of solvent can have a dramatic impact on photochromism. Modifying the solvent composition can change the isomerisation quantum yield significantly,⁹⁹ or even turn off photoisomerisation entirely.¹⁰⁰ A more subtle problem is differential stabilisation of the ground and various excited states by solvent, shifting the energy of electronic transitions and modifying excited-state dynamics compared to the intrinsic photoswitch. If theoretical calculations used to support experiments are to properly describe the electronic structure and dynamics, they must properly account for influence of the solvent environment on the photophysics.¹⁰¹ The simplest approach is to treat the solvent as a non-interacting polarisable dielectric, a route that is only qualitatively useful and not universally available for highly-accurate electronic structure calculations.¹⁰² Explicit treatment of solvent molecules and their electronic response to resonant excitation is necessary to provide quantitative predictions, but comes at a large computational cost due to the above-linear scaling with the number of electrons for almost all electronic structure theories.¹⁰³ Gas-phase spectroscopic measurements, which either lack solvent or allow for controlled microsolvation,¹⁰⁴ therefore provide an ideal comparison with electronic structure calculations to investigate complex chromophores such as photoswitches.

The simplest azobenzenes are not protonated at neutral pH, and so an acid must be added,

typically to a methanolic or aqueous solution of the azobenzene, to form the protonated species. Both solvents and the conjugate base of the acid are strongly hydrogen-bonding and interaction with the azonium proton will perturb the chromophore's electronic structure.¹⁰⁵ Avoiding chromophore-solvent interaction is therefore crucial to observing the intrinsic photochemistry of the protonated azonium ions. Neutral azobenzene has been the focus of numerous gas-phase spectroscopic studies, including resonance-enhanced two-photon ionisation and time-resolved photoelectron spectroscopies,^{37,106} which provide high energy and time resolution, respectively. Protonated azobenzene has been the focus of only one gas-phase spectroscopic investigation, described in Section 1.1.1, which hinted at photoisomerisation following electronic excitation,⁵⁸ motivating the study described in Chapter 3.

Solvation can also shift the energy of the MLCT transitions in metal bipyridyl complexes, presumably due to the large transition dipole associated with charge transfer.⁷² As mentioned above, coupling of MLCT and MC triplet states depends on the energy gap between them. Modification of MLCT energy levels by solvent will alter the mixing and rate of transfer between triplet states, affecting the excited-state dynamics. As such, isomerisation in ruthenium sulfoxide molecules is strongly influenced by solvation.^{107,108} Additionally, coordinating solvents such as acetonitrile or methanol can displace the sulfoxide ligands after excitation, due to the repulsive nature of the triplet surfaces.³² Avoiding perturbation by solvent, allowing a comparison to theory, is the major motivation for studying these complexes in the gas phase. Investigation of photoisomerisation in an isolated ruthenium bis-sulfoxide complex is detailed in Chapter 4.

1.2 Ferrocenium radical cation

The ferrocenium radical cation (FeCp_2^+), where Cp is η^5 -cyclopentadienyl, is the one-electron oxidised form of ferrocene (FeCp_2), the prototypical organometallic molecule (Figure 1.6).^{109,110} Ferrocene has been of interest since its discovery in 1951 due to its unusual geometry with an uncommon C_5 axis of symmetry, although its exact point group depends strongly on the conditions and its environment.^{111–113} Metallocene complexes with most transition metals have been reported, with possibly the most well-known families being the titanocenes and zirconocenes, which are popular catalysts for olefin polymerisation.^{114,115}

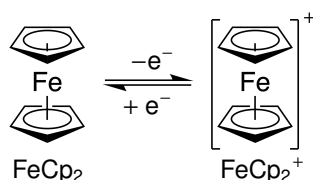


Figure 1.6: The ferrocene/ferrocenium one-electron redox couple.

The widest application of the ferrocene/ferrocenium redox pair is as an electrochemical stan-

dard for non-aqueous solvent systems.^{116–118} Compounds derived from ferrocene or containing functional groups based on ferrocene have been proposed for use as medical agents to treat diseases including cancer and malaria.^{119–121} The redox properties of the couple have been exploited to imbue electrochemical selectivity of ferrocene-containing pharmaceutical compounds towards biological targets, including proteins involved in cell metabolism.¹²² Ferrocene/ferrocenium-based electrolytes have been proposed as safer replacements for iodine/triiodide redox mediators in dye-sensitised solar cells.¹²³ Conjugated organic polymers containing ferrocenium units have been demonstrated to imbue highly-tunable magnetic properties to materials.¹²⁴

Metallocene complexes, sharing ferrocenium’s “sandwich” structure but containing different metal atoms, are also of interest due to their unusual symmetry and energy levels. Recent efforts have demonstrated that the metallocene geometry is a useful motif in single molecule magnets (SMMs),^{125–127} which have been proposed for use as qubits for quantum computing,¹²⁸ as the active units in high-density data storage,¹²⁹ and in molecular spintronics.¹³⁰ The high axial symmetry and approximately cylindrical structure have been suggested to increase the barrier to magnetic reversal and therefore to extend the lifetime of the magnetic states.^{131,132} While the most successful metallocenium single-molecule magnets are based on dysprosium, with some complexes exhibiting magnetic hysteresis up to 60 K (illustrated in Figure 1.7),¹²⁵ methyl-substituted ferrocenium cations have also been demonstrated to act as SMMs.¹³³ Rationalisation of the magnetic behaviour in metallocenium SMMs requires detailed knowledge of their electronic structure, which is strongly perturbed by the crystal field.

The low-lying electronic states of ferrocenium can be derived by single-electron ionisation from the occupied *d*-orbitals of Fe(II) and the π -orbitals from the Cp ligands,^{134,135} as illustrated

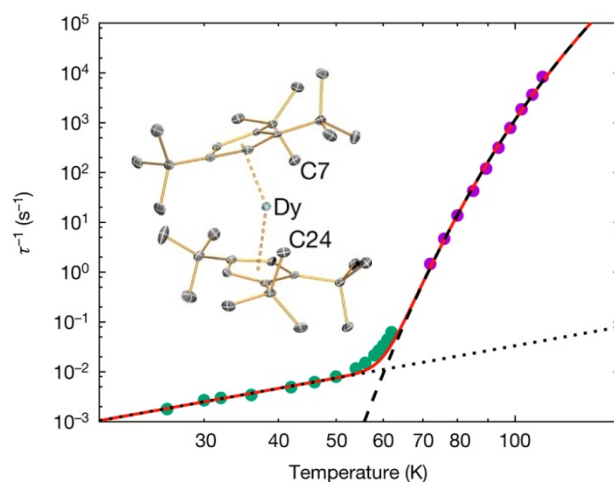


Figure 1.7: Dysprosocenium organometallic complexes are the best-performing single molecule magnets to date. They exhibit large barriers to magnetic reversal, apparently due to the axial symmetry and cylindrical structure, and correspondingly have long-lived retention of magnetisation at liquid nitrogen temperatures. Adapted with permission from Goodwin *et al.*¹²⁵. Copyright 2017 Springer Nature.

in Figure 1.8. The ground state corresponds to ionisation from the degenerate $d_{xy}/d_{x^2-y^2}$ orbitals on Fe. The lowest excited state arises from a hole in the d_{z^2} orbital and excitation to it from the ground state is therefore forbidden.¹³⁶ The first bright state arises from a hole in the Cp π -orbitals with the dipole-allowed transition from the ground state occurring at around 16000 cm^{-1} .¹³⁷ The spectroscopic properties of ferrocenium and its derivatives reflect its electronic structure. The allowed ligand-to-metal charge transfer transition occurs in the visible and so is important to consider if ferrocenium-based compounds are to be used in optical materials. The SMM behaviour arises from transitions between the states derived from d -orbital ionisation.¹³³ Furthermore, electronic spectra of ferrocenium provide benchmarks for electronic structure theories, which might provide insight into effective SMM candidates based on ferrocenium or other metallocene structures.

Nearly all electronic spectra of the ferrocenium cation to date have been recorded in condensed media, including powders and frozen rare gases,^{138,139} where the matrix crystal field can shift or even split energy levels including due to counterion interactions and site packing effects. Chapter 5

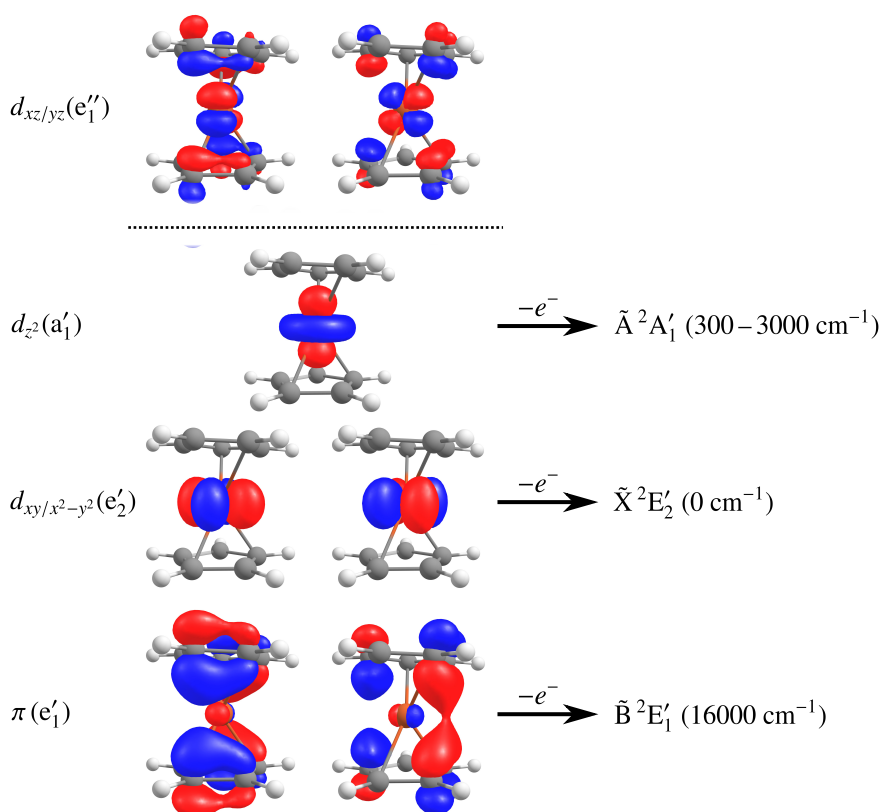


Figure 1.8: Frontier molecular orbitals of ferrocene and ferrocenium. Qualitative orbital labels and symmetries are given on the left. Right-facing arrows indicate ionisation from the orbital, with relative energies and term symbols for the low-lying electronic states of ferrocenium shown on the right. Energies are given relative to the $\tilde{X}^2E_2' \leftarrow \tilde{X}^1A_1'$ adiabatic ionisation energy. The dotted line represents the HOMO-LUMO gap.

describes spectroscopy of isolated ferrocenium ions measured through photodissociation of their weakly-bound complexes with single rare gas atoms. The experimental spectra are supported by multireference electronic structure calculations, which lay the foundations for more sophisticated theoretical treatments.

1.3 Tropylium cation

The tropylium cation (Tr^+ , C_7H_7^+) is the least studied of the three simplest 6π aromatic molecules depicted in Figure 1.9. Benzene (Bn , C_6H_6) has been of interest to chemists since elucidation of its bonding by Kekulé, allegedly resulting from an epiphany during a dream.¹⁴⁰ The cyclopentadienide anion (Cp^- , C_5H_5^-) is one of the classical organometallic ligands, a component of the prototypical organometallic molecule ferrocene and the oxidised ferrocenium discussed in Section 1.2. Both Bn and Cp^- are common ligands in organometallic chemistry, with applications in catalysis,^{114,115,141} medicinal and biological science,¹⁴² and advanced materials.¹⁴³ In contrast, Tr^+ plays a lesser role in organometallic chemistry, with relatively few complexes synthesised.¹⁴⁴ It has been demonstrated as an organometallic ligand in the “piano stool” complex $[(\text{C}_7\text{H}_7)\text{FeCO}_3]^+$.¹⁴⁵ Use of Tr^+ as a reagent in organic synthesis has been reported, such as for accessing substituted cycloheptatrienes and in the α -oxidation of aliphatic amines.^{146,147}

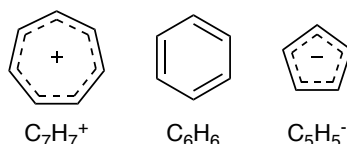


Figure 1.9: Skeletal structures of the simplest 6π -electron aromatic molecules: tropylium (C_7H_7^+), benzene (C_6H_6), and the cyclopentadienide anion (C_5H_5^-).

In organic mass spectrometry, however, the Tr^+ ion has been of great interest since it was demonstrated to be formed through electron impact ionisation of toluene.^{148,149} It had been assumed that the major C_7H_7^+ product from toluene would be the benzylium cation, produced by loss of a hydrogen atom from the methyl substituent; however, all hydrogen positions in the resulting C_7H_7^+ cations were found to be equivalent, implying that Tr^+ is a major product ion from toluene. Reactivity studies, following methylene transfer to aromatic molecules, indicate that Bz^+ must also be produced from toluene,¹⁵⁰ although the ratio of Tr^+ to Bz^+ is unclear. A conversion mechanism was proposed on the basis of electronic structure calculations, with Tr^+ formed from the toluene cation *via* the 1-cycloheptatrienyl radical cation, as supported by time-resolved photoionisation mass spectrometry experiments, kinetic energy release studies, and statistical rate theory calculations.^{151,152} The interconversion barrier proceeding through the 1-cycloheptatrienyl cation is on the order of 300 kJ/mol (illustrated in Figure 1.10) and so is unlikely to occur once the initial energy from ionisation is dissipated.¹⁵³

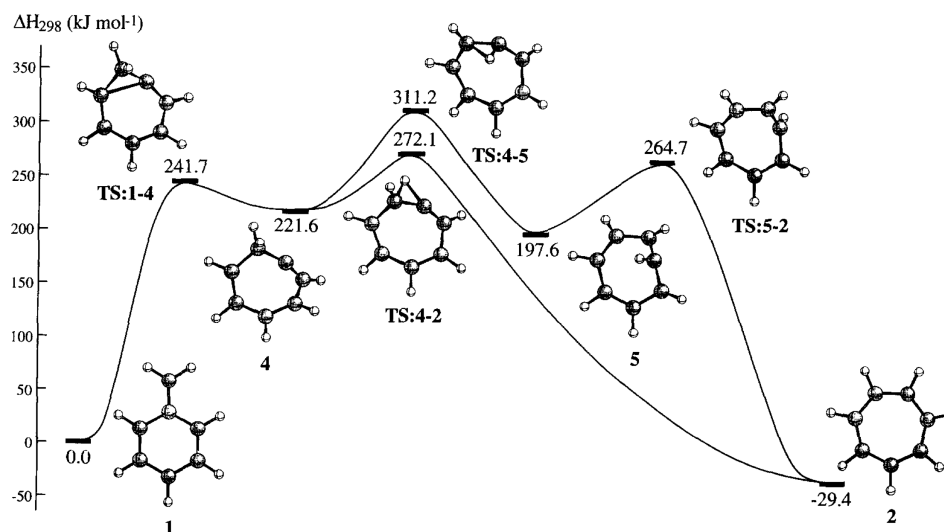


Figure 1.10: Proposed interconversion mechanism between Tr^+ (**2**) and Bz^+ (**1**) via the 1-cycloheptatrienyl cation (**4**) at the G2(MP2/SVP) level of theory. Reproduced with permission from Smith and Hall¹⁵³. Copyright 1997 Elsevier.

Recently, focus has turned to spectroscopic identification of the tropylium and benzylium structures following their formation through ionisation of hydrocarbon precursors. Previously, only isotopic labelling or ion-neutral reactivity had been used to distinguish the isomers. Several infrared spectra have been reported for Tr^+ and Bz^+ though photodissociation of their weakly-bound complexes with rare gas atoms,^{154,155} as well as multiphoton dissociation of substituted analogues.^{156–158}

The low-lying electronic spectrum of Tr^+ is derived from a single-electron HOMO-LUMO transition, which yields states of E'_3 and E'_1 symmetries.¹⁵⁹ The situation is analogous in the UV spectrum of Cp^- , where the lowest transitions are to states of E'_2 and E'_1 symmetries, and similar to that of Bn , which possesses transitions to B_{2u} , B_{1u} , and E_{1u} states.¹⁶⁰ Transitions are allowed to states of E'_1 , E'_1 , and E_{1u} symmetries in Tr^+ , Cp^- , and Bn , respectively, whereas transitions to the other states are forbidden and can only gain intensity through vibronic coupling. While the electronic spectrum of Bn has been rigorously analysed,¹⁶¹ the spectra of Tr^+ and Cp^- are relatively poorly understood. The ultraviolet (UV) spectrum of Cp^- is difficult to study in the gas phase as even the lowest electronically-excited states lie above the electron detachment energy (1.808 ± 0.006 eV).¹⁶² The difficulty in studying Tr^+ stems from interference by its isomer Bz^+ and from neutral benzyl radicals, which both possess intense transitions at overlapping wavelengths in the UV, contaminating the electronic spectra.¹⁶³

Gas-phase electronic spectra have been reported for the vibrationally-cooled Bz^+ isomer of C_7H_7^+ through photodissociation both of the bare ions and of complexes with rare gas atoms.^{164,165} No corresponding spectrum of Tr^+ has been reported to date. The best resolved

spectrum of Tr^+ was recorded in a 6 K neon matrix,¹⁶³ although the signal-to-noise ratio rendered interpretation of the vibrational structure difficult. The first electronic spectrum of gas-phase Tr^+ was recorded through photodissociation of its weakly-bound complexes with argon. The theoretical analysis of its spectrum, involving electronic structure calculations, group theory, and vibronic coupling simulations, is presented within Chapter 6.

1.4 Gas-phase ion spectroscopy

Obtaining spectra of molecular ions in the gas phase has several major benefits compared to studying the same ions in condensed media. The technique which has provided the best resolved spectra of molecular ions in the condensed phase is matrix isolation spectroscopy, where the target ions or molecules are deposited as a dilute guest inside a frozen inert matrix (typically a rare gas such as neon or argon).^{166–169} A range of molecular ions including ferrocenium and tropylium have been spectroscopically investigated within neon matrices by Maier and coworkers.^{139,163,170} However, even though rare-gas matrices represent one of the least perturbing condensed-phase environments, matrix-isolation spectra of ions often show additional structure or broadened features due to interaction with the matrix. In contrast, spectra of gas-phase molecular ions are representative of the intrinsic electronic structure of the species. Comparison of measured and theoretically predicted spectra is greatly simplified for gas-phase ions.¹⁰¹ Many ions are unstable in condensed media and degrade through intermolecular reactions with nearby species on the timescale of the spectroscopic experiment, including the tropylium ion which hydrolyses in aqueous solvent.¹⁷¹ In high vacuum, the reactive ions undergo few collisions and so their lifetime can be on the order of milliseconds or longer.¹⁷² Finally, gas-phase ions can be conveniently manipulated and separated using electromagnetic fields and ion optics,¹⁷³ such that spectra can be recorded of ions with well-defined mass-to-charge ratios m/z . This section provides an overview of the techniques which have enabled routine measurement of electronic spectra for a range of molecular ions. Emphasis is given to techniques directly relevant to the molecules discussed within this thesis, namely molecular photoswitches and the ferrocenium and tropylium cations.

The first known spectra of molecular ions in the gas phase were recorded through emission from the “negative” glow of direct current (DC) electrical discharges, with the observed species including N_2^+ , O_2^+ , and CO^+ .^{174–176} Later studies employed flash discharges, pulse radiolysis, and UV photoionisation to increase sample density. This early period in molecular ion spectroscopy was reviewed in 1971,¹⁷⁷ and at that time only 39 molecular ions had been spectroscopically detected, of which 32 were observed through emission. All molecular ions observed were di- or tri-atomic, with the exception of the diacetylene ion (C_4H_2^+).¹⁷⁸ The magnetic resonance spectrum of the H_2^+ ion was measured by detecting the H^+ photodissociation products in the first mass-resolved ion spectroscopy experiment.^{179,180}

Techniques developed by the Dunbar, Maier, and Tuckett groups made spectroscopic investigations of polyatomic ions, such as fluorinated benzene radical cations, achievable in the gas phase.^{181–184} Sample vapours were introduced as effusive beams into a vacuum chamber, wherein the molecular species were ionised with beams of electrons with energies between 20–100 eV. The resulting ions were generated in electronically, vibrationally, and rotationally excited states, with their electronic spectra recorded through dispersion of the emission through a spectrometer or by means of photodissociation with tunable light from a lamp. The use of electron impact ionisation, a standard technique from mass spectrometry, opened the door to a range of elegant experiments on mass-selected molecular ions, such as measuring the electric transition dipole moment orientation of CH_3Cl^+ in the molecular frame through polarisation experiments within the magnetic field of a modified ion cyclotron resonance (ICR) mass spectrometer.¹⁸⁵ Around the same time, fast beams of CH_3Cl^+ ions were Doppler-tuned into resonance with a polarised argon ion laser, with the photodissociation yields confirming the transition dipole orientation assignments from the ICR experiments.¹⁸⁶ Tandem triple quadrupole mass spectrometers were soon developed by the Vestal and Morrison groups for the measurement of photodissociation spectra of ions with higher throughput and sensitivity than achievable in ICR-based instruments.^{187,188} Photodissociation spectra of atmospherically-relevant cations, including the O_4^+ and CO_2CO_2^+ radicals, were measured in drift tube mass spectrometers, the predecessors of tandem ion mobility-mass spectrometers.¹⁸⁹

The main drawback of electron impact ionisation of warm molecules in effusive beams is that the ions are produced in a range of quantum states, manifested as broadened spectra which are difficult to interpret. The next major advance relevant to this thesis involved cooling the molecules during and after electron impact ionisation *via* adiabatic expansion, where the vapour of the molecular species under investigation is transferred from a high pressure source through a pinhole and into high vacuum.¹⁸³ The internal degrees of freedom in the molecules are dramatically cooled, with typical rotational temperatures inside molecular beam being below 10 K and vibrational temperatures usually less than an order of magnitude higher. The beam is crossed with the ionising electrons during expansion, such that the excess energy is dissipated rapidly, leaving internally-cooled ions distributed within only a few quantum states. Some action of the cold ions is then probed, generally emission or photodissociation, as a function of wavelength.^{184,190,191} At this point, free jet expansions had already been extensively utilised in laser spectroscopy of neutral species, whereby one could measure rotationally-resolved spectra for molecules as large as tetracene and phthalocyanine.¹⁹² The application of jet cooling to molecular ions allowed accurate spectroscopic and molecular parameters to be attained routinely for molecules with tens of atoms. Wide slit jets have allowed for direct absorption spectroscopy of certain molecular ions.¹⁹³ Furthermore, electronic spectra of mass-selected and jet-cooled ions can be measured by isolating ions with a single m/z from the molecular beam by means of standard mass spectrometric techniques and inducing photodissociation with a tunable laser,¹⁹⁴

the core principle behind resonance-enhanced photodissociation (REPD) spectroscopy.

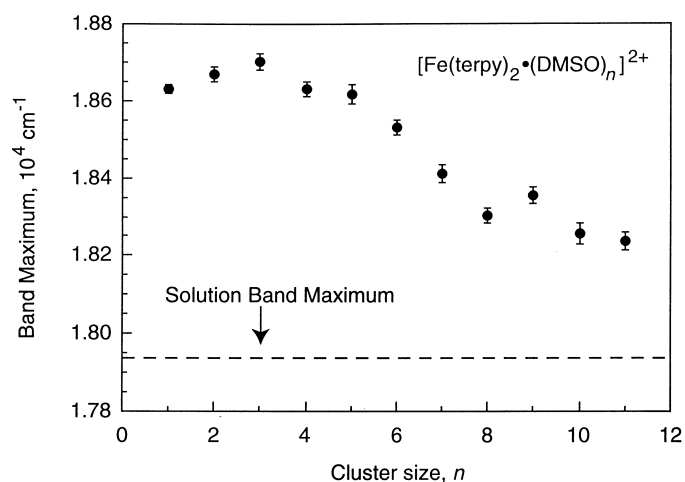


Figure 1.11: Shift in the photodissociation action spectrum band maximum of an electro sprayed $[\text{Fe}(\text{terpy})_2]^{2+}$ complex as a function of the number of clustered dimethylsulfoxide (DMSO) molecules. As the number of microsolvating DMSO molecules increases, the band maximum wavenumber approaches the bulk solution value. Adapted with permission from Spence *et al.*¹⁰⁴ Copyright 1998 American Chemical Society.

A major milestone relevant to the spectroscopic investigations of molecular photoswitches in this thesis was the development of electrospray ionisation (ESI), and in particular its application to spectroscopy of relatively large, non-volatile polyatomic ions. ESI was first developed as a modification of the jet expansion technique described in the previous paragraph. Solutions were sprayed from a narrow capillary held at a high electrical potential (2–10 kV), with charged droplets forming and evaporating until only a single gas-phase charged particle was left, which was analysed in a standard mass spectrometer.¹⁹⁵ Its application to soft ionisation and mass spectrometric investigation of large biomolecules would later win Fenn the Nobel Prize in Chemistry.^{196,197} Using ESI, non-volatile ions can be gently transferred from solution into the gas phase, where they can be probed mass spectrometrically or spectroscopically. The first application of ESI to ion spectroscopy was by Posey and coworkers in recording the laser photodissociation spectrum of polypyridyl complexes of iron(II) and ruthenium(II) over their MLCT transitions.^{104,198,199} Microsolvated cluster ions of the metal complex and solvent molecules were generated using ESI ionisation and mass selected, before being irradiated with tunable light. The charged dissociation products were isolated using a second mass selection stage and measured as a function of laser wavelength. The microsolvated clusters were demonstrated to display a red shift, approaching the bulk solution value as the number of solvating molecules increased as illustrated in Figure 1.11.¹⁰⁴

Perhaps the greatest challenge in gas-phase ion spectroscopy is observing a response to the absorption of light. Coulombic repulsion limits the ion density such that it is usually difficult to measure an attenuation in light intensity as it passes through the sample. In general, gas-phase

ion spectroscopy experiments observe some *action* induced after absorption of a photon by an ion.²⁰⁰ Such observable actions include fluorescence (or more generally emission, which includes phosphorescence and luminescence) and photodissociation, as mentioned previously.^{177,201} Photodetachment of an electron from a negative ion provides another observable action.²⁰² Photoelectron (PE) spectroscopy, where the kinetic energy of the emitted electron is measured at a given photon wavelength, can provide detailed information about resonances in both the initial and final species, which differ by one electron and one of which must be an ion (an electron is detached from an anion to yield a neutral molecule, or a neutral molecule is photoionised to a cation).²⁰³ Improvements to PE spectral resolution have been realised by measuring only the slowest (lowest kinetic energy) electrons.^{204–206} Other techniques which have been employed include laser magnetic resonance,^{207,208} velocity modulation spectroscopy,²⁰⁹ reaction inhibition or enhancement in fast ion beams and ion traps,^{210,211} and cavity ring-down spectroscopy.^{212,213} In cases where ions can be generated in high densities, direct absorption spectroscopy is possible, with multiple-pass cells and slit jets helping to maximise the effective path length.^{193,214,215} This is not an exhaustive list of gas-phase ion spectroscopic techniques, and the relevant reviews should be consulted for further information.^{177,184,194,200,216}

1.4.1 Photoisomerisation action (PISA) spectroscopy

The technique used to study photoisomerisation in the azobenzene and ruthenium sulfoxide photoswitches is photoisomerisation action (PISA) spectroscopy, which relies on measuring the photoisomerisation yields between isomers of electronically-excited molecules as a function of wavelength.^{217,218} Discrimination of isomers is achieved using ion mobility spectrometry (IMS), whereby isomeric ions are spatially and temporally separated on the basis of their drift mobility in an inert buffer gas through which they are propelled by a weak electric field.²¹⁹ The ions undergo numerous collisions with the buffer gas and move with a velocity inversely proportional to their orientationally-averaged collision integral with the buffer gas. Compact ions tend to have a small collision integral and drift more quickly than extended ions which have large collision integrals. The ions therefore separate along the length of the drift region, with compact isomers reaching the end before extended isomers. Isolation of a single isomer population to be probed spectroscopically is realised by means of an ion gate at the end of a first drift sector, which is pulsed open to allow only a subset of ions to pass.²²⁰ In this way, an isomer-selected ion packet can be probed, as illustrated in Figure 1.12.

Immediately after isomer selection, and at the start of a second drift region, the isomer-selected ion packet is overlapped with the output of a tunable light source. Resonant excitation of electronic transitions can lead to unimolecular chemical processes including photoisomerisation and photodissociation. The photoproducts are separated from the parent ions in the second drift region, before the ions are transferred through a mass spectrometer and detected. Photoisomeri-

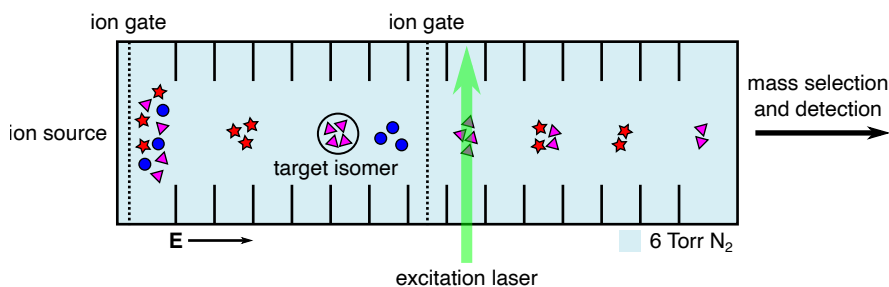


Figure 1.12: Schematic depiction of the tandem ion mobility spectrometer developed for photoisomerisation action (PISA) spectroscopy. Ion packets are injected into a drift region, where isomers separate through collisions with the N_2 buffer gas. The target isomer is selected by opening a second ion gate, while all other ions are discarded. The isomer of interest is irradiated with a pulse of tunable light, which can induce transformation into an isomeric photoproduct. The product photoisomer ions are separated from the parent isomer in a second drift region, after which the ions are mass selected and detected.

sation is manifested as a new ion packet with the same mass-to-charge ratio m/z but a different arrival time at the detector than the parent.²¹⁷ Photodissociation is detected through ions appearing at a different m/z and arrival time to the parent. The PISA spectra are built up by plotting the photoisomer yield normalised by the light intensity as a function of wavelength.

The PISA signal is proportional to the product of the absorption cross section and the quantum yield of isomerisation at that wavelength. In the simplest case, where the isomerisation yield is independent of wavelength, the PISA spectrum is identical to the absorption spectrum. More generally, the isomerisation yield depends on excitation wavelength, due to excited-state barriers to isomerisation, by accessing energetically-overlapping excited states, or from rapid ground-state thermal reversion before quenching by buffer gas, and so the PISA and absorption spectra can

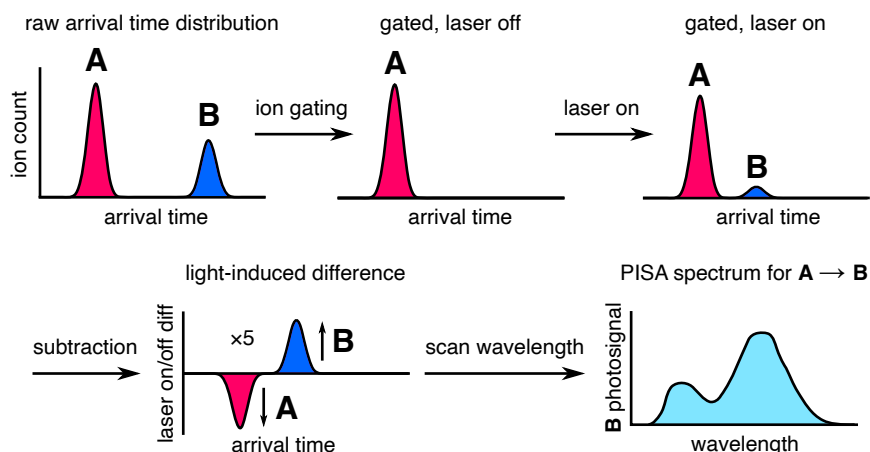


Figure 1.13: Procedure to record PISA spectra. The raw arrival time distribution (ATD) is recorded to identify isomers present. Ion packets, corresponding to the isomer of interest, are gated yielding an ATD free of other ions. Irradiating isomer **A** yields a signal corresponding to photoisomer **B**, while the intensity of the **A** signal decreases correspondingly. The laser on/off difference ATD shows this more clearly. The PISA spectrum is built up by recording the **B** photoproduct signal while scanning the laser wavelength.

differ. Measuring the absorption and PISA spectra would allow one in principle to extract relative isomerisation quantum yields as a function of wavelength. If a molecule does not photoisomerise, its PISA spectrum cannot be measured even if it strongly absorbs light. In these cases, other responses such as fluorescence or photodissociation would be required to measure an electronic action spectrum. Indeed, PISA spectroscopy does not represent the only combination of IMS with laser spectroscopy; IMS has been used to provide isomer selectivity for laser-induced fluorescence,²²¹ photoelectron spectroscopy,^{222,223} and photodissociation spectroscopy.^{224–227} The ion mobility technique has also been applied to measurements of relative photoisomerisation yields as a function of wavelength for molecules in solution.⁹²

In the case of molecular switches, PISA spectroscopy allows the wavelength dependence for photoisomerisation to be measured in the absence of solvent. By combining the isomer specificity with mass selection after the drift regions, the different forms of the photoswitches can be separated based on their drift mobilities and the isomer of interest can be isolated from the other forms. Individual action spectra can be collected for each isomer of the photoswitch without the need to purify populations in solution.⁹¹ Due to the short timescale of the experiment (10^{-3} – 10^{-2} s) compared to the timescale for thermal reversion in many molecular switches, even relatively unstable isomers can be isolated and studied.⁹² The identity of each species in the PISA experiments can be confirmed through careful sample preparation, analysis of the electronic spectrum, and modelling of relative drift mobilities in the chosen buffer gases.²²⁸

The initial application of PISA spectroscopy was to cyanine dyes,^{217,229} before focus turned to molecular switches of biological and nanotechnological relevance including the retinal protonated Schiff base and organic photoswitches.^{91,230–233} This thesis describes efforts towards understanding isomerisation behaviour in two such photoswitches based on protonated azobenzene molecules and ruthenium sulfoxide coordination complexes, as detailed in Chapters 3 and 4 respectively.

1.4.2 Resonance-enhanced photodissociation (REPD) spectroscopy

Resonance-enhanced photodissociation (REPD) spectroscopy is used to measure electronic spectra of the ferrocenium and tropylium cations, as described within Chapters 5 and 6. In the simplest implementation of REPD, the photodissociation yield of the isolated chromophore is monitored as a function of excitation wavelength.¹⁸¹ Fragmentation can occur if the sum of the photon energy and the chromophore's internal energy exceeds the molecule's lowest dissociation energy. Dissociation can occur directly from the electronically-excited state through coupling to a repulsive state or indirectly through statistical ground-state dissociation following internal conversion.²⁰⁰ The REPD signal obtained through excitation of the bare chromophore is the product of the absorption cross-section and the photodissociation yield at that wavelength.

In the work described in this thesis, a variant of REPD spectroscopy is employed, whereby

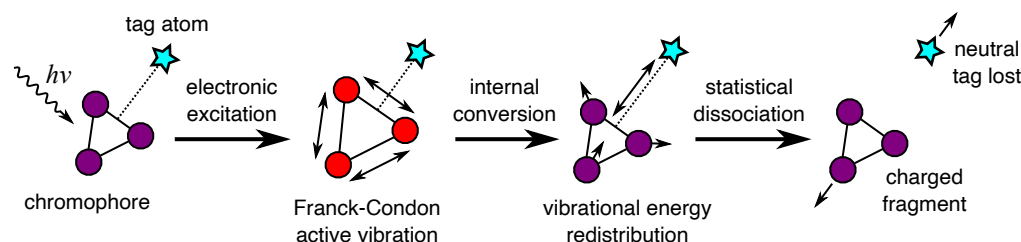


Figure 1.14: Principle behind tag-atom REPD spectroscopy. The chromophore in a weakly-bound complex with a rare gas “tag” atom is resonantly excited by an incoming photon. The energy from electronic excitation is transferred into vibrational energy following internal conversion and statistical energy redistribution. Eventually the weak non-covalent bond is broken, yielding the bare chromophore ion, which is detected as a function of photon energy.

weakly-bound complexes between the ferrocenium or tropylium cations and a rare gas atom (the “tag”) are generated in a molecular beam and mass selected, such that only the charged complexes left in the ion beam. Production of the bare chromophore ion upon resonant excitation is monitored instead of a charged fragment from the chromophore itself.²³⁴ Because the non-covalent bond between rare gas atoms and molecular cations is on the order of 10–1000× weaker than covalent bonds, dissociation to lose the tag atom is probable. The low binding energy of the rare gas atoms confers a second advantage to the technique, in that charged chromophores must be vibrationally cool in order to bind to the tag atoms.²³⁵ As mentioned previously in Section 1.4, bare chromophore ions generated through electron impact can be vibrationally warm, even in supersonic beams. Spectra gathered from warm ions tend to be congested and difficult to interpret, due mainly to vibrational hot bands, exemplified in the only previous gas-phase spectrum of the ferrocenium cation.²³⁶ In contrast, the weakly-bound complexes only support vibrational levels below the binding energy of the rare gas atom, reducing the probability of hot bands congesting the spectrum.

One possible mechanism for tag atom loss following electronic excitation is depicted in Figure 1.14 and briefly described here.²³⁷ Resonant excitation of the chromophore in the weakly-bound complex generates an electronically-excited state, with the intensity of the transition to a particular vibronic level governed by the Franck-Condon principle. The initially-prepared state internally converts to the ground electronic state, with the electronic energy redistributed into the internal degrees of freedom. The result is a highly vibrationally excited complex in the ground electronic state, which rapidly dissociates losing the tag atom. The excited complex can also couple to a repulsive surface and directly predissociate to lose the tag atom. Alternatively, the excited complex can relax through fluorescence, which can again lead to dissociation if fluorescence occurs to a vibrational level above the tag atom dissociation limit. In any case, the chromophore cation fragment normalised by light intensity is detected as a function of wavelength to yield the REPD spectrum.

Tag-atom REPD spectroscopy was first developed by Okumura and Lee to measure the

vibrational spectra of small cluster ions, including the cationic hydrogen clusters $\text{H}_3^+(\text{H}_2)_n$,²³⁸ the hydronium clusters $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$,²³⁹ and the non-classical protonated ethane C_2H_7^+ .²⁴⁰ Vibrational REPD spectroscopy has been widely applied to explore systems of fundamental importance, including the structural dynamics of hydration shells around protons and electrons in water clusters,^{241–248} and the electronic structure of small transition metal complexes and clusters.^{249,250} Electronic REPD spectroscopy has been applied to a range of systems, such as aromatic cations bound to rare gas atoms,^{251–253} fundamental biomolecules including DNA bases and amino acids,^{254–256} and coordination complexes modelling enzymatic active sites.^{257–259} The studies described within Chapters 5 and 6 involve application of the tag-atom REPD technique to the ferrocenium and tropylium ions, prototypical organometallic and aromatic cations, respectively, using argon and neon as tag atoms.

1.5 Scope of this thesis

This thesis describes spectroscopic studies on molecular photoswitches, protonated azobenzenes and ruthenium sulfoxide coordination complexes, and on the ferrocenium and tropylium cations. Chapter 2 contains descriptions of the custom-built tandem mass spectrometers in which these experiments were performed, an outline of the tunable light source used, and a brief overview of the supporting electronic structure calculations. The work described within the remainder of this thesis is divided into two sections. The first section describes the investigation of isomerisation in molecular photoswitches using photoisomerisation action spectroscopy. The first study, presented in Chapter 3, focused on protonated azobenzenes, which are prototypical organic photoswitches. The second study, described in Chapter 4, involves an investigation of the linkage isomerisation in ruthenium sulfoxide coordination complexes. The second section details the investigation of high-symmetry molecular cations using photodissociation action spectroscopy. Chapter 5 describes a combined experimental and theoretical study on the ferrocenium cation, where electronic spectroscopy provides insight into how electronic and molecular structure cannot be disentangled in this highly symmetric species. Finally, a combined *ab initio* and group theoretical investigation of the tropylium cation is described within Chapter 6.

Chapter 2

Methods

This chapter describes the two different spectrometers used for recording electronic spectra of molecular ions, that were utilised for the studies presented within this thesis. The first instrument is a tandem ion mobility-mass spectrometer used to measure the photoisomerisation yields of electrosprayed, isomer-selected protonated azobenzene and ruthenium sulfoxide photoswitch cations. The second instrument is a tandem mass spectrometer used to measure photodissociation of complexes between either ferrocenium or tropylium cations and rare gas atoms, that are generated by electron impact ionisation in a supersonic expansion. The operating principles behind the two instruments have been briefly described in Sections 1.4.1 and 1.4.2; the technical details of their implementation are provided within this chapter in Sections 2.1.1 and 2.1.2. The UV-visible optical parametric oscillator (OPO) employed as a light source for the spectroscopic measurements is described in Section 2.1.3. The chapter concludes with the theoretical background and practical details for the electronic structure calculations, performed to support the experimental action spectra, in Sections 2.2.1 and 2.2.2, respectively.

2.1 Experimental details

2.1.1 Photoisomerisation action (PISA) instrument

The photoisomerisation action (PISA) spectra of protonated azobenzenes and ruthenium sulfoxide photoswitches were measured using a tandem ion mobility-mass spectrometer, which was built in the Bieske group laboratory in 2012–2013 and has been progressively modified since. The following sections give a general overview of the instrument; the relevant publications and theses should be consulted for more detailed information.^{218,260,261}

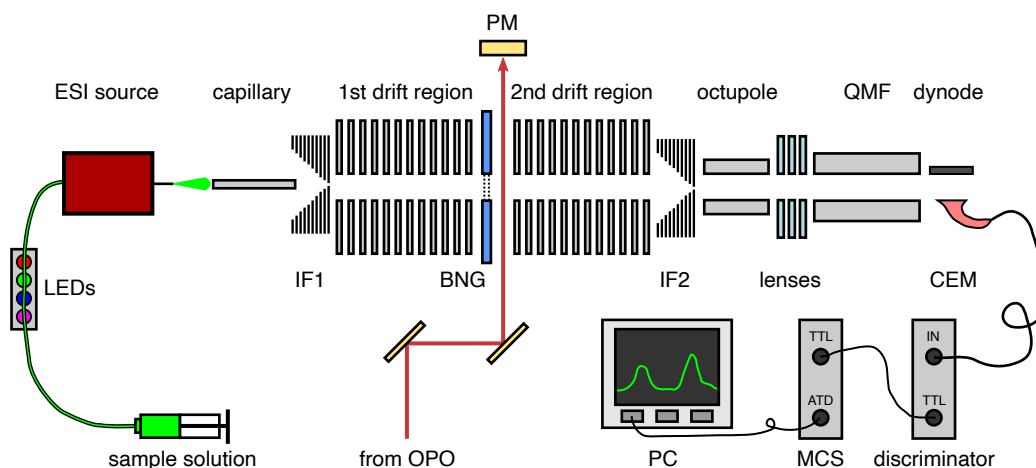


Figure 2.1: Schematic illustration of the tandem ion mobility-mass spectrometer in the Bieske group laboratory. Abbreviations: LED, light-emitting diode; ESI, electrospray ionisation; IF, ion funnel; BNG, Bradbury-Nielsen ion gate; PM, power meter; OPO, optical parametric oscillator; QMF, quadrupole mass filter; CEM, channel electron multiplier; TTL, transistor-transistor logic; ATD, arrival time distribution; MCS, multichannel scaler; PC, personal computer.

The tandem ion mobility-mass spectrometer is schematically illustrated in Figure 2.1. Gas-phase photoswitch cations are generated in an ESI source and accumulated in the first ion funnel. An electrostatic gate at the end of the funnel is pulsed open to allow packets of ions into a first drift region. Here, the isomeric ions are separated on the basis of their drift mobility as they are propelled by a weak electric field through N_2 buffer gas, with compact isomers drifting quickly and extended isomers drifting slowly. A single isomer family is selected using a Bradbury-Nielsen ion gate (BNG) and exposed to the output of a tunable OPO. The photoproducts resulting from unimolecular photochemical processes are separated according to their drift mobility from the parent isomer in a second drift region. The ions are then collected by the second ion funnel and transported within an octupole ion guide through a differentially pumped region, before mass selection in a quadrupole mass filter (QMF) and detection at a channel electron multiplier (CEM). The ATD is built up as a histogram of ion counts as a function of their arrival time at the detector. The difference between the OPO-on and OPO-off ATDs normalised by the OPO power as a function of wavelength gives the PISA spectrum for the selected isomer of the protonated

azobenzene or ruthenium sulfoxide photoswitch.

2.1.1.1 Sample preparation and ion source

The photoswitch samples are prepared as solutions in methanol (azobenzenes) or acetonitrile (ruthenium sulfoxides) at concentrations of around 10^{-5} M. Trace acetic acid ($\ll 1\%$) is added to the azobenzene solutions to aid protonation. Sample solutions are shielded from light, unless otherwise noted, to prevent photoisomerisation in solution. The solutions are pushed through the ESI tip at $10\ \mu\text{L}/\text{min}$ by a syringe pump (Kent Scientific, Genie Plus). The electrosprayed ions are entrained in the N_2 sheath gas flow and pass through a heated (480 K) stainless steel capillary held around 10 mm from the ESI tip, which transfers the ions into the drift region. The ESI tip is biased at +3 kV relative to the transfer capillary to ensure a stable ion count for the duration of the experiment. The transfer capillary is held at the same potential as the entrance electrode of the first ion funnel (around +5 kV relative to ground). Desolvation is aided by a flow of hot N_2 gas over the transfer capillary orifice and through heating of the capillary itself using a resistive heater.

After the ions pass through the transfer capillary, they are accumulated within a radio-frequency (RF) ion funnel. The funnel consists of stainless steel ring electrodes with decreasing internal diameter down the length of the funnel. Alternate rings are connected through $1\ \text{M}\Omega$ resistors and capacitively coupled to an 800 kHz RF potential with a typical amplitude of $80\ \text{V}_{\text{pp}}$. A 100 V DC gradient is applied along the length of the funnel, such that the ions are propelled to the exit of the funnel by the DC field while radially confined by the RF potential. The pressure in the funnel is around 6 Torr with the ions thermalising to near room temperature through collisions with the buffer gas. The funnel is terminated by a 90% transmittance mesh held at 20 V above both the final electrode and the entrance of the drift region, which prevents the ions from leaving. To inject ions into the IMS, the potential on the mesh is switched at 40 Hz to the same potential as the beginning of the drift region for $100\ \mu\text{s}$ allowing packets of ions to exit the funnel.

2.1.1.2 IMS drift region

The IMS drift region is comprised of stainless steel ring electrodes, where the first five electrodes are spaced apart by 5 mm and the remainder are spaced by 12 mm. The electrodes are sequentially connected by $1\ \text{M}\Omega$ resistors to form a voltage divider. With the ion source held at 5100 V, the DC drift field is maintained at around 45 V/cm. The pressure in the drift region is around 6 Torr, which is maintained by introducing nitrogen (N_2) buffer gas at $0.6\ \text{sl}/\text{min}$ while pumping with a two-stage rotary vane pump (E2M28, Edwards, $28\ \text{m}^3/\text{hr}$).

When operated as a single-stage IMS, the ion packets are separated along the full length of the drift region ($\approx 0.9\ \text{m}$), giving maximum separation. However, a pulsed BNG approximately halfway down the drift region allows for operation as a tandem IMS-IMS-MS instrument enabling

isomer- and mass-selective spectroscopy.²⁶² The BNG consists of two overlaid rows of nichrome wire (0.1 mm diameter) with individual strands are spaced by 0.6 mm. To transmit ions, the two rows are both set to the same potential as the drift electrodes at that points. To block ions, the potential of one row of wires is raised by 18 V relative to the other row. The ion trajectories are skewed sideways such that the ions are collected by one row of wires and lost. By pulsing the BNG open as the isomer of interest arrives at the gate, all ions except those in the selected packet are filtered out.

2.1.1.3 Ion activation using light

Ions of different mobilities are separated temporally and spatially in the first drift region, and this separation is utilised to perform isomer-specific spectroscopy experiments. The BNG is opened for a brief period to introduce an ion packet with a chosen mobility into the second IMS stage. Immediately after the ion gate, the packet is overlapped with the output of a tunable light source, generally an optical parametric oscillator (EKSPLA NT342B) that is described in more detail in Section 2.1.3.

Resonant excitation of the drifting ions leads to their promotion to electronically-excited states, which can decay either radiatively or non-radiatively. Radiative decay, either fluorescence or phosphorescence, leads to regeneration of the original ion with no change in mobility. Non-radiative decay of the excited state can induce a unimolecular reaction in the ion, which can occur on either of the excited or ground electronic states and can lead to photodissociation or photoisomerisation. Photodissociation is observed as a change in mass-to-charge ratio (m/z), whereas photoisomerisation, the focus of Chapters 3 and 4, results in a change in the drift mobility of the ion and therefore modification of the ATD. Alternatively, the unimolecular reaction could occur sufficiently slowly that the internal energy of the ion is quenched through collisions with buffer gas molecules, so that the ion returns to its electronic ground state thermalised to room temperature. In this case, there is no change in the arrival time distribution. The change in signal induced by light is background-corrected by recording a light-off ATD for each light-on ATD; as the experiment runs at 40 Hz, the OPO is operated at 20 Hz.

2.1.1.4 Mass selection and ion detection

Following separation in the two IMS drift sectors, the ions are transferred into a differentially pumped chamber by a series of electrostatic optics and guides. Firstly, the ions are radially collected and focused by a second RF ion funnel before being transferred through a 0.35 mm orifice into an octupole ion guide. The neutral buffer gas is pumped away in this differentially pumped region by a turbomolecular pump (Edwards EXT255H, 220 L/s) backed by a rotary vane pump (Edwards RV12, 14 m³/hr). The ion funnel and octupole guide RF electrical potentials are generated by custom-built power supplies.²⁶³ Thin wires running parallel alongside the octupole

rods generate a potential gradient which drives the ions through the guide. The ions then pass through a 5 mm orifice, guided by several electrostatic lenses, into the detector chamber where the ions are selected on the basis of their mass-to-charge ratio (m/z) by a quadrupole mass filter (Extrel C50, 1/2" rod diameter), operated with either of two commercial power supplies (Extrel C50, 1.2 MHz or Ardara Technologies, 800 KHz). Finally, the ions are detected by a combination of a stainless steel conversion dynode (-4 kV) and a channel electron multiplier (CEM, Photonis Channeltron 4870E, -2.45 kV). The detection chamber is pumped by a turbomolecular pump (Pfeiffer TMH 260, 230 L/s) backed by a rotary vane pump (Edwards RV3, 4 m³/h).

The signal from the CEM is detected by an amplifier/discriminator (Advanced Research Instruments F-100T). The discriminator sends a transistor-transistor logic (TTL) signal for each ion arrival event to a multichannel scaler (FAST ComTec, MCS-3), which builds up the ATD, a histogram of ion signal as a function of arrival time at the detector, which is transferred to a standard desktop computer for processing.

2.1.1.5 Power supplies and synchronisation

The high voltage in the ion funnel and drift region is provided by three computer-controllable dual-channel power supplies (iseg NHQ 216L and 213M, ± 6 kV and ± 3 kV, respectively) inside a nuclear instrumentation module (NIM) crate (Ortec 401C). One 6 kV power supply provides the potential gradient along the ion funnel, with the first and last electrodes held at 5200 V and 5100 V, respectively. The drift field is set by two power supplies providing 2520 V (± 6 kV) and 350 V (± 3 kV) potentials to the drift electrode immediately after the BNG and to the start of the second RF ion funnel, respectively. The linear potential gradient of around 45 V/cm is maintained by 1 M Ω resistors between drift electrodes. The DC biases on the ESI tip, the second ion funnel, and octupole ion guide are provided by custom-built power supplies.

Synchronisation of all pulsed events, including ion injection, opening of the BNG, and the OPO output timing, is performed with a four-channel digital pulse generator (Stanford Research Systems DG535) in combination with a two-channel pulse generator (Berkeley Nucleonics Model 575). Tagging of ATDs as "OPO-on" or "OPO-off" is achieved using a custom-built circuit based on D-type flip-flop integrated circuits triggered from the OPO Q-switching circuit.

2.1.2 Resonance-enhanced photodissociation (REPD) instrument

The resonance-enhanced photodissociation (REPD) spectra of the ferrocenium and tropylium ions described in Chapters 5 and 6 were measured using a custom-built mass spectrometer, which couples an ion source capable of generating jet-cooled beams of atomic and molecular ions with a tandem mass spectrometer and a tunable OPO (described in Section 2.1.3).²⁶⁴ The mass spectrometer has been described extensively and is schematically illustrated in Figure 2.2.^{164,264,265}

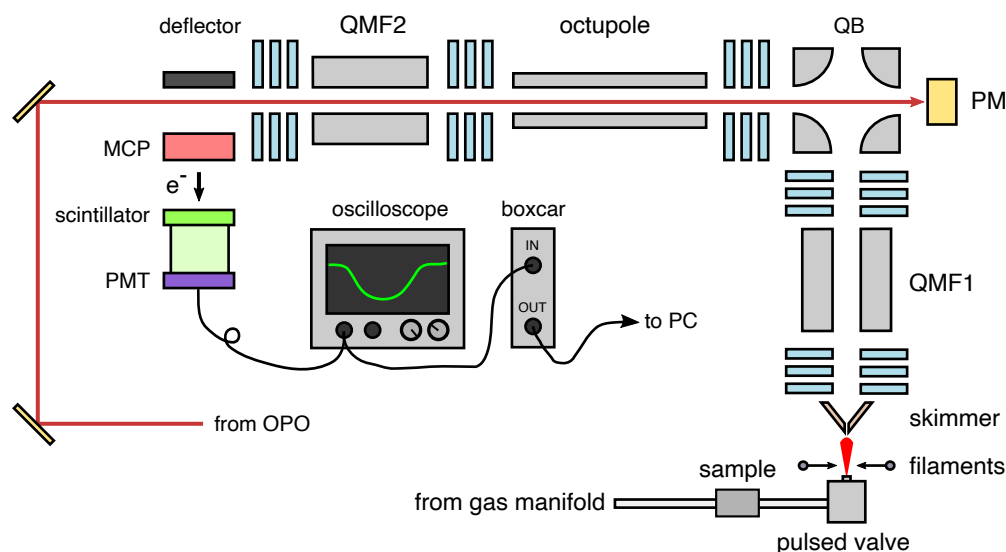


Figure 2.2: Schematic illustration of the tandem mass spectrometer for resonance-enhanced photodissociation (REPD) spectroscopy. Abbreviations: QMF, quadrupole mass filter; PM, power meter; QB, quadrupole bender; MCP, microchannel plate; PMT, photomultiplier tube; OPO, optical parametric oscillator; PC, personal computer.

A neutral precursor for the ion of interest (ferrocene, in the case of the ferrocenium cation detailed in Chapter 5, or cycloheptatriene, for tropylium in Chapter 6) is entrained in pressurised Ne or Ar, which is expanded into vacuum through a pulsed valve. The seeded gas jet is overlapped with an electron beam to ionise the target molecules, which form weakly-bound complexes with carrier gas atoms in the supersonic expansion. The ion beam passes through a skimmer before the charged complexes are selected on the basis of their mass-to-charge ratio m/z in QMF1, after which they are deflected orthogonally and transferred into an octupole ion guide. Here, the charged complexes are overlapped with the counter-propagating output of a tunable OPO which induces photodissociation of the weakly-bound clusters upon resonant electronic excitation. The fragment ions are selected in QMF2 before impinging on a detector sufficiently sensitive to observe single ions. The REPD action spectra are built up by measuring the photofragment ion signal normalised by OPO power as a function of irradiation wavelength.

2.1.2.1 Vacuum system

The REPD spectrometer is enclosed in a series of five differentially-pumped vacuum chambers. The ion source region is pumped by a 6" diffusion pump (Varian VHS-6, 2400 L/s) backed by a dual-stage rotary vane pump (Varian SD-1400, 60 m³/h). The typical working and base pressures in this chamber are around 10⁻⁴ Torr and 10⁻⁶ Torr, respectively. The skimmer assembly acts as a differential wall separating the source chamber, which has a large gas load, from the rest of the apparatus, which has mainly the gas load from the gas passing through the skimmer. The QMF1 region behind the skimmer is pumped by a turbomolecular pump (Pfeiffer Balzers TPH

330, 330 L/s) backed by a dual-stage rotary pump (Edwards RV12, 17 m³/h). The quadrupole bender region is pumped by a larger turbomolecular pump (Leybold TMP450, 450 L/s) backed by another dual-stage rotary pump (Varian SD-700, 30 m³/h). The octupole/QMF2 stage and detector region are each pumped by a turbomolecular pump (Oerlikon Leybold Turbovac 151, 145 L/s and Pfeiffer TMH 260, 230 L/s, respectively), both backed by the same rotary pump (Edwards RV5, 7 m³/h). Three liquid nitrogen cold traps are available for cryopumping water vapour in the source, QMF1, and octupole regions. Combined, the pumping system achieves base and working pressures in the octupole region of 10⁻⁸ and 10⁻⁷ Torr, respectively.

2.1.2.2 Ion source

Vibrationally and rotationally cooled complexes of cations with rare gas atoms are formed in an ion source comprised of a supersonic expansion crossed by an electron beam. A neutral precursor for the ion of interest (ferrocene for ferrocenium, cycloheptatriene for tropylium) is diluted in a pressurised rare gas carrier (typically around 1% sample in 4 bar Ar or Ne) and introduced into vacuum through a pulsed solenoid valve (General Valve, Series 9, 500 μ m orifice, 250 μ s typical opening time). The backing gas carrying the analyte expands adiabatically, during which the vibrational and rotational energies of the analyte are reduced through collisions. Shortly after exiting the valve orifice and early in the expansion process, the gas pulse is intercepted by a pulsed electron beam (typically $\sim$ 500 eV), generated from two rhenium filaments on either side of the expansion. The cations of interest are likely formed through a combination of direct ionisation by the electron beam, Penning ionisation by metastable carrier gas atoms,²⁶⁶ and charge transfer from ionised carrier gas atoms. The ionised molecular beam continues to expand and cool following ionisation. Complexes between the ions with the carrier gas atoms form through three-body collisions when the internal energy of the ions falls below the binding energy of the rare gas atoms to the molecular ion.

The central part of the expansion is selected after ionisation with an electroformed nickel skimmer (Beam Dynamics, 1.5 mm aperture, typically positioned around 40 mm from the pulsed valve orifice). The ion beam then passes into QMF1 *via* a series of electrostatic ion lenses. The ions are likely to possess typical rotational temperatures around 30 K, as determined from the rovibrational spectra of species formed in similar ion sources.²⁶⁴ Vibrational cooling is somewhat less efficient than rotational cooling, with vibrational temperatures generally on the order of 10–100 K.¹⁹²

2.1.2.3 Mass selection and ion optics

The charged complexes are selected on the basis of their mass-to-charge ratio in a first QMF (QMF1 in Figure 2.2). They are then deflected orthogonally into an octupole ion guide to separate the ion beam from the neutral beam. Inside the octupole ion guide, the ion clusters are exposed

to the output of a tunable OPO. Absorption of light is manifested as dissociation of the weakly-bound clusters, leading to formation of a fragment cation with different m/z . These fragment ions are selected in QMF2 before impinging on an ion detector.

The two mass filters, QMF1 and QMF2 in Figure 2.2, are each comprised of four cylindrical rods with diameters $3/4''$ and $1/2''$, respectively. The rods are arranged along the long edges of a square prism, with opposing pairs of parallel rods electrically connected. Opposite phases of a 1 MHz RF waveform are applied to each of the two pairs of rods and a DC offset is applied between the pairs, with the ratio of the RF amplitude to the DC offset determining which m/z values have stable trajectories through the QMF. The ions' kinetic energy is set by applying a common DC bias to all four rods. High ion kinetic energy increases transmission but reduces mass resolution, and vice versa. The superimposed RF and DC potentials to the QMFs are generated by commercial control units (both Extrel Model 14).

The DC quadrupole bender, used to separate the charged complexes from the neutral beam, is comprised of four electrodes with quarter-circle cross sections. Opposing electrodes are electrically connected to form two pairs. The quadrupole DC field formed through application of opposing potentials to the two electrode pairs serves to steer the charged complexes orthogonally into an octupole guide, where they are exposed to tunable UV-visible radiation. Plate electrodes above and below the bender electrodes serve to control the vertical trajectory of the ions. The DC voltages applied to the DC bender, the skimmer, and most electrostatic lenses (indicated in blue in Figure 2.2) are supplied by a custom-built 20-channel ± 200 V power supply.

The octupole is comprised of eight parallel cylindrical rods (3.2 mm diameter, 600 mm length). Alternate rods are electrically connected to form two sets of rods. Opposing phases of an RF waveform are applied to each set of rods, generating the confining potential. The RF voltage is generated by a commercial transceiver (Yaesu FT-450) and coupled to the octupole by an impedance-matching unit (Yaesu Musen FC-700). A common DC bias applied to all eight rods modulates the ion kinetic energy through the octupole.

2.1.2.4 Ion detection and data acquisition

In the REPD apparatus, the ions are collected by a high-gain (10^9 – 10^{12}) detector capable of efficiently sensing single ions. The ions are deflected off-axis onto the front face of a microchannel plate (MCP, Del Mar Photonics, 34 mm active area), which acts as an electron multiplier. The amplified electrons are accelerated into a scintillator disc behind the microchannel plate (MCP), with the luminescence guided onto a photomultiplier tube (PMT) through a glass light guide. The voltages for the MCP, scintillator, and PMT are provided by separate power supplies (two Stanford Research Systems PS350 units and Bertan 205A-01R, respectively). The PMT signal is split and sent to a digital oscilloscope (Tektronix TDS 620) for viewing and to a gated boxcar integrator (Stanford Research Systems SR250) for recording. The output of the boxcar integrator

tuned from 410–710 nm and 710–2600 nm, respectively, through rotation of the BBO-2 crystals. The idler photons have orthogonal polarisation with respect to the signal and are removed using a Rochon polariser following the OPO output coupler, before the signal beam is directed to the output. Alternatively, ultraviolet light from 225–410 nm can be generated inside type-1 β -barium borate (BBO-1) crystals using either sum-frequency generation (SFG, 296–410 nm) or second-harmonic generation (SHG, 225–296 nm). In either case, the remaining visible OPO signal photons are removed using a Pellin-Broca prism, before the UV light is directed to the output aperture.

The Nd³⁺:YAG pump laser typically operates at 600 mJ/pulse, which after frequency-tripling provides around 100–120 mJ per pulse at 355 nm as measured with a calibrated photodiode. The OPO signal output is typically >5 mJ per pulse, monitored using a thermopile power meter (Ophir 3A-P-SH). Normally, the power is attenuated using a Glan-Taylor polariser immediately prior to introduction into the experimental apparatus. For PISA experiments, the beam profile is formed using an aperture to a rectangle of approximately 20×10 mm² to overlap the ion packets. The OPO bandwidth is generally <5 cm⁻¹ in the visible and <8 cm⁻¹ in the UV. When necessary, the wavelength is calibrated using a commercial wavemeter (High Finesse/Ångstrom LSA) with absolute accuracy better than 0.6 cm⁻¹/20 GHz.

2.2 Theoretical details

Electronic structure theory calculations were performed in order to interpret the spectroscopic data presented in this thesis. Specifically, molecular geometries and their relative energies were used to determine which isomers were likely responsible for features in the arrival time distributions of the protonated azobenzene and ruthenium sulfoxide photoswitches. From these geometries and the associated electronic wavefunctions, partial charges were calculated and used as input to estimate the collision cross sections of the predicted isomers. Calculated electronic excitation energies were used to assign measured spectra. The spin-orbit splitting in the ferrocenium cation was investigated using multireference perturbation theory in order to assign observed vibronic levels. In the case of the tropylium cation, calculations of vibronic couplings provided insight into intensity borrowing in the electronically-excited states.

This section first describes the physical basis of the calculations, starting from the Schrödinger equation and the Hartree-Fock method. Various approximations to the exact electronic energy are then outlined, concluding with a brief description of the pertinent details for the computational methods employed in Chapters 3–6.

2.2.1 Physical background

Electronic structure theory, in the context of this thesis, aims to solve the non-relativistic time-independent Schrödinger equation:

$$\hat{\mathcal{H}}\Psi = E\Psi \quad (2.1)$$

where $\hat{\mathcal{H}}$ is the Hamiltonian operator for the system of electrons and nuclei and Ψ is the many-particle wavefunction.²⁷² The Hamiltonian $\hat{\mathcal{H}}$ can be represented as:

$$\begin{aligned} \hat{\mathcal{H}} &= T(\mathbf{R}, \mathbf{r}) + V(\mathbf{R}, \mathbf{r}) \\ &= T_N(\mathbf{R}) + T_e(\mathbf{r}) + V_{eN}(\mathbf{r}, \mathbf{R}) + V_{NN}(\mathbf{R}) + V_{ee}(\mathbf{r}) \\ &\approx T_e(\mathbf{r}) + V_{eN}(\mathbf{r}; \mathbf{R}) + V_{NN}(\mathbf{R}) + V_{ee}(\mathbf{r}) = \hat{\mathcal{H}}_{\text{BO}} \end{aligned} \quad (2.2)$$

where the T and V are the kinetic and potential energies, respectively, with $\mathbf{R}$ and $\mathbf{r}$ referring to the nuclear and electronic coordinates.²⁷³ T and V can be partitioned into the nuclear (N) and electronic (e) components. Under the Born-Oppenheimer approximation, the nuclei are assumed to be frozen with respect to electronic motion. Therefore, the nuclear kinetic energy $T_N(\mathbf{R})$ is set to zero, and the interaction potential between electrons and nuclei becomes a function of only the electronic coordinates at a given nuclear geometry (that is, $V_{eN}(\mathbf{r}; \mathbf{R})$ is an explicit function of $\mathbf{r}$ and a parametric function of $\mathbf{R}$).

The electronic Schrödinger equation, obtained by substituting Equation 2.2 into Equation 2.1, is then solved in a basis of one-electron spin-orbitals $\chi(\mathbf{x})$, which are the product of a spatial orbital $\psi(x, y, z)$ and a spin function $\alpha(\omega)$ or $\beta(\omega)$.²⁷⁴ The electronic wavefunction Ψ_e is constructed as a linear combination of Slater determinants Ψ_{SD} , which have the required antisymmetry according to Pauli's exclusion principle, in a basis of n spin-orbitals with spatial and spin coordinates $\mathbf{x}_n$:

$$\Psi_{\text{SD}} = \frac{1}{\sqrt{n!}} \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) & \dots & \chi_n(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) & \dots & \chi_n(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\mathbf{x}_n) & \chi_2(\mathbf{x}_n) & \dots & \chi_n(\mathbf{x}_n) \end{vmatrix} \quad (2.3)$$

In the simplest approach, Ψ_e is approximated by a single Slater determinant, which is called the Hartree-Fock (HF) approximation.²⁷³ The ground-state electronic energy is found through variational optimisation of the molecular orbitals. The HF approach, however, neglects electron correlation, the effect of electron-electron interaction beyond the mean-field description. The electron correlation problem can be roughly divided into static and dynamic correlation. Static correlation corresponds to situations where electronic states cannot be properly described by a single Slater determinant, such as in bond breaking, open-shell transition metal complexes, and low-spin diradicals.²⁷⁵ Dynamic correlation considers spontaneous electron-electron interaction

and the inability for HF to properly describe interelectronic cusps;²⁷⁶ its neglect generally degrades accuracy. The following sections outline several approaches used to recover the correlation contribution to the electronic energy.

2.2.1.1 Full configuration interaction

The entire electron correlation contribution of a molecule, and therefore its exact electronic energy, can be recovered through the full configuration interaction (CI) approach.²⁷⁷ In full CI, the wavefunction is expressed as the linear combination of all Slater determinants possible in the molecule:

$$|\Psi\rangle = \underbrace{c_0 |\Phi_0\rangle}_{\text{reference}} + \underbrace{\sum c_i^a |\Phi_i^a\rangle}_{\text{singles}} + \underbrace{\sum c_{ij}^{ab} |\Phi_{ij}^{ab}\rangle}_{\text{doubles}} + \dots \quad (2.4)$$

where $|\Phi_i^a\rangle$ corresponds to a Slater determinant related to a reference determinant $|\Psi_0\rangle$ by an electronic excitation from an orbital i to another orbital a , and c_i^a is the weight of that determinant in the sum. The computational cost of the full CI approach outlined in Equation 2.4 grows factorially with the number of spin-orbitals; however, it captures entirely both static and dynamic correlation in the electronic wavefunction. A range of approaches have been developed to tackle both the static and dynamic correlation problems with lower computational requirements, many of which are inspired by full CI. These methods are outlined in the next subsections.

2.2.1.2 Multiconfigurational self-consistent field theory

Static correlation, or the improper description of an electronic state by a single Slater determinant, is a key problem in the study of excited states and open-shell transition metal complexes. The most common solution is multiconfigurational self-consistent field (MCSCF) theory, where the electronic wavefunction is represented as a linear combination of Slater determinants, with the determinants selected from a subset of full CI.²⁷⁷

The most common approach, and the one employed in the work presented in this thesis, designates a number of electrons to be distributed within a similar number of spin-orbitals, with static correlation captured by full CI inside this subspace.^{278,279} The remainder of the orbitals are left either doubly occupied or doubly unoccupied. The complete active space configuration interaction (CASCI) wavefunction is found by optimising the determinant coefficients c_i in

$$|\Psi_{\text{CASCI}}\rangle = \sum_i^{\text{CAS}} c_i |\Phi_i\rangle \quad (2.5)$$

The complete active space self-consistent field (CASSCF) wavefunction and the corresponding energies are obtained by simultaneous variational optimisation of the MCSCF orbitals and coefficients c_i . CASSCF captures most of the static correlation, so long as the required determinants to

describe the multiconfigurational character are within the chosen active space. A small part of the dynamical correlation is also described by the CASCI expansion. Perturbation theory (PT) can then recover most of the remaining dynamical correlation. In this thesis, multi-reference (MR) PT approaches such as n -electron valence state second-order perturbation theory (NEVPT2) and complete active space second-order perturbation theory (CASPT2) are employed on top of CASSCF to describe multiconfigurational electronic states of transition metal complexes in Chapters 4 and 5.^{280–282}

2.2.1.3 Coupled cluster theory

An alternative approach to the CI method for capturing the dynamical electron correlation is the coupled cluster (CC) theory,²⁸³ which expresses the correlated wavefunction as the action of an exponential operator on a reference wavefunction:

$$|\Psi_{\text{CC}}\rangle = e^{\hat{\mathcal{T}}} |\Phi_0\rangle, \quad \hat{\mathcal{T}} = \sum_i t_i^a |\Phi_i^a\rangle + \sum_{ij} t_{ij}^{ab} |\Phi_{ij}^{ab}\rangle + \dots \quad (2.6)$$

The reference is usually a HF wavefunction and so CC theory is typically a single reference method. At infinite order, the CC and CI theories give identical energies, making CC formally equivalent to full CI and therefore exact, but both scale factorially with the number of orbitals. By truncating to single and double excitations and including an estimate of the triples excitation contribution using PT—the so-called CCSD(T) approach—relative energies with accuracies of around 0.1 eV can be achieved for many systems where static correlation plays only a minor role.²⁸⁴ Excitation energies can be calculated using various forms of CC theory through linear response theory or the equation-of-motion (EOM) approach, the latter of which can also compute ionisation and electron attachment energies with respect to an initial reference state.^{285,286} Approaches such as the EOM-CCSD applied in Chapter 6 provide excitation energies accurate to within 0.3–0.5 eV, when the excited states can be predominantly described as single excitations from the ground state. States consisting of double or higher excitations from the reference state require higher order levels of the CC expansion (e.g. EOM-CCSDT, EOM-CCSDTQ), and so their proper description is only feasible for molecules consisting of a handful of atoms. CC theory is used to calculate relative electronic energies for the protonated azobenzene and ruthenium sulfoxide photoswitch isomers and for the tropylium and benzylium isomer cations. Approaches based on EOM-CC theory provide electronic excitation energies for the protonated azobenzenes and the ferrocenium and tropylium molecular cations.

2.2.1.4 Density functional theory

Density functional theory (DFT) in its formulation by Kohn and Sham describes the electronic wavefunction as a functional of the electronic density.²⁸⁷ The electronic wavefunction, depending on the spatial coordinates of each electron, is replaced with a wavefunction depending only on

the total electronic density. The energy is then a functional of the electronic density ρ :

$$E[\rho] = T[\rho] + E_{\text{eN}}[\rho] + J[\rho] + E_{\text{xc}}[\rho] \quad (2.7)$$

where T is the kinetic energy, E_{eN} is the electron-nucleus Coulomb attraction, J is the electron-electron Coulomb repulsion, and E_{xc} is the exchange-correlation functional. DFT is formally exact if all components of $E[\rho]$ can be computed exactly. However, while the first three terms of Equation 2.7 can be easily calculated, the exact expression for E_{xc} is unknown. Approximate expressions for E_{xc} have been derived as functionals of the density ρ ,²⁸⁸ its first derivative $\nabla\rho$,²⁸⁹ and the kinetic energy density τ ,²⁹⁰ as well as “hybrid” functionals incorporating HF exchange.²⁹¹

Due to E_{xc} capturing electron correlation in its formulation, DFT tends to be significantly more accurate than HF and competitive in accuracy with CC theory including single and double excitations.²⁹² The computational cost is usually on the same order as or lower than HF, typically around two orders of magnitude faster than coupled cluster expansion with single and double excitations (CCSD).²⁹³ Electronic gradients and Hessians with respect to nuclear displacement can be computed easily, making DFT useful when searching potential energy surfaces of molecules for minimum energy geometries. The major disadvantage of DFT is the lack of a clear hierarchy of accuracy: while more advanced exchange-correlation functionals tend to be more accurate, there is no guarantee they will give accurate results for any given system and there is no clear path to systematically improving their accuracy.²⁹²

Time-dependent density functional theory (TDDFT) provides a means of calculating excitation energies for molecules within the DFT framework.²⁹⁴ The time-dependent density is modelled by the linear response to a weak electric field, with the poles and residues of the density response function providing the excitation energies and oscillator strengths, respectively. Under the adiabatic approximation, the TDDFT equations simplify to an eigenvalue problem, avoiding time propagation and numerical integration of the electronic density. The relative energetics are typically within 0.5 eV of experimental values for single-particle excitations to valence excited states, competitive with EOM-CC theory but with the lower computational cost of DFT.²⁹⁵ The TDDFT description of transitions to doubly-excited states and states of Rydberg or charge transfer character can be qualitatively incorrect due to the adiabatic approximation and the incorrect long-range behaviour of the DFT density, respectively. Corrections have been developed for proper fall off of the density at long range,^{296,297} although robust treatment of double excitations in TDDFT remains elusive.²⁹⁸

2.2.1.5 Spin-orbital basis functions

The basis of spin-orbitals in which the electronic Schrödinger equation is solved comprises another major approximation. The molecular orbitals χ are formulated as a linear combination of one-electron atomic orbitals:

$$\chi = \sum_{i=1}^N C_i \tilde{\chi}_i \quad (2.8)$$

where $\tilde{\chi}_i$ are the basis functions and N is the number of atomic orbital basis functions.²⁹⁹ The coefficients C_i are modified during the electronic structure calculations to optimise the electronic wavefunctions. A complete one-electron basis set will model the molecular orbitals exactly but is practically not feasible as the required basis set is infinite in size. Truncated sets of basis functions are required with the goal of approximating the complete basis limit, balancing accuracy with computational cost. In the applications presented in this thesis, Gaussian-type basis functions were employed,²⁷⁴ with the form:

$$R(r) = Y(\theta, \phi) A r^n e^{-\alpha r^2} \quad (2.9)$$

where $Y(\theta, \phi)$ is a spherical harmonic, A is a normalisation factor, n is the principal quantum number, and α is an adjustable exponent controlling the radial extent. While Slater-type basis functions derived from the $1s$ hydrogenic orbitals more accurately model the orbital shapes for small values of N , Gaussian-type functions are not much less accurate in the large- N limit and make electronic integral operations significantly faster.³⁰⁰ To reduce the computational cost further, the basis sets are contracted, where subgroups of basis functions within the set are defined, with a single coefficient controlling the contribution of the whole group to the molecular orbitals.

In the work presented later, the employed basis sets are generally at least split-valence “triple-zeta” quality, meaning that three contracted basis functions are used to describe each valence atomic orbital but only a single contracted function is used for the core orbitals. As the cost of most quantum chemical calculations grows polynomially with the number of basis functions (for example, HF scales with the fourth power of the number of basis functions), the basis set size is often a limiting factor in the accuracy of computed values.²⁷³

2.2.1.6 Collision cross section prediction

The IMS data for the protonated azobenzene and ruthenium sulfoxide ions are interpreted with the aid of predicted collision cross sections. The drift time t_d of an ion through a region of buffer gas under the influence of a weak electric field is inversely proportional to its drift mobility K :

$$t_d = \frac{l}{v_d} = \frac{l}{KE} \quad (2.10)$$

where l is the length of the drift region, v_d the drift velocity, and E the electric field strength. K is itself a function of the reduced field strength E/N , with N the number density of the buffer gas. The Mason-Schamp equation provides an estimate for K in the low-field limit:

$$K = \frac{3}{16} \frac{qe}{N} \sqrt{\frac{2\pi}{\mu kT}} \frac{1}{\Omega} \quad (2.11)$$

where qe is the ion charge, μ the reduced mass of the ion-buffer gas collision pair, k the Boltzmann constant, T the temperature, and Ω the orientationally-averaged collision cross section.³⁰¹

Using the trajectory method as implemented in the MOBCAL program of Jarrold and coworkers,³⁰² Ω for the ion of interest is numerically estimated by propagating ion-buffer gas collision trajectories. The trajectory simulations are generally performed on a potential energy surface generated by assuming atom-atom potentials describe the ion-neutral interaction. This requires as input the ion geometry and partial charges for each atom.³⁰³ As implemented in MOBCAL, the Lennard-Jones potential between the ion and nitrogen buffer gas is supplemented by ion-induced dipole and ion-quadrupole potentials,^{302,304} with a total interaction potential given by:

$$V(r, z) = 4\epsilon \underbrace{\sum_{i=0}^n \left[\left(\frac{\sigma}{r_i} \right)^{12} - \left(\frac{\sigma}{r_i} \right)^6 \right]}_{\text{Lennard-Jones "12-6"}} + \underbrace{\frac{\alpha(qe)^2}{2n^2} \sum_{i=0}^n \frac{1}{r_i^4}}_{\text{Ion-induced dipole}} + \underbrace{\sum_{j=1}^3 \sum_{i=0}^n \frac{q_i q_j e^2}{r_{ij}}}_{\text{Ion-quadrupole}} \quad (2.12)$$

The i subscript denotes summation over the n atoms in the ion of the atom-buffer gas distance r and atomic partial charges q , and α is the polarisability of the buffer gas. The empirical parameters ϵ and σ are extracted from fitting to benchmark measurements.³⁰³ The input parameters r and q are typically obtained from DFT calculations. The value of Ω is then calculated for the ions of interest, protonated azobenzenes and ruthenium sulfoxide cations in this thesis, which can be compared to experimental values of Ω . This trajectory-based approach involves two major approximations, that the ion geometry is static and that the interaction potential can be treated as a sum of atom-atom potentials. Molecular dynamics simulations employing electric fields have been used to capture molecular flexibility,³⁰⁵ whereas to date use of more accurate interaction potentials beyond atom-atom potentials has been limited to calculation of transport properties of only small ions.^{306,307}

2.2.2 Computational details

Electronic structure calculations are conducted to aid interpretation of experimental spectra. In Chapters 3–5, these calculations play a supporting role, whereas Chapter 6 describes a predominantly theoretical study. The quantum chemical calculations include finding minimum energy geometries, computing harmonic frequencies, estimating vertical excitation energies and state

splittings, and simulating vibronic structure and coupling. The majority of theoretical results are gathered using a combination of DFT methods, MCSCF supplemented with MRPT, and several CC theories, described within the previous section. The practical aspects of those approaches, pertinent to this thesis, are outlined here and detailed within the chapters themselves.

In all cases, minimum energy ground-state geometries are calculated using DFT, as it provides roughly equivalent accuracy to CC methods at several orders of magnitude lower cost.²⁹² A range of density functionals are employed, including ω B97X-D,³⁰⁸ TPSS,²⁹⁰ PBE0,³⁰⁹ and PW6B95,³¹⁰ all with empirical dispersion corrections.^{308,311} These functionals are chosen either due to their reliable performance on similar systems or because of their lack of empirical parametrisation so as to avoid fitting bias.²⁹²

Geometry optimisations are performed to find stationary points on the potential energy surfaces using the gradients of the electronic energy with respect to nuclear displacement.³¹² The Hessian matrices, containing the second derivatives of the energy with respect to displacement, are computed at the optimised geometries to confirm that the stationary points correspond to minima on the potential energy surfaces.³¹³ The harmonic frequencies obtained from diagonalising the mass-weighted Hessian are then used to assign vibronic bands in Chapters 5 and 6 for ferrocenium and tropylium, respectively, and to provide estimates of the vibrational zero-point energy to correct the electronic energies for all molecular ions within this thesis.

Excitation energies from the ground to higher electronic states are calculated under the vertical and adiabatic approximations.³¹⁴ In the vertical approximation, the energy difference is calculated between the two states at the ground-state geometry, whereas the adiabatic or 0-0 approximation takes the energy difference with both states at their minimum-energy geometries, optionally corrected for the difference in vibrational zero-point energies. The excitation energies are obtained using TDDFT (protonated azobenzenes in Chapter 3 and ruthenium sulfoxides in Chapter 4), EOM-CC (Chapters 3, 5, and 6 for protonated azobenzenes, ferrocenium, and tropylium, respectively), or MCSCF approaches optionally improved with MRPT (Chapters 4–6).

Vibronic band profiles for Tr^+ are modelled using the Franck-Condon approach in Chapter 6. Briefly, according to Fermi’s golden rule, the intensity of a vibronic transition is proportional to the squares of the vibrational wavefunction overlap integral and the transition dipole moment.³¹⁵ The vibrational wavefunctions are approximated with one- and two-dimensional harmonic oscillators,³¹⁶ while the transition dipole moment is computed through to first order with respect to nuclear displacement to include the Herzberg-Teller vibronic coupling effect. The simulated spectra are obtained through a Fourier transform of the electric dipole autocorrelation function.³¹⁷ The linewidth is adjusted to best match the experimental spectrum by convoluting the autocorrelation function with an exponential damping function.

The electronic structure calculations are performed using the GAUSSIAN,^{318,319} ORCA,^{320,321} PSI4,³²² and MOLCAS programs.³²³ The MOBCAL program is used to calculate collision cross sections.³⁰²

Chapter 3

Photoisomerization of protonated azobenzenes in the gas phase

Introduction to Chapter 3

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3.1 Abstract

Due to their high photoisomerization efficiencies, azobenzenes and their functionalized derivatives are used in a broad range of molecular photoswitches. Here, the photochemical properties of the *trans* isomers of protonated azobenzene (ABH^+) and protonated 4-aminoazobenzene (NH_2ABH^+) cations are investigated in the gas phase using a tandem ion mobility spectrometer. Both cations display a strong photoisomerization response across their $S_1 \leftarrow S_0$ bands, with peaks in their photoisomerization yields at 435 nm and 525 nm, respectively, red-shifted with respect to the electronic absorption bands of the unprotonated AB and NH_2AB molecules. The experimental results are interpreted with the aid of supporting electronic structure calculations considering the relative stabilities and geometries of the possible isomers and protomers, and vertical electronic excitation energies.

3.2 Introduction

Azobenzene (AB) is the simplest azoarene compound that displays *cis-trans* isomerization around the azo ($-\text{N}=\text{N}-$) bond in response to light (Figure 3.1). The dynamics of the photoisomerization process have been the subject of considerable debate, with the current consensus being that excitation of the $S_2 \leftarrow S_0$ transition (≈ 365 nm, oscillator strength ≈ 0.8), which has $\pi\pi^*$ character, is followed by rapid internal conversion to the S_1 state on a timescale of a few hundred femtoseconds.³⁷ In turn, molecules in the S_1 state undergo internal conversion to the S_0 state through a conical intersection seam at a geometry intermediate between those of the *trans* and *cis* isomers.^{39,324} The quantum yield for isomerization, which at the absorption maximum of the $S_2 \leftarrow S_0$ band is ≈ 0.25 ,^{35,38,47} depends on wavelength due to overlapping excited state absorption bands and dynamics on coupled excited state potential energy surfaces.^{39,324} The $S_1 \leftarrow S_0$ transition (≈ 420 nm) in the *trans* isomer has $n\pi^*$ character and is symmetry-forbidden, whereas the same transition in the *cis* isomer is weakly allowed.³⁹ The thermal *cis-trans* isomerization of azobenzene and substituted derivatives in solution has also been the subject of numerous studies.^{35,325} Although the rate of *cis-trans* isomerization depends on the solvent, unsubstituted *cis* azobenzenes typically have half-lives of around 2 days at 298 K corresponding to isomerization barriers of 80–120 kJ/mol.³⁵ The *cis-trans* isomerization can be hastened by excitation of the *cis* isomer to the S_1 state, a property that has been exploited to design substituted azobenzenes with controllable photoswitching between *cis* and *trans* isomers with visible light of different colours.³²⁶

The efficient, ultrafast photoisomerization of azobenzene and its substituted derivatives has led to their application in a range of molecular photoswitches, including in biological probes,³¹ in mechanical and optical materials,^{1,327} and in photopharmacology.^{328–330} There is considerable interest in shifting the absorptions of both *trans* and *cis* isomers of azobenzene

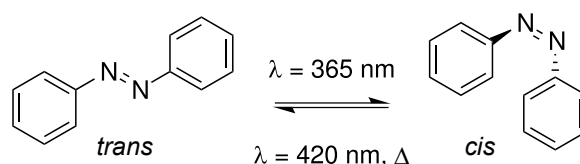


Figure 3.1: In solution, neutral *trans*-azobenzene readily converts to *cis*-azobenzene following the absorption of near-UV light, whereas *cis*-azobenzene reverts back to *trans*-azobenzene thermally or with exposure to 420 nm light.

to longer wavelengths for application in medicine and photopharmacology, as human tissue is translucent to red and near-infrared light but opaque to blue and UV light.⁵² There are several approaches to red-shifting the absorption profile of azobenzenes,⁵² with the most common route involving *ortho*- or *para*-substitution of both benzene rings with electron donating or withdrawing groups, which decreases the HOMO-LUMO gap. For example, Hecht and coworkers synthesized a series of *ortho*-fluorinated azobenzenes for which the *cis* isomers possess bright and red-shifted $S_1(n\pi^*)$ transitions,³²⁶ achieving separated absorption profiles for the *cis* and *trans* isomers. Another approach to modifying the absorption profile involves coordinating the azo-group to a strongly electron-withdrawing BF_2 group, which has the effect of red-shifting the absorption into the near-infrared while maintaining the isomerization quantum yield above 70%.^{331,332} The third approach to red-shifting the transition, first detailed by Woolley and co-workers,^{49,51} is protonation of the azo group to give an azonium protomer. The azonium ions exhibit a red shift which can exceed 100 nm, that is caused by delocalization of the positive charge over the π -system, and stabilization of the LUMO.⁵⁸ For azobenzenes with hydrogen bond acceptors such as methoxy groups incorporated at the *ortho*-position, the azo group can become sufficiently basic to be protonated at physiological pHs, leading to absorption maxima in the 560–620 nm range. These photoswitching moieties can be grafted at the *para*-positions with short polypeptides or enzymes to allow *in vivo* control of peptide conformation and drug activity with red light.^{49–52,54}

Although the dynamics of neutral azobenzenes have been thoroughly studied both in solution and in the gas phase, less is known about the protonated species. Féraud *et al.*⁵⁸ recently measured the $S_1 \leftarrow S_0$ photodissociation (PD) spectra of protonated azobenzene (ABH^+) and protonated 4-(dimethylamino)azobenzene cations (NMe_2ABH^+) in a cryogenic ion trap, showing that the $\pi\pi^*$ transition was significantly red-shifted compared to the unprotonated molecules. Although the authors could not directly observe photoisomerization for either of these protonated azobenzenes in the gas phase, they postulated a similar excited state isomerization mechanism to that established for azobenzene based on the presence of a pronounced 41 cm^{-1} vibronic progression, assigned to a vibrational mode involving torsion around the $N=N$ bond. Furthermore, geometry optimization on the S_1 surface starting from the ground state *trans*- ABH^+ geometry yielded a twisted chair-like structure intermediate between the *trans* and *cis* geometries, indicating that isomerization may result from $S_1 \leftarrow S_0$ excitation.

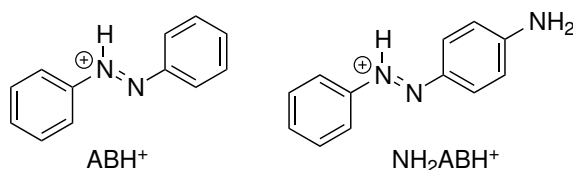


Figure 3.2: Structures of the *trans* protonated azobenzenes considered in this study.

Here we extend the earlier photodissociation investigations by probing the photoisomerization responses of the protonated *trans*-azobenzene cation and protonated *trans*-4-aminoazobenzene cation (NH_2ABH^+), shown in Figure 3.2, in the gas phase. The experimental strategy involves separating the *trans* and *cis* azobenzene cations in a tandem drift-tube ion mobility spectrometry (IMS) exploiting their different collision cross sections with N_2 buffer gas. Following their separation and selection in a first IMS stage, individual azobenzene isomers are photoexcited with wavelength tuneable radiation, with separation of the resulting photoisomers in the second IMS stage. By measuring the photoisomer yield against wavelength one derives a photoisomerisation action (PISA) spectrum that is a convolution of the absorption spectrum and a wavelength-dependent photoisomerization response. This strategy has been deployed previously by our group and by others to investigate the photoisomerization of a range of molecular systems.^{91,217,218,232,333} A PISA spectrum potentially provides complementary information to a photodissociation (PD) spectrum, which represents a convolution of the absorption spectrum and a wavelength-dependent photodissociation response. Questions we seek to answer include, whether the protonated azobenzenes undergo photoisomerization in the gas phase, is there a resemblance between the PISA and photodissociation (PD) spectra of the protonated azobenzene molecule, and how does a substituent amino group influence the photochemical properties of the azobenzene molecule.

3.3 Methods

3.3.1 Experimental approach

The experimental setup has been described previously.^{91,217,218,232} Briefly, the ABH^+ and NH_2ABH^+ cations were investigated using a tandem ion mobility-mass spectrometer illustrated in Figure 3.3, which allows mobility-selected ions to be exposed to tunable light from an optical parametric oscillator (OPO). Note that Figure 3.3 depicts the apparatus as a linear drift tube for simplicity, whereas the actual instrument includes S-bends at the beginning and end of the drift region.^{217,218,232} These S-bends have no effect on the operation of the instrument.

Azobenzene cations electrosprayed from methanol (10^{-5} M, 1% acetic acid) were accumulated in an ion funnel (IF1) and injected into the drift region in 100 μs pulses at 20 Hz through an ion gate (IG1). Azobenzene (98%) and 4-aminoazobenzene (98%) were purchased from

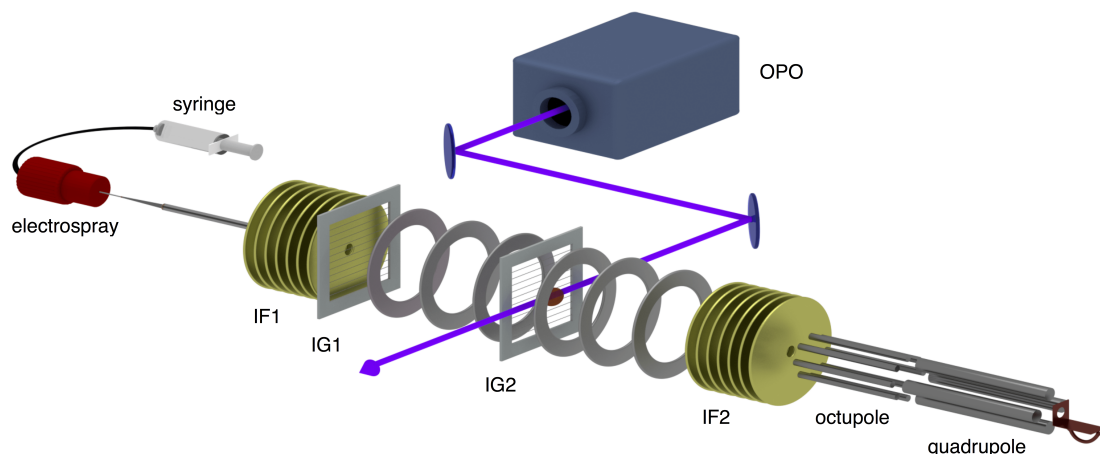


Figure 3.3: Representation of the tandem ion mobility mass spectrometer, showing the electrospray ionization source, first ion funnel (IF1), first ion gate (IG1), second ion gate (IG2), second ion funnel (IF2), and optical parametric oscillator (OPO).

Sigma-Aldrich (Castle Hill, Australia) and used without further purification. The ion packets were propelled through the drift region by an electric field ($E = 44 \text{ V/cm}$) and separated according to their collision cross sections with N_2 buffer gas ($\approx 6 \text{ Torr}$). At the end of the drift region, the ions were collected radially by a second ion funnel (IF2) and guided through a differentially pumped stage by an octupole ion guide, before being mass-selected by a quadrupole mass filter and striking the Channeltron detector which was connected to a multichannel scaler. An arrival time distribution (ATD) was built up as a histogram representing ion count versus arrival time. The mobility resolution for the protonated azobenzene cations was typically $t_d/\Delta t_d \approx 75$. Collision cross sections were measured as described previously.³³⁴

Photoisomerisation action (PISA) spectra of protonated azobenzene cations were obtained by operating the ion mobility spectrometer in tandem mode. A Bradbury-Nielsen electrostatic ion gate (IG2) halfway along the drift region was used to select the target isomer by opening it for $100 \mu\text{s}$ at an appropriate delay with respect to the first gate. The selected ions were irradiated 15 mm after IG2 with light from a tunable OPO (energy flux $\approx 1 \text{ mJ/cm}^2/\text{pulse}$). The OPO light beam had approximately a $5 \text{ mm} \times 20 \text{ mm}$ profile where it overlapped the ion packet. The OPO was pulsed at 10 Hz, irradiating every second ion packet. In this way, light-off and light-on ATDs were collected, the difference between which revealed the photoisomerization response. The photoisomerisation action (PISA) spectrum was obtained by plotting the photoisomer yield against OPO wavelength.

3.3.2 Computational approach

In order to identify the important gas-phase species, ground state geometries of the ABH^+ and NH_2ABH^+ cations were optimized and zero-point energies were obtained at the $\omega\text{B97X-D/6-}$

311+G(2df,p) level of theory using Gaussian 09.^{308,318,335} In turn, single point energies were calculated using the ORCA 3.0.3 program package at the DLPNO-CCSD(T)/cc-pVTZ level of theory.^{320,336–339} With the cc-pVTZ basis set, this method provides energies within 4 kJ/mol of the complete CCSD(T) values while being several orders of magnitude less computationally demanding.^{337,338}

The equilibrium geometry of *trans*-ABH⁺ was found to be planar at the ω B97X-D/6-311+G(2df,p) level of theory, unlike the previously published twisted structure.⁵⁸ However, as discussed in Section 7.1, the energy difference between the planar and non-planar structures and the barrier separating them are small (≤ 1 kJ/mol), such that the molecule should be quasi-planar at 300 K. Therefore, the planar DFT geometry was used for calculating vertical excitation energies.

Vertical excitation energies (VEEs) were determined using the EOM-CC2 and linear-response TDDFT (CAM-B3LYP) methods.^{297,340,341} The EOM-CC2 method is known to reliably predict singlet excited state energies for a range of organic chromophores, often giving good agreement with CASPT2.³⁴² The CAM-B3LYP density functional was chosen due to incorporation of range-separated exact exchange to account for charge transfer.^{343,344} The VEE calculations used the def2-TZVP basis set for ABH⁺ and aug-cc-pVDZ for NH₂ABH⁺.^{345,346}

Collision cross sections for the isomers of ABH⁺ were modelled using the trajectory method in a version of MOBCAL parametrized for N₂ buffer gas.^{302,303,347} The input charge distributions were calculated using the Merz-Kollman scheme from ω B97X-D/6-311+G(2df,p) charge densities.³⁴⁸

3.4 Results and discussion

3.4.1 Protonated azobenzene (ABH⁺) cation

The arrival time distribution of ABH⁺ electrosprayed from methanol solution, shown in Figure 3.4, displays two peaks, the relative intensities of which depend upon the amplitude of the RF drive voltage applied to ion funnel (IF)1. With low RF drive voltage, the ions are collected gently, so that the ATD is likely to represent the relative populations of the nascent, electrosprayed *trans* and *cis* ABH⁺ isomers. On the other hand, at high RF voltage, the electrosprayed ions are subject to energetic collisions with the buffer gas in IF1, inducing isomerization and driving the isomer populations towards a quasi-equilibrium between the various gas-phase isomers.^{349,350}

The ω B97X-D/6-311+G(2df,p) and DLPNO-CCSD(T)/cc-pVTZ calculations predict that *trans*-ABH⁺ is more stable than *cis*-ABH⁺ by 29 kJ/mol and 26 kJ/mol, respectively. The slower isomer (ATD peak centred at ≈ 11.0 ms, measured collision cross section 139 ± 1 Å²), which dominates at high IF1 RF drive voltage, is therefore likely to be the *trans*-ABH⁺ isomer, with

the faster isomer being the *cis*-isomer (measured collision cross section $137 \pm 1 \text{ \AA}^2$). Calculated cross sections for the *trans*- and *cis*-ABH⁺ isomers were both $142 \pm 1 \text{ \AA}^2$, where the uncertainty reflects the range of calculated values delivered by the Trajectory Method of MOBCAL.^{302,303,347} The presence of both *trans*- and *cis*-ABH⁺ peaks in the ATD obtained with low IF1 drive voltage demonstrates that the two isomers are separated by a substantial energy barrier, otherwise they would interconvert in the drift tube. The barrier for *trans* to *cis* conversion is estimated to be at least 80 kJ/mol (from RI-MP2/cc-pVDZ calculations), significantly larger than the thermal energy of the drifting ions at 300 K.

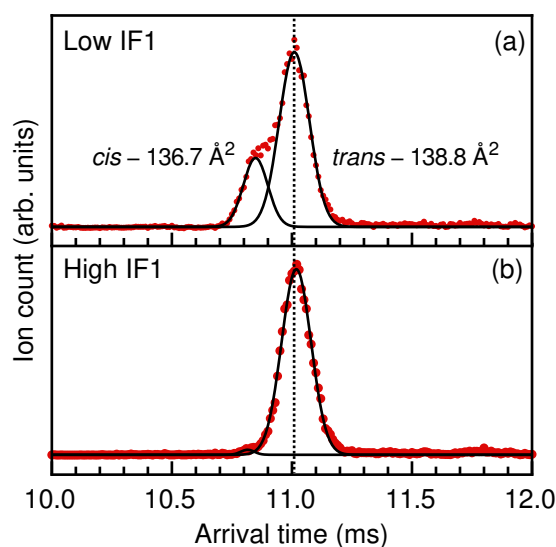


Figure 3.4: Arrival time distributions for ABH⁺ with low (a) and high (b) RF drive voltages to IF1. Experimental collision cross sections (estimated uncertainty of $\pm 1 \text{ \AA}^2$) are given for each peak (see Section 7.1 for details).

Exposing *trans*-ABH⁺ to light over the 370–500 nm range causes isomerization to *cis*-ABH⁺. This behaviour is apparent in Figure 3.5a, which shows a light-off ATD and a light-on/off difference ATD obtained with 440 nm irradiation of *trans*-ABH⁺. There is clear depletion of the *trans* peak and appearance of the *cis* isomer peak at shorter arrival time. Note that because the ions are irradiated halfway along the drift region, the *cis* isomer photo-appearance peak is situated approximately halfway between the parent *trans* peak and the *cis* peak in Figure 3.5a. The collision cross section of the photo-isomer corresponds to the cross-section for *cis*-ABH⁺ (both $137 \text{ \AA}^2$). Although photoisomerization is the dominant process, the depletion signal exceeds the enhancement signal by around 15 % due to photodissociation.

Plotting the integrated *cis*-ABH⁺ photo-appearance signal as a function of wavelength gives the *trans* to *cis* PISA spectrum shown in Figure 3.5b. The PISA spectrum exhibits a single band spanning the 480–370 nm range with a maximum at $\approx 435 \text{ nm}$, which is assigned to the $S_1 \leftarrow S_0$ transition on the basis of electronic structure calculations and its similarity to the band in the

photodissociation (PD) action spectrum of Féraud *et al.*⁵⁸ The PD action spectrum, which was recorded under cryogenic conditions at ≈ 40 K, displays a resolved vibrational progression with 41 cm^{-1} spacing near the band onset that was assigned to a low frequency torsional mode around the azo bond, corresponding to the isomerization coordinate. Our results clearly demonstrate that excitation of the $S_1 \leftarrow S_0$ band leads to isomerization in the gas phase.

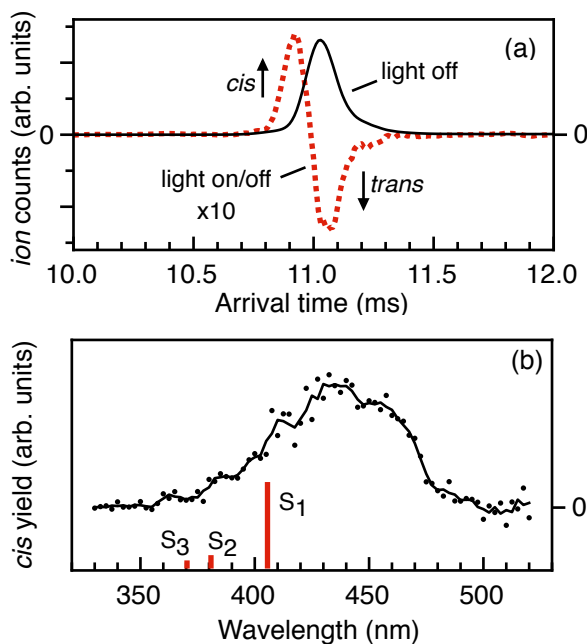


Figure 3.5: (a) Arrival time distribution with high RF drive voltage for *trans*-ABH⁺ with the light off (solid black curve) and the difference in the light on and light off arrival time distributions at 440 nm (dashed red curve). The enhancement and depletion signals differ in area by $\approx 15\%$ due to photodissociation. (b) PISA spectrum of *trans*-ABH⁺, normalised for total ion count and light fluence. Red lines indicate wavelengths and intensities of vertical electronic excitations calculated at the EOM-CC2/def2-TZVP level of theory.

Table 3.1: Calculated vertical excitation energies [eV (nm)] and oscillator strengths for ABH⁺ compared with experimental values. All calculations were performed using the def2-TZVP basis set.

Method	LUMO $\leftarrow$ HOMO		LUMO $\leftarrow$ HOMO-1		LUMO $\leftarrow$ HOMO-2	
	$S_1 \leftarrow S_0$	f	$S_2 \leftarrow S_0$	f	$S_3 \leftarrow S_0$	f
EOM-CC2	3.0 (406)	1.00	3.4 (364)	0.04	3.5 (359)	0.02
CAM-B3LYP	3.2 (382)	0.80	3.6 (345)	0.07	3.6 (341)	0.04
Exp.	2.85 (435)					

Calculated vertical excitation energies (VEEs) and oscillator strengths for ABH⁺, which are summarized in Table 3.1, are consistent with the calculations of Féraud *et al.*⁵⁸ In contrast to *trans*-azobenzene in which the S_1 state is optically-dark with $n\pi^*$ character and the S_2 state is optically-bright with $\pi\pi^*$ character, the S_1 state of the protonated azobenzene cation is bright with $\pi\pi^*$ character, whereas the S_2 and S_3 states are approximately degenerate and are associated

with charge transfer from the phenyl rings to the azo group. The S_1 VEE predicted by EOM-CC2 agrees with the PISA spectrum band maximum, whereas there is poorer correspondence with the TDDFT values. We note that TDDFT provides an inadequate description of vertical excitations in heteroarene systems due to considering only singles excitations,³⁵¹ whereas EOM-CC2 includes approximate treatment of double excitations.³⁴² A rigorous treatment of the excited states requires inclusion of both static and dynamic electron correlation effects using multireference methods.^{342,352–354}

The EOM-CC2 calculations suggest that the $S_2 \leftarrow S_0$ and $S_3 \leftarrow S_0$ transitions should be very weak with oscillator strengths of 0.02–0.04 (a factor of 25–50 weaker than the $S_1 \leftarrow S_0$ transition). The PISA spectrum shows only a weak photoisomerization response associated with these transitions and an even lower photodissociation yield (less than 15 % of the photoisomerization response). In contrast, the PD spectrum of ABH^+ reported by Féraud *et al.* shows a strong photodissociation signal for the S_2 and S_3 excited states with prominent peaks at 405 and 390 nm.⁵⁸ The difference in the ABH^+ photodissociation response for the S_2 and S_3 excited states for the two experiments may be linked to differences in laser intensity and buffer gas pressure, which will affect respectively the probability for multiphoton absorption and rate of collisional deactivation.

Unfortunately, due to low signal levels it was not possible to record a corresponding PISA spectrum of the *cis*- ABH^+ isomer. As shown in Figure 3.4, at low RF drive voltage to IF1, the *cis* isomer constitutes $\approx 30\%$ of the signal. However, the total ion count is very low due to poor ion collection. At high RF drive voltage to IF1 the total ion count is much higher, but the *cis*- ABH^+ isomer ions are almost completely converted to *trans*- ABH^+ isomer ions before their injection into the drift region.

In summary, protonation of the azo group significantly red-shifts the $\pi\pi^*$ transition compared to the corresponding transition in neutral *trans*-azobenzene (435 nm compared to 365 nm). Facile photoisomerization is observed for the $S_1 \leftarrow S_0$ transition, demonstrating that protonation is an effective way to red-shift the azobenzene photoisomerization response for practical applications.

3.4.2 Protonated 4-aminoazobenzene (NH_2ABH^+) cation

We turn now to consider the protonated 4-aminoazobenzene (NH_2ABH^+) cation, in which a single phenyl ring is *para*-substituted with an electron-donating amino group. The NH_2ABH^+ molecule has three likely protomers, with the proton either attached to one of the two azo N atoms, or to the amino group (Figure 3.6). The ATD for NH_2ABH^+ , shown in Figure 3.7a, exhibits a single peak irrespective of the RF drive voltage to IF1, suggesting either a single isomer is present or there are several isomers with very similar collision cross sections. As shown in Figures 3.7a and b, exposing the NH_2ABH^+ isomer to light of wavelengths between 410 and 540 nm causes

isomerization to a faster species with a maximum response at 525 nm. The transformation presumably corresponds to a *trans* to *cis* photoisomerization.

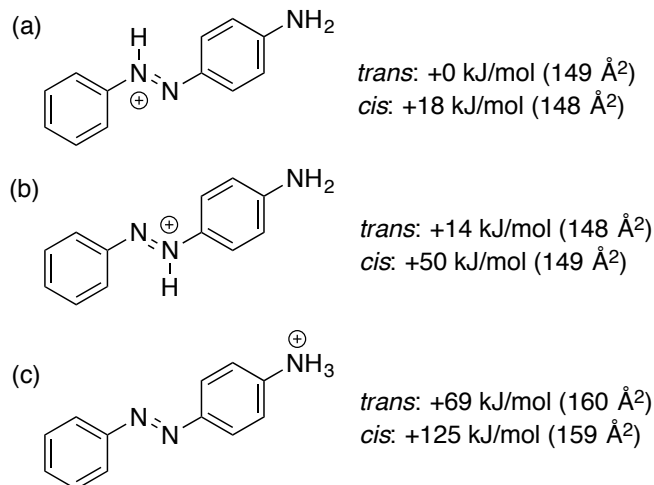


Figure 3.6: Structures of *trans*-NH₂ABH⁺ protomers. Energies calculated at the DLPNO-CCSD(T)/cc-pVTZ// ω B97X-D/6-311+G(2df,p) level of theory are given relative to the energy of the *trans*-(a) protomer. Calculated collision cross sections with N₂ are given in parentheses.

Calculations conducted at the DLPNO-CCSD(T)/cc-pVTZ// ω B97X-D/6-311+G(2df,p) level of theory identified the isomers shown in Figure 3.6. For the *trans* isomers, protonation on the azo N-atom most distant from the amino-substituted ring (*trans*-(a)) is preferred over protonation on the other azo N atom (*trans*-(b)) by 14 kJ/mol, whereas the isomer with the proton located on the amino nitrogen atom (*trans*-(c)) lies 69 kJ/mol higher in energy. The energetic ordering of the *cis* protomers parallels that of the *trans* protomers. The *cis*-(a) protomer is more stable than the *cis*-(b) and *cis*-(c) protomers by 32 kJ/mol and 107 kJ/mol, respectively, and is 18 kJ/mol less stable than the *trans*-(a) protomer. Given the relative energies of the various isomers one might expect that *trans*-(a) should be the predominant gas-phase protomer. On the basis of calculated collision cross sections, given in Figure 3.6, one would predict only a small difference between the arrival times of the four *cis*- and *trans*- isomers of protomers (a) and (b), with the *trans* and *cis* isomers of protomer (c) having significantly longer arrival times. As for ABH⁺, the calculated collision cross sections for the azo-protonated NH₂ABH⁺ isomers are slightly larger than the measured cross sections, suggesting that an azo-protonated *trans*-NH₂ABH⁺ protomer is the observed species.

To connect the PISA spectrum shown in Figure 3.7b to one of the two azo-protomers of *trans*-NH₂ABH⁺, we consider the vertical excitation energies for each protomer calculated at the EOM-CC2/aug-cc-pVDZ level of theory (Table 3.2). First, the anilinium-like protomer (c) can be excluded, as only the optically-dark S₁ state lies in the visible, with the bright S₂ state occurring in the UV as for neutral azobenzene.³⁷ Protomers (a) and (b) are both predicted to have bright S₁ ← S₀ transitions in the visible centred at 441 and 498 nm, respectively. Protomer (a) is

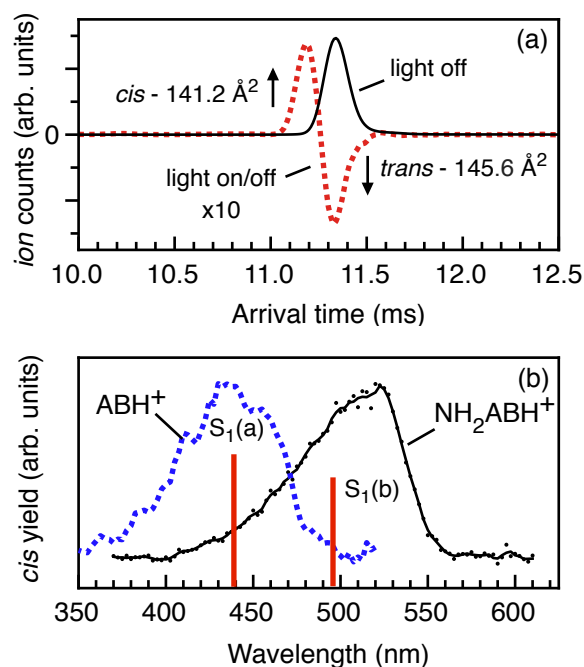


Figure 3.7: (a) ATDs of *trans*-NH₂ABH⁺ with the light-off ATD (black) and the difference in the light-on and light-off arrival time distributions at 515 nm (dashed red curve). Collision cross sections are given with an uncertainty of ± 1 Å² (*trans*) and ± 1.5 Å² (*cis*). The depletion and enhancement signals balance to within 5% proving that photoisomerization is the dominant process at this wavelength. (b) PISA spectrum of *trans*-NH₂ABH⁺. Red lines indicate wavelengths and intensities of vertical S₁ ← S₀ transitions of protomers (a) and (b) (see Figure 3.6) calculated at the EOM-CC2/aug-cc-pVDZ level. For comparison, the PISA spectrum of ABH⁺ is shown as a blue dotted curve.

calculated to be 14 kJ/mol more stable than protomer (b) and should therefore be the dominant form. However, the vertical excitation energy for protomer (b) better matches the experimental band maximum. Given that the CC2 method has a mean absolute deviation of 0.32 eV for VEEs in typical heteroarene compounds with a maximum deviation of 1.5 eV,³⁴² the calculated vertical excitation energies do not provide grounds for a definite spectral assignment. It is of course possible that protomers (a) and (b) both contribute to the PISA spectrum, in which case their relative contributions could possibly be distinguished through hole burning experiments.

The main band in the PISA spectrum of NH₂ABH⁺ is red-shifted by 90 nm with respect to the corresponding band of ABH⁺ (525 nm versus 435 nm) and has a steeper band onset (Figure 3.5). The spectral shift can be attributed to the *para* electron-donating amino group in NH₂ABH⁺ increasing electron density in the delocalized π -system relative to ABH⁺, and consequently increasing the energy of the HOMO and reducing the HOMO-LUMO gap. These differences are consistent with trends derived from the PD spectra for ABH⁺ and NMe₂ABH⁺ reported by Feráud *et al.*⁵⁸ In summary, the PISA spectra show that a combination of protonation and *para*-substitution with an electron-donating group shifts the absorption of the *trans*-NH₂ABH⁺

Table 3.2: Vertical excitation energies [eV (nm)] and oscillator strengths for *trans*-NH₂ABH⁺ protomers calculated at the EOM-CC2/aug-cc-pVDZ level of theory. The experimental value is listed at the bottom.

Protomer	LUMO←HOMO		LUMO←HOMO-1		LUMO←HOMO-2	
	S ₁ ← S ₀	<i>f</i>	S ₂ ← S ₀	<i>f</i>	S ₃ ← S ₀	<i>f</i>
(a)	2.8 (441)	1.31	3.8 (330)	0.01	4.2 (298)	0.01
(b)	2.5 (498)	1.18	3.7 (338)	0.01	3.9 (316)	0.02
(c)	2.7 (460)	0.00	3.8 (324)	0.82	4.0 (313)	0.06
Exp.	2.36 (525)					

cation into the green region of the spectrum, while the molecule still retains the *trans*-to-*cis* isomerization required for its use as a molecular photoswitch.

3.5 Conclusions

Photoisomerisation action (PISA) spectra measured for *trans*-ABH⁺ and *trans*-NH₂ABH⁺ in the visible region exhibit a single photoisomerization band assigned in both cases as the $\pi\pi^*$ S₁ ← S₀ transition. The NH₂ABH⁺ spectrum has a maximum at 525 nm, which is red-shifted from the ABH⁺ spectrum maximum at 435 nm due to stabilization of the HOMO by the electron-donating amino group. No photoisomerization response was discernible for the S₂ ← S₀ or S₃ ← S₀ transitions of ABH⁺ or NH₂ABH⁺, similar to the situation for the higher $\pi\pi^*$ transitions of neutral *trans*-azobenzene.³⁷ Overall, the PISA spectra are consistent with previously reported PD spectra of ABH⁺ and NMe₂ABH⁺, although the bands are broader due to the higher temperature in the drift tube (close to 300 K) compared to the cryogenic ion trap used for the PD measurements (40 K).⁵⁸ Perhaps most significantly we have shown that protonation of azobenzenes leads to a significant red-shift in their absorption maxima in the gas phase while retaining the *trans* to *cis* isomerization response required for their application as photoswitch molecules. Ultimately, the results demonstrate that ion mobility spectrometry coupled with laser spectroscopy is a useful strategy for investigating the photoswitching behaviour of isolated protonated azobenzenes.

Chapter 4

Linkage photoisomerization of an isolated ruthenium sulfoxide complex

Introduction to Chapter 4

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4.1 Abstract

Ruthenium sulfoxide complexes undergo thermally-reversible linkage isomerization of sulfoxide ligands from S- to O-bound in response to light. Here, we report photoisomerization action spectra for a ruthenium bis-sulfoxide molecular photoswitch, $[\text{Ru}(\text{bpy})_2(\text{bpSO})]^{2+}$, providing the first direct evidence for photoisomerization of a transition metal complex in the gas phase. The linkage isomers are separated and isolated in a tandem drift tube ion mobility spectrometer and exposed to tunable laser radiation provoking photoisomerization. Direct switching of the S,S-isomer to the O,O-isomer following absorption of a single photon is the predominant isomerization pathway in the gas phase, unlike in solution, where stepwise isomerization is observed with each sulfoxide ligand switching in turn. The change in isomerization dynamics is attributed to rapid vibrational quenching that suppresses isomerization in solution. Supporting electronic structure calculations predict the wavelengths and intensities of the peaks in the photoisomerization action spectra of the S,S- and S,O-isomers, indicating that they correspond to metal-to-ligand charge transfer (MLCT) and ligand-centered $\pi\pi^*$ transitions.

4.2 Introduction

Photochromic molecules reversibly switch from one state to another in response to light, converting photonic energy into the internal molecular energy required for molecular rearrangement.⁵ Photochromic molecules have been proposed for use as light-activated molecular switches for applications that include photopharmacology, light-harvesting, energy storage, and for non-linear optical materials.^{14,355–358}

Over the last two decades, a range of photochromic ruthenium complexes have been developed, exploiting light-induced linkage isomerization of sulfoxide ligands on a ruthenium polypyridyl core.^{32,80,85,359} In solution, these complexes have photoisomerization quantum yields up to 0.79 with thermal half-lives extending to several hours or longer.^{360,361} Density functional theory (DFT) calculations suggest isomerization is initiated on an excited ³MLCT (metal-to-ligand charge transfer) surface and then proceeds along surfaces with predominantly MC (metal centered) character in a non-adiabatic manner.^{82,86} Spectroscopic measurements show that the ³MLCT surface is present throughout the isomerization, and imply strong mixing between this surface and the MC surface, which is formally Ru-S σ^* (antibonding) in nature.^{360,361} Direct comparison of theoretical predictions with experimental data is often difficult due to strong solvent perturbation of excited state energy levels in ruthenium polypyridyl complexes.¹⁹⁹ Moreover, even simple ruthenium polypyridyls display complex photochemistry which underpins their roles as photosensitizers in dye-sensitized solar cells and as photopharmacological agents.^{362,363}

In a step towards characterizing the inherent (solvent-free) photochemistry of a ruthenium-based photoswitch molecule, we have probed the photoisomerization of the ruthenium bis-

sulfoxide complex $[\text{Ru}(\text{bpy})_2(\text{bpSO})]^{2+}$ ($\text{Ru}(\text{bpSO})$), where bpy = 2,2'-bipyridine, bpSO = 1,2-bis(phenylsulfinyl)ethane) in the gas phase. As shown in Figure 4.1, the $\text{Ru}(\text{bpSO})$ complex has three stable linkage isomers, as each of the two sulfoxide groups can be either S- or O-bound, giving S,S-, S,O-, and O,O- $\text{Ru}(\text{bpSO})$ isomers. Earlier studies on the S,S-isomer in solution have shown two photons are required to reach the O,O-isomer; exposing the S,S-isomer solution to 355 nm light produces the S,O-isomer, and subsequent 400 nm irradiation yields the O,O-isomer.³⁶¹ No direct isomerization from the S,S- to the O,O-isomer occurs. In contrast, we demonstrate that in the gas phase, a single photon can generate the O,O-isomer directly from the S,S-isomer with minor formation of the S,O-isomer. This direct conversion has been previously observed in the related $[\text{Ru}(\text{bpy})_2(\text{OSSO})]^{2+}$ ($\text{Ru}(\text{OSSO})$, OSSO = dimethylbis(methylsulfinylmethyl)silane) and $[\text{Ru}(\text{bpy})_2(\text{F-bpSO})]^{2+}$ ($\text{Ru}(\text{F-bpSO})$, F-bpSO = 1,2-bis(2-fluorophenylsulfinyl)ethane) complexes in solution, where double isomerization was proposed to be facilitated by low barriers on the excited-state triplet manifold leading to rapid quasi-statistical equilibration before non-adiabatic relaxation to the ground state.³⁶⁴ Results from the present study suggest that solvation affects isomerization dynamics in these systems and that gas-phase investigations can provide key insight into the intrinsic photochemistry of transition metal complexes.

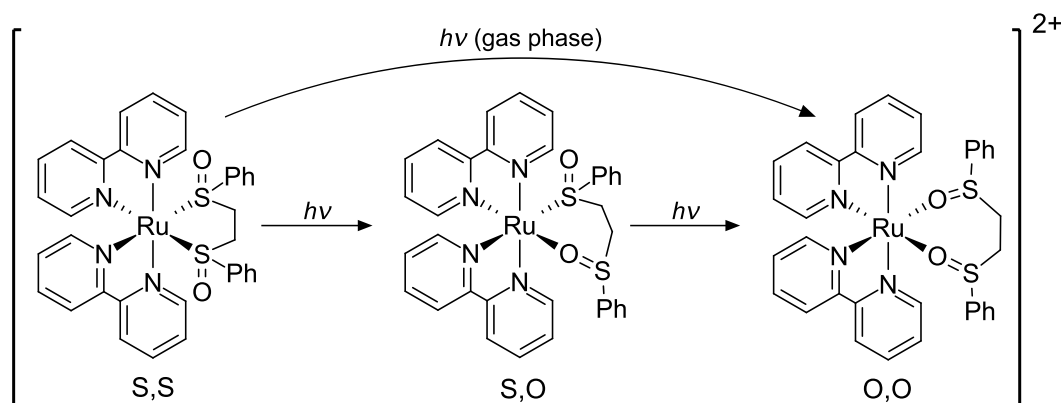


Figure 4.1: Photoinduced linkage isomerization in the $\text{Ru}(\text{bpSO})$ complex. Stepwise isomerization from the S,S- to the S,O- and O,O-isomers is observed in solution, whereas direct isomerization from the S,S- to the O,O-bound-isomer is the predominant process in the gas phase.

The present investigation complements previous gas-phase spectroscopic investigations of ruthenium complexes, which have mainly focused on ruthenium polypyridyl complexes such as the prototypical photosensitizer $[\text{Ru}(\text{bpy})_3]^{2+}$, which has been extensively studied in solution.^{73,74} In pioneering work, Posey and coworkers obtained an electronic spectrum of $[\text{Ru}(\text{bpy})_3]^{2+}$ in the gas phase observing a progressive red shift in MLCT bands with increasing microsolvation.^{104,198,199} More recently, photodissociation action spectra have been recorded for ruthenium bipyridyl complexes in a range of oxidation states.^{365–367} However, these earlier studies employed techniques that were not suited to following structural changes such as isomerization. To our knowledge, the present study reports the first observation of the photoisomerization of a

transition metal complex in the gas phase.

4.3 Methods

4.3.1 Experimental procedure

The photoisomerization of Ru(bpSO) was investigated using a purpose-built tandem ion mobility-mass spectrometer coupled with a tunable optical parametric oscillator (OPO) system. The experimental apparatus has been described previously.^{217,218} Electrosprayed ions from a 10^{-4} M solution of S,S-Ru(bpSO) in acetonitrile were injected as 100 μ s pulses at 40 Hz into a drift tube ion mobility stage, where the ions were separated spatially and temporally on the basis of their drift mobility in 6 Torr N₂ buffer gas with an applied electric field of ≈ 40 V/cm. The separated isomers then passed through a quadrupole mass filter and were detected using a channeltron electron multiplier. The arrival time distribution (ATD) of the ions was built up by plotting the ion signal as a function of arrival time at the detector. In order to measure photoisomerization action (PISA) spectra, the isomer of interest was selected using a pulsed electrostatic ion gate halfway along the drift tube. Immediately after the ion gate, alternate ion packets were exposed to the output of a pulsed UV-visible OPO (EKSPLA NT342B, 20 Hz, <0.35 mJ/cm⁻² per pulse), generating laser-off and laser-on ATDs. The effect of light on the ions is manifested in the difference between the laser-on and laser-off ATDs. The photoisomerization action spectrum was generated by plotting the photoisomer yield as a function of OPO wavelength.

Isomerically pure S,S-Ru(bpSO) was synthesized according to a previously-published procedure and its isomeric purity confirmed using UV-vis and NMR spectroscopy.³⁶¹ The S,O-Ru(bpSO) and O,O-Ru(bpSO) ions were generated by either UV irradiation of the S,S-isomer in solution or by ion activation in the first RF ion funnel, as described below. Experiments were performed in the dark to avoid isomerization in solution prior to electrospraying.

4.3.2 Computational procedure

Supporting electronic structure calculations were performed using a combined density functional theory (DFT) and *ab initio* approach. Geometries and harmonic frequencies were optimized at the TPSS-D3(BJ)/def2-TZVP level of theory.^{290,345,368,369} Single point energies were then calculated at the DLPNO-CCSD(T)/def2-TZVP level.^{337,338} Vertical excitation energy calculations to simulate absorption spectra were performed at the PBE0/def2-TZVP and NEVPT2(14,13)/def2-TZVP levels of theory — further details are given in Section 7.2.^{345,368,370} All electronic structure calculations were performed using the ORCA 4.0 program package.^{320,321}

4.4 Results and discussion

First, arrival time distributions (ATDs) of electrosprayed Ru(bpSO) were gathered operating the instrument as a single ion mobility drift tube under different ion source conditions; resulting ATDs are shown in Figure 4.2. A clear dependence on the source conditions was found: a single peak with an arrival time of 10.72 ms was observed with a low radio-frequency (RF) drive voltage on the source ion funnel (Figure 4.2a), whereas two additional slower peaks with arrival times of 10.99 and 11.20 ms were observed when the RF drive voltage was increased (Figure 4.2b). As the electrosprayed solution consisted purely of the S,S-isomer, the fastest isomer can be confidently assigned to S,S-Ru(bpSO). Exposure of the S,S-Ru(bpSO) isomers in solution to UV light prior to electrospraying and with a low RF drive voltage yielded the ATD shown in Figure 4.2c, where three later peaks are observed, in addition to the S,S-Ru(bpSO) peak. The slower two isomers in Figure 4.2b with arrival times of 10.99 and 11.20 ms are assigned to the S,O-Ru(bpSO) and O,O-Ru(bpSO) isomers, respectively, on the basis of prior studies³⁶¹ which found that upon exposure to UV light S,S-Ru(bpSO) in solution yields S,O-Ru(bpSO) and O,O-Ru(bpSO) isomers. These assignments are also consistent with the appearance of S,O-Ru(bpSO) and O,O-Ru(bpSO) at higher RF drive voltages, as electronic structure calculations indicate that these isomers lie significantly higher in energy than the S,S-Ru(bpSO) isomer (by 1800–2500 and 4200–4400 cm^{-1} for S,O-Ru(bpSO) and O,O-Ru(bpSO), respectively; Table 7.5).^{321,337,338} As discussed below, PISA spectra of the S,S- and S,O-isomers are consistent with their condensed-phase absorption spectra, further supporting the ATD peak assignments.

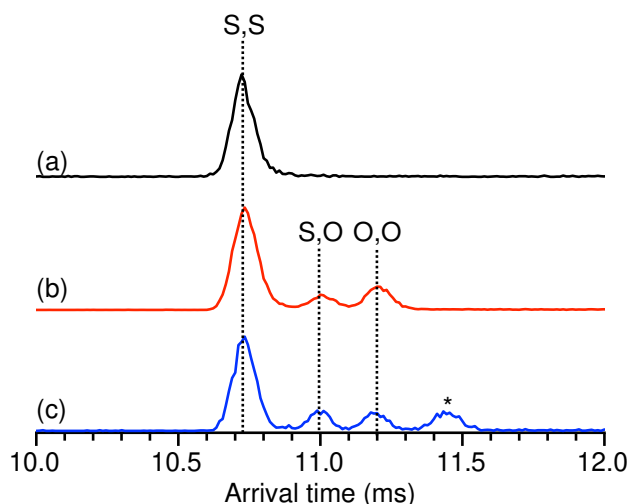


Figure 4.2: Arrival time distributions for electrosprayed solutions of pure S,S-Ru(bpSO). (a) Low RF drive voltage for the source ion funnel. (b) High RF drive voltage for the source ion funnel. (c) Exposure of the solution to 360 nm light and low RF drive voltage on the source ion funnel. The peak labelled with an asterisk corresponds to a Ru(bpSO)-MeCN adduct that traverses the drift region intact and then dissociates to yield bare Ru(bpSO) in the exit region of the drift region prior to mass selection.

Next, the effect of light on the gas-phase S,S-Ru(bpSO) ions was investigated by exposing

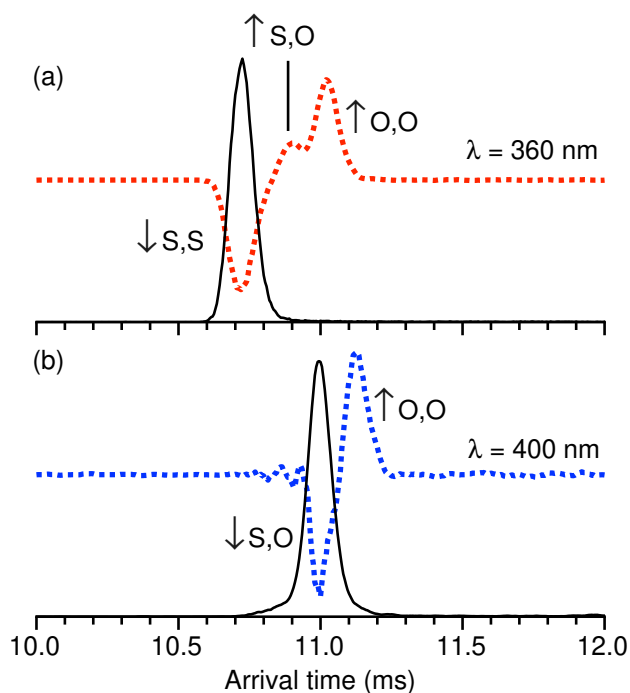


Figure 4.3: Example light-on/light-off difference ATDs for (a) S,S-Ru(bpSO) gathered at 360 nm (red) and (b) S,O-Ru(bpSO) at 400 nm (blue) superimposed over the light-off ATDs (black). In each case, the difference ATD was generated by subtracting the light-off ATD from the light-on ATD.

them to tunable radiation from the OPO (following selection with the electrostatic ion gate). As shown in Figure 4.3a, two slower isomers are formed from S,S-Ru(bpSO) at 360 nm (near the band maximum of the condensed-phase MLCT transition). Plotting the yield of these photoproducts as a function of wavelength produced the PISA spectrum shown in Figure 4.4. Two distinct bands are apparent with maxima at 345 nm ($29,400\text{ cm}^{-1}$) and at 310 nm ($32,350\text{ cm}^{-1}$). No wavelength or power dependence was observed in the photoisomerization branching ratio (Figures 7.3 and 7.4) and so the PISA spectrum corresponds to the sum of the S,O- and O,O-Ru(bpSO) isomer yields. The lower energy band peaking at 345 nm is close to the analogous band maximum in solution at 335 nm ($29,850\text{ cm}^{-1}$), which has been assigned to a MLCT transition from the ruthenium center to the bipyridyl ligands.³⁶¹ Similarly, the higher energy band peaking at 310 nm is close to the band assigned to bipyridyl-localized $\pi\pi^*$ transitions for S,S-Ru(bpSO) in solution (319 nm, $31,350\text{ cm}^{-1}$).³⁶¹ It was not possible to measure below 290 nm due to background signal caused by photoionization of trace contaminants in the drift region. Overall, the gas-phase PISA spectrum is similar to the absorption spectrum of S,S-Ru(bpSO) in solution,³⁶¹ reinforcing assignment of the earliest ATD peak in Figure 4.2 to the S,S-Ru(bpSO) isomer.

In order to confirm band assignments, excited state calculations were performed using time-dependent density functional theory (TDDFT, details in Section 7.2).^{290,336,345,368} The TDDFT-simulated spectrum is shown below the experimental PISA spectrum in Figure 4.4,

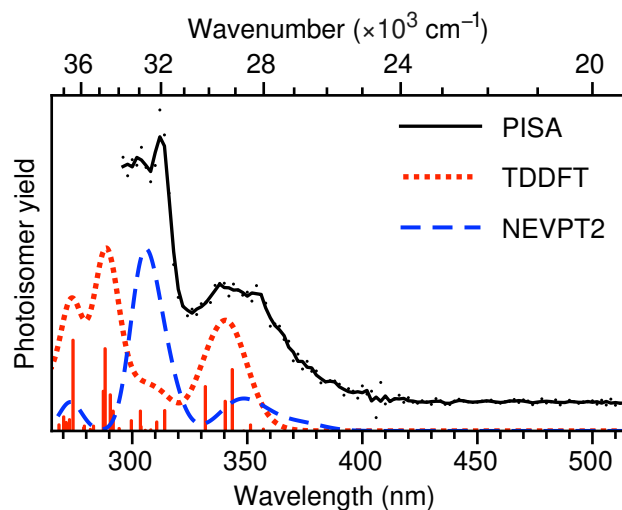


Figure 4.4: Gas-phase PISA spectrum for S,S-Ru(bpSO) corresponding to aggregate S,O- and O,O-Ru(bpSO) yields as a function of wavelength (black) and calculated TDDFT absorption spectrum (red dotted). The calculated NEVPT2 absorption spectrum is plotted for reference (blue dashed, further details in Section 7.2).

along with a spectrum generated using multireference NEVPT2 theory to confirm that TDDFT provides at least a qualitatively correct description for the present system (see Section 7.2 for computational details).³⁷⁰ As shown in Figure 4.4, the TDDFT calculations predict two major absorption bands for S,S-Ru(bpSO) at 340 nm ($29,440\text{ cm}^{-1}$) and 290 nm ($34,640\text{ cm}^{-1}$). The calculated electronic character of the transitions agrees well with previous assignments,³⁶¹ with the low energy transition at 340 nm corresponding to MLCT associated mainly with the bipyridyl ligands with a minor component connected with the bpSO phenyl rings, and the higher energy transition at 290 nm corresponding to bipyridyl-centered $\pi\pi^*$ transitions. Kohn-Sham orbitals responsible for the calculated transitions are depicted in Table 7.4.

The NEVPT2 calculations are able to treat MLCT excited states accurately.³⁷¹ The discrepancy of $<1000\text{ cm}^{-1}$ between the TDDFT and NEVPT2 calculations for the MLCT bands suggests that TDDFT performs reasonably at least for this system (vertical excitation energies are tabulated along with a quantitative discussion of relative performances in Section 7.2). There is poorer agreement between TDDFT and NEVPT2 calculations for the higher energy band, with a difference of around 30 nm ($\sim 3000\text{ cm}^{-1}$). For reasons of economy, and because the TDDFT approach provides a reasonable qualitative description of the excited state character, for the S,O-Ru(bpSO) isomer only the TDDFT approach was used.

Given that $\pi\pi^*$ excitation leads to isomerization, there must be efficient conversion from the initial $^1\pi\pi^*$ state to the $^3\text{MLCT}$ state from which photoisomerization occurs.⁸² However, it is unclear whether internal conversion (IC) to a $^1\text{MLCT}$ state precedes intersystem crossing (ISC), which is known to occur on a femtosecond timescale in ruthenium polypyridyls,^{73,74} or whether

rapid ISC yields a $^3\pi\pi^*$ state before internal conversion to the $^3\text{MLCT}$ manifold. To elucidate the mechanism, we are presently performing wavelength-dependent transient absorption studies to probe the dynamics following $\pi\pi^*$ excitation.

Significantly, whereas direct isomerization is observed from the S,S-isomer to the O,O-isomer in the gas phase, stepwise isomerization *via* the S,O-isomer was observed in solution.³⁶¹ Power dependence studies (Figure 7.3) indicate that in the gas phase the branching ratio between the S,O- and O,O-Ru(bpSO) photoproducts does not depend on light fluence at both band maxima, and therefore both single and double isomerizations are triggered by absorption of a single photon. Likewise, the branching ratio for formation of S,O-Ru(bpSO) and O,O-Ru(bpSO) does not vary with wavelength (Figure 7.4). Together, these results suggest that the thermal reversion barriers are sufficiently high on the ground state potential energy surface to prevent back-isomerization of the S,O and O,O-isomers under the present experimental conditions.³⁷² Support for this interpretation comes from DFT calculations on the closely related $[\text{Ru}(\text{bpy})_2(\text{dmsO})_2]^{2+}$ complex (dmsO = dimethyl sulfoxide), which predict that barriers to thermal reversion on the ground state potential energy surface are ≥ 85 kJ/mol, compared to barriers on the triplet MC and MLCT surfaces of ≈ 20 kJ/mol.⁸⁶ Although the present system differs from this model system through presence of a chelating linker between the sulfoxides, the electronic character of the triplet state surfaces should be comparable.

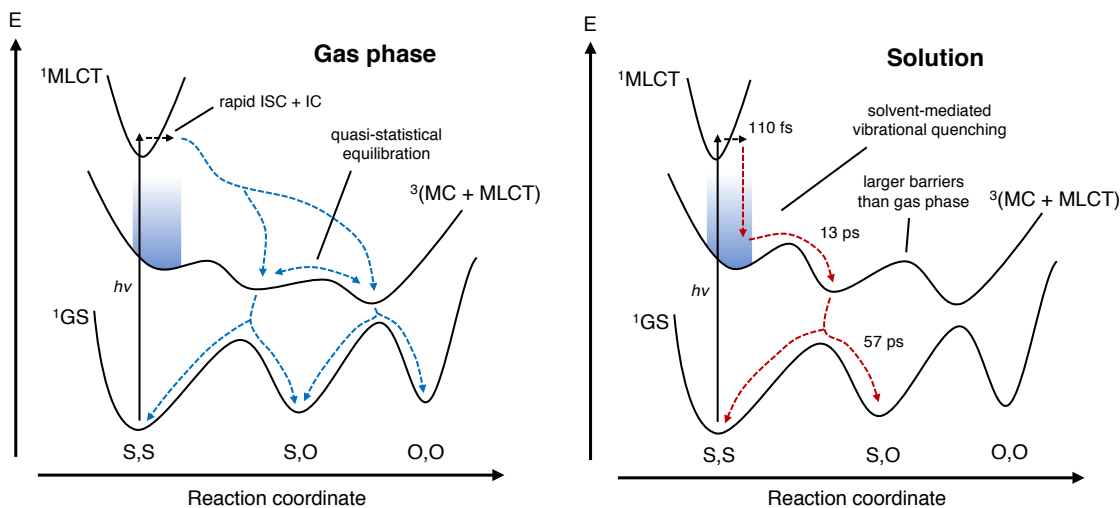


Figure 4.5: Schematic potential energy surfaces for S,S-Ru(bpSO) isomerization in the gas phase (left) and in solution (right). Relaxation timescales in solution are taken from King *et al.*³⁶¹

Schematic potential energy surfaces (PESs) shown in Figure 4.5 illustrate the proposed mechanisms for isomerization dynamics for S,S-Ru(bpSO) in the gas phase and in solution. They are based on the experimental results from the present study and from King *et al.*,³⁶¹ as well as DFT calculations of Boggio-Pasqua and coworkers on the closely related $[\text{Ru}(\text{bpy})_2(\text{dmsO})_2]^{2+}$ complex.^{82,86} Although the previous theoretical work considered the MC and MLCT states to

be distinct, we discuss the lowest triplet surface in Ru(bpSO) as a mixed surface with varying MC and MLCT character for the following reasons: the two states are similar in energy,⁸⁶ multi-configurational character has been predicted in low-lying triplet states of ruthenium coordination complexes,³⁷³ and Kohn-Sham density functional theory has difficulty describing such mixed states.³⁷⁴ Future computational studies using appropriate multireference methods may be able to elucidate the electronic character of the triplet surface. Note that for simplicity the reaction coordinate is depicted as being one-dimensional, whereas in reality a multidimensional reaction coordinate likely exists along which direct S,S- to O,O- isomerization can occur.

The different rates of vibrational quenching in solution and in the gas phase are probably responsible for the difference in isomerization dynamics. Specifically, vibrational energy transfer to the solvent (i.e. thermalization) is usually complete on a sub-200 ps timescale, although the rate is solvent dependent. This timescale is on the same order as the timescale for isomerization of the present system in solution,³⁶¹ as illustrated in Figure 4.5. Assuming S,S- to O,O-Ru(bpSO) photoisomerization occurs on the excited state surface in a sequential manner, vibrational energy transfer to solvent causes excited state molecules in the S,O geometry to be trapped before they can further isomerize to O,O-Ru(bpSO). In contrast, vibrational energy quenching in the present gas-phase experiment is much slower, taking place through ion-molecule collisions occurring every few nanoseconds, with hundreds of collisions required to thermalize the ions. Gas-phase ions therefore remain vibrationally energized on the excited-state surface, allowing the excited state population to sequentially propagate through the transient S,O-isomer to form O,O-Ru(bpSO). This is consistent with studies on Ru(OSSO) and Ru(F-bpSO) in solution, which suggested a mixture of S,O- and O,O-isomers results from a quasi-statistical equilibrium on the ³MLCT surface, where interconversion between excited-state isomers is rapid compared to deactivation to the singlet electronic ground state.³⁶⁴

The direct S,S- to O,O-Ru(bpSO) isomerization in the gas phase might also be related to the strength of the Ru-S bond on the triplet surface. As discussed above and illustrated in Figure 4.5, the triplet states of Ru(bpSO) are thought to have mixed MC and MLCT character. MC character is formally antibonding towards the sulfoxide ligands and should induce weaker Ru-S bonds, while MLCT character should have no significant impact on the Ru-S bond strength. One might expect that the MC character of the lowest triplet state should be enhanced relative to MLCT character in the gas phase because there is no solvent to stabilize the separated charges associated with MLCT.³⁷⁵ For these reasons we hypothesize that weaker Ru-S bonds on the isomerizing triplet surface in the gas phase should promote formation of the S,O- and O,O-Ru(bpSO) isomers, while suppressing recovery of S,S-Ru(bpSO). We note that this hypothesis is consistent with previous solution studies considering changes in Ru-S bond strengths following incorporation of electron-withdrawing groups (EWGs) into the bpSO ligand, such as fluorination of the phenyl groups or insertion of a silane group in the alkyl linker.³⁶⁴ EWGs decrease the electron donating

character of the sulfur atoms, leading to longer, weaker Ru-S bonds, allowing direct S,S- to O,O-Ru(bpSO) conversion.³⁶⁴

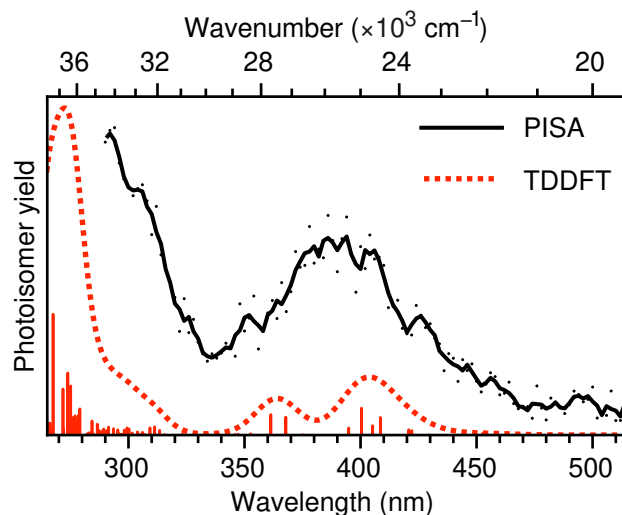


Figure 4.6: Gas-phase PISA spectrum of S,O-Ru(bpSO) corresponding to O,O-Ru(bpSO) yield as a function of wavelength (black) and the TDDFT-simulated absorption spectrum (red). Further details of the calculation are given in Section 7.2.

The S,O-isomer also undergoes photoisomerization in the gas phase. As shown in Figure 4.3b irradiation of isolated S,O-Ru(bpSO) yields a light-on/light-off difference ATD in which depletion of the S,O-Ru(bpSO) peak is matched by growth in a later peak with an arrival time consistent with O,O-Ru(bpSO). Notably, formation of the S,S-isomer was not observed. The lack of reverse photoisomerization is consistent with the PES presented in Figure 4.5, as the S,S-Ru(bpSO) isomer lies energetically uphill on the excited triplet surface, while barriers on ground-state singlet surface are sufficiently large to prevent thermal reversion before thermalization by buffer gas. The PISA spectrum, generated by monitoring the O,O-isomer yield as a function of wavelength, is plotted in Figure 4.6 along with a TDDFT-simulated spectrum. The PISA spectrum exhibits a lower energy band with a maximum at ≈ 395 nm (MLCT), and another band with an onset at 330 nm and increasing in intensity to shorter wavelength (bpy-centered $\pi\pi^*$ transition). Over the measured region, the gas-phase PISA spectrum is again very similar to the solution absorption spectrum.³⁶¹

Finally, no photoisomerization was observed for O,O-Ru(bpSO) over the 295–600 nm range and hence no PISA spectrum could be measured. This is consistent with solution studies that demonstrated thermal but not photochemical reversion from O,O-Ru(bpSO) to S,O-Ru(bpSO) and S,S-Ru(bpSO).³⁶¹ Although we have no estimate for the barrier height for reversion in this system, the barriers must be sufficiently large that thermal isomerization rate following return to the ground electronic state is much less than $k \ 10^8\text{--}10^9 \text{ s}^{-1}$, the collision rate of ions with the buffer gas molecules in our experiment. As with S,O-Ru(bpSO), these observations are consistent

with the proposed potential energy surfaces.

4.5 Conclusions

We report gas-phase photoisomerization action spectra for the S,S- and S,O-Ru(bpSO) photo-switching complexes. The two isomers display ligand-centered electronic transitions in the UV and MLCT transitions in the visible, which both lead to photoisomerization via a triplet surface. In the gas phase, absorption of a single photon induces isomerization directly from the S,S- to the O,O-bound isomer, whereas in solution double linkage isomerization is likely suppressed by a combination of solvent-mediated vibrational quenching and increased Ru-S bond strength in the excited state. We aim to continue these gas-phase studies by examining the roles of the chelate linker and of metal-centered excited states in the photoisomerization of metal-sulfoxide complexes, in similar ruthenium complexes and in analogous osmium compounds.^{364,376,377} Comparison of condensed and gas-phase PISA spectra should allow us to directly assess the effect of solvation on photoisomerization.⁹² Additionally, studies of osmium polypyridyl complexes, which, due to strong spin-orbit coupling, have bright $T_1 \leftarrow S_0$ transitions, may allow direct optical access to the $^3\text{MLCT}$ surface and provide an alternative route to initiating photoisomerization.³⁷⁸

Chapter 5

Electronic spectroscopy of the ferrocenium cation

Introduction to Chapter 5

This chapter is based on a manuscript in preparation for submission to a peer-reviewed journal as “Scholz, M. S., Muller, G., Bartlett, N. I., Jacovella, U., Bieske, E. J. *Electronic spectrum of the ferrocenium cation*”. It has been adapted to fit within the thesis and does not represent the final form of the manuscript to be submitted. The supplementary information which will accompany the manuscript is reproduced in Section 7.3.

Chapter begins here

5.1 Abstract

Gas-phase electronic spectra of the ferrocenium cation (FeCp_2^+ , $\text{Cp} = \eta^5\text{-cyclopentadienyl}$) are obtained over the $15600\text{--}18000\text{ cm}^{-1}$ (640–560 nm) range by monitoring photodissociation of the $\text{FeCp}_2^+\text{-Ne}$ and $\text{FeCp}_2^+\text{-Ar}$ complexes in a custom-built tandem mass spectrometer. Bands corresponding to the origin of the $\tilde{\text{B}}^2\text{E}'_1 \leftarrow \tilde{\text{X}}^2\text{E}'_2$ charge-transfer transition are observed at 15830 cm^{-1} ($\text{FeCp}_2^+\text{-Ne}$) and 15809 cm^{-1} ($\text{FeCp}_2^+\text{-Ar}$). The spectra exhibit vibronic structure with the dominant progression of 285 cm^{-1} corresponding to the totally-symmetric ring-metal-ring stretching mode ν_4 . Weak bands in the electronic spectra may arise from vibronic coupling or spin-orbit coupling. Coupled cluster and multireference calculations are performed to estimate the relative energies and splitting of the low-lying electronic states in FeCp_2^+ , which are found to be in reasonable agreement with the experiment values.

5.2 Introduction

The ferrocene molecule (FeCp_2 , $\text{Cp} = \eta^5\text{-cyclopentadienyl}$), the prototypical organometallic complex, was first reported in 1951.^{109,110,379–381} Its orange color is due to a parity-forbidden dd^* transition at around 23000 cm^{-1} ; the first allowed transition occurs in the UV at approximately 50000 cm^{-1} .^{382,383} In the gas phase, FeCp_2 possesses an eclipsed D_{5h} geometry in its $^1\text{A}'_1$ ground state, as confirmed by gas electron diffraction experiments and electronic structure calculations.^{111,384–386} In crystalline lattices, FeCp_2 is highly disordered at room temperature but at low temperatures assumes an eclipsed geometry.^{112,387} Recent studies indicate conversion between the staggered and eclipsed conformations of FeCp_2 has a barrier on the order of several hundred cm^{-1} .^{113,388}

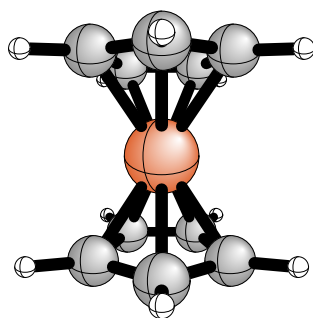


Figure 5.1: Geometry of the ferrocenium (FeCp_2^+) cation showing the sandwich structure. Orange, grey, and white spheres represent iron, carbon, and hydrogen atoms, respectively.

Ferrocenium (FeCp_2^+ , Figure 5.1) is the monocationic oxidized form of ferrocene. The $\text{FeCp}_2/\text{FeCp}_2^+$ one-electron redox couple is the standard reference couple for non-aqueous electrochemistry and has been proposed for use as the active electrolyte in dye-sensitized solar cells.^{116,123} The rate of electron transfer depends strongly on energy level overlap between donor

and acceptor, and so knowledge of energy levels is crucial in quantitative electrochemistry and when designing solar cell dyes.³⁸⁹ Additionally, as electronic transitions tend to occur in the UV-visible range, they may overlap with absorption by the active dyes, reducing the efficiency of the solar cells.

Vibronically-resolved electronic spectra provide insights into the electronic ground and excited states of molecular ions such as FeCp_2^+ . The first vibronically-resolved electronic spectrum of FeCp_2^+ cations over the $\tilde{\text{B}}^2\text{E}'_1 \leftarrow \tilde{\text{X}}^2\text{E}'_2$ band system, recorded by Gray and coworkers in 10 M LiCl aqueous solutions,¹³⁷ exhibited vibrational structure beginning at 16200 cm^{-1} with a spacing of 280 cm^{-1} , that was assigned to a totally-symmetric ring-metal stretching mode. This band system is associated with ligand-to-metal charge transfer (LMCT), from the π -systems of the Cp ligands to a d_{xy/x^2-y^2} orbital on the Fe atom. A better resolved spectrum recorded for $[\text{Fe}(\text{C}_5\text{H}_5)_2]\text{PF}_6$ powders at 4.2 K was reported by the same group several years later.¹³⁸ The spectrum exhibited a band around 200 cm^{-1} above the origin transition, that was assigned as a transition to the upper spin-orbit component of the $\tilde{\text{B}}^2\text{E}'_1$ state. Subsequent absorption and magnetic circular dichroism (MCD) spectra, measured by Rowe and McCaffery in poly(methacrylic acid) matrices at 9 K,³⁹⁰ suggested the energy gap between the two $\tilde{\text{B}}^2\text{E}'_1$ spin-orbit components is rather on the order of 500 cm^{-1} .

Spectra obtained for FeCp_2^+ cations in cryogenic rare gas matrices featured significantly improved resolution and narrower linewidths. Electronic MCD spectra, recorded in 15 K Ar matrices by Taylor,³⁹¹ suggested the vibronic band at $+500\text{ cm}^{-1}$ with negative molar ellipticity instead corresponds to the ν_{16} ring-tilting normal mode, the mode predominantly responsible for Jahn-Teller (JT) activity in the $\tilde{\text{X}}^2\text{E}'_2$ state. The best resolved electronic spectrum of FeCp_2^+ to date was recorded by Maier and coworkers for FeCp_2^+ deposited in a 6 K Ne matrix.¹³⁹ A progression in the ring-metal stretching mode was clearly apparent along with peaks associated with several other totally-symmetric modes. The peaks in the dominant vibronic progression appeared to be split into multiplets, likely due to the existence of FeCp_2^+ in different lattice sites. Additionally, a progression beginning at $+502\text{ cm}^{-1}$ with spacing of around 300 cm^{-1} was proposed to correspond to combination levels of the ring-metal stretch with a low frequency bending vibration.

Here, we report electronic spectra of $\text{FeCp}_2^+\text{-Ne}$ and $\text{FeCp}_2^+\text{-Ar}$ in the gas phase, recorded using REPD spectroscopy. The dissociation energy of the attached rare gas atom is far less than the energy of the electronic transition, such that dissociation is likely to occur following either a non-radiative transition or fluorescence to a vibrationally excited level in the ground electronic state. The only previous gas-phase spectrum of FeCp_2^+ was recorded using multiphoton dissociation in an ICR mass spectrometer.²³⁶ Because absorption of several photons was required to dissociate the FeCp_2^+ cations, which were at room temperature, the spectral resolution was poor and it was not possible to resolve the vibronic structure apparent in the neon matrix spectrum or

the 4.2 K powder spectrum. The present spectra feature vibronic linewidths of $\approx 15 \text{ cm}^{-1}$, less than for the Ne matrix spectrum. Interpretation of the spectra is supported by multireference *ab initio* calculations, providing new insights into the low-lying electronic states of the FeCp_2^+ ion.

5.3 Electronic structure of ferrocenium

We begin by discussing the electronic structure of the FeCp_2^+ cation, which has been the focus of several theoretical and experimental studies.^{138,391–397} The energy level scheme is illustrated in Figure 5.2. The five iron 3d orbitals (with orbital angular momentum $\ell = 2$) are degenerate for the free Fe^{3+} ion, but are split by the ligand field depending on their orbital angular momentum projection m_ℓ . Under D_{5h} symmetry, the $m_\ell = 0$ orbital transforms as a'_1 (d_{z^2}), the $m_\ell = \pm 1$ orbitals as e'_1 (d_{xz} and d_{yz}), and the $m_\ell = \pm 2$ orbitals as e'_2 (d_{xy} and $d_{x^2-y^2}$), with the energetic ordering $e'_2 \approx a'_1 < e'_1$. The FeCp_2^+ ion has a low spin d^5 configuration and exists as a doublet with spin angular momentum projection $m_s = \pm 1/2$. Through spin-orbit coupling (SOC), the spin and orbital angular momenta are coupled and the total angular momentum projection is given by $m_j = m_l \pm m_s$. The e'_2 orbitals split into $|m_j = \pm 5/2\rangle$ and $|m_j = \pm 3/2\rangle$ substates, and similarly the e'_1 orbitals divide into $|m_j = \pm 3/2\rangle$ and $|m_j = \pm 1/2\rangle$ substates. Since the SOC-induced splitting is relatively small ($< 1000 \text{ cm}^{-1}$), the close-lying $|m_j = \pm 5/2\rangle$ and $|m_j = \pm 3/2\rangle$ spin-orbit components of the e'_2 state interact and further separate via a pseudo-Jahn-Teller (PJT) effect, thereby lowering the molecular symmetry from D_{5h} . The e'_1 $|m_j = \pm 3/2\rangle$ and $|m_j = \pm 1/2\rangle$ components are expected to interact in a similar manner. The a'_1 orbital has $m_\ell = 0$ and so gives a

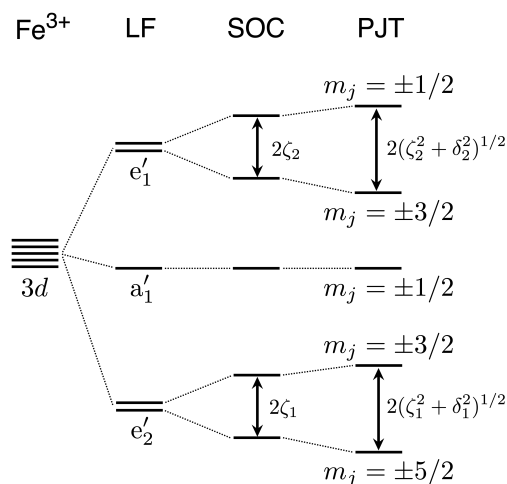


Figure 5.2: Energy level diagram for FeCp_2^+ , illustrating splitting of the five degenerate 3d orbitals of the free Fe^{3+} ion by the ligand field (LF), spin-orbit coupling (SOC), and a pseudo-Jahn-Teller (PJT) effect. ζ is the SOC constant and δ is a parameter describing distortion away from D_{5h} symmetry. The subscripts 1 and 2 indicate values in the $\tilde{X}^2E'_2$ and $\tilde{B}^2E'_1$ states, respectively.

$|m_j = \pm 1/2\rangle$ state. Finally, each electronic state is further split into a pair of Kramers doublets, which are degenerate in the absence of an applied magnetic field.

Molecular orbital theory and Koopmans' theorem suggest the FeCp_2^+ ground state should be of ${}^2A'_1$ symmetry, where FeCp_2 is ionized from the d_{z^2} -like a'_1 orbital. However, a series of early electron paramagnetic resonance (EPR) spectroscopy and magnetic susceptibility studies established a ${}^2E'_2$ ground state for the ferrocenium cation in condensed phases.^{383,392} The equatorial and axial components of the g -tensor were shown to be highly anisotropic and incompatible with an ${}^2A'_1$ ground state. Rapid spin-lattice relaxation leading to line broadening when above cryogenic temperatures was attributed to the presence of the $|m_j = \pm 3/2\rangle$ Kramers doublet a few hundred cm^{-1} above the $|m_j = \pm 5/2\rangle$ ground state.³⁹³ He(I) PE spectroscopy provided unambiguous evidence for the same ${}^2E'_2$ ground state in the gas phase.³⁹⁸ PE and Raman spectroscopy experiments suggested a state of ${}^2A'_1$ symmetry lies between 200–3000 cm^{-1} above the electronic ground state,^{398–400} agreeing with temperature-dependent magnetic susceptibility measurements that indicated thermal population of an electronically-excited state with lower magnetic moment occurs at higher temperatures.¹³⁷ Inelastic neutron scattering (INS) measurements reveal an electric dipole-forbidden transition at 510 cm^{-1} carrying intensity consistent with magnetic excitation to the excited $|m_j = \pm 3/2\rangle$ Kramers doublet of the $\tilde{X}^2E'_2$ ground state.³⁹⁶

In this study, we probe electronic transitions between the $\tilde{X}^2E'_2$ and $\tilde{B}^2E'_1$ states of FeCp_2^+ . The $|m_j = \pm 5/2\rangle$ $\tilde{X}^2E'_2$ state is reasonably certain to be the ground state, on the basis of the condensed-phase magnetic and EPR data, the gas-phase PE spectra, and electronic structure calculations reported below. Under the assumption m_j is a good quantum number, only transitions to the $|m_j = \pm 3/2\rangle$ component of the $\tilde{B}^2E'_1$ state should be allowed from the $|m_j = \pm 5/2\rangle$ ground state. Note that the electronic structure calculations described later in Section 5.5 are spin-free and describe SOC only perturbatively. In the absence of SOC, the e'_2 components interact via a JT effect instead, and the coupling is described within this framework in the resulting discussion. We use D_{5h} labelling even when the molecular symmetry is reduced to C_{2v} , due to the established convention of using the high-symmetry D_{5h} or D_{5d} nomenclature in the metallocene literature.

5.4 Experimental methods

Electronic spectra reported in this work were gathered using a custom-built tandem mass spectrometer, which has been described previously and in detail in Section 2.1.2.^{264,401} Briefly, molecular cations and their complexes with rare gas atoms were generated by passing neon or argon carrier gas over a heated ferrocene sample at ≈ 375 K. The gas mixture passed through a pulsed valve (General Valve, Series 9, 200 μs opening time) before expanding supersonically into the source chamber. The expanding gas mixture was bombarded with electrons near the

nozzle orifice to create FeCp_2^+ which clustered with Ne or Ar atoms. The ions were extracted through a skimmer, after which the tagged complexes ($\text{FeCp}_2^+\text{-Ne}$, $\text{FeCp}_2^+\text{-Ar}$) were mass-selected with a quadrupole mass filter and deflected by a quadrupole bender into an octupole ion guide. Here, the ions were overlapped with the output of a tunable OPO (EKSPLA NT342B, bandwidth $\sim 5\text{ cm}^{-1}$, pulse length 3–5 ns). Resonant excitation of $\text{FeCp}_2^+\text{-Ne}$ or $\text{FeCp}_2^+\text{-Ar}$ was detected by monitoring FeCp_2^+ photofragment ions, which were mass-selected by a second quadrupole mass filter. The photodissociation action spectra were built up by plotting the photodissociation yield normalized by OPO power as a function of photon energy. The OPO wavelength was calibrated using a commercial wavemeter (High Finesse/Ångstrom LSA). The rotational temperature of the FeCp_2^+ ions was estimated to be $\approx 40\text{ K}$ on the basis of rotationally-resolved spectra of ions generated using similar ion sources.²⁵³

5.5 Computational methods

Ground-state geometry optimizations and harmonic frequency calculations were performed at the DFT PBE0-D3(BJ)/def2-TZVPP level of theory.^{309,311,402} Stability analyses were performed at all stationary points to confirm convergence to the lowest electronic state of the given symmetry had been obtained. The “SuperFine” integration grid was employed with very tight convergence criteria to account for numerical noise on the flat potential energy surfaces.

Vertical excitation energies were computed using the ionization potential variant of the equation-of-motion coupled cluster method with single and double excitations (EOM-IP-CCSD) with the quadruple- ζ def2-QZVP basis set.^{285,402} These calculations employed the DLPNO, resolution-of-the-identity (RI) and the chain-of-spheres exchange approximations.^{403,404} The error introduced by the DLPNO approximation with the TightPNO cutoffs is around 400 cm^{-1} , far smaller than the uncertainty of the underlying EOM-IP-CCSD method.⁴⁰³

Refined vertical excitation energies and oscillator strengths for the low-lying electronic states were calculated by multistate second-order perturbation theory using a state-averaged CASSCF reference wavefunction (i.e. MS-CASPT2).^{278,282} The reference wavefunction employed an active space encompassing the 5 $3d$ orbitals on Fe and 4 pairs of correlating π and π^* orbitals from the Cp ligands (13 electrons in 13 orbitals).³⁹⁷ The default IPEA shift of 0.25 a.u. was used. The calculations were performed using C_{2v} symmetry, the point group of the $\tilde{X}^2E'_2$ ground state. State averaging was employed separately over three states of A_1 symmetry (i.e. one each of the $\tilde{X}^2E'_2$ and $\tilde{B}^2E'_1$ components and the $\tilde{A}^2A'_1$ state) and two states of B_1 symmetry (the other of the two substates for both the $\tilde{X}^2E'_2$ and $\tilde{B}^2E'_1$ states) before the wavefunctions were mixed and oscillator strengths calculated using the spin-orbit restricted active space state interaction (SO-RASSI) method.⁴⁰⁵ The ANO-RCC basis (quadruple- ζ contraction to $7s6p4d3f2g1h$ for Fe, $5s4p3d2f1g$ for C, and $4s3p2d1f$ for H) was used along with the DKH2 scalar relativistic

correction.^{406–408} The Cholesky decomposition and RI approximations were employed to decrease computational cost.⁴⁰⁹

DFT calculations were performed with the GAUSSIAN 16 program,³¹⁹ whereas wavefunction theory calculations were run using the MOLCAS 8.1 and ORCA 4.2 packages.^{321,323} Further information on the theoretical methods employed is available in Section 2.2.1.

5.6 Results and discussion

5.6.1 Electronic structure calculations

We first discuss the electronic structure calculations, starting with prediction of electronic state ordering in FeCp_2^+ . DFT calculations indicate the ground state is doubly degenerate with ${}^2E'_2$ electronic symmetry, consistent with the discussion in Section 5.3. Geometry optimization gives minima with C_{2v} structures, indicating symmetry lowering from D_{5h} due to the JT effect. The C_{2v} geometry agrees with the results of Pierloot.³⁹⁷ However, D_{5h} geometries have also been reported for the $\tilde{X}^2E'_2$ state of FeCp_2^+ .^{139,410} It is likely these calculations had converged to the low-lying $\tilde{A}^2A'_1$ state, which has a non-degenerate electronic configuration and is likely to retain a D_{5h} geometry. Stability analysis of the ${}^2A'_1$ wavefunction at the D_{5h} geometry suggests that it lies higher in energy than the ${}^2E'_2$ wavefunction even at the D_{5h} geometry. Furthermore, harmonic frequencies calculated at the $\tilde{A}^2A'_1$ minimum-energy geometry match the previously reported wavenumbers for a D_{5h} ground-state geometry.¹³⁹ The harmonic frequencies for the $\tilde{X}^2E'_2$ and $\tilde{A}^2A'_1$ states are compiled in Table 5.1.

Further calculations using the EOM-IP-CCSD and MS-CASPT2 methods were performed to confirm the ground state of FeCp_2^+ has ${}^2E'_2$ electronic symmetry and to establish the energetic ordering of the lowest excited states. The results are summarized in Table 5.2. First, we employed the EOM-IP-CCSD method at the DFT-optimized ${}^2E'_2$ minimum-energy geometry using neutral ferrocene to provide the reference wavefunction. Predicting a vertical ionization energy of 53700 cm^{-1} , 800 cm^{-1} above the experimental value,⁴¹¹ EOM-IP-CCSD should provide accurate energetic data for the low-lying electronic states of FeCp_2^+ that can be reached through single ionization from ferrocene. The EOM-IP-CCSD calculations confirm the lowest electronic state is of ${}^2E'_2$ electronic symmetry, and place the ${}^2A'_1$ state 6200 cm^{-1} above the ground electronic state, in line with photoelectron spectra.³⁹⁸ The lowest allowed transition is expected to be to the LMCT $\tilde{B}^2E'_1$ state around 18600 cm^{-1} above the ground state, consistent with previous experimental and theoretical results.¹³⁹

The doubly-degenerate $\tilde{X}^2E'_2$ and $\tilde{B}^2E'_1$ states are calculated to be split by 1050 and 30 cm^{-1} , respectively, with the EOM-IP-CCSD method. The splitting at this level of theory contains only the contribution from the JT distortion of the ground state geometry while neglecting SOC entirely. MS-CASPT2 calculations were performed in order to refine the state energies, to estimate

Table 5.1: Computed frequencies for FeCp_2^+ in the $\tilde{X}^2E'_2$ and $\tilde{A}^2A'_1$ states at the DFT PBE0-D3(BJ)/def2-TZVPP level of theory. All vibrational frequencies are unscaled. Modes are ordered according to the Mulliken convention in the D_{5h} point group; the ordering and correlating irreducible representations upon descent to C_{2v} are also provided. The coordinate system in C_{2v} is such that the xz -plane is approximately parallel to the Cp ligands and bisects the Fe atom.

Mode no.		Irrep.		$\tilde{\nu}_{\text{calc}} (\text{cm}^{-1})$		Description
D_{5h}	C_{2v}	D_{5h}	C_{2v}	$\tilde{X}^2E'_2$	$\tilde{A}^2A'_1$	
ν_1	ν_1	a'_1	a_1	3278	3280	C-H stretch
ν_2	ν_6	a'_1	a_1	1159	1149	Cp ring breathing
ν_3	ν_{11}	a'_1	a_1	875	859	C-H out-of-plane bend
ν_4	ν_{15}	a'_1	a_1	302	309	Cp-Fe-Cp symmetric stretch
ν_5	ν_{21}	a''_1	a_2	1293	1286	C-H in-plane bend
ν_6	ν_{29}	a''_1	a_2	23	32	Cp-Fe-Cp torsion
ν_7	ν_{34}	a'_2	b_1	1294	1287	C-H in-plane bend
ν_8	ν_{43}	a''_2	b_2	3277	3279	C-H stretch
ν_9	ν_{48}	a''_2	b_2	1160	1151	Cp ring breathing
ν_{10}	ν_{53}	a''_2	b_2	878	860	C-H out-of-plane bend
ν_{11}	ν_{56}	a''_2	b_2	511	494	Cp-Fe-Cp antisymmetric stretch
ν_{12}	ν_2/ν_{30}	e'_1	a_1/b_1	3267/3267	3270	C-H stretch
ν_{13}	ν_4/ν_{32}	e'_1	a_1/b_1	1476/1470	1462	C-H in-plane bend
ν_{14}	ν_8/ν_{36}	e'_1	a_1/b_1	1045/1037	1035	C-H in-plane bend
ν_{15}	ν_{12}/ν_{39}	e'_1	a_1/b_1	847/859	880	C-H out-of-plane bend
ν_{16}	ν_{14}/ν_{41}	e'_1	a_1/b_1	447/226	452	Cp-Fe-Cp rock
ν_{17}	ν_{16}/ν_{42}	e'_1	a_1/b_1	149/22	121	Cp-Fe-Cp bend
ν_{18}	ν_{17}/ν_{44}	e''_1	a_2/b_2	3267/3266	3269	C-H stretch
ν_{19}	ν_{19}/ν_{46}	e''_1	a_2/b_2	1476/1477	1464	C-H in-plane bend
ν_{20}	ν_{23}/ν_{50}	e''_1	a_2/b_2	1040/1040	1033	C-H in-plane bend
ν_{21}	ν_{25}/ν_{52}	e''_1	a_2/b_2	888/890	870	C-H out-of-plane bend
ν_{22}	ν_{28}/ν_{57}	e''_1	a_2/b_2	364/363	370	Cp-Fe-Cp slide
ν_{23}	ν_3/ν_{31}	e'_2	a_1/b_1	3252/3256	3261	C-H stretch
ν_{24}	ν_5/ν_{33}	e'_2	a_1/b_1	1411/1422	1419	Cp in-plane deformation
ν_{25}	ν_7/ν_{35}	e'_2	a_1/b_1	1082/1095	1104	C-H in-plane bend
ν_{26}	ν_9/ν_{37}	e'_2	a_1/b_1	975/968	973	C-H out-of-plane bend
ν_{27}	ν_{10}/ν_{38}	e'_2	a_1/b_1	911/894	880	Cp in-plane deformation
ν_{28}	ν_{13}/ν_{40}	e'_2	a_1/b_1	620/611	615	Cp out-of-plane deformation
ν_{29}	ν_{18}/ν_{45}	e''_2	a_2/b_2	3255/3252	3257	C-H stretch
ν_{30}	ν_{20}/ν_{47}	e''_2	a_2/b_2	1407/1397	1387	Cp in-plane deformation
ν_{31}	ν_{22}/ν_{49}	e''_2	a_2/b_2	1085/1081	1074	C-H in-plane bend
ν_{32}	ν_{24}/ν_{51}	e''_2	a_2/b_2	964/975	955	C-H out-of-plane bend
ν_{33}	ν_{26}/ν_{54}	e''_2	a_2/b_2	837/839	840	Cp in-plane deformation
ν_{34}	ν_{27}/ν_{55}	e''_2	a_2/b_2	602/597	602	Cp out-of-plane deformation

the magnitude of SOC-induced splitting, and to predict the oscillator strengths for electronic transitions arising from the $\tilde{X}^2E'_2$ ground state. The MS-CASPT2 energetics agree with the EOM-IP-CCSD values, with the major discrepancy being the energy of the $\tilde{A}^2A'_1$ state. The ground state splitting is estimated to be 1570 cm^{-1} , 520 cm^{-1} larger than the spin-free EOM-IP-CCSD value. This value is also somewhat larger than the 510 cm^{-1} value extracted from INS measurements,³⁹⁶ although the gas-phase energies are not directly comparable to the experimental data for crystalline samples. Furthermore, the $\tilde{B}^2E'_1$ state is predicted to be split by almost 800 cm^{-1} with transitions to either of the spin-orbit sublevels carrying roughly equal oscillator strengths of $f \approx 7 \times 10^{-3}$. Following the $\Delta m_j = 0, \pm 1$ selection rule, the $|m_j = \pm 1/2\rangle \leftarrow |m_j = \pm 5/2\rangle$ transition should be forbidden in D_{5h} symmetry. The symmetry reduction in the $\tilde{X}^2E'_2$ ground state predicted from DFT geometry optimization is likely responsible for the relaxation of selection rules, such that the transition becomes weakly allowed. The JT effect in d^5 metallocenes is generally dynamic and weak, such that the equilibrium (vibrationally-averaged) geometry retains D_{5h} symmetry,³⁹⁵ and it is unclear to what degree the experimentally-sampled geometry will resemble the C_{2v} minimum-energy geometry.

Table 5.2: Calculated vertical excitation energies ($\tilde{\nu}$, cm^{-1}) at the EOM-IP-CCSD/def2-QZVP and MS-CASPT2/ANO-RCC-QZVP levels of theory for FeCp_2^+ . Angular momentum projection (m_j) quantum numbers are given assuming D_{5h} symmetry. Oscillator strengths (f , a.u.) were computed using SO-RASSI from the MS-CASPT2 wavefunctions.

State	m_j	$\tilde{\nu}$ (EOM-IP-CCSD)	$\tilde{\nu}$ (MS-CASPT2)	f
$\tilde{X}^2E'_2$	$\pm 5/2$	0	0	
$\tilde{X}^2E'_2$	$\pm 3/2$	1050	1570	2.3×10^{-5}
$\tilde{A}^2A'_1$	$\pm 1/2$	6190	3720	3.8×10^{-6}
$\tilde{B}^2E'_1$	$\pm 3/2$	18560	19640	7.5×10^{-3}
$\tilde{B}^2E'_1$	$\pm 1/2$	18590	20400	6.6×10^{-3}

The $\tilde{A}^2A'_1 \leftarrow \tilde{X}^2E'_2$ transition is expected to occur in the infrared region outside the spectral range investigated in this study. The $\tilde{A}^2A'_1$ state is predicted using MS-CASPT2 to lie 3720 cm^{-1} above the $\tilde{X}^2E'_2$ state (vertically), while PE spectroscopy indicates the gap is around 2800 cm^{-1} . Furthermore, the $\tilde{A}^2A'_1 \leftarrow \tilde{X}^2E'_2$ transition is formally forbidden by symmetry in the D_{5h} point group. The MS-CASPT2 calculations in Table 5.2 show that, assuming a weak distortion due to the JT effect but without explicit treatment of vibronic coupling, excitation to the $\tilde{A}^2A'_1$ state should be three orders of magnitude weaker than to the $\tilde{B}^2E'_1$ state.

The $\tilde{B}^2E'_1 \leftarrow \tilde{X}^2E'_2$ transition corresponds to LMCT from the Cp ligands to the metal center. The donor Cp ligand π -electrons are strongly bonding, whereas the acceptor Fe d_{xy} and $d_{x^2-y^2}$ orbitals contribute minimally to bonding. Therefore, the LMCT transition is likely to cause weakening of the Fe-Cp bonding with corresponding elongation of the metal-ligand bonds. As a result, extended progressions in ν_4 , the normal mode associated with a totally-symmetric

Cp-Fe-Cp stretching motion and illustrated in Figure 5.3, are the major vibrational features in electronic spectra of FeCp_2^+ recorded in crystals, powders, and matrices.^{138,139,390} The gas-phase spectrum is also expected to be dominated by progressions in ν_4 .

It was not feasible to compute the excited-state geometry or vibrational frequencies in order to simulate a vibronic spectrum under the Franck-Condon approximation. Because the $\tilde{\text{B}}^2\text{E}'_1$ state transforms as the same irreducible representations ($\text{A}_1 \oplus \text{B}_1$) as the $\tilde{\text{X}}^2\text{E}'_2$ ground state upon reduction to C_{2v} , it was not possible to converge DFT calculations to the $\tilde{\text{B}}^2\text{E}'_1$ state by means of symmetry restrictions. Time-dependent density functional theory gave relative energies and oscillator strengths inconsistent with the CASPT2 calculations, suggesting the single-reference method is insufficient for describing the excited electronic states. The large active space required at the CASSCF level (13 electrons in 13 orbitals) renders harmonic frequency calculations impracticable. A recent investigation of substituted ferrocenium complexes indicates smaller active spaces can describe the important electronic structure if sufficient correlation is added to the CASSCF reference.¹³³ Recently developed analytical CASPT2 gradients may provide a means for calculating frequencies for excited states of FeCp_2^+ as a prerequisite for Franck-Condon simulations of the vibronic spectrum.^{412,413}

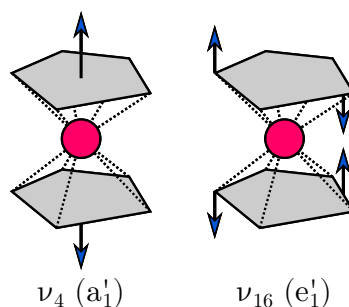


Figure 5.3: Illustration of the ν_4 and ν_{16} normal modes in FeCp_2^+ .

Having established a picture of the low-lying electronic states of FeCp_2^+ , we turn to a discussion of geometric parameters of FeCp_2^+ and its charged complexes with neon and argon. As previously mentioned, the $\tilde{\text{X}}^2\text{E}'_2$ minimum-energy geometry possesses C_{2v} symmetry, in accordance with symmetry lowering *via* the JT effect. The major distortion arises from a rocking motion involving the metal center and both Cp rings, with two edges from the eclipsed Cp ligands brought closer together and two vertices pushed apart. The shortest and longest C-C distances between the two Cp ligands at the C_{2v} minimum-energy geometry are 3.34 Å and 3.52 Å, respectively. The normal mode associated with this rocking motion, and hence the JT distortion, is ν_{16} of e'_1 symmetry, depicted in Figure 5.3. The symmetry of the JT-active mode is consistent with the prediction from group theory and its assignment to ν_{16} is in line with previous investigations of d^5 metallocenes.^{391,395} The same investigations suggested the JT stabilization energy, conferred through distortion to a geometry of lower symmetry, is likely lower than the

energy of a single quantum in ν_{16} in the $\tilde{X}^2E'_2$ state of FeCp_2^+ . A detailed investigation of the JT effect in FeCp_2^+ is outside the scope of this work, and so due to its likely small impact we proceed under the assumption the JT effect is dynamic and negligible in the ground state of FeCp_2^+ .

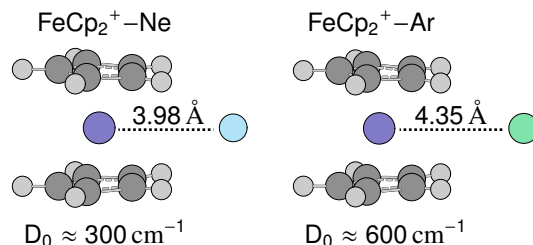


Figure 5.4: Optimized geometries and dissociation energies for the $\text{FeCp}_2^+\text{-Ne}$ and $\text{FeCp}_2^+\text{-Ar}$ cluster ions determined at the PBE0-D3(BJ)/def2-TZVPP level of theory.

Next, we briefly discuss the structures of the complexes of FeCp_2^+ with neon and with argon. In both cases, DFT geometry optimizations yielded only one stable geometry, with the rare gas atom in the equatorial plane between the Cp ligands; the optimized geometries are depicted in Figure 5.4. The rare gas atoms favor binding to FeCp_2^+ where the Cp edges come together. Attempts to find other binding modes in the $\tilde{X}^2E'_2$ ground state were unsuccessful, with all inputs yielding the structures shown in Figure 5.4. Binding of the rare gas atom along the D_5 axis represents a minimum in the $D_{5h} \tilde{A}^2A'_1$ excited state, and presumably such a structure might be stable in the $\tilde{X}^2E'_2$ ground state if a dynamic JT effect restores effective D_{5h} symmetry. $\text{FeCp}_2^+\text{-Ne}$ is more fragile than $\text{FeCp}_2^+\text{-Ar}$, with dissociation energies of around 300 cm^{-1} and 600 cm^{-1} , respectively, consistent with the lower polarizability of Ne compared to Ar. The $\text{FeCp}_2^+\text{-Ne}$ bond ($3.98 \text{ \AA}$, measured between the iron and neon atoms) is shorter than the $\text{FeCp}_2^+\text{-Ar}$ bond ($4.35 \text{ \AA}$), in line with the difference in atomic radii. We note that the equatorial binding of a rare gas atom to FeCp_2^+ removes the orbital degeneracy; however, the rare gas atom has a minor effect on the FeCp_2^+ geometry (generally $\Delta r < 0.002 \text{ \AA}$), and we assume the symmetry breaking effects induced by the rare gas atom are negligible.

5.6.2 Experimental results and discussion

The electronic spectra of the $\text{FeCp}_2^+\text{-Ne}$ and $\text{FeCp}_2^+\text{-Ar}$ complexes over the $15600\text{--}18000 \text{ cm}^{-1}$ ($640\text{--}560 \text{ nm}$) range, measured using REPD spectroscopy monitoring FeCp_2^+ photofragments, are shown in Figure 5.5. The binding energies of Ne and Ar are far less than the $\tilde{B}^2E'_1 \leftarrow \tilde{X}^2E'_2$ transition energy, such that in the absence of radiative decay the REPD spectrum likely resembles the absorption spectrum. Note that no FeCp^+ or Fe^+ photofragments were observed. Previous gas-phase multiphoton dissociation experiments performed in a room-temperature ICR mass spectrometer indicate that the lowest dissociation channel for FeCp_2^+ lies 40000 cm^{-1} above the ground state,²³⁶ far above the energy of a single photon in the present experiment. The $\text{FeCp}_2^+\text{-Ne}$ spectrum is sharp and well resolved, whereas the $\text{FeCp}_2^+\text{-Ar}$ spectrum displays broader bands

and a more congested vibronic structure. The origin transition of $\text{FeCp}_2^+-\text{Ne}$ lies at 15830 cm^{-1} , blue-shifted by approximately 20 cm^{-1} compared to the transition for FeCp_2^+ in a 6 K neon matrix (15810 cm^{-1}). The origin band of $\text{FeCp}_2^+-\text{Ar}$ is split into several peaks, with the lowest energy peak at 15809 cm^{-1} and the most intense peak at 15837 cm^{-1} . A similar multiplet structure was observed in the Ne matrix spectrum, albeit with the lowest energy band the most intense and with two weaker bands at $+25$ and $+63\text{ cm}^{-1}$.¹³⁹ Possibly, the multiplet structure is associated with a lowering of symmetry of the FeCp_2^+ cations induced by intermolecular perturbations between the ion and its rare gas tag or matrix; a brief discussion of this possibility is presented later. The vertical excitation energies, using the MS-CASPT2 and EOM-IP-CCSD theories and listed in Table 5.2, are in reasonable agreement with experiment. The $\tilde{\text{B}}^2\text{E}'_1 \leftarrow \tilde{\text{X}}^2\text{E}'_2$ transition is predicted to occur at 19640 cm^{-1} using MS-CASPT2, around 4000 cm^{-1} above the experimental value but in good agreement with the previous prediction of Maier and coworkers.¹³⁹ Presumably, the adiabatic excitation energy at the same level of theory would show better agreement with experiment, by accounting for geometric relaxation in the excited state.

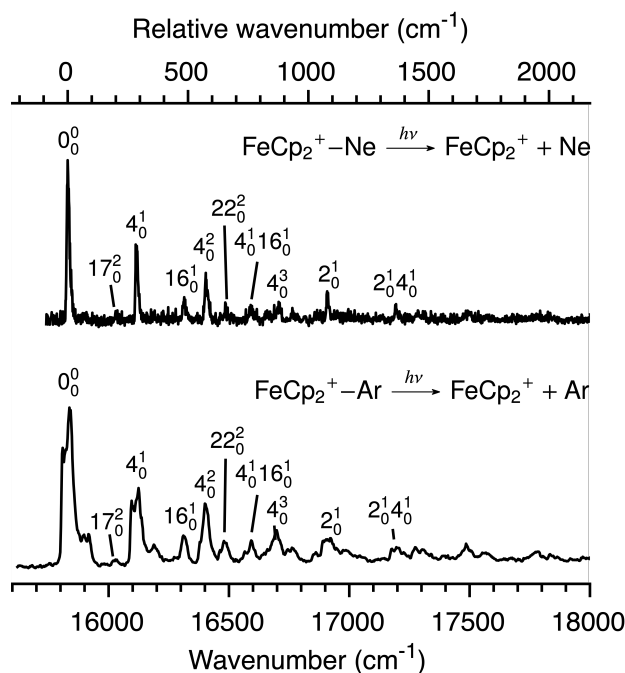


Figure 5.5: The REPD spectra of $\text{FeCp}_2^+-\text{Ne}$ (top) and $\text{FeCp}_2^+-\text{Ar}$ (bottom). The more intense vibronic bands are labelled. Peak wavenumbers and assignments are given in Table 5.3. A relative wavenumber axis is provided for the $\text{FeCp}_2^+-\text{Ne}$ spectrum; the $\text{FeCp}_2^+-\text{Ar}$ origin transition is displaced by -21 cm^{-1} along this axis.

Because the $\text{FeCp}_2^+-\text{Ne}$ electronic spectrum is simpler than the $\text{FeCp}_2^+-\text{Ar}$ spectrum, we discuss it first. The origin band is the most intense transition, indicating there is little change in geometry upon electronic excitation. The peak splitting observed in the Ne matrix spectrum, where bands are split into triplets, is absent in the $\text{FeCp}_2^+-\text{Ne}$ spectrum. This indicates the splitting

is not an intrinsic property of the FeCp_2^+ cation, but rather is associated with an interaction between FeCp_2^+ and the Ne matrix, and is perhaps due to occupation of different matrix sites. The vibronic structure is dominated by a progression spaced by $\sim 285 \text{ cm}^{-1}$ extending to at least three quanta, corresponding to the totally-symmetric ν_4 mode, the ring-metal-ring stretching vibration. The same progression is observed for electronic spectra of FeCp_2^+ in cryogenic matrices, single crystals, and powders.^{137–139,390,391} The FeCp_2^+ -Ne spectrum exhibits narrower bands than that of FeCp_2^+ in a Ne matrix, albeit with a lower signal-to-noise ratio.

Table 5.3: Vibronic band energies ($\tilde{\nu}$, cm^{-1}), relative positions ($\Delta\tilde{\nu}$, cm^{-1}), and assignments for transitions in the FeCp_2^+ -Ne and FeCp_2^+ -Ar electronic spectra.

FeCp_2^+ -Ne		FeCp_2^+ -Ar		Assignment
$\tilde{\nu}$	$\Delta\tilde{\nu}$	$\tilde{\nu}$	$\Delta\tilde{\nu}$	
15830	0	15809	0	0_0^0
-	-	15837	28	
-	-	15897	88	
16036	198	16029	220	17_0^2
16112	282	16096	287	4_0^1
-	-	16124	315	
-	-	16188	379	
16314	484	16311	502	16_0^1
16404	574	16400	591	4_0^2
16485	655	16479	670	22_0^2
16590	760	16593	784	$4_0^1 16_0^1$
16706	876	16699	890	4_0^3
16908	1078	16904	1095	2_0^1
17191	1361	17196	1387	$2_0^1 4_0^1$

Our assignments for the weaker features in the FeCp_2^+ -Ne spectrum generally mirror those for the Ne matrix spectrum.¹³⁹ After the progression in ν_4 , the next most intense bands lie at 16908 cm^{-1} ($+1078 \text{ cm}^{-1}$) and 17191 cm^{-1} ($+1361 \text{ cm}^{-1}$) and correspond to the 2_0^1 and $2_0^1 4_0^1$ transitions, respectively, where ν_2 is associated with totally-symmetric breathing of the Cp rings. Weaker features at 16485 cm^{-1} ($+655 \text{ cm}^{-1}$) and 16036 cm^{-1} ($+198 \text{ cm}^{-1}$) likely correspond to the 22_0^2 (a sliding motion of the Fe atom between the Cp ligands) and 17_0^2 (a bending motion along the Cp-Fe-Cp axis) transitions, respectively. The $\tilde{\text{B}}^2\text{E}'_1 \leftarrow \tilde{\text{X}}^2\text{E}'_2$ LMCT transition, as stated previously, is predicted to result in an elongation of the metal-ligand bonds, consistent with the experimental data. Charge transfer from the Cp π -systems is likely to weaken the carbon-carbon bonds of the aromatic ligands, explaining the Franck-Condon activity of the ν_2 Cp ring breathing mode, although it is much weaker than the dominant ν_4 mode.

We turn to discuss features in the spectrum which have challenged assignment in condensed-

phase spectra. The band at 16314 cm^{-1} ($+484\text{ cm}^{-1}$) has previously been assigned to either the 16_0^1 vibronic transition or to the origin transition of $\tilde{B}^2E'_1 |m_j = \pm 1/2\rangle$ substate.^{139,390,391} We prefer assignment of the $+484\text{ cm}^{-1}$ feature to the 16_0^1 transition, which was first proposed based on the sign of the band's molar ellipticity in a cryogenic MCD spectrum.³⁹¹ Excitation of single quanta of the non-totally-symmetric ν_{16} mode was asserted to arise from vibronic coupling *via* the JT effect in the ground state. Our DFT geometry optimizations indicate ν_{16} is the major contributor for JT distortion in the $\tilde{X}^2E'_2$ state, in line with group theoretical considerations.^{391,395} Anomalous intensity for the 16_0^1 vibronic transition, arising from the JT effect in the ground state,³⁹¹ is therefore plausible. A hitherto unassigned feature in the neon matrix spectrum at $+943\text{ cm}^{-1}$ can then be assigned to the 16_0^2 vibronic transition.¹³⁹ This band cannot be attributed to a single quantum of any other mode, at least on the basis of the ground-state vibrational frequencies in Table 5.1, nor can it be readily assigned to any transitions to the $\tilde{B}^2E'_1 |m_j = \pm 1/2\rangle$ substate.

The other plausible assignment of the $+484\text{ cm}^{-1}$ feature is to the $\tilde{B}^2E'_1 |m_j = \pm 1/2\rangle$ origin transition. Our electronic structure calculations predict the $\tilde{B}^2E'_1$ state to be split by 760 cm^{-1} due to SOC and structural distortion. We note that the origin transition to the $\tilde{B}^2E'_1 |m_j = \pm 1/2\rangle$ substate is also expected to have a negative molar ellipticity consistent with the MCD spectra.³⁹⁰ However, the transitions to the $|m_j = \pm 3/2\rangle$ and $|m_j = \pm 1/2\rangle$ substates are predicted by our MS-CASPT2 calculations to have similar oscillator strengths ($f = 7.5 \times 10^{-3}$ and 6.6×10^{-3} , respectively). In the $\text{FeCp}_2^+-\text{Ne}$ spectrum, the origin and $+484\text{ cm}^{-1}$ bands differ by an order of magnitude in intensity, at odds with the calculated oscillator strengths. No other bands carry sufficient intensity to be the $|m_j = \pm 1/2\rangle$ origin transition. Additionally, the band at $+943\text{ cm}^{-1}$ in the Ne matrix spectrum is difficult to reconcile with excitation of a single quantum of a vibration in the $|m_j = \pm 1/2\rangle$ substate.¹³⁹ It is possible that the approximately equal oscillator strengths for excitation to the $|m_j = \pm 3/2\rangle$ and $|m_j = \pm 1/2\rangle$ substates arise from artefactual symmetry breaking: the MS-CASPT2 calculations were performed in the C_{2v} minimum energy geometry, ignoring the JT effect and only perturbatively treating SOC. The two generally cannot be modelled as decoupled effects, as SOC is expected to quench the JT effect and vice versa.⁴¹⁴ Furthermore, SOC can modify the selection rules for which modes induce JT coupling.⁴¹⁵ Fully relativistic calculations are required to completely describe SOC and therefore any JT effect in FeCp_2^+ ,^{416,417} although such calculations are beyond the scope of this study. We hope the present spectra and interpretation provide a starting point for future theoretical investigations.

Another possibility is that the $+484\text{ cm}^{-1}$ band and the apparent progression in ν_4 built up on it are associated with a $\tilde{B}^2E'_1 (|m_j = \pm 1/2\rangle) \leftarrow \tilde{X}^2E'_2 (|m_j = \pm 3/2\rangle)$ transition, with excitation arising from the upper spin-orbit substate of the electronic ground state. However, the energy gap between the $\tilde{X}^2E'_2$ spin-orbit components is likely to be large enough ($500\text{--}1500\text{ cm}^{-1}$) that the upper level should not be significantly populated in the present experiment. The $+484\text{ cm}^{-1}$ band

has also been variously attributed to the $4_0^1 17_0^2$ combination transition and to the $|m_j = \pm 1/2\rangle$ 4_0^1 transition, with the latter assignment requiring that the $+198\text{ cm}^{-1}$ feature is associated with the origin to the $\tilde{B}^2E'_1 |m_j = \pm 1/2\rangle$ substate.^{138,139,390} The intensities of bands in the gas-phase spectra, however, are inconsistent with these assignments, as the intensities of a progression in ν_4 should follow the pattern for the dominant ν_4 progression built on the origin.

The FeCp_2^+ -Ar REPD spectrum is similar to the FeCp_2^+ -Ne spectrum, with the main vibronic structure due to a ν_4 progression spaced by $\sim 285\text{ cm}^{-1}$. Transitions to other Franck-Condon-allowed vibronic levels are also observed, as in the FeCp_2^+ -Ne spectrum. The bands in the FeCp_2^+ -Ar spectrum are significantly broader than the analogous bands obtained for FeCp_2^+ -Ne. Moreover, all bands display unresolved substructure, with each peak apparently divided into multiplets. The higher binding energy of Ar is perhaps partially responsible for the broad peaks in the FeCp_2^+ -Ar spectrum. The FeCp_2^+ chromophore in the charged complexes with Ar can have a higher internal energy before the complex dissociates, whereas the weaker bond between FeCp_2^+ and Ne mandates that the complex has a lower internal energy or else it will dissociate.

The cause of the peak splitting in the FeCp_2^+ -Ar spectrum is unclear. It is unlikely to be related to the specific electronic structure of the FeCp_2^+ -Ar complex. Rather, it is possible band splitting in the gas phase is associated with breaking of degeneracy, with the presence of Ar removing the degeneracy of the $\tilde{X}^2E'_2$ state and leading to separate transitions between split substates. It is plausible that the interaction of a single Ne atom is sufficiently weak that the degeneracy breaking is so small as to be unobservable, whereas Ar has an observable effect due to a stronger intermolecular interaction. Furthermore, interaction between FeCp_2^+ and rare gas atoms, either in the gas-phase complex or solid matrix, possibly increases the JT distortion of FeCp_2^+ in its $\tilde{X}^2E'_2$ ground state towards a static C_{2v} geometry, with argon likely to have a stronger effect than neon.³⁹⁴ Ultimately, explanation of the multiplet structure is not feasible with the current spectral resolution and the employed level of theory. In principle, visible-visible hole-burning spectra should help decide whether the band multiplets in the FeCp_2^+ -Ar spectrum arise from symmetry breaking or different binding sites for Ar (i.e. a gas-phase site effect). The small oscillator strength of the transition frustrated our attempts at such experiments.

5.7 Conclusions

In summary, we report the vibrationally-resolved spectrum for the $\tilde{B}^2E'_1 \leftarrow \tilde{X}^2E'_2$ transition of FeCp_2^+ , recorded using REPD spectroscopy of the weakly-bound FeCp_2^+ -Ne and FeCp_2^+ -Ar complexes. The origin of the transition lies at 15830 cm^{-1} for FeCp_2^+ -Ne and 15809 cm^{-1} for FeCp_2^+ -Ar. Vibronic progressions associated with the ν_4 totally-symmetric stretching mode with a spacing of around 285 cm^{-1} dominate the spectra, consistent with previous observations.^{138,139} Other Franck-Condon-allowed transitions are active, including excitation of a single quantum of

the totally-symmetric ν_2 mode, as well as transitions to levels with two quanta each of ν_{17} and ν_{22} . The spectrum of FeCp_2^+ measured as a complex with Ne exhibits the best spectral resolution to date, although the Ne matrix spectrum has a better signal-to-noise ratio.¹³⁹ Splitting of spectral features observed in the Ne matrix is not present in the FeCp_2^+ -Ne REPD spectrum, whereas the FeCp_2^+ -Ar spectrum displays broader peaks with unresolved substructure. A C_{2v} geometry is predicted for FeCp_2^+ in the $\tilde{X}^2E'_2$ ground state at the DFT PBE0-D3(BJ)/def2-TZVPP level of theory, which is consistent with geometric distortion along ν_{16} via the JT effect. A band around 484 cm^{-1} above the origin likely corresponds either to the forbidden 16_0^1 transition, which gains intensity through vibronic coupling associated with the JT effect, or to a transition to the higher-energy spin-orbit component of the $\tilde{B}^2E'_1$ state. We hope the present work serves as a starting point for high-resolution spectroscopic studies preferably of the bare FeCp_2^+ ion in the gas phase, as the rotational substructure of the vibronic bands may provide information on the structural dynamics and vibronic couplings at play in the fundamental FeCp_2^+ cation.

Supplementary material

See Section 7.3 for the optimized $\tilde{X}^2E'_2$ and $\tilde{A}^2A'_1$ geometries of FeCp_2^+ .

Acknowledgements

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Chapter 6

Vibronic coupling in the tropylium cation

Introduction to Chapter 6

This chapter presents a theoretical investigation into the electronic structure of the tropylium cation $C_7H_7^+$. The experimental spectrum was recorded by Dr. Ugo Jacovella and is reproduced here with his permission. The work described within this chapter will comprise part of a manuscript, currently in preparation for submission to a peer-reviewed journal.

Chapter begins here

6.1 Introduction

The tropylium molecular ion ($c\text{-C}_7\text{H}_7^+$, Tr^+) has been of chemical and physical interest since at least 1931, when Hückel predicted it to be unusually stable on account of being aromatic with 6 π -electrons.⁴¹⁸ The first synthesis of a Tr^+ compound, tropylium bromide, was reported in 1891,⁴¹⁹ but it was only around 60 years later that the aromatic nature of the Tr^+ ion was confirmed using vibrational spectroscopy.¹⁷¹ Its D_{7h} equilibrium geometry was determined based on the simplicity of its vibrational spectra, both in solution and in powders,^{420,421} and from its ^1H nuclear magnetic resonance (NMR) spectrum.⁴²²

Well-resolved gas-phase vibrational spectra of both Tr^+ and its fellow C_7H_7^+ isomer, benzylium (Bz^+), have been obtained by infrared photodissociation spectroscopy.^{154,155} The spectra provide unambiguous proof of their structures in the gas phase (sketched in Figure 6.1). The structural analysis has been supported by electronic structure calculations for both C_7H_7^+ isomers,^{154,155,163,165,423,424} which confirm the ground-state geometries of Tr^+ and Bz^+ have D_{7h} and C_{2v} symmetries, respectively.

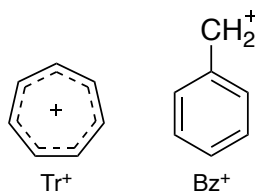


Figure 6.1: Skeletal structures for tropylium (Tr^+) and its higher-energy isomer benzylium (Bz^+).

The electronic spectrum of Tr^+ is poorly understood compared to its vibrational spectrum. In contrast, the UV-visible spectrum of Bz^+ has been reported and analysed by several groups.^{163–165} The electronic spectrum of Tr^+ was first recorded in acidic solution through UV-visible absorption, with a single weak band apparent at 275 nm.¹⁷¹ Analysis using molecular orbital theory and the Pariser-Parr semi-empirical Hamiltonian led to assignment of the band to a forbidden $S_1\ ^1E'_3 \leftarrow S_0\ ^1A'_1$ transition.¹⁵⁹ The transition to the formally-dark state was proposed to gain intensity through vibronic coupling with a bright state of similar energy, although the coupling mechanism was not discussed. A higher energy band was predicted to occur around 195 nm corresponding to a transition to the $S_2\ ^1E'_1$ state, which is dipole-allowed and should be bright by analogy to the equivalent transition in benzene.⁴²⁵

The first vibrationally-resolved electronic spectrum of Tr^+ was recorded through direct absorption by mass-selected C_7H_7^+ ions deposited in a 6 K neon matrix.¹⁶³ The spectrum was dominated by contributions from Bz^+ and neutral benzyl radicals, which possess nearby transitions that are far more intense than those originating from Tr^+ . However, a series of bands was observed starting at 36350 cm^{-1} (275.1 nm) and spaced by around 840 cm^{-1} . The band system was assigned to a dipole-allowed $^1A_2'' \leftarrow ^1A_1'$ transition in Tr^+ on the basis of TDDFT

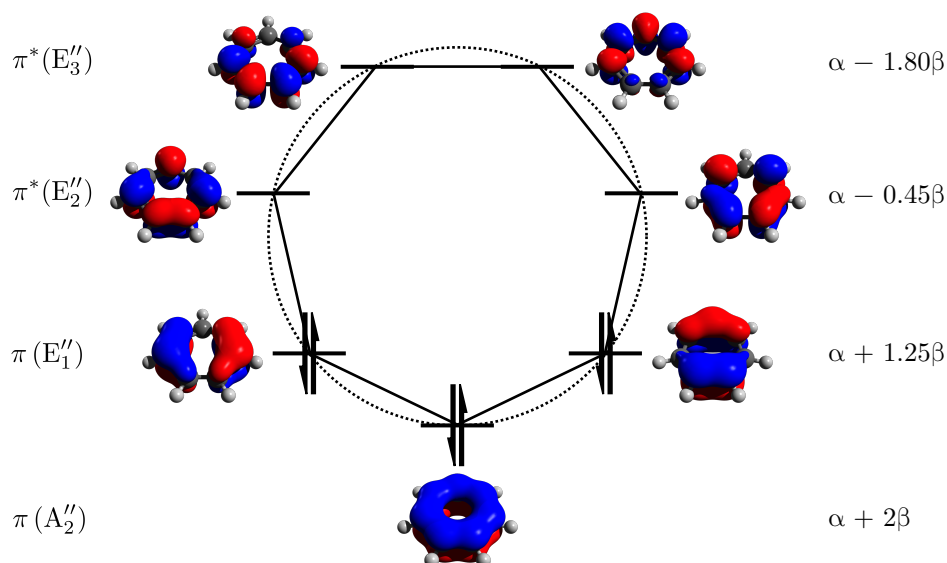


Figure 6.2: Frost diagram for Tr^+ showing the π -orbital system. Orbital labels and Hückel theory energies, in terms of the Coulomb integral α and the resonance integral β , are given on the left and right sides, respectively. Blue and red isosurfaces indicate opposite wavefunction phases. The molecular orbitals were computed at the RHF/STO-3G level of theory.

calculations, at odds with its previous assignment to a forbidden transition.¹⁵⁹

Assignment of the tropylium cation's electronic spectrum is partially motivated by a desire to spectroscopically differentiate between Tr^+ and Bz^+ . These two ions are key intermediates in hydrocarbon combustion and radical chemistry and in organic mass spectrometry.¹⁴⁹ Deuterium labelling experiments indicate that both Tr^+ and Bz^+ are major products from electron impact-induced dissociation of alkylbenzenes such as toluene.¹⁴⁸ Although the precise mechanism for Tr^+ formation from the tolyl radical cation (C_7H_8^+) is not entirely clear,¹⁴⁹ the current consensus is that it is likely formed through an intermediate cycloheptatrienyl radical cation.^{153,426} The main method for distinguishing Tr^+ and Bz^+ has been through measuring the rate of methylene cation (CH_2^+) transfer to toluene to form C_8H_9^+ . Tr^+ does not react with toluene whereas Bz^+ readily transfers its methylene group to yield C_8H_9^+ and neutral benzene.¹⁵⁰ However, reactivity-based studies are inherently invasive, whereas spectroscopy provides a means for *in situ* detection of Tr^+ and Bz^+ components in hydrocarbon flames and plasmas.

In this chapter, electronic spectra of argon-tagged Tr^+ ions are analysed using electronic structure calculations, group theory, and vibronic coupling simulations. The electronic spectra were obtained through resonance-enhanced photodissociation (REPD) of Tr^+ -Ar complexes using the tandem mass spectrometer described in Section 2.1.2. The ground-state geometries of Tr^+ and Tr^+ -Ar were optimised using DFT and the character of the $S_1 \leftarrow S_0$ transition was determined using EOM-CCSD calculations. The Herzberg-Teller and Jahn-Teller vibronic

coupling mechanisms in the S_1 state were then investigated using MCSCF and vibronic coupling theories to elucidate the intensity borrowing effects at play in the $S_1 \leftarrow S_0$ transition of Tr^+ .

6.2 Methods

The REPD spectrum of Tr^+ was recorded by Dr. Ugo Jacovella using the custom-built tandem mass spectrometer described in detail in Section 2.1.2. The spectrum was recorded through resonant photodissociation of weakly-bound Tr^+ -Ar complexes. Briefly, Tr^+ -Ar complexes were generated through electron impact ionisation of a cycloheptatriene-argon mixture as it expanded adiabatically into vacuum. The complexes were mass-selected and irradiated with tunable UV light; absorption of light was monitored through detection of ionic photofragments corresponding to bare Tr^+ at m/z 91. The REPD spectrum was built up by plotting the Tr^+ yield normalised by light fluence as a function of UV wavelength.

Interpretation of the electronic spectrum using electronic structure theory is the focus of this chapter. Ground state geometry optimisations for Tr^+ , its complexes with Ar, and Bz^+ were performed using the DFT PW6B95-D3(BJ)/jul-cc-pVTZ level of theory, where D3(BJ) denotes an empirical dispersion correction.^{310,311,427} The jul-cc-pVTZ basis set offers comparable performance to its fully-augmented equivalent but at significantly lower computational cost.⁴²⁷ The harmonic zero-point energies were calculated at the same level. The single-point energies were then refined using the DLPNO-CCSD(T)/aug-cc-pVQZ level of theory.^{346,428} Vertical excitation energies and oscillator strengths for transitions to the S_1 and S_2 states were computed using the EOM-CCSD/aug-cc-pVTZ level of theory.^{285,346} The EOM-CCSD method was chosen as it has a typical accuracy of around 3000 cm^{-1} for excitation energies without systematic bias depending on excited-state character.⁴²⁹ Ground- and excited-state geometry optimisations for the purposes of vibronic coupling simulations were performed using the CASSCF MCSCF method with the def2-TZVP basis.^{279,345} The chosen active space contained the entire π -system in Tr^+ , i.e. 6 electrons within the 7 π -orbitals (illustrated in Figure 6.2). Harmonic frequencies and transition dipole moment derivatives were calculated at the same level of theory. State-specific orbitals and gradients were computed in all cases except for potential energy surface scans, which were performed with orbitals averaged over the lowest three states, that is, the S_0 state and the two degenerate components of the S_1 state. These calculations were performed within the Gaussian 16 and ORCA 4.1 programs.^{319,321}

6.3 Results and interpretation

The REPD spectrum of Tr^+ -Ar complexes in the gas phase is plotted in Figure 6.3a. A number of bands over the $35000\text{--}40000\text{ cm}^{-1}$ range (285–250 nm) are apparent, consistent with the neon matrix spectrum. At least seven peaks are apparent in the spectrum, with more features appearing

as shoulders or poorly resolved sidebands.

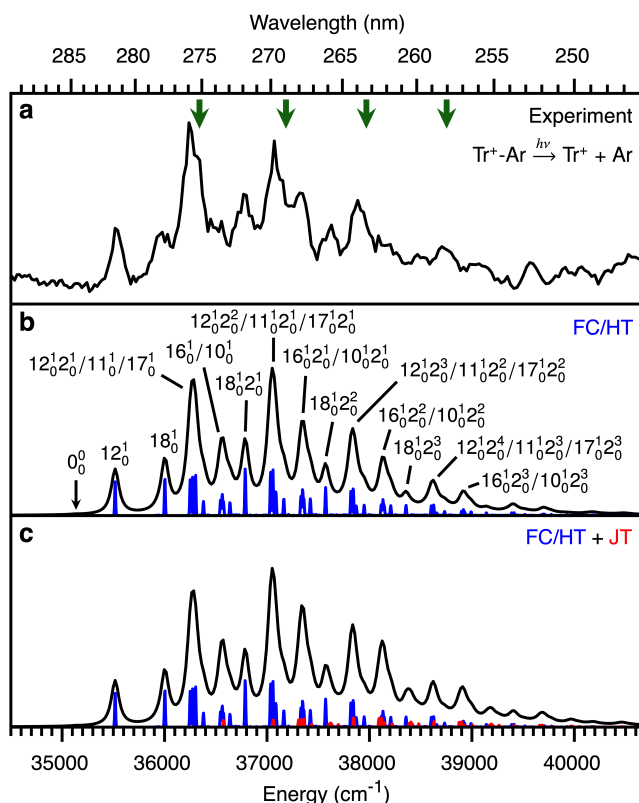


Figure 6.3: a) Experimental REPD spectrum of $\text{Tr}^+\text{-Ar}$ complexes, monitoring Tr^+ photofragments. Green arrows above the experimental spectrum indicate the band maxima from the neon matrix spectrum reported by Nagy *et al.*¹⁶³ b) Simulated spectrum computed under the Franck-Condon approximation including the Herzberg-Teller (HT) coupling contribution. The convoluted spectrum incorporates an artificial broadening of 100 cm^{-1} full width at half maximum to best match the experimental spectrum. c) Simulated spectrum including treatment of the JT effect on top of HT coupling, with bands arising from the JT effect shown in red.

The green arrows above the experimental spectrum in Figure 6.3a indicate band maxima from the neon matrix absorption spectrum.¹⁶³ These four bands were assigned to the dipole-allowed ${}^1A_2'' S_1 \leftarrow {}^1A_1' S_0$ origin and a progression in the totally-symmetric ring stretching mode ν_2 extending to three quanta (i.e. 0_0^0 , 2_0^1 , 2_0^2 , and 2_0^3). These assignments were based on vertical excitation energies, state symmetries, and oscillator strengths from TDDFT calculations. However, the assignment of the excited state to one of ${}^1A_2''$ symmetry is incompatible with previous theoretical studies which predicted an ${}^1E_3'$ excited state.¹⁵⁹ The ground state of Tr^+ is unambiguously of ${}^1A_1'$ symmetry with three doubly-occupied π - and four empty π^* -orbitals. No excitations within the π -system of the ${}^1A_1'$ state in Tr^+ produce a state of ${}^1A_2''$ symmetry. Either a $\sigma\pi^*$ or $\pi\sigma^*$ excitation is required to yield a ${}^1A_2''$ state. However, both options are unlikely to be lower in energy than a frontier $\pi\pi^*$ transition.⁴³⁰ In contrast, HOMO (E_1') to LUMO (E_2'') $\pi\pi^*$ excitation would give rise to states of E_3' and E_1' symmetries, in line with the semi-empirical

calculations of Murrell and Longuet-Higgins.¹⁵⁹

To clarify the nature of the $S_1 \leftarrow S_0$ transition, electronic structure calculations were performed focussing on the geometries and energies of Tr^+ , $\text{Tr}^+\text{-Ar}$, and Bz^+ in their S_0 ground states, and of Tr^+ in its S_1 excited state. First, the ground state geometries of Tr^+ , $\text{Tr}^+\text{-Ar}$, and Bz^+ were optimised using DFT, and the resulting geometries are depicted in Figure 6.4. As expected, the equilibrium geometry of Tr^+ has D_{7h} symmetry, while that of Bz^+ has C_{2v} symmetry. In line with previous studies, Tr^+ is found to be more stable than Bz^+ , which is calculated to lie 33 kJ/mol higher in energy. The most stable $\text{Tr}^+\text{-Ar}$ isomer possesses C_{7v} symmetry, with the Ar atom lying above the Tr^+ plane along the C_7 axis, and has a dissociation energy of 531 cm^{-1} . Alternative binding sites exist with the Ar atom in the Tr^+ plane bound to either one or two hydrogen atoms. However, these complexes lie several hundred cm^{-1} higher in energy.

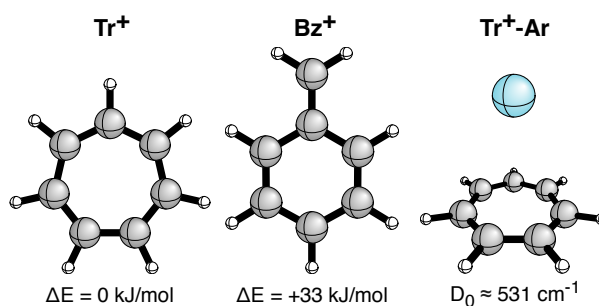


Figure 6.4: Optimised geometries for Tr^+ , Bz^+ , and $\text{Tr}^+\text{-Ar}$ at the PW6B95-D3(BJ)/jul-cc-pVTZ level of theory. Relative energies (Tr^+ and Bz^+) and dissociation energies ($\text{Tr}^+\text{-Ar}$) at the DLPNO-CCSD(T)/aug-cc-pVQZ are given below each structure.

The DFT D_{7h} S_0 geometry for Tr^+ was used as input for EOM-CCSD vertical excitation energy and oscillator strength calculations. The two lowest electronic transitions are calculated to be the S_1 $^1E'_3 \leftarrow S_0$ $^1A'_1$ transition at 39585 cm^{-1} and the S_2 $^1E'_1 \leftarrow S_0$ $^1A'_1$ transition at 53770 cm^{-1} , consistent with group theoretical considerations. The former transition is forbidden by symmetry and has a calculated oscillator strength of $f = 0$, whereas the latter allowed transition is strong with $f = 0.77$. These calculations are in line with those of Murrell and Longuet-Higgins,¹⁵⁹ but disagree with the TDDFT calculations of Nagy *et al.*,¹⁶³ which predict the S_1 state to have $^1A'_2$ symmetry and to lie at 44440 cm^{-1} , almost 5000 cm^{-1} above the EOM-CCSD value and 8000 cm^{-1} above the most intense feature in the experimental spectrum. On the basis of the EOM-CCSD calculations, the S_1 state is assigned to one of $^1E'_3$ symmetry with the bright S_2 $^1E'_1$ state lying somewhat higher in energy, in line with the calculations of Murrell and Longuet-Higgins.¹⁵⁹

The S_1 $^1E'_3 \leftarrow S_0$ $^1A'_1$ transition is forbidden by symmetry, as $\Gamma(S_0) \otimes \Gamma(S_1) \not\supset \Gamma(\mu)$, where μ is the electric dipole moment, and so to be accessible the S_1 $^1E'_3$ state must vibronically couple to a bright state. The EOM-CCSD calculations indicate the S_2 $^1E'_1$ state, which lies around

14000 cm^{-1} above the $S_1 \ ^1E'_3$ state, has a large oscillator strength ($f = 0.77$), and that the $S_1 \leftarrow S_0$ transition likely gains intensity through coupling between S_1 and S_2 . Vibronic coupling lends intensity to the analogous $S_1 \ ^1B_{2u} \leftarrow S_0 \ ^1A_{1g}$ transition in benzene,¹⁶¹ where, as in Tr^+ , the HOMO-LUMO transition is forbidden by symmetry. The transition to the dark $S_1 \ ^1B_{2u}$ state gains intensity through coupling to the bright $S_3 \ ^1E_{1u}$ state *via* ν_6 , a normal mode of e_{2g} symmetry.¹⁶¹

The spectrum of Tr^+ was analysed using the HT model for vibronic coupling, whereby vibrational displacement along coupling normal modes breaks D_{7h} symmetry lending intensity to otherwise forbidden vibronic transitions.⁴³¹ The HT model arises from Fermi's golden rule, which states the oscillator strength f of a vibronic transition is proportional to the square of the transition dipole moment $\vec{\mu}$:

$$f(\omega) \propto \frac{4\omega^3 n^2}{3\hbar c^3} |\vec{\mu}(\mathbf{Q})|^2 \delta(E'' - E' \pm \hbar\omega) \quad (6.1)$$

where ω is the photon energy, n the refractive index, c the speed of light, $\mathbf{Q}$ the nuclear coordinates, and E'' and E' are the energies of the ground and excited vibronic levels. Transitions with non-zero values of $\vec{\mu}$ will carry intensity. The HT vibronic coupling model assumes that $\vec{\mu} = \langle \Psi'' | \mu | \Psi' \rangle$ (where Ψ'' and Ψ' are the ground- and excited-state vibronic wavefunctions, respectively) varies slowly with $\mathbf{Q}$, such that Taylor expansion of $\vec{\mu}$ around the equilibrium geometry of either the ground or excited state $\mathbf{Q} = 0$ gives:

$$\vec{\mu}(\mathbf{Q}) = \vec{\mu}_0 + \sum_i \left. \frac{\delta \vec{\mu}}{\delta Q_i} \right|_{\mathbf{Q}=0} Q_i + \dots \quad (6.2)$$

Truncation at zeroth order yields the Condon approximation, which assumes the transition dipole is independent of displacement along the nuclear degrees of freedom. For allowed transitions, the zeroth-order contribution dominates. When $\vec{\mu}_0$ is zero by symmetry, higher-order terms become significant. For the $S_1 \leftarrow S_0$ transition in benzene, $\vec{\mu}_0$ is zero and truncation of $\vec{\mu}(\mathbf{Q})$ at first order, considering a linear dependence of $\vec{\mu}$ upon distortion along uncoupled coordinates, is sufficient to account for the spectrum. Indeed, benzene is a benchmark case for HT-coupling implementations in electronic structure packages.^{317,431} For molecules with very high symmetry such as the nitrate anion (D_{3h}), the zeroth- and first-order contributions to the transition dipole can be zero and second- or higher-order terms must be considered.⁴³²

It is likely vibronic coupling through a HT mechanism provides intensity for the $S_1 \ ^1E'_3 \leftarrow S_0 \ ^1A'_1$ transition of Tr^+ , as for the $S_1 \ ^1B_{2u} \leftarrow S_0 \ ^1A_{1g}$ transition of benzene. To first order, the symmetries of the HT active modes, which couple a dark state to a nearby bright state, are given by $\Gamma(\Psi_{\text{bright}}) \otimes \Gamma(\Psi_{\text{dark}}) \supseteq \Gamma(\vec{\nu})$, where Ψ_{bright} and Ψ_{dark} are the electronic wavefunctions of the bright and dark states, respectively, and $\vec{\nu}$ is the set of active modes. In the case of Tr^+ ,

$\Gamma(\Psi_{\text{dark}})$ is E'_3 and, on the basis of the previous arguments, $\Gamma(\Psi_{\text{bright}})$ is E'_1 . Therefore, the irreducible representations of the coupling modes are $e'_2 \oplus e'_3$. Transitions to S_1 $^1E'_3$ vibrational levels transforming as either e'_2 or e'_3 will gain intensity through HT coupling at first order to the S_2 $^1E'_1$ state, while levels transforming as any other irreducible representation should remain dark. It is worth emphasising that the origin of the S_1 $^1E'_3 \leftarrow S_0$ $^1A'_1$ transition should carry no intensity and remains forbidden.

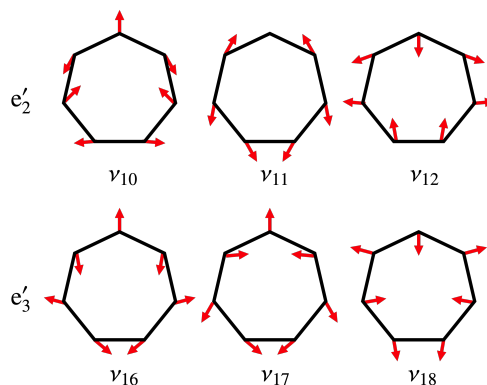


Figure 6.5: Schematic illustration of the HT-active normal modes in the S_1 state of Tr^+ . Only modes localised to the carbon backbone are depicted. Hydrogen atoms are omitted for clarity.

The DFT calculations suggest eight vibrational modes transform as either e'_2 or e'_3 and so can contribute to intensity borrowing: ν_9 – ν_{12} are of e'_2 symmetry and ν_{15} – ν_{18} are of e'_3 symmetry. The highest frequency modes, ν_9 and ν_{15} , are C–H stretches. The most intense bands in the electronic spectrum will be those which most strongly couple the S_1 state to the bright S_2 state. As the S_1 $^1E'_3$ and S_2 $^1E'_1$ states are both of $\pi\pi^*$ character, the difference in C–H bonding is likely to be minimal between these states, and so ν_9 and ν_{15} should only be weakly HT-active. The remaining six modes, corresponding to displacement of the carbon backbone, are depicted in Figure 6.5. In all cases, these in-plane vibrations provide intensity through coupling to the e'_1 transition dipole moment component perpendicular to the C_7 axis.

To help assign the observed spectrum shown in Figure 6.3a, the electronic spectrum of Tr^+ was modelled using a Franck-Condon simulation, with the transition dipole moment $\vec{\mu}$ including HT vibronic coupling to first order. The value of $\vec{\mu}$ to first order was determined numerically with electronic wavefunctions and transition dipole moment derivatives computed as described in Section 6.2. The expansion of $\vec{\mu}$ in $\mathbf{Q}$ was performed around the $^1E'_3$ excited-state geometry. The electronic spectrum of Tr^+ was modelled using a time-dependent version of the Franck-Condon method as implemented in ORCA,³¹⁷ where the vibronic spectrum is obtained from the Fourier transform of the electric dipole autocorrelation function. The S_0 and S_1 harmonic frequencies were scaled by 0.915 and the simulation origin offset by $+2990 \text{ cm}^{-1}$ to best reproduce the experimental band system.

Table 6.1: Positions ($\tilde{\nu}_{\text{exp}}$) and assignments for peaks in the $S_1 \leftarrow S_0$ band system of Tr^+ . The experimental and calculated relative wavenumbers ($\Delta\tilde{\nu}_{\text{exp}}$ and $\Delta\tilde{\nu}_{\text{calc}}$, respectively) are given with respect to the calculated origin at 35130 cm^{-1} .

$\tilde{\nu}_{\text{exp}} (\text{cm}^{-1})$	Assignment	$\Delta\tilde{\nu}_{\text{exp}} (\text{cm}^{-1})$	$\Delta\tilde{\nu}_{\text{calc}} (\text{cm}^{-1})$
35530	12_0^1	400	390
35985	18_0^1	855	880
36245	11_0^1	1115	1132
36245	$12_0^1 2_0^1$	1115	1175
26245	17_0^1	1115	1249
36550	16_0^1	1420	1429
36550	10_0^1	1420	1519
36785	$18_0^1 2_0^1$	1655	1665
37075	$11_0^1 2_0^1$	1945	1917
37075	$12_0^1 2_0^2$	1945	1960
37075	$17_0^1 2_0^1$	1945	2034
37325	$16_0^1 2_0^1$	2195	2214
37325	$10_0^1 2_0^1$	2195	2304
37615	$18_0^1 2_0^2$	2485	2450
37890	$11_0^1 2_0^2$	2760	2702
37890	$12_0^1 2_0^3$	2760	2745
37890	$17_0^1 2_0^2$	2760	2819
38090	$16_0^1 2_0^2$	2960	2999
38090	$10_0^1 2_0^2$	2960	3089

The resulting simulated spectrum for the $S_1 \ ^1E'_3 \leftarrow S_0 \ ^1A'_1$ transition of Tr^+ is plotted in Figure 6.3b. The simulation agrees qualitatively with the experimental spectrum up to 3000 cm^{-1} above the origin. The origin is calculated to occur at 35130 cm^{-1} with zero oscillator strength and is absent from the spectrum. The bands at 35530 , 35985 , 36245 , and 36550 cm^{-1} correspond to false origins arising from excitation of single quanta of the six HT-active vibrational modes (ν_{10} – ν_{12} and ν_{16} – ν_{18}). Progressions extending to at least three quanta of ν_2 , the totally-symmetric a'_1 ring-breathing mode, are built on each of the false origins. The transitions corresponding to single quanta of ν_2 built on each of the false origins are predicted to carry around the same intensity as the false origins themselves. Most of the higher energy peaks have contributions from several transitions due to the similar frequencies of the HT-active modes and of ν_2 itself.

The progressions in the ring-breathing mode ν_2 suggest a significant change in C–C bond length occurs upon electronic excitation. This is consistent with the $\pi\pi^*$ character of the HOMO–LUMO $S_1 \leftarrow S_0$ transition, where a bonding π -electron is excited to an anti-bonding π^* -orbital (see Figure 6.2), implying the C–C bond should lengthen upon excitation. Indeed, the CASSCF calculations indicate the mean C–C bond length increases by $0.020 \text{ \AA}$ from $1.397 \text{ \AA}$ to $1.417 \text{ \AA}$.

A similar, albeit larger, bond length increase occurs in benzene after excitation to S_1 (0.044 Å).¹⁶¹ The mean change in Tr^+ C–H bond length following S_1 $^1E'_3$ excitation is calculated to be –0.001 Å with the largest change equal to –0.003 Å.

While C–C bond elongation is the major structural change upon excitation to S_1 , the molecular symmetry is also reduced from D_{7h} to C_s predominantly through an in-plane distortion of e'_1 symmetry. This distortion is consistent with one caused by the JT effect, whereby a non-linear molecule in an orbitally-degenerate electronic state undergoes distortion to lower its potential energy and molecular symmetry, removing the electronic degeneracy.⁴³³ The JT effect is a form of vibronic coupling where the components of the degenerate electronic state are coupled by at least one degenerate vibrational mode. Transitions between vibronic energy levels involving JT-active coupling modes obey altered selection rules, such that transitions to otherwise forbidden vibronic levels can be observed in electronic spectra.^{434,435} The spectral analysis presented to this point does not account for JT vibronic coupling, as each vibrational mode has been treated as a decoupled harmonic oscillator. Similarly, the geometry optimisations predict a minimum-energy geometry for the S_1 state with lower than D_{7h} symmetry. However, it is not clear whether the vibrationally-averaged structure has reduced symmetry or is delocalised over D_{7h} and C_s geometries. To explore these issues, we follow the work of Longuet-Higgins and of Miller to investigate the impact of the JT effect on Tr^+ and its electronic spectrum.^{316,436}

The S_1 $^1E'_3$ state in Tr^+ is subject to the $E \otimes e$ JT effect, where both the electronic state and the symmetry-lowering mode are doubly degenerate.⁴³³ The irreducible representations of the normal modes which couple the degenerate components of the electronic state are given by $[\Gamma(\Psi_e) \otimes \Gamma(\Psi_e)] \supseteq \Gamma(\vec{\nu})$, where the square brackets indicate only the symmetric component with respect to nuclear permutation, and Ψ_e and $\vec{\nu}$ are the electronic wavefunction and the set of JT-active normal modes, respectively. In the case of the S_1 $^1E'_3$ state in Tr^+ , normal modes of $a'_1 \oplus e'_1$ symmetry are expected to couple the degenerate electronic states. Totally-symmetric a'_1 modes cannot lower the molecular symmetry, leaving only the degenerate e'_1 vibrations as those which can lower the potential energy. Of the e'_1 modes, ν_7 is predominantly responsible for lowering the symmetry in the S_1 $^1E'_3$ state, according to CASSCF geometry optimisations and illustrated in Figure 6.6a. As stated above, the minimum-energy geometry of Tr^+ in the S_1 state is calculated to be C_s , instead of C_{2v} as symmetry arguments would suggest. This discrepancy is likely due to symmetry breaking in the CASSCF calculations; the deviation from exact C_{2v} symmetry are an order of magnitude smaller than the distortion induced by ν_7 .

The JT distortion of a molecule can be broadly categorised as static or dynamic. The former situation has the vibrationally-averaged geometry trapped within the distorted well,⁴³⁷ whereas the latter scenario implies the geometry is delocalised over both the high- and low-symmetry configurations, even if the minimum-energy geometry is distorted.³¹⁶ A static JT effect has a large stabilisation energy E_{JT} compared to the frequency of the distorting mode ω_{JT} , whereas

E_{JT} and ω_{JT} are normally similar in the dynamic case. In order to gauge the strength of the JT effect induced by ν_7 in the S_1 $^1E'_3$ state, the CASSCF potential energy surface was followed along the two components of the doubly-degenerate ν_7 mode and the totally-symmetric ν_2 mode. The scans were performed by taking steps in dimensionless mass-weighted normal coordinates simultaneously along all three modes. The instability of the S_1 state with respect to distortion in accordance with the JT effect is illustrated in Figure 6.6b, which depicts the potential energy as a function of ν_2 and one component of ν_7 on the x - and y -axes, respectively. The D_{7h} geometries represent a seam along Q_2 on the S_1 potential energy surface, with a minimum at $Q_2 \approx 1.5$, with lower energy geometries accessible through relatively small distortions along Q_7 ($Q_7 \approx \pm 0.5$).

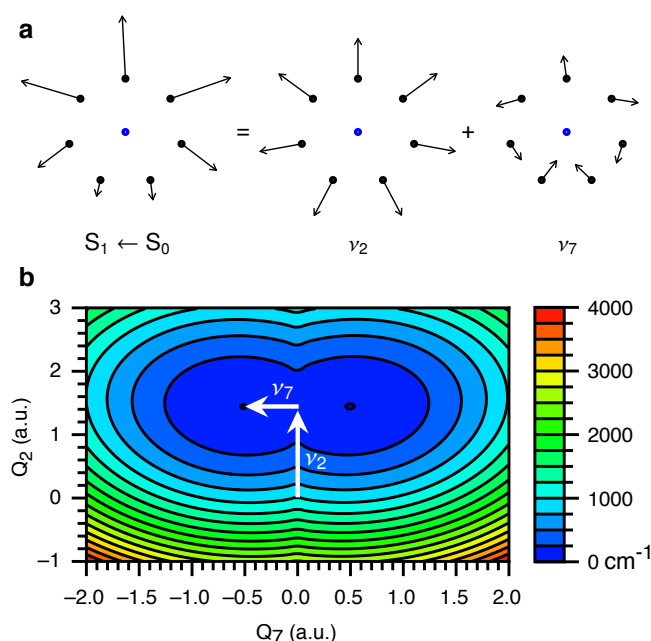


Figure 6.6: a) Decomposition of the geometry change upon $S_1 \leftarrow S_0$ excitation into contributions from ν_2 and ν_7 . The geometry changes are magnified by 50 $\times$ and hydrogen atoms are omitted for clarity. The blue dots represent the molecules' centres of mass. b) Potential energy surface scans along the Q_2 and Q_7 normal coordinates to illustrate the topology of the S_1 surface, with the origin representing the S_0 minimum-energy geometry. Contour lines are separated by 250 cm^{-1} .

The potential energy surface displayed in Figure 6.6b implies the minimum-energy geometry of Tr^+ in the S_1 $^1E'_3$ state has lower symmetry than D_{7h} . However, the stabilisation energy is small ($E_{JT} < 200 \text{ cm}^{-1}$) compared to the frequency of ν_7 ($\omega_7 \approx 600\text{--}1000 \text{ cm}^{-1}$), and so the lowest vibrational level probably lies above the D_{7h} seam. To explore this possibility, the potential energy surface was followed along both components of ν_7 at a fixed value of $Q_2 = 1.5$. The results from this scan are depicted in Figures 6.7a and 6.7b.

The surfaces have circular symmetry to within 25 cm^{-1} (the separation of the contour lines), with negligible barrier to pseudorotation along the minimum energy moat. This suggests the

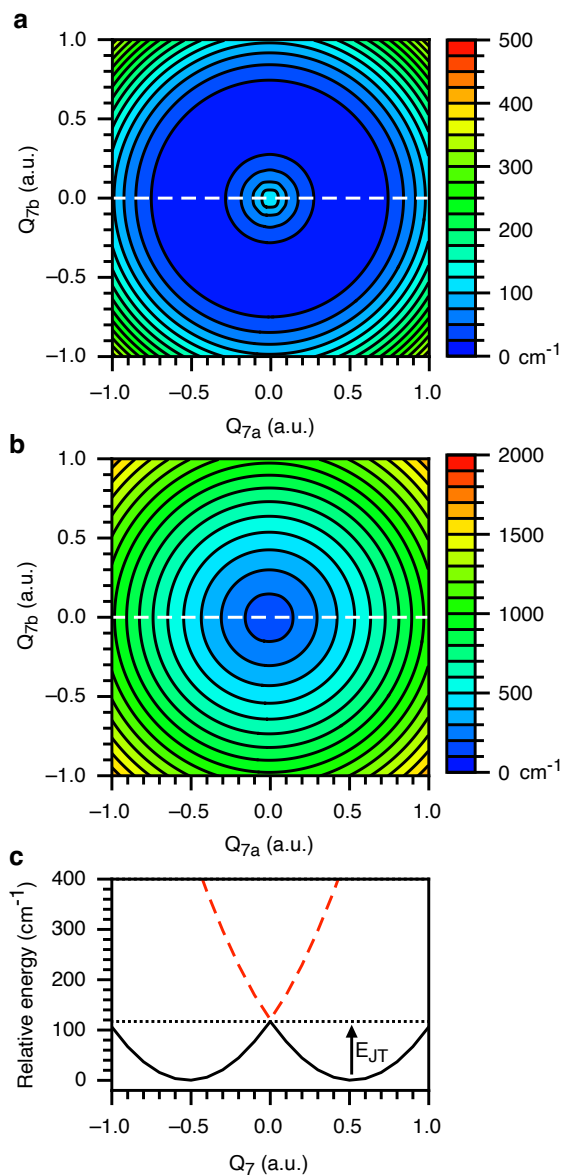


Figure 6.7: Potential energy surfaces for the two S_1 $^1E'_3$ state components split by the JT effect. The lower energy surface (a) and higher energy surface (b) have contour lines separated by 25 and 100 cm^{-1} , respectively. Energies are given relative to the lowest point on the lower energy surface. The surfaces were calculated at $Q_2 = 1.5$ where the potential energy is lowest. Slices through the potential energy surfaces (c), taken at the points indicated by white dashed lines, show the conical intersection at $Q_7 = 0$. The black and red curves represent the lower and upper adiabatic surfaces, respectively. The JT stabilisation energy E_{JT} is indicated by the black dotted line.

distortion is caused only by a linear Jahn-Teller vibronic coupling, as a quadratic Jahn-Teller effect would induce barriers along the pseudorotation coordinate, breaking circular symmetry.⁴³⁶ A conical intersection between the upper and lower surfaces is evident at $Q_7 = 0$; this conical intersection represents a single point along the intersection seam apparent in Figure 6.6b. Slices through the potential energy surfaces, along the white dashed lines in Figure 6.7a and 6.7b, are shown in Figure 6.7c. E_{JT} , the energy difference between the conical intersection and the bottom of the potential moat, is calculated to be 118 cm^{-1} . By fitting the surface slices to a quadratic function,⁴³⁸ the value of ω_{JT} is estimated to be 899 cm^{-1} . As E_{JT} is smaller than ω_{JT} , the lowest vibronic level likely lies above or near the high-symmetry conical intersection ($Q_7 = 0$ in Figure 6.7c), and the $S_1 \ ^1E'_3$ state cannot be considered as having a static, distorted equilibrium geometry. Rather, the geometry would be delocalised over a combination of the distorted geometries and the high-symmetry D_{7h} geometry. The probability density would possess a maximum in the moat but would be non-zero at the high-symmetry geometry.⁴³⁶

In order to calculate the lowest vibronic levels and to estimate the impact of JT activity on the electronic spectrum, the vibronic wavefunctions were determined following the approach of Longuet-Higgins and coworkers.^{316,439} The vibronic wavefunctions were approximated as:

$$\Psi = \psi^+ e^{i\theta} + \psi^- e^{-i\theta} \quad (6.3)$$

where ψ^+ and ψ^- represent the diabatic wavefunctions before interaction and θ is the angular coordinate of the electronic state. The model Hamiltonian was given by a two-dimensional harmonic oscillator:

$$\hat{\mathcal{H}}_0 = \frac{1}{2} \left(r^2 - \frac{\delta^2}{\delta r^2} - \frac{1}{r} \frac{\delta}{\delta r} - \frac{1}{r^2} \frac{\delta^2}{\delta \phi^2} \right) \quad (6.4)$$

perturbed by a mixing operator:

$$\hat{\mathcal{H}}' = kr \left(e^{i(2\theta-\phi)} + e^{-i(2\theta-\phi)} \right) \quad (6.5)$$

where r and ϕ are the polar vibrational coordinates in terms of the two degenerate normal modes. The dimensionless parameter k is given by:

$$k^2 = \frac{2E_{JT}}{E_{ZPE}} \quad (6.6)$$

where E_{ZPE} is the zero-point energy of the uncoupled doubly-degenerate ω_{JT} (i.e. E_{ZPE} is 899 cm^{-1}).³¹⁶ Together, these equations yield an expression for the vibronic energy levels:

$$\begin{bmatrix} \hat{\mathcal{H}}_0 - E & kre^{-i\phi} \\ kre^{i\phi} & \hat{\mathcal{H}}_0 - E \end{bmatrix} \begin{bmatrix} \psi_{\ell_v}^+ \\ \psi_{\ell_v}^- \end{bmatrix} = 0 \quad (6.7)$$

where the quantum number ℓ_v indicates the vibronic angular momentum. Following the ap-

proaches of Longuet-Higgins, Leach, and respective coworkers,^{316,439,440} the energy levels were numerically evaluated by expansion of $\psi_{\ell_v}^{+/-}$ in a basis of isotropic 2-dimensional harmonic oscillator wavefunctions. The final eigenvalue problem for a given value of ℓ_v was given by:

$$\begin{bmatrix} \ell_v + 1 - E & k\sqrt{\ell_v + 1} & 0 & 0 & \dots \\ k\sqrt{\ell_v + 1} & \ell_v + 2 - E & k\sqrt{1} & 0 & \dots \\ 0 & k\sqrt{1} & \ell_v + 3 - E & k\sqrt{\ell_v + 2} & 0 \\ 0 & 0 & k\sqrt{\ell_v + 2} & \ell_v + 4 - E & \ddots \\ \vdots & \vdots & 0 & \ddots & \ddots \end{bmatrix} \begin{bmatrix} a_1 \\ a_2 \\ a_3 \\ a_4 \\ \vdots \end{bmatrix} = 0. \quad (6.8)$$

Diagonalisation of Equation 6.8 yielded the vibronic energy levels for a given ℓ_v in units of ω_{JT} . A better quantum number than ℓ_v , however, is the JT quantum number j , given by $j = \ell_v + \Lambda/2$ in D_{7h} , where Λ is the electronic angular momentum projection. The selection rule for transitions between JT-active vibronic levels is $\Delta j = \pm 1/2$.³¹⁶ The $v_7 = 0$ level of the S_0 ground state has zero vibronic angular momentum ($\ell_v = 0$) and electronic angular momentum ($\Lambda = 0$), giving $j = 0$. The S_1 excited state has $\ell_v = -v, -v + 1, \dots, v - 1, v$ and $\Lambda = \pm 1$, giving $j = \pm 1/2, \pm 3/2, \dots$. Transitions to the $S_1 |v \geq 0, j = \pm 1/2\rangle$ vibronic levels should be allowed and contribute to the spectrum, whereas transitions to $j = \pm 3/2, \pm 5/2, \dots$ are forbidden in the absence of a quadratic JT effect.⁴⁴¹

The only parameter in this model is k , which was calculated using Equation 6.6 using the values of E_{JT} and ω_{JT} extracted from the potential energy slices shown in Figure 6.7c. Expansion in a basis of 1000 harmonic oscillator functions followed by numerical diagonalisation was performed using a script written in the Julia programming language (provided in Section 7.4).⁴⁴² The resulting vibronic energy levels are depicted in Figure 6.8a. The lowest level ($|0, \pm 1/2\rangle$) lies at 805 cm^{-1} relative to the energy minimum ($Q_7 \approx \pm 0.5$), approximately 686 cm^{-1} above E_{JT} . As a result, the S_1 state is expected to exhibit a very weak and dynamic JT effect. The next accessible levels are $|1, \pm 1/2\rangle$ and $|2, \pm 1/2\rangle$ at 1864 cm^{-1} and 2650 cm^{-1} , respectively. The $|1, \pm 3/2\rangle$ level, which is not accessible by transitions from the ground state, is predicted to lie at 1550 cm^{-1} .

The model of Longuet-Higgins and coworkers can be used to predict the relative intensities for transitions from the vibrationless level of the ${}^1A'_1$ ground state to the JT-active vibrational levels of the ${}^1E'_3$ state,³¹⁶ providing an indication of the impact of the JT effect on the electronic spectrum of Tr^+ . The intensities are provided by the elementwise square of the eigenvectors from Equation 6.8.⁴⁴⁰ Relative intensities for the lowest $j = \pm 1/2$ levels are plotted in Figure 6.8b compared to the $v = 0$ band, with the lowest three transitions predicted to carry relative intensities of 1.00, 0.21, and 0.01, respectively. In the case of dipole-allowed transitions, adding the

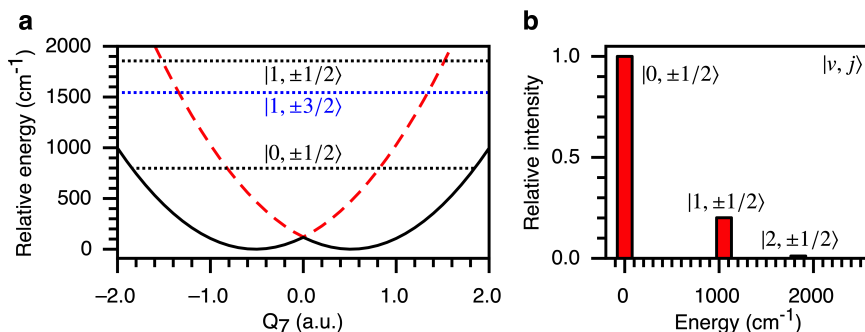


Figure 6.8: a) Slices through the Q_7 potential energy surfaces from Figure 6.7. The vibronic energy levels computed using Equation 6.8 are depicted by dotted lines, with the $j = \pm 1/2$ and $j = \pm 3/2$ levels in black and blue, respectively. b) Relative intensities predicted for transitions to each vibronic level indicated in a).

JT-induced modes from this model to the usual Franck-Condon simulation reconstructs the experimental spectrum rather well.^{436,440}

In the case of Tr^+ , the $S_1 \leftarrow S_0$ electronic transition is dipole-forbidden with intensity arising from HT coupling. Transitions to combination levels of the JT-active ν_7 with the HT-induced false origins and progressions (e.g. $12_0^1 7_0^1$, $12_0^1 7_0^1 2_0^1$, ...) are not expected to affect the HT intensity borrowing, as the HT- and JT-active vibrational modes are orthogonal to one other. Transition dipole moment surface scans, obtained by simultaneously displacing Tr^+ along the JT-active ν_7 and HT-active ν_{12} modes, also suggest that the intensity borrowing effect is not substantially altered by displacement along the ν_7 coordinate. The treatment of the JT-active ν_7 mode therefore begins by performing the spectral simulation as previously described without explicit consideration of JT activity, corresponding to excitations to the $|0, \pm 1/2\rangle$ levels. To treat excitation including quanta of ν_7 ($|1, \pm 1/2\rangle$, $|2, \pm 1/2\rangle$, ...), combination progressions in ν_7 are added to each band in the JT-free spectrum with intensities given in Figure 6.8b (for example, the bands in the 12_0^1 , $12_0^1 7_0^1$ and $12_0^1 7_0^1 2_0^1$ progression have relative intensities of 1.00, 0.21, 0.01, respectively).

The resulting simulation, including consideration of the JT-active ν_7 mode, is plotted in Figure 6.3c, where the sticks in blue and red correspond to transitions to $|v = 0, j = \pm 1/2\rangle$ and $|v > 0, j = \pm 1/2\rangle$ levels, respectively. The transitions to $|1, \pm 1/2\rangle$ and $|2, \pm 1/2\rangle$ levels overlap the $|0, \pm 1/2\rangle$ false origins and progressions in ν_2 , as the totally-symmetric ν_2 , the JT-active ν_7 , and the HT-active modes all have frequencies on the order of 1000 cm^{-1} . As a result, no new features are apparent in the simulated spectrum upon inclusion of ν_7 , but the features at higher energy gain intensity relative to the low-energy bands. The resolution of the REPD spectrum in Figure 6.3a precludes observing JT-induced vibronic transitions. Ideally, the $S_1 \leftarrow S_0$ electronic spectrum would be measured using bare, cold Tr^+ to yield a better resolved spectrum. Alternatively, measurement of REPD spectra using helium or neon as the tag atom, which generally yield sharper spectra than argon, may provide a path to higher spectral resolution.

6.4 Conclusion and outlook

This chapter has described the theoretical analysis of the $S_1\ ^1E'_3 \leftarrow S_0\ ^1A'_1$ transition of Tr^+ . The REPD spectrum, recorded through resonant photodissociation of weakly-bound Tr^+ -Ar complexes, exhibits weak and broad bands over the 35000–40000 cm^{-1} range which are consistent with previously recorded spectra in condensed phases.¹⁶³ EOM-CCSD electronic structure calculations and group theoretical arguments support assignment of the transition as being to a dark state of $^1E'_3$ symmetry. Franck-Condon simulations, incorporating HT vibronic coupling to first order, indicate the spectrum is comprised of progressions in the totally-symmetric ν_2 ring-breathing mode built on six false origins. These false origins are associated with vibrational levels of the S_1 state which borrow intensity from the nearby bright $S_2\ ^1E'_1$ state, in accordance with predictions from group theory.

Electronic structure calculations confirm the molecular structure of Tr^+ in its $S_0\ ^1A'_1$ ground state is D_{7h} . Multiconfigurational calculations indicate the $S_1\ ^1E'_3$ state exhibits a dynamical JT effect, with a minimum energy geometry of lower symmetry than the ground state. Potential energy surface scans suggest linear JT coupling is weak and quadratic JT coupling is negligible, allowing pseudorotation between equivalent distorted structures. As a result, the impact of the JT effect on the electronic spectrum is expected to be small, with a slight intensity increase for features in the high-energy region of the spectrum. Spectra of the cooled bare Tr^+ molecule, or of Tr^+ -He or Tr^+ -Ne complexes, will likely have better resolution enabling individual vibrational contributions to be distinguished. A more accurate estimation of the impact of the JT effect on the $^1E'_3$ state might then be possible. More accurate electronic structure calculations should provide a better understanding of the JT activity to guide interpretation of higher resolution spectra. The CASSCF calculations lack treatment of dynamical correlation, and so MRPT or MRCI methods should improve accuracy of the potential energy surfaces.

The fate of Tr^+ in the S_1 state is not obvious from the REPD spectrum or the electronic structure calculations. Depending on the fluorescence quantum yield, laser-induced fluorescence experiments may provide complementary information to the REPD spectra. Non-radiative processes including intersystem crossing play a key role in the S_1 photophysics of benzene,^{443,444} and the S_1 state in Tr^+ may undergo similar photochemical processes. Time-resolved spectroscopic experiments should provide insight into the S_1 decay mechanisms, although the low ion density in the gas phase and weakness of the $S_1 \leftarrow S_0$ transition mean such experiments will not be straightforward. Photoelectron spectroscopy starting from the tropyli radical C_7H_7 might also provide information on the cation's vibronic energy levels,⁴⁴⁵ but the strong JT effect in C_7H_7 ($E_{\text{JT}} = 1043\text{ cm}^{-1}$) will probably complicate the analysis.^{446,447}

Chapter 7

Supporting information

7.1 Supporting information for Chapter 3

This section contains the supporting information for Chapter 3. It was originally available alongside the published article at doi:10.1021/acs.jpca.7b05902 and is reproduced here with permission. Figure and table numbers have been adjusted to reflect their position within the thesis.

Typical experimental timings

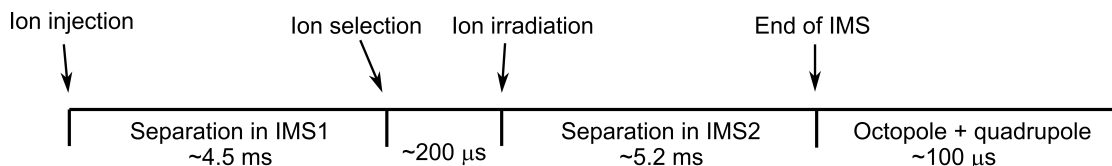


Figure 7.1: Schematic illustration showing ordering and typical durations of stages in the present experiment.

ABH⁺ equilibrium geometry

Feráud *et al.* used the RI-MP2/cc-pVDZ level of theory to propose that the *trans*-isomer is non-planar, with the phenyl ring more distant from the protonation site twisted out of plane by 18°. ⁵⁸ With the larger cc-pVTZ basis set, both the C₁ twisted and C_s planar geometries are found to be local minima, whereas only the planar structure is a minimum at the DFT ωB97X-D/6-311+G(2df,p) level. Single-point energies at the DLPNO-CCSD(T)/cc-pVTZ level indicate that the twisted geometry lies slightly lower in energy than the planar geometry (by 0.6 kJ/mol).

A relaxed scan around the N–N–C–C coordinate at the RI-MP2/cc-pVTZ level suggests that the planar geometry is a minimum lying slightly higher in energy (0.7 kJ/mol) than the twisted

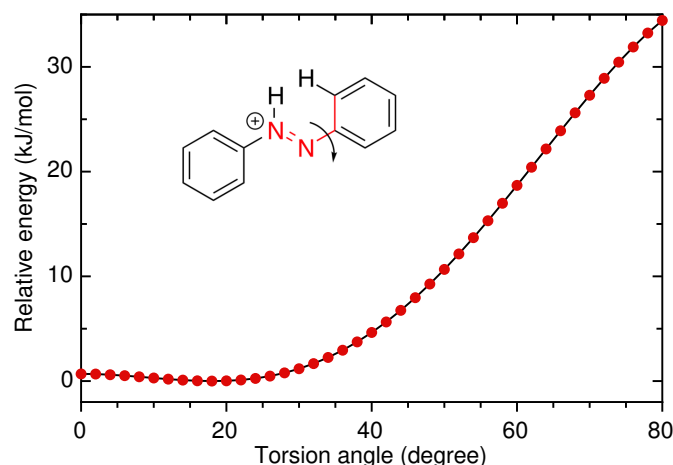


Figure 7.2: Potential energy curve for torsion around the indicated dihedral angle for ABH^+ . The curve was calculated at the RI-MP2/cc-pVTZ level, with all coordinates except for the indicated dihedral angle relaxed at each point. The RI-MP2/cc-pVTZ calculations were performed using the ORCA 3.0.3 program.³²⁰

minimum. Relaxation from the planar geometry to the twisted geometry at the RI-MP2/cc-pVTZ level has a tiny barrier. Beyond 18° , the energy rises steeply and is above 30 kJ/mol by 80° . Due to the low, flat potential energy curve in the torsional coordinate, at 300 K the molecule will execute large amplitude vibrational motion, and should have a quasi-planar structure. A scan over the analogous coordinate in *trans* NH_2ABH^+ displays a single minimum at the planar geometry.

Collision cross sections

The approach to measuring collision cross sections has been explained in ref. 91. Briefly, the drift mobility (K) of a drift ion is given by the Mason-Schamp equation:

$$K = \frac{3ze}{16N} \sqrt{\frac{2\pi}{\mu k_B T}} \left(\frac{1}{\Omega} \right) = \frac{l^2}{t_d V} \quad (7.1)$$

where ze is the molecular charge, N the buffer gas number density, μ the reduced mass of the ion and buffer gas, k_B the Boltzmann constant, T the temperature, and Ω the orientationally-averaged collision cross section.

Equation 7.1 can be rearranged to give a linear relationship between the collision cross section Ω and the arrival time at the detector t_d :

$$\Omega = A t_d \mu^{-1/2} \quad (7.2)$$

where A is a constant which describes the temperature and pressure dependence, and is determined

by linear regression of literature collision cross sections against measured arrival times for a series of tetraalkylammonium cations.^{303,448} Once A is known, the collision cross sections for ABH^+ and NH_2ABH^+ can be determined. These values are shown in Table 7.1.

Table 7.1: Measured (Ω_m) and calculated (Ω_c) collision cross sections for isomers of ABH^+ and NH_2ABH^+ .

Molecule	Ω_m ($\text{\AA}^2$)	Ω_c ($\text{\AA}^2$)
ABH^+		
<i>trans</i>	138.8	142
<i>cis</i>	136.7	142
NH_2ABH^+		
<i>trans</i> isomer a	145.6	149
<i>trans</i> isomer b		148
<i>trans</i> isomer c		160
<i>cis</i> isomer a	141.2	148
<i>cis</i> isomer b		149
<i>cis</i> isomer c		159

Calculated geometries of ABH⁺**7.1.0.1 Planar *trans*-ABH⁺ (DFT, ω B97X-D/6-311+G(2df,p))**

C	-3.89331	-0.71555	-2.06611
C	-2.54422	-0.61889	-1.82548
C	-2.06466	-0.84638	-0.52320
C	-2.94923	-1.16704	0.51352
C	-4.30317	-1.26074	0.25733
C	-4.77152	-1.03560	-1.02770
H	-4.27745	-0.54342	-3.06296
H	-1.88999	-0.36895	-2.65352
H	-2.54595	-1.33588	1.50383
H	-4.99105	-1.50807	1.05483
H	-5.83232	-1.10789	-1.23393
N	-0.74545	-0.78619	-0.12751
N	0.15654	-0.51042	-0.93936
C	1.52487	-0.43280	-0.60030
C	2.40684	-0.11220	-1.62548
C	1.95549	-0.66832	0.70056
C	3.75698	-0.02499	-1.34027
H	2.04748	0.06742	-2.63354
C	3.30658	-0.57668	0.96589
H	1.24488	-0.91596	1.47713
C	4.20467	-0.25673	-0.04798
H	4.45794	0.22348	-2.12602
H	3.66621	-0.75560	1.97073
H	5.26200	-0.18826	0.17426
H	-0.06214	-0.32134	-1.92172

7.1.0.2 Planar *trans*-ABH⁺ (RI-MP2/cc-pVTZ)

C	-3.86375239707663	-0.71268158293154	-2.07880182538195
C	-2.50844731496143	-0.62233722126573	-1.81053438706186
C	-2.06051471321711	-0.85288873620490	-0.49572927921864
C	-2.97100720569819	-1.17003852926064	0.52728649644614
C	-4.32544465592822	-1.25594537840748	0.24009314112522
C	-4.77251356988500	-1.02781701047538	-1.06029535862708
H	-4.22118088951549	-0.53851105985191	-3.08369703867081
H	-1.83839331086398	-0.37765559569232	-2.62593608238237
H	-2.58455901161350	-1.33985556685440	1.52246016957290
H	-5.02927609269543	-1.49904724598454	1.02277919469048
H	-5.82719358545049	-1.09406776843607	-1.28848298664516
N	-0.74821181331685	-0.80288999269777	-0.05687297482172
N	0.15697051279348	-0.51927156103571	-0.89426411642760
C	1.51356860733297	-0.43824902117414	-0.57970191044530
C	2.37816006397709	-0.11097398947702	-1.63075209936928
C	1.96811027243000	-0.67485738000928	0.72340213489696
C	3.73775531019238	-0.01765431102539	-1.36977623981187
H	1.99226648754245	0.06574303711827	-2.62759322501635
C	3.32832974085207	-0.57627833685489	0.96090061313875
H	1.26721903775025	-0.92487939871806	1.50541396814270
C	4.20974055717733	-0.24980142569289	-0.07775193801347

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H	4.42329003574354	0.23357810593217	-2.16552500251771
H	3.70972058458408	-0.75316174066834	1.95602582028782
H	5.26895903914866	-0.17699161725054	0.12493217544904
H	-0.08357568930199	-0.33046667308148	-1.87457924933887

7.1.0.3 Twisted *trans*-ABH⁺ (RI-MP2/cc-pVTZ)

C	-3.86592299919885	-0.36520290279639	-1.94747863354252
C	-2.52642492858077	-0.24584859749932	-1.61382053437280
C	-2.05635738141130	-0.89371560734003	-0.45548910551254
C	-2.93189438725280	-1.61114938185926	0.37697563773136
C	-4.26547002306607	-1.73454850774481	0.01600973731966
C	-4.73177755107038	-1.11792715211970	-1.14548400987120
H	-4.24696751324761	0.14511987840622	-2.82061803951821
H	-1.89152278744816	0.40047570524185	-2.20864811767006
H	-2.53460239237155	-2.07193581564329	1.27054403694780
H	-4.94280889775466	-2.29927767792174	0.64016321503550
H	-5.77481501161857	-1.20015376013235	-1.41767411140226
N	-0.74252025906566	-0.88468433881928	-0.01888513423004
N	0.14561834362572	-0.56632682020463	-0.86396558618505
C	1.50289485705450	-0.45193176267409	-0.56967343756553
C	2.35329476642644	-0.17226465057486	-1.64625228034090
C	1.97266422821399	-0.61494534065276	0.73963104670646
C	3.71512970511952	-0.06008870852850	-1.40598751322253
H	1.95420743832034	-0.04942543251603	-2.64597982953245
C	3.33512879695957	-0.50027473689639	0.95566620303517
H	1.28062156451876	-0.82132128531606	1.54225261764258
C	4.20285611999695	-0.22483537143047	-0.10917535031223
H	4.39064989665000	0.15424825073474	-2.22089752761648
H	3.72880572319068	-0.62054870414069	1.95447112087911
H	5.26381259233250	-0.13550011056892	0.07748250607691
H	-0.12235990032259	-0.39153716900325	-1.84143691047976

7.1.0.4 *cis*-ABH⁺ (DFT, ω B97X-D/6-311+G(2df,p))

C	-2.52275	2.46377	1.24807
C	-1.52758	1.78810	0.58545
C	-1.23523	0.45811	0.96981
C	-1.96691	-0.15010	2.01022
C	-2.94852	0.55104	2.67478
C	-3.22439	1.85581	2.29138
H	-2.76396	3.47813	0.95849
H	-1.00284	2.27644	-0.21985
H	-1.73066	-1.17466	2.26766
H	-3.50272	0.08583	3.47886
H	-4.00023	2.41238	2.80344
N	-0.32012	-0.40975	0.43826
N	0.52955	-0.15365	-0.44212
C	0.86237	1.08898	-1.09935
C	0.40825	1.30171	-2.38940
C	1.65369	2.00447	-0.42484
C	0.73998	2.49423	-3.01383

H	-0.20027	0.55904	-2.89109
C	1.97798	3.18866	-1.06537
H	2.00391	1.79703	0.57903
C	1.51763	3.43367	-2.35227
H	0.39203	2.68563	-4.02065
H	2.59675	3.91856	-0.55955
H	1.77563	4.36138	-2.84704
H	1.08485	-0.96743	-0.69824

NH₂ABH⁺

All NH₂ABH⁺ geometries were calculated at the DFT ω B97X-D/6-311+G(2df,p) level of theory.

7.1.0.5 *trans*-(a)

C	-3.28869	-0.26547	1.70642
C	-1.90637	-0.19205	1.70178
C	-1.27712	0.98648	1.31266
C	-2.02724	2.09931	0.92544
C	-3.40404	2.01674	0.93313
C	-4.03498	0.83782	1.32247
H	-3.78306	-1.17989	2.00832
H	-1.29644	-1.03718	1.99637
H	-1.52311	3.00802	0.62557
H	-3.99716	2.87227	0.63514
H	-5.11684	0.78401	1.32477
C	2.12762	1.90099	1.05414
C	2.81776	3.04984	0.68884
C	2.82450	0.75368	1.43703
C	4.20251	3.06858	0.70212
H	2.25437	3.92587	0.39453
C	4.20404	0.75999	1.45359
H	2.26997	-0.13170	1.71682
C	4.86210	1.92040	1.08476
H	4.73890	3.96720	0.41681
H	4.75099	-0.12890	1.74994
N	0.12929	0.95301	1.34440
N	0.71145	1.99489	1.00284
N	6.34532	1.92513	1.11108
H	6.71101	2.80310	0.73772
H	6.70591	1.82074	2.06285
H	6.73222	1.16596	0.54532

7.1.0.6 *trans*-(b)

C	-3.39067	-0.12851	1.90259
C	-2.00933	-0.14765	1.87132
C	-1.31583	0.91152	1.28248
C	-2.01174	1.96785	0.67844
C	-3.38946	1.96806	0.70584
C	-4.07878	0.92821	1.32531

H	-3.93140	-0.94091	2.37005
H	-1.44490	-0.96107	2.30897
H	-1.50322	2.76116	0.14057
H	-3.93654	2.77059	0.22838
H	-5.16143	0.93869	1.33888
C	2.15545	1.82908	1.10744
C	2.79145	3.05935	0.91751
C	2.90340	0.65817	1.27761
C	4.15781	3.12871	0.90180
H	2.20895	3.96531	0.78350
C	4.26690	0.72652	1.26337
H	2.39963	-0.28887	1.41787
C	4.93013	1.96209	1.07649
H	4.64976	4.08196	0.75503
H	4.85156	-0.17591	1.39349
N	0.06769	0.80092	1.34175
N	0.76704	1.81239	1.12500
N	6.27287	2.01804	1.06293
H	6.75818	2.88758	0.93007
H	6.83054	1.19155	1.18623
H	0.31592	2.71772	0.95644

7.1.0.7 trans-(c)

C	-3.39776	-0.22773	1.68233
C	-2.01407	-0.22551	1.70106
C	-1.33616	0.92769	1.32992
C	-2.01005	2.07760	0.94094
C	-3.39183	2.05789	0.92805
C	-4.08656	0.91189	1.29651
H	-3.93642	-1.12123	1.96960
H	-1.47108	-1.11546	2.00233
H	-1.45961	2.96355	0.65635
H	-3.93320	2.94569	0.62756
H	-5.16889	0.90933	1.28217
C	2.148350	1.80204	1.08862
C	2.80594	2.99442	0.70090
C	2.93657	0.68412	1.47226
C	4.16372	3.08253	0.69085
H	2.19224	3.83815	0.41117
C	4.29103	0.76463	1.46478
H	2.48776	-0.25402	1.77862
C	4.94447	1.96782	1.07329
H	4.65279	4.00119	0.39182
H	4.88975	-0.08922	1.75785
N	0.07732	0.88329	1.36448
N	0.80562	1.86279	1.04928
N	6.27712	2.03231	1.07081
H	6.75827	2.87260	0.79796
H	6.84164	1.24503	1.34116
H	0.48403	-0.00242	1.66433

7.1.0.8 cis-(a)

C	-1.80301	-1.80700	-0.30710
C	-1.03693	-1.07774	0.58609
C	-0.71507	0.24086	0.29069
C	-1.21942	0.85768	-0.84904
C	-2.01909	0.13074	-1.71502
C	-2.29575	-1.20431	-1.45648
H	-2.03926	-2.84150	-0.09186
H	-0.68076	-1.51649	1.51023
H	-1.02221	1.90599	-1.03586
H	-2.43938	0.61215	-2.58950
H	-2.91971	-1.76890	-2.13799
C	1.59529	1.67512	-0.33483
C	1.80822	2.92532	-0.90661
C	2.10950	0.52806	-0.93574
C	2.49345	3.03191	-2.10181
H	1.43408	3.80994	-0.40708
C	2.81510	0.62792	-2.11915
H	1.95508	-0.43947	-0.47662
C	2.98338	1.87815	-2.68209
H	2.64801	4.00569	-2.55402
H	3.21821	-0.26408	-2.58658
N	0.04972	0.94460	1.27016
N	1.02734	1.63085	0.97181
N	3.76434	1.99062	-3.93737
H	3.47549	2.80936	-4.47662
H	4.76788	2.07762	-3.75510
H	3.62652	1.17032	-4.53148

7.1.0.9 cis-(b)

C	3.67677	-1.88213	2.15317
C	2.75039	-1.65602	1.15336
C	1.77482	-0.66833	1.32095
C	1.78380	0.15280	2.45828
C	2.74984	-0.04750	3.41905
C	3.67911	-1.07669	3.28201
H	4.41443	-2.66545	2.03884
H	2.75581	-2.23532	0.23877
H	1.07348	0.96047	2.57034
H	2.78505	0.60059	4.28526
H	4.42102	-1.23409	4.05500
C	-1.13620	0.25288	1.26647
C	-2.11517	1.20762	0.97739
C	-1.19879	-0.47580	2.45856
C	-3.10667	1.47935	1.88180
H	-2.08616	1.75242	0.03939
C	-2.20096	-0.22258	3.35356
H	-0.48019	-1.25441	2.67368
C	-3.17144	0.77215	3.09815
H	-3.85088	2.23292	1.65663
H	-2.25922	-0.80134	4.26725

N	0.95835	-0.48776	0.21193
N	-0.19932	-0.01381	0.24857
N	-4.14154	1.02668	3.99418
H	-4.84671	1.71978	3.81659
H	-4.21080	0.50618	4.85050
H	-0.56045	0.15569	-0.68933

7.1.0.10 cis-(c)

C	-2.52518	-2.42802	2.30550
C	-1.86494	-1.74328	1.29750
C	-2.02081	-0.36911	1.21395
C	-2.83203	0.33222	2.09127
C	-3.48654	-0.36481	3.09455
C	-3.32877	-1.73941	3.20344
H	-2.41570	-3.50202	2.38520
H	-1.23252	-2.26509	0.58942
H	-2.94273	1.40540	1.99321
H	-4.12519	0.16683	3.78832
H	-3.84438	-2.27950	3.98748
C	0.69475	0.91131	1.18941
C	1.89205	1.60530	0.84503
C	0.59548	0.35947	2.50600
C	2.91649	1.74965	1.72233
H	1.95587	2.01841	-0.15379
C	1.61848	0.50275	3.38350
H	-0.28502	-0.17610	2.82406
C	2.80670	1.19920	3.02229
H	3.81631	2.28103	1.43842
H	1.53857	0.08292	4.37909
N	-1.33184	0.34967	0.17447
N	-0.18141	0.88662	0.18064
N	3.79810	1.32724	3.90113
H	4.64576	1.81547	3.66486
H	3.73142	0.94007	4.82739
H	-1.81100	0.46343	-0.71122

7.2 Supporting information for Chapter 4

This section contains the supporting information for Chapter 4. It was originally available alongside the published article at doi:10.1021/acs.inorgchem.8b00871 and is reproduced here with permission. Figure and table numbers have been adjusted to reflect their position within the thesis.

Computational details

Geometry optimizations were performed at the TPSS/def2-TZVP level of theory using Grimme's D3 dispersion correction with Becke-Johnson damping.^{290,336,345} Harmonic frequencies were calculated using finite differences ($\Delta x = 0.005$ Bohr) to confirm the identity of local minima and to calculate zero-point energies. No symmetry constraints were enforced during optimization. Single-point energies were calculated at the DLPNO-CCSD(T)/def2-TZVP level of theory, which is benchmarked to give relative energies to within $\sim 400\text{ cm}^{-1}$ of the canonical CCSD(T) values for main-group elements.^{337,338}

Vertical excitation energies were calculated using linear-response time-dependent density functional theory at the PBE0/def2-TZVP level of theory using the same dispersion correction as for geometry optimization.^{345,368} The first 45 singlet excited states were calculated for each isomer and conformer. These calculations were performed using the scalar-relativistic zeroth-order relativistic approximation (ZORA), where spin-orbit contributions were neglected as they have been shown to be of minimal impact in the predicted absorption spectrum.^{378,449} Relativistically-recontracted basis sets were used for both the orbital and auxiliary terms.

For all DFT calculations, the resolution of the identity (RIJ) and chain of spheres (COSX) approximations were applied using the appropriate auxiliary basis set.^{404,450} Tight integration grids were used (Grid5). The DLPNO-CCSD(T) calculations were performed using the def2-TZVP/C correlation-fitting basis set. Tight SCF convergence was enforced throughout. All electronic structure calculations were performed using the ORCA 4.0 package.^{320,321}

Collision cross sections were calculated using the trajectory method in the MOBCAL program parametrized for nitrogen buffer gas.^{302,347} Input partial charges were calculated from the TPSS/def2-TZVP densities using the CHELPG scheme as implemented in ORCA. Lennard-Jones parameters for ruthenium were assumed to be the same as for iron.

Reference NEVPT2 simulation

In order to confirm the applicability of the TDDFT approach for calculating excited states in the Ru(bpSO) system, the ZORA-PBE0-D3(BJ)/def2-TZVP simulated absorption spectrum was compared against a simulated spectrum using the n -electron valence state perturbation theory at second order (NEVPT2) approach.^{280,281}

A complete active space self-consistent field (CASSCF) theory wavefunction using an active space of 14 electrons distributed in 13 orbitals was used as the zeroth-order wavefunction. The active space was chosen by visual inspection of Kohn-Sham guess orbitals and included the five ruthenium $4d$ orbitals, two pairs of bonding and anti-bonding π orbitals on the bipyridine ligands, and two pairs of bonding and anti-bonding π orbitals on the bpSO phenyl rings.

The state-specific strongly-contracted NEVPT2 method was used for this study, whereas the reference CASSCF wavefunction was averaged over the ground state and 20 lowest-lying singlet excited states. The def2-TZVP basis set including a scalar-relativistic effective core potential on ruthenium was employed, along with the appropriate auxiliary basis sets for the RI and COSX approximations.

The S,S-Ru(bpSO) ground state was found to be comprised almost exclusively of the low-spin d^6 configuration with a CASSCF weight of 0.95. Both the single-reference DLPNO-CCSD(T) and DFT methods should therefore accurately describe the ground state.

Table 7.2: Example electronic transitions for the S,S-Ru(bpSO) isomer calculated using NEVPT2(14,13)/def2-TZVP and TD-PBE0/def2-TZVP levels of theory.

Method	Transition	Wavelength (nm)	Energy (cm^{-1})	Oscillator strength
NEVPT2	MLCT	352.4	28377	0.078
	MLCT	346.0	28910	0.064
	$\pi\pi^*$	314.0	31848	0.343
	$\pi\pi^*$	304.8	32808	0.996
TDDFT	MLCT	343.5	29116	0.057
	MLCT	331.8	30143	0.041
	$\pi\pi^*$	290.4	34431	0.034
	$\pi\pi^*$	288.2	34687	0.076
	$\pi\pi^*$	287.4	34791	0.037

Example vertical excitation energies and corresponding oscillator strengths are given in Table 7.2 using TDDFT and the reference NEVPT2 values for the S,S-Ru(bpSO) isomer. While 45 and 20 excited states were calculated using TDDFT and NEVPT2, respectively, only the transitions with the largest oscillator strengths are listed. For the MLCT transitions, excitation energies agree to within a few thousand cm^{-1} , with poorer agreement for the high energy $\pi\pi^*$ band. Oscillator strengths also differ somewhat, but without experimental data, it is difficult to judge accuracies. However, overall the TDDFT results agree at least qualitatively with the high level NEVPT2 reference at a fraction of the computational cost. As shown in the main text, the TDDFT absorption spectrum models the experimental PISA spectrum reasonably well.

Calculated CASSCF and Kohn-Sham orbitals

Table 7.3: CASSCF natural orbitals depicting the active space used in the NEVPT2 calculations.

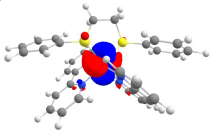
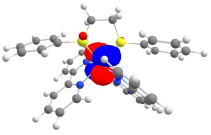
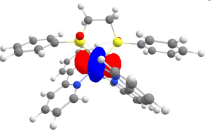
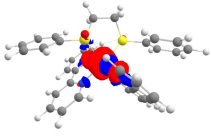
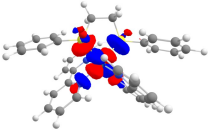
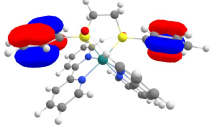
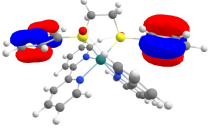
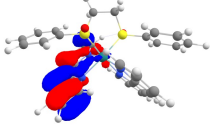
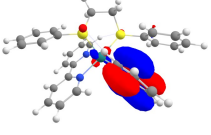
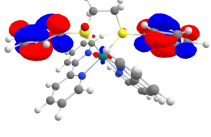
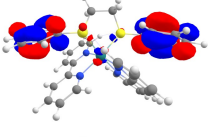
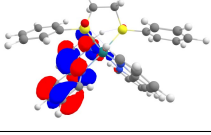
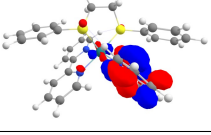
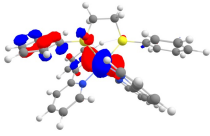
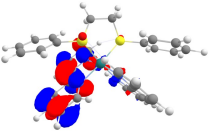
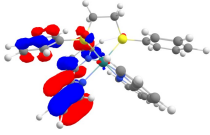
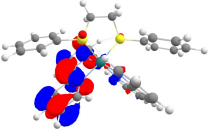
Character			
d			
d^*			
π (phenyl)			
π (bpy)			
π^* (phenyl)			
π^* (bpy)			

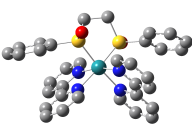
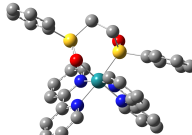
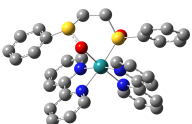
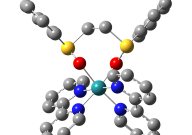
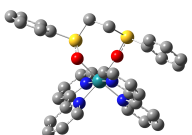
Table 7.4: Representative Kohn-Sham orbitals responsible for transitions predicted by TDDFT.

Transition	Donor	Acceptor
MLCT		
$\pi\pi^*$		

Calculated structures, energies and collision cross sections

Calculated energies of the Ru(bpSO) isomers at the DLPNO-CCSD(T)/def2-TZVP//TPSS-D3(BJ)/def2-TZVP level of theory are given in Table 7.5. Cartesian coordinates for the structures are given at the end of Section 7.2. The S,S-isomer optimization was started from the experimental crystal structure geometry. No evidence for diastereomers at the chiral sulfur atoms was observed in solution, for either Ru(bpSO) or its synthetic precursor, by ^1H -NMR spectroscopy or X-ray crystallography.³⁶¹ For the S,O- and O,O-isomers, two conformers each were calculated depending on whether the phenyl rings on the bpSO ligand are π -stacked with the bpy ligands. Two energies and two collision cross sections are given for each S,O- and O,O-isomer, corresponding to π -stacked and non- π -stacked conformers.

Table 7.5: Calculated geometries and relative energies (ΔE) for the S,S-, S,O-, and O,O-Ru(bpSO) isomers using the DLPNO-CCSD(T) (CC) and TPSS (DFT) methods with the def2-TZVP basis set, and the corresponding measured and calculated collision cross sections (Ω_m and Ω_c). Hydrogen atoms have been omitted for clarity.

Isomer	Geometry	ΔE^a (CC) (cm^{-1})	ΔE^a (DFT) (cm^{-1})	Ω_m^b ($\text{\AA}^2$)	Ω_c ($\text{\AA}^2$)
S,S		0	0	253	275
S,O (non- π -stacked)		2460	2880	260	285
S,O (π -stacked)		1830	2820	260	274
O,O (non- π -stacked)		4380	4690	265	303
O,O (π -stacked)		4250	4790	265	283

^aEnergies given in cm^{-1} relative to the S,S-Ru(bpSO) isomer;

^bMeasured collision cross sections have an uncertainty of $\pm 2 \text{ \AA}^2$.

Measured collision cross sections

The method for measuring collision cross sections has been previously explained.⁴⁵¹ The drift mobility of an ion in a weak electric field is given by the Mason-Schamp equation:

$$K = \frac{3ze}{16N} \sqrt{\frac{2\pi}{\mu k_B T}} \left(\frac{1}{\Omega} \right) = \frac{l^2}{t_d V} \quad (7.3)$$

where ze is the ion's charge, N the buffer gas number density, μ the reduced mass of the ion and buffer gas, k_B the Boltzmann constant, T the temperature, and Ω the orientationally-averaged collision cross section.

Equation 7.3 can be rearranged to give an ion's collision cross section as a function of its arrival time at the detector:

$$\Omega = A \frac{t_d z}{\sqrt{\mu}} \quad (7.4)$$

The parameter A was extracted by linear regression of literature collision cross sections against measured drift times for a series of tetraalkylammonium cations. The extracted collision cross sections are given in Table 7.5.

Branching ratio for formation of S,O-Ru(bpSO) and O,O-Ru(bpSO) isomers

Power dependence

Power dependence studies were performed to confirm that the S,O-Ru(bpSO) and O,O-Ru(bpSO) isomers were formed from S,S-Ru(bpSO) following absorption of a single photon. The ratio of S,O-Ru(bpSO) to O,O-Ru(bpSO) photoproduct counts was measured as a function of the light fluence. The product ratios were extracted by fitting the laser-on/laser-off difference ATDs with a sum of three Gaussian functions, to model depletion of the S,S-isomer and formation of the S,O- and O,O-isomers. Plots of the O,O to S,O branching ratio against light fluence at 315 nm and 360 nm are shown in Figure 7.3, where the dotted lines indicate a weighted least-squares fit to the data points. No net depletion due to photodissociation was observed even at the highest power.

Wavelength dependence

The branching ratio for photo-induced transformation of S,S-Ru(bpSO) to the S,O- to O,O-Ru(bpSO) isomers is plotted as a function of wavelength in Figure 7.4. Measurements were performed with light fluences of $<0.35 \text{ mJ cm}^{-2}$ per pulse. The branching ratio was found to be independent of wavelength. Therefore, the PISA spectrum in Figure 4 of the main manuscript was built up as the sum of the S,O- and O,O-Ru(bpSO) photoyields.

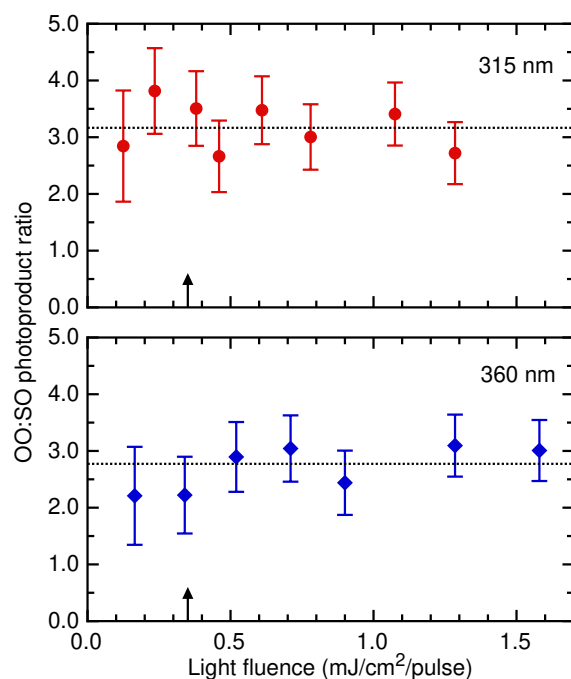


Figure 7.3: Branching ratio for O,O- to S,O-Ru(bpSO) photoproducts with respect to the light fluence at 315 nm (top) and 360 nm (bottom). The lines correspond to branching ratios of O,O- to S,O-Ru(bpSO) of 3.2 (top) and 2.8 (bottom). The vertical arrows indicate the upper limit to the light fluences used in the present experiment (0.35 mJ cm^{-2} per pulse).

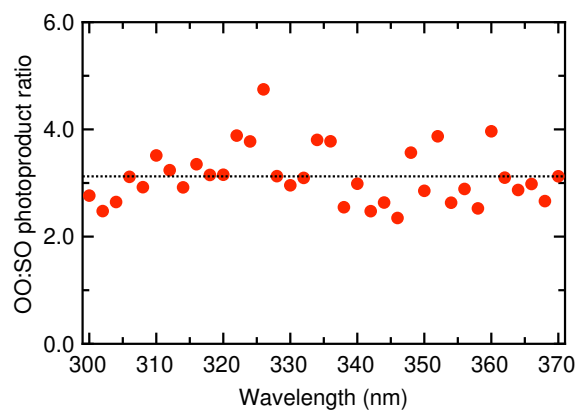


Figure 7.4: Dependence of the branching ratio for O,O- to S,O-isomer photoproducts on irradiation wavelength. The dotted line indicates an unweighted mean branching ratio of O,O- to S,O-isomers of 3.1.

Cartesian coordinates for calculated structures

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Coordinates from ORCA-job SS

C	4.66540515337006	4.29773296468724	2.57983413797633
H	3.98723188333641	3.96679827508700	1.80457519555054
C	5.87998701668864	3.66236987559408	2.79556281212503
H	6.15453207148602	2.81034755771635	2.18381476835942
C	6.72276923527380	4.14244690982269	3.79646202584155
C	6.31739697204949	5.24133438718562	4.54413826279472
H	6.96171383910643	5.63735385595915	5.31960846570648
C	5.08254189119057	5.83957746623741	4.28492059401673
C	4.56587231247982	7.00151597164057	5.01049856263711
C	5.22215750162954	7.57586765187694	6.10016908473518
H	6.16869728523907	7.16917214459550	6.43474804872815
C	4.65708594957984	8.65905791950111	6.76190458980766
H	5.16140850610225	9.10813657949658	7.61106560832600
C	3.43206489020922	9.14550349693291	6.31328229287222
H	2.94328759016552	9.98532783951884	6.79494592933685
C	2.82287548611808	8.54519710221604	5.21897650947671
H	1.87843097839559	8.90101326990570	4.81924640830147
C	1.11736789496878	5.50730983316953	5.52370398808972
H	1.68754507342025	6.31500021238929	5.96369140204843
C	0.22636653194782	4.75872725276494	6.27990871973894
H	0.10245083408369	4.97947201265537	7.33425719956326
C	-0.49313679914636	3.73928726672169	5.65949192341768
H	-1.20335021316663	3.13973328922633	6.21901772874828
C	-0.28714779851617	3.50311485246239	4.30590211780823
H	-0.84214104556150	2.72188693710201	3.80118416331549
C	0.62743559705866	4.28426286871829	3.59627656738314
C	0.91048025087997	4.11469917211897	2.16988624169779
C	0.37929068026586	3.07328466480364	1.40647272315731
H	-0.26815627865510	2.34063266200006	1.87260984752229
C	0.68223816823868	2.97452133551442	0.05468702611189
H	0.27123168838520	2.16853341802776	-0.54413897883031
C	1.53089945734063	3.92670501082002	-0.50595868183056
H	1.80741114487787	3.89475717108825	-1.55416827224132
C	2.04682079774513	4.93383481863239	0.29886193845007
H	2.74368129745188	5.67176154492731	-0.08514849253967
C	-1.68635786811033	7.12413528899790	3.37953363332768
H	-1.42080814328252	7.73516165303626	4.23539002430227
C	-2.90868988635080	6.45777366762049	3.32117876631902
H	-3.60172544601811	6.53654270564477	4.15273704634458
C	-3.24985273424152	5.71430322061452	2.18996546018935
H	-4.20962502154619	5.20954310301181	2.14295639444578
C	-2.37096666349671	5.63722976367962	1.10804779908280
H	-2.64695275007532	5.07988032177830	0.21845059556265
C	-1.13957370835571	6.28810535026693	1.15506757610679
H	-0.46526034881678	6.22040702759666	0.30881890288269
C	-0.81141933175295	7.02740292261792	2.29411800010417
C	1.13715476083966	8.52191700147251	0.83923851409425
H	1.04388299621739	7.71642783998633	0.10705016723137

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H	0.39229903594207	9.29841056015053	0.64715262322996
C	2.54851226660034	9.07879530373472	0.90550390479425
H	2.62171959807851	9.90483974446897	1.61488581647522
H	2.92706177094246	9.38722586263566	-0.07228600678241
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C	6.33005541194734	8.08486857820625	1.84431132797521
H	6.41714346558142	7.24435847641225	1.16413783749262
C	7.45699694029410	8.67926854392918	2.41126496264430
H	8.44265439215015	8.28983615437517	2.17695166042449
C	7.31943823000719	9.78160511136796	3.25534064422498
H	8.20061447179959	10.24906293218484	3.68331684569902
C	6.05302184607240	10.30089926154048	3.53561208669376
H	5.94878680749239	11.17123987722051	4.17567677200487
C	4.91698151805811	9.71520361378691	2.98296531299564
H	3.93779221166109	10.12275381937016	3.20883889359493
N	4.26589904842664	5.35983541038336	3.30614230620771
N	3.36882491982831	7.49475060387807	4.56749905873583
N	1.31831223930112	5.28466301080371	4.21014863282859
N	1.74900811112185	5.04249017622891	1.61443885929246
O	0.52434011600545	9.02343039899997	3.39485871434749
O	4.17594534945979	7.03059379206581	0.22623284474813
Ru	2.51457430970692	6.47363601047131	2.95053673189625
S	0.76665804366655	7.85251907179500	2.50783534806167
S	3.67663011034209	7.72373194789561	1.44532442459729
H	7.68123264330234	3.67202975812141	3.98888918916716

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Coordinates from ORCA-job SO

C	4.62135884838552	4.29532059224327	2.67138159465384
H	3.87948530992312	3.96538322462346	1.95614088790048
C	5.83776563038113	3.64316959526963	2.81090483120289
H	6.05038388551121	2.77601664315980	2.19565110126006
C	6.76183916289620	4.12145380967875	3.73884007761446
C	6.42989222091016	5.23824077386697	4.49648190056406
H	7.13211107296053	5.63326610474177	5.22104934630729
C	5.19229549763785	5.85761020228098	4.31952388246965
C	4.74624018921206	7.03323999400801	5.06944468075569
C	5.47786409492578	7.64516132682167	6.08897606469032
H	6.45801402750672	7.26791602118748	6.35525897005864
C	4.94045342971267	8.73278988393863	6.76729517255255
H	5.50018712592694	9.21210449830852	7.56342466549131
C	3.66996823855853	9.18779512611962	6.41370412397234
H	3.20772078424092	10.02598323054525	6.92346547589626
C	2.98915305416815	8.55144086393131	5.38563952256542
H	2.00226527575707	8.86050750507044	5.05952723223173
C	1.47646097817214	5.42473477743022	5.87804846612883
H	2.20062239898080	6.11749345489076	6.28656073279556
C	0.61133660159387	4.72075071972602	6.70348908110108
H	0.66349811077193	4.85973835073151	7.77757259249561
C	-0.31062516148972	3.84918456823420	6.12569730760092
H	-1.00675999577044	3.28858363590449	6.74062607105950
C	-0.31861290399897	3.70465147949984	4.74368222199646
H	-1.02296363217331	3.02977817941226	4.27252035014979

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C	0.58419889023993	4.43012036336493	3.96268170004366
C	0.68968120290658	4.30992983286603	2.50868765509969
C	-0.04378219280264	3.38576795429071	1.76316122729913
H	-0.76780987421964	2.74954577821696	2.25725002462680
C	0.16577689342047	3.26859162130454	0.39526126502469
H	-0.40016943076781	2.55115783104792	-0.18925496035556
C	1.13162574247329	4.07898865344533	-0.19642953637617
H	1.35625709696840	4.01348241007279	-1.25550734067249
C	1.82626272380668	4.99010342780298	0.58637916592728
H	2.60121440186279	5.62686191048765	0.17110141303050
C	-1.85591373092720	6.62228902925026	2.79376707900736
H	-1.64553772840573	6.94643746067109	3.80851283748412
C	-2.87369074256217	5.70872509821770	2.53817510648533
H	-3.46512718946277	5.32020099089982	3.36133967512906
C	-3.15263435252233	5.31956704521827	1.22576373851926
H	-3.96317811045346	4.62537066420620	1.02744877638455
C	-2.40692661506204	5.83578552079305	0.16636173188077
H	-2.63139131704257	5.54221669290674	-0.85408877991026
C	-1.37367826190115	6.74224014732300	0.40631089613520
H	-0.81288624476417	7.14513784317128	-0.42942482433329
C	-1.10283668022832	7.12069249961002	1.72317655117882
C	1.13629489456468	8.50510786481098	0.68431265812046
H	1.24824764300022	7.51499888865817	0.23523336556214
H	0.61916374616895	9.16760028347877	-0.01568228474348
C	2.48495949572033	9.09381617435519	1.10032996824228
H	2.39778653582399	9.82643423543036	1.90552325782655
H	2.99508331144991	9.54564995366538	0.24546382125177
C	5.02981054777717	8.62247883416467	2.20789529608747
C	6.26642353277070	8.07719405569476	1.85812837571289
H	6.30862015992042	7.21594307624078	1.19991524599955
C	7.42842745656159	8.67733461731718	2.34226687362000
H	8.39614423101381	8.27146473573368	2.06493661672038
C	7.34782541534837	9.80466156796265	3.16021507961886
H	8.25528853726906	10.27573346748164	3.52455396601241
C	6.10339088780410	10.34331363216020	3.49569095058956
H	6.04229770710234	11.23251616382985	4.11517131882641
C	4.93358834727337	9.75130004260588	3.02590092392376
H	3.97265429167039	10.17559274871933	3.29424067287937
N	4.29286371661494	5.38019773355268	3.40331857071764
N	3.51139790187344	7.50100860643948	4.71855411922266
N	1.46669609340878	5.29672342632491	4.53593862300472
N	1.60879797450389	5.13484570713588	1.91557284408948
O	0.96727193498203	7.84590004096179	3.30469964087276
O	4.00632506941636	7.03677149815458	0.36609643708440
Ru	2.57388860362983	6.46562440655288	3.20526724990353
S	0.06814456250688	8.40080416352365	2.17015326761378
S	3.59088367447915	7.72186694409276	1.62277819312661
H	7.72309500208828	3.63582979415976	3.86797519299090

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Coordinates from ORCA-job SO_nostack

C	4.61084590372636	4.54142804723805	2.86106967472800
H	3.93026489948628	4.20830022913897	2.08770189234901

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C	5.79336842993727	3.86830015450440	3.13244505844124
H	6.04314150422646	2.98031163070668	2.56235091426357
C	6.63607393131766	4.35098804152048	4.13277468447934
C	6.25821482682163	5.49187882363914	4.83048441395796
H	6.89727064453836	5.89198933398348	5.60870564675490
C	5.05678127978863	6.13001768679551	4.52171569332820
C	4.57086996776435	7.33580237777077	5.19453265158606
C	5.19120699245023	7.94020808361760	6.29007929840526
H	6.10216809485371	7.51827088260854	6.69786178345251
C	4.63534388951214	9.08161603690128	6.85510001697804
H	5.11056003122644	9.55868574635898	7.70565508961622
C	3.45164477408957	9.59413433110045	6.31955818845245
H	2.97769109556164	10.47490040375149	6.73864742984136
C	2.86865081954774	8.94924127903121	5.23853403935703
H	1.93446356358121	9.27589072998433	4.79320957001556
C	1.32517758667671	5.83050519456842	5.78509682209190
H	1.99954457366756	6.56514403428225	6.20497660737077
C	0.45151310798007	5.11779568926262	6.59310041215152
H	0.44532419585926	5.29522999067699	7.66271956331865
C	-0.40363213430785	4.18803145241630	6.00383551594861
H	-1.10363730217939	3.61667900114720	6.60419548071783
C	-0.34287170698945	4.00234275097902	4.62854692707529
H	-0.99609500836199	3.28284573938851	4.14979981413732
C	0.56217563896473	4.74390140029621	3.86471104610728
C	0.72484325438380	4.59682669116795	2.41822998560575
C	0.01733802579325	3.66303685013888	1.65803145827393
H	-0.71533804868799	3.02312664764098	2.13498781031189
C	0.26108514660487	3.54571754584928	0.29537618246517
H	-0.28195028702750	2.81965654162810	-0.30033995456074
C	1.22141799653232	4.37581000699066	-0.27930462157611
H	1.45685394273650	4.32327543882216	-1.33666034397875
C	1.88960578922364	5.29580218705107	0.51649988642369
H	2.62882594405573	5.97644778568083	0.10746859256530
C	-1.18935174488050	10.39408613460533	2.43086671678619
H	-0.38311012267418	10.74962563088979	3.06520835710990
C	-2.43115715432739	11.01844813319843	2.44819682512057
H	-2.59481668543165	11.87624790959909	3.09253414020325
C	-3.46710531724122	10.54671814871440	1.63333687758325
H	-4.43041603436375	11.04660985356152	1.64796398824180
C	-3.27382050385747	9.44115285367704	0.80588536172037
H	-4.08143819659889	9.07929820325871	0.17812859196908
C	-2.03884973545477	8.79341615768218	0.78878722485180
H	-1.87353066185318	7.92616856181965	0.15624427774927
C	-1.00814875933995	9.28588515340381	1.59484151134927
C	1.67966759939998	9.74472541661733	0.95900982948280
H	1.81261305244169	9.56437648666265	-0.11062311349366
H	1.19101307654409	10.70867486943531	1.11356826567098
C	3.01233996165453	9.70525092007011	1.69931911547412
H	2.89812481938723	9.96447792119958	2.75329163357797
H	3.72594855279476	10.37961630950824	1.21751380818245
C	5.42375665809984	8.30228891110517	2.09640425380759
C	6.36655367751316	7.47594949428940	1.47992954296462

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H	6.05420200843551	6.78001690614364	0.70871815046394
C	7.70597504499289	7.59310502096663	1.84498482434153
H	8.44928576361222	6.96539897137644	1.36380533024816
C	8.09263160539380	8.52864223840250	2.80676437081091
H	9.13931992402506	8.62597177078660	3.07713964094313
C	7.14119100387331	9.35648456024213	3.40456726975675
H	7.44541860163439	10.10034715777752	4.13425757006771
C	5.79528234450495	9.24376424288955	3.05846241557414
H	5.06250811378202	9.89068995017479	3.52864255797500
N	4.23966428075689	5.65239817168208	3.53113903163297
N	3.41502021785629	7.84866114955182	4.67727753344433
N	1.38579248923348	5.65942123315622	4.44908231984399
N	1.65652383627749	5.42083578704859	1.84400660173155
O	0.93528535420749	8.13227155305927	3.00882696096524
O	3.72790943327365	7.63273294829490	0.18062814964454
Ru	2.58034432504298	6.76781568952700	3.14067431437272
S	0.52476485061487	8.40278292085654	1.52026346356022
S	3.71679294261406	8.01538776893589	1.62104539989786
H	7.56919401470238	3.84892612319128	4.36439965591760

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Coordinates from ORCA-job 00_onestack

C	4.26528096793077	3.75722539456034	3.35053349002736
H	3.52561293913714	3.45505153470189	2.62092710405462
C	5.38265678962547	2.97933821457453	3.60886677533145
H	5.51634719258836	2.04662516029759	3.07213954819751
C	6.31273089340804	3.41472229112922	4.55320787193608
C	6.07362942873036	4.61131561426657	5.2165277726663
H	6.77167732008188	4.96789744626670	5.96493623240808
C	4.92840514888432	5.35577677622755	4.92837764803591
C	4.55805679843102	6.59155524498284	5.61379520262124
C	5.29671925743824	7.18182793834408	6.64202406098739
H	6.23776702332743	6.74404029737567	6.95388806513022
C	4.81666941665561	8.32492509762739	7.26957508399956
H	5.38071553092645	8.78749366631111	8.07246819644519
C	3.59426915266419	8.85730542504732	6.85463914118067
H	3.17575120218506	9.74128619746871	7.32328129960781
C	2.90608362451052	8.24126353629118	5.82062657321385
H	1.96176546919335	8.61821142068650	5.44571934264080
C	0.92051573947529	5.15275978409001	5.93821493640955
H	1.57298681606964	5.81549356344578	6.49223001314029
C	-0.08014991057759	4.42570946812351	6.56364246214913
H	-0.21456191564778	4.51906546050878	7.63566803416862
C	-0.89214792724358	3.58527713530113	5.79997290557354
H	-1.68181345348979	3.00339185680666	6.26280137387166
C	-0.66387349197449	3.50405203594104	4.43223237219609
H	-1.27692794093767	2.85926842372474	3.81322307411995
C	0.35722616890391	4.25514641661770	3.84812850391183
C	0.69692266866857	4.22541433940069	2.42901882808352
C	0.09931323927884	3.39306017734786	1.48088289504276
H	-0.71208919071416	2.73694474944668	1.77302415162207
C	0.55772601813885	3.39691462857551	0.16915181843230
H	0.10294108797489	2.75003659354588	-0.57324767763517

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C	1.62599068422909	4.23127626037806	-0.16746294738824
H	2.03408294806298	4.24676714281982	-1.17225581018831
C	2.17903837392002	5.04473947983435	0.80915402837402
H	3.02347136272053	5.69814495648621	0.61422241660574
C	-1.72953670895861	6.74220210056871	2.82823900451974
H	-1.58389097342367	7.08192954605388	3.84933065801649
C	-2.74759335749741	5.84501893950510	2.52034645573604
H	-3.40437204154814	5.48938733126068	3.30782716680625
C	-2.93882277215200	5.42856000769517	1.20121418836209
H	-3.74879260958333	4.74732394156561	0.96006285375438
C	-2.10423738180204	5.90064192006121	0.18807817465701
H	-2.25801546043328	5.58321568264418	-0.83828641889965
C	-1.07151034643022	6.79059357476710	0.48163040018924
H	-0.43688959070627	7.15030411247841	-0.31937770419838
C	-0.89013086471222	7.20006627176348	1.80497519497894
C	1.40322067120243	8.51752607718585	0.88326721892889
H	1.71231391673155	7.50162395243952	0.63389725721777
H	0.79739441301212	8.93396142528839	0.07164513363868
C	2.60614494977871	9.42675595565192	1.11831962705420
H	2.32344106250373	10.45140994614080	1.37806128654928
H	3.22090144679470	9.44465723321621	0.21472966510397
C	5.24451058443594	9.48766976791263	1.96097680748743
C	5.89773616648761	8.99055237411593	0.82804842768425
H	5.46809507259320	8.17411961905007	0.25584478135984
C	7.12187577612355	9.54551879172731	0.47062671156546
H	7.64927905843340	9.17161149452919	-0.40107928752685
C	7.67227511519468	10.58435266078620	1.22994069801370
H	8.62492918130065	11.01516634258749	0.93853704233117
C	7.01214963733885	11.06595005573766	2.36025292093429
H	7.44755954023314	11.86693408085566	2.94866044677808
C	5.79161571727892	10.50947566636191	2.74226742937561
H	5.27102251057136	10.86338661842243	3.62761913078535
N	4.03133672924836	4.93194973474099	3.97932842904167
N	3.37042270673712	7.13269731989706	5.20020677913611
N	1.14599720871730	5.08537079518372	4.60567617339941
N	1.71979976078844	5.06846866020164	2.08186334144314
O	1.12710891112852	7.80513692132538	3.48675353530309
O	3.75639334962420	7.29594146113749	2.27492621137767
Ru	2.49917969332475	6.18504157713431	3.60308139020577
S	0.29948551536372	8.43194972037186	2.33766363305328
S	3.68735576572265	8.83648294256954	2.50242195315893
H	7.19974821400179	2.83071164851172	4.77297849110394

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Coordinates from ORCA-job 00_nostack

C	4.17962010229852	4.69506948297048	3.19207493314494
H	3.36077868572328	4.14815620545435	2.74261822641226
C	5.38522551655408	4.08102100690439	3.49147985154192
H	5.51263334307103	3.02618877720585	3.27453793833955
C	6.41096050996638	4.83358888344456	4.06551947750700
C	6.18017990443071	6.17742272997522	4.33034765367665
H	6.95474865304088	6.78441752724543	4.78474263271573
C	4.94582843839604	6.74985753951138	4.01807607401328

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C	4.58313618844248	8.13604536315096	4.30093237950536
C	5.41146329966358	9.06776000504510	4.93164086481577
H	6.42102049509029	8.79189877514767	5.21354431390052
C	4.93405727912259	10.34362308750416	5.20513607385123
H	5.56867942423945	11.07263419777288	5.69742958867610
C	3.62198304156064	10.66377076985199	4.84702478109102
H	3.20423928063565	11.64258656501464	5.05563407183046
C	2.84518132756813	9.70704332022414	4.21370929789974
H	1.82279141679767	9.89679418028733	3.90687039401018
C	1.31818720914879	6.76461484082074	5.77671338353446
H	2.04792761969059	7.54640150564817	5.94384470572711
C	0.52284194936148	6.28201903947582	6.80371977536790
H	0.63507598276478	6.69318919198597	7.80086845564257
C	-0.40686771063299	5.27687458982979	6.53293352499849
H	-1.04552962062632	4.88279689494795	7.31585261573370
C	-0.49297217288885	4.78366584097199	5.23733040766356
H	-1.19887567519163	3.99625996272305	4.99946678010282
C	0.33555212066985	5.29610641624701	4.23743569435966
C	0.36214315890395	4.81365363352488	2.85923133278207
C	-0.42499549430908	3.77312428800187	2.35952047782549
H	-1.15106569872157	3.28694278948319	3.00079733874109
C	-0.26721916383954	3.35777906572051	1.04307023945156
H	-0.87143005698208	2.54855931315961	0.64727908788518
C	0.68983059946970	3.99140966028302	0.24623871996216
H	0.85647058045626	3.68871441541673	-0.78173220668473
C	1.43670812148974	5.02577663459547	0.78653956766531
H	2.18936747037774	5.55984372452714	0.21756290494491
C	-2.40862747607365	9.44663679248489	0.36559162182850
H	-2.46298759919968	8.67514732883891	-0.39835524175196
C	-3.38531345266120	10.43691862870640	0.43719488053739
H	-4.19916666144606	10.44130050559850	-0.28045840792834
C	-3.32544014950212	11.40802488639383	1.43986493411534
H	-4.09493836656901	12.17113992137626	1.49669342895694
C	-2.29262376554445	11.39287777412731	2.37791193290334
H	-2.25963545516797	12.14080767345911	3.16370791316778
C	-1.30084103319983	10.41357698499961	2.31642491260827
H	-0.50528751044269	10.36962800102378	3.05130336093636
C	-1.36914781667780	9.46208827930896	1.30022449254112
C	0.89590456915807	8.86368755955207	-0.20193033417668
H	1.37740812385405	8.00371591819028	-0.67389151233933
H	0.19144220287316	9.31546168438102	-0.90451265646164
C	1.89872429131327	9.87505614337077	0.32306747401519
H	1.55029467005589	10.37941935048669	1.22765628208572
H	2.15725985596909	10.62171918859033	-0.43173003697575
C	4.26506121645749	8.97037862564453	-0.82637082704090
C	4.29579837212216	7.77204337992761	-1.53731647592663
H	3.86408103807516	6.87428315150977	-1.11012553273754
C	4.91885759817666	7.75515877585345	-2.78552703174347
H	4.95634372116714	6.83117582986900	-3.35368420627176
C	5.49705347905021	8.91663714929076	-3.29878376299211
H	5.98277938248422	8.89457453339692	-4.26897831911814
C	5.46969199106960	10.10493948351520	-2.56452343798405

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H	5.93497794939899	11.00234813394802	-2.95896667675440
C	4.85926737644617	10.13840763582029	-1.31309225179163
H	4.85538164404134	11.05459053736039	-0.72797514016838
N	3.94900703192636	6.00620195553620	3.43491455790590
N	3.30710123063389	8.46778152841062	3.93034863515082
N	1.23415706647222	6.29887127801683	4.50889623977618
N	1.27898683221903	5.44617174067081	2.06242273054992
O	0.71234379223062	8.36524853944018	2.46349372644179
O	3.12426531896980	7.56929702963693	1.07465199167289
Ru	2.27602752845550	7.00169408611553	2.94274377513337
S	-0.14216340293126	8.17130702273193	1.17925972844087
S	3.50076134261587	9.04954340310417	0.78534250660566
H	7.36651893843747	4.38088933523863	4.30660536815429

7.3 Supporting information for Chapter 5

This section contains the supporting information for Chapter 5 in the form of the calculated $\tilde{X}^2E'_2$ and $\tilde{A}^2A'_1$ equilibrium geometries.

$\tilde{X}^2E'_2$ equilibrium geometry of FeCp_2^+

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Equilibrium geometry of $\text{Fe}(\text{Cp})_2^+$ at PBE0-D3(BJ)/def2-TZVPP

C	-0.711866	1.668476	-0.976599
C	0.711866	1.668476	-0.976599
C	1.145441	1.724440	0.374477
C	0.000000	1.761034	1.202093
C	-1.145441	1.724440	0.374477
H	-1.348855	1.629171	-1.846438
H	1.348855	1.629171	-1.846438
H	2.169880	1.708636	0.713815
H	0.000000	1.762014	2.281685
H	-2.169880	1.708636	0.713815
C	-0.711866	-1.668476	-0.976599
C	-1.145441	-1.724440	0.374477
C	0.711866	-1.668476	-0.976599
H	-1.348855	-1.629171	-1.846438
C	0.000000	-1.761034	1.202093
H	-2.169880	-1.708636	0.713815
C	1.145441	-1.724440	0.374477
H	1.348855	-1.629171	-1.846438
H	0.000000	-1.762014	2.281685
H	2.169880	-1.708636	0.713815
Fe	0.000000	0.000000	-0.000272

$\tilde{A}^2A'_1$ equilibrium geometry of FeCp_2^+

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Equilibrium geometry of the A state of $\text{Fe}(\text{Cp})_2^+$ at PBE0-D3(BJ)/def2-TZVPP

C	-0.000000	1.209291	1.670133
C	-1.150104	0.373691	1.670133
C	-0.710803	-0.978337	1.670133
C	0.710803	-0.978337	1.670133
C	1.150104	0.373691	1.670133
H	-0.000000	2.287655	1.637833
H	-2.175689	0.706924	1.637833
H	-1.344650	-1.850752	1.637833
H	1.344650	-1.850752	1.637833
H	2.175689	0.706924	1.637833
C	0.000000	1.209291	-1.670133
C	1.150104	0.373691	-1.670133
C	-1.150104	0.373691	-1.670133
H	0.000000	2.287655	-1.637833
C	0.710803	-0.978337	-1.670133
H	2.175689	0.706924	-1.637833
C	-0.710803	-0.978337	-1.670133
H	-2.175689	0.706924	-1.637833
H	1.344650	-1.850752	-1.637833
H	-1.344650	-1.850752	-1.637833
Fe	0.000000	0.000000	0.000000

$\tilde{X}^2E'_2$ equilibrium geometry of $\text{FeCp}_2^+-\text{Ar}$

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Equilibrium geometry of $\text{Fe}(\text{Cp})_2^+-\text{Ar}$ at PBE0-D3(BJ)/def2-TZVPP

C	-0.7118213231	-1.6669267937	0.6335367219
C	0.7118215754	-1.6669267832	0.6335365848
C	1.145408609	-1.7247392949	-0.7173910775
C	-0.0000000083	-1.7621150584	-1.5450650397
C	-1.1454086161	-1.7247393119	-0.7173908569
H	-1.3477584529	-1.6239249269	1.5038044403
H	1.3477588722	-1.6239249069	1.5038041807
H	2.1698205264	-1.7090311373	-1.0567892343
H	-0.000000187	-1.7638360336	-2.6246512223
H	-2.1698205992	-1.7090311695	-1.0567888164
C	-0.7118213479	1.6669267162	0.6335369254
C	-1.1454086417	1.7247393928	-0.7173906463
C	0.7118215507	1.6669267267	0.6335367883
H	-1.347758477	1.6239247337	1.5038046385
C	-0.0000001092	1.7621152574	-1.5450648246
H	-2.1698206246	1.7090312766	-1.0567886078
C	1.1454085834	1.7247394098	-0.717390867
H	1.3477588481	1.6239247537	1.5038043789
H	-0.0000002132	1.7638363643	-2.624651007
H	2.1698205011	1.7090313088	-1.0567890257
Fe	0.0000000196	0.0000000262	-0.3441283998
Ar	0.0000004384	-0.0000002392	4.0045007557

$\tilde{X}^2E'_2$ equilibrium geometry of $\text{FeCp}_2^+-\text{Ne}$

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Equilibrium geometry of $\text{Fe}(\text{Cp})_2^+-\text{Ne}$ at PBE0-D3(BJ)/def2-TZVPP

C	-0.7118447538	-1.6674117462	0.6502662319
C	0.7118450467	-1.6674117179	0.650266098
C	1.1454293492	-1.7247399441	-0.7007149101
C	-0.0000000567	-1.7619480059	-1.5283380446
C	-1.1454293083	-1.7247399897	-0.7007146946
H	-1.3483863525	-1.6260106537	1.520248262
H	1.3483868073	-1.6260106	1.5202480083
H	2.1698571367	-1.7091244063	-1.040085325
H	-0.0000001582	-1.7636747743	-2.6079248168
H	-2.1698571602	-1.7091244927	-1.0400849168
C	-0.7118448202	1.6674117913	0.6502660205
C	-1.145429377	1.7247398463	-0.7007149133
C	0.7118449803	1.6674118196	0.6502658865
H	-1.3483864172	1.6260107837	1.5202480558
C	-0.0000001268	1.7619478031	-1.528338268
H	-2.1698572283	1.7091242654	-1.0400851335
C	1.1454292805	1.7247398919	-0.7007151288
H	1.3483867426	1.6260108374	1.5202478021
H	-0.0000002284	1.7636744346	-2.6079250404
H	2.1698570686	1.7091243518	-1.0400855417
Fe	0.0000000213	-0.0000000252	-0.3270688149
Ne	0.0000003958	0.0000002272	3.6543207722

7.4 Supporting information for Chapter 6

This section contains the supporting information for Chapter 6 in the form of the Julia script used to calculate the $S_1 \ ^1E'_3$ JT energy levels.

```
#!/usr/bin/env julia

using LinearAlgebra

# fit gives  $V(x) = 449.6679 * x^2 + 460.8571 * x + 118.3046$ 
#
# Longuet-Higgins says  $V(x) = (\omega/2) * x^2 +/- b*x$ 
omega = 899.3358

# k is defined as the ZPE of the degenerate vibration w/o JT coupling
# =>  $k^2 = 2 * E_{jt} / ZPE$ 

# From diabatic curves in Fig. 4
E_jt = 118

# From fit
ZPE = 2 * omega / 2

# Linear JT coupling parameter  $k^2 = 2 * 118 / 899 = 0.262$ 
k = sqrt(2 * E_jt / ZPE)

# Basis size
l = 1000

println("k^2= ", k^2, "\n")

for m = 0.0 : 4.0
    # Diagonal values
    dv = m .+ Array{Float64,1}(1 : l)

    # Off-diagonal values
    ev = sqrt.(ceil.(Array{Float64,1}(1:l) ./ 2) + m .* rem.(Array{Float64,1}(1:l), 2))

    # Build the Hamiltonian
    H = SymTridiagonal(dv, k*ev[1:end-1])

    # And diagonalize
    vals, vecs = eigvals(H), eigvecs(H)

    println(m)
    println("energies(cm-1)= ", vals[1:10] .* omega .+ E_jt)
    println("relative_intensities= ", (vecs[1:10,1] .^ 2) ./
        maximum(vecs[1:10,1] .^ 2))
    println()
end
```

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2. Scholz, M. S., Bull, J. N., Carrascosa, E., Kosgei, G. K., Rack, J. J., Bieske, E. J. Linkage photoisomerization of an isolated ruthenium sulfoxide complex: sequential versus concerted rearrangement. *Inorg. Chem.* **2018**, *57* (9), 5701–5706.

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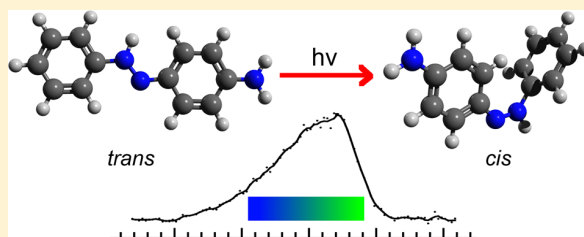
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Photoisomerization of Protonated Azobenzenes in the Gas Phase

Michael S. Scholz,[†] James N. Bull,[†] Neville J. A. Coughlan,^{‡,†} Eduardo Carrascosa,[†]
Brian D. Adamson,^{§,†} and Evan J. Bieske^{*,†}[†]School of Chemistry, University of Melbourne, Melbourne, Australia[‡]Department of Chemistry, University of Oxford, Oxford, United Kingdom[§]Sandia National Laboratories, Livermore, California 94551, United States

Supporting Information

ABSTRACT: Because of their high photoisomerization efficiencies, azobenzenes and their functionalized derivatives are used in a broad range of molecular photoswitches. Here, the photochemical properties of the *trans* isomers of protonated azobenzene (ABH^+) and protonated 4-aminoazobenzene (NH_2ABH^+) cations are investigated in the gas phase using a tandem ion mobility spectrometer. Both cations display a strong photoisomerization response across their $S_1 \leftarrow S_0$ bands, with peaks in their photoisomerization yields at 435 and 525 nm, respectively, red-shifted with respect to the electronic absorption bands of the unprotonated AB and NH_2AB molecules. The experimental results are interpreted with the aid of supporting electronic structure calculations considering the relative stabilities and geometries of the possible isomers and protomers and vertical electronic excitation energies.



INTRODUCTION

Azobenzene (AB) is the simplest azoarene compound that displays *cis*–*trans* isomerization around the azo ($-\text{N}=\text{N}-$) bond in response to light (Figure 1). The dynamics of the

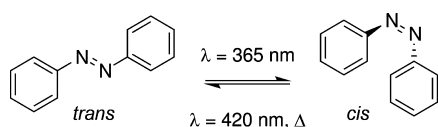


Figure 1. In solution, neutral *trans*-azobenzene readily converts to *cis*-azobenzene following the absorption of near-UV light, whereas *cis*-azobenzene reverts back to *trans*-azobenzene thermally or with exposure to 420 nm light.

photoisomerization process have been the subject of considerable debate, with the current consensus being that excitation of the $S_2 \leftarrow S_0$ transition (≈ 365 nm, oscillator strength ≈ 0.8), which has $\pi\pi^*$ character, is followed by rapid internal conversion to the S_1 state on a time scale of a few hundred femtoseconds.¹ In turn, molecules in the S_1 state undergo internal conversion to the S_0 state through a conical intersection seam at a geometry intermediate between those of the *trans* and *cis* isomers.^{2,3} The quantum yield for isomerization, which at the absorption maximum of the $S_2 \leftarrow S_0$ band is ≈ 0.25 ,^{4–6} depends on wavelength due to overlapping excited state absorption bands and dynamics on coupled excited state potential energy surfaces.^{2,3} The $S_1 \leftarrow S_0$ transition (≈ 420 nm) in the *trans* isomer has $n\pi^*$ character and is symmetry-forbidden, whereas the same transition in the *cis* isomer is weakly allowed.³ The thermal *cis*–*trans* isomerization

of azobenzene and substituted derivatives in solution has also been the subject of numerous studies.^{4,7} Although the rate of *cis*–*trans* isomerization depends on the solvent, unsubstituted *cis*-azobenzenes typically have half-lives of around 2 days at 298 K, corresponding to isomerization barriers of 80–120 kJ/mol.⁴ The *cis*–*trans* isomerization can be hastened by excitation of the *cis* isomer to the S_1 state, a property that has been exploited to design substituted azobenzenes with controllable photo-switching between *cis* and *trans* isomers with visible or light of different colors.⁸

The efficient, ultrafast photoisomerization of azobenzene and its substituted derivatives has led to their application in a range of molecular photoswitches, including in biological probes,⁹ in mechanical and optical materials,^{10,11} and in photopharmacology.^{12–14} There is considerable interest in shifting the absorptions of both *trans* and *cis* isomers of azobenzene to longer wavelengths for application in medicine and photopharmacology, as human tissue is translucent to red and near-infrared light but opaque to blue and UV light.¹⁵ There are several approaches to red-shifting the absorption profile of azobenzenes,¹⁵ with the most common route involving *ortho*- or *para*-substitution of both benzene rings with electron donating or withdrawing groups, which decreases the HOMO–LUMO gap. For example, Hecht and co-workers synthesized a series of *ortho*-fluorinated azobenzenes for which the *cis* isomers possess bright and red-shifted $S_1(n\pi^*)$ transitions,⁸ achieving separated absorption profiles for the *cis* and *trans* isomers.

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Another approach to modifying the absorption profile involves coordinating the azo group to a strongly electron withdrawing BF_2 group, which has the effect of red-shifting the absorption into the near-infrared while maintaining the isomerization quantum yield above 70%.^{16,17} The third approach to red-shifting the transition, first detailed by Woolley and co-workers,^{18,19} is protonation of the azo group to give an azonium protomer. The azonium ions exhibit a red-shift which can exceed 100 nm that is caused by delocalization of the positive charge over the π -system and stabilization of the LUMO.²⁰ For azobenzenes with hydrogen bond acceptors such as methoxy groups incorporated at the *ortho*-position, the azo group can become sufficiently basic to be protonated at physiological pHs, leading to absorption maxima in the 560–620 nm range. These photoswitching moieties can be grafted at the *para*-positions with short polypeptides or enzymes to allow *in vivo* control of peptide conformation and drug activity with red light.^{15,18,19,21,22}

Although the dynamics of neutral azobenzenes have been thoroughly studied both in solution and in the gas phase, less is known about the protonated species. Féraud et al.²⁰ recently measured the $S_1 \leftarrow S_0$ photodissociation (PD) spectra of protonated azobenzene (ABH^+) and protonated 4-(dimethyl-amino)azobenzene cations (NMe_2ABH^+) in a cryogenic ion trap, showing that the $\pi\pi^*$ transition was significantly red-shifted compared to the unprotonated molecules. Although the authors could not directly observe photoisomerization for either of these protonated azobenzenes in the gas phase, they postulated a similar excited state isomerization mechanism to that established for azobenzene based on the presence of a pronounced 41 cm^{-1} vibronic progression, assigned to a vibrational mode involving torsion around the $\text{N}=\text{N}$ bond. Furthermore, geometry optimization on the S_1 surface starting from the ground state *trans*- ABH^+ geometry yielded a twisted chairlike structure intermediate between the *trans* and *cis* geometries, indicating that isomerization may result from $S_1 \leftarrow S_0$ excitation.

Here we extend the earlier photodissociation investigations by probing the photoisomerization responses of the protonated *trans*-azobenzene cation and protonated *trans*-4-aminoazobenzene cation (NH_2ABH^+), shown in Figure 2, in the gas phase.

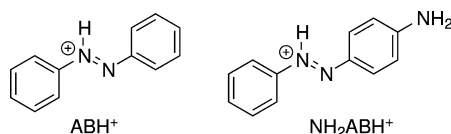


Figure 2. Structures of the *trans* protonated azobenzenes considered in this study.

The experimental strategy involves separating the *trans* and *cis* azobenzene cations in a tandem drift-tube ion mobility spectrometer (IMS) exploiting their different collision cross sections with N_2 buffer gas. Following their separation and selection in a first IMS stage, individual azobenzene isomers are photoexcited with wavelength tunable radiation, with separation of the resulting photoisomers in the second IMS stage. By measuring the photoisomer yield against wavelength, one derives a photoisomerization action (PISA) spectrum that is a convolution of the absorption spectrum and a wavelength-dependent photoisomerization response. This strategy has been deployed previously by our group and by others to investigate the photoisomerization of a range of molecular systems.^{23–27} A

PISA spectrum potentially provides complementary information to a photodissociation (PD) spectrum, which represents a convolution of the absorption spectrum and a wavelength-dependent photodissociation response. Questions we seek to answer include the following: do the protonated azobenzenes undergo photoisomerization in the gas phase, is there a resemblance between the PISA and PD spectra of the protonated azobenzene molecule, and how does a substituent amino group influence the photochemical properties of the azobenzene molecule?

METHODS

Experimental Approach. The experimental setup has been described previously.^{23–26} Briefly, the ABH^+ and NH_2ABH^+ cations were investigated using a tandem ion mobility mass spectrometer illustrated in Figure 3, which allows mobility-selected ions to be exposed to tunable light from an optical parametric oscillator (OPO). Note that Figure 3 depicts the apparatus as a linear drift tube for simplicity, whereas the actual instrument includes S-bends at the beginning and end of the drift region.^{23–25} These S-bends have no effect on the operation of the instrument.

Azobenzene cations electrosprayed from methanol (10^{-5} M , 1% acetic acid) were accumulated in an ion funnel (IF1) and injected into the drift region in 100 μs pulses at 20 Hz through an ion gate (IG1). Azobenzene (98%) and 4-aminoazobenzene (98%) were purchased from Sigma-Aldrich (Castle Hill, Australia) and used without further purification. The ion packets were propelled through the drift region by an electric field ($E = 44\text{ V/cm}$) and separated according to their collision cross sections with N_2 buffer gas ($\approx 6\text{ Torr}$). At the end of the drift region, the ions were collected radially by a second ion funnel (IF2) and guided through a differentially pumped stage by an octupole ion guide, before being mass-selected by a quadrupole mass filter and striking the channeltron detector which was connected to a multichannel scaler. An arrival time distribution (ATD) was built up as a histogram representing ion count versus arrival time. The mobility resolution for the protonated azobenzene cations was typically $t_d/\Delta t_d \approx 75$. Collision cross sections were measured as described previously.²⁸

Photoisomerization action (PISA) spectra of protonated azobenzene cations were obtained by operating the ion mobility spectrometer in tandem mode. A Bradbury-Nielsen electrostatic ion gate (IG2) halfway along the drift region was used to select the target isomer by opening it for 100 μs at an appropriate delay with respect to the first gate. The selected ions were irradiated 15 mm after IG2 with light from a tunable OPO (energy flux $\approx 1\text{ mJ/cm}^2/\text{pulse}$). The OPO light beam had approximately a $5\text{ mm} \times 20\text{ mm}$ profile where it overlapped the ion packet. The OPO was pulsed at 10 Hz, irradiating every second ion packet. In this way, light-off and light-on ATDs were collected, the difference between which revealed the photoisomerization response. The photoisomerization action (PISA) spectrum was obtained by plotting the photoisomer yield against OPO wavelength.

Computational Approach. In order to identify the important gas-phase species, ground state geometries of the ABH^+ and NH_2ABH^+ cations were optimized and zero-point energies were obtained at the $\omega\text{B97X-D}/6\text{-311+G}(2\text{df,p})$ level of theory using Gaussian 09.^{29–31} In turn, single point energies were calculated using the ORCA 3.0.3 program package at the DLPNO-CCSD(T)/cc-pVTZ level of theory.^{32–36} With the cc-

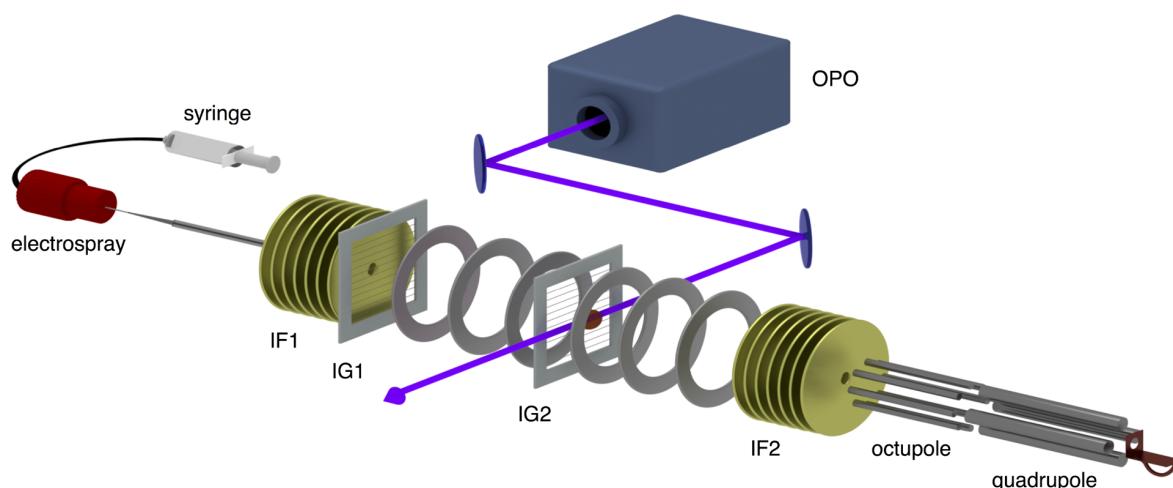


Figure 3. Representation of the tandem ion mobility mass spectrometer, showing the electrospray ionization source, first ion funnel (IF1), first ion gate (IG1), second ion gate (IG2), second ion funnel (IF2), and optical parametric oscillator (OPO).

pVTZ basis set, this method provides energies within 4 kJ/mol of the complete CCSD(T) values while being several orders of magnitude less computationally demanding.^{34,35}

The equilibrium geometry of *trans*-ABH⁺ was found to be planar at the ω B97X-D/6-311+G(2df,p) level of theory, unlike the previously published twisted structure.²⁰ However, as discussed in the [Supporting Information](#), the energy difference between the planar and nonplanar structures and the barrier separating them are small (≤ 1 kJ/mol), such that the molecule should be quasi-planar at 300 K. Therefore, the planar DFT geometry was used for calculating vertical excitation energies.

Vertical excitation energies (VEEs) were determined using the EOM-CC2 and linear-response TDDFT (CAM-B3LYP) methods.^{37–39} The EOM-CC2 method is known to reliably predict singlet excited state energies for a range of organic chromophores, often giving good agreement with CASPT2.⁴⁰ The CAM-B3LYP density functional was chosen due to incorporation of range-separated exact exchange to account for charge transfer.^{41,42} The VEE calculations used the def2-TZVP basis set for ABH⁺ and aug-cc-pVDZ for NH₂ABH⁺.^{43,44}

Collision cross sections for the isomers of ABH⁺ were modeled using the trajectory method in a version of MOBCAL parametrized for N₂ buffer gas.^{45–47} The input charge distributions were calculated using the Merz–Kollman scheme from ω B97X-D/6-311+G(2df,p) charge densities.⁴⁸

RESULTS AND DISCUSSION

Protonated Azobenzene (ABH⁺) Cation. The arrival time distribution of ABH⁺ electrosprayed from methanol solution, shown in [Figure 4](#), displays two peaks, the relative intensities of which depend upon the amplitude of the RF drive voltage applied to IF1. With low RF drive voltage, the ions are collected gently, so that the ATD is likely to represent the relative populations of the nascent, electrosprayed *trans*- and *cis*-ABH⁺ isomers. On the other hand, at high RF voltage, the electrosprayed ions are subject to energetic collisions with the buffer gas in IF1, inducing isomerization and driving the isomer populations toward a quasi-equilibrium between the various gas-phase isomers.^{49,50}

The ω B97X-D/6-311+G(2df,p) and DLPNO-CCSD(T)/cc-pVTZ calculations predict that *trans*-ABH⁺ is more stable than *cis*-ABH⁺ by 29 and 26 kJ/mol, respectively. The slower isomer

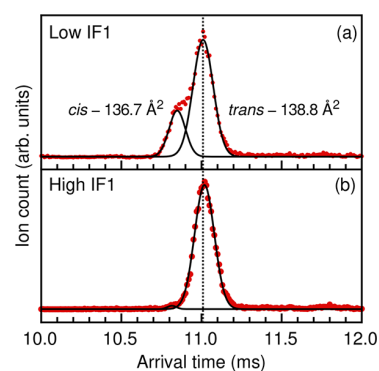


Figure 4. Arrival time distributions for ABH⁺ with low (a) and high (b) RF drive voltages to IF1. Experimental collision cross sections (estimated uncertainty of ± 1 Å²) are given for each peak (see [Supporting Information](#) for details).

(ATD peak centered at ≈ 11.0 ms, measured collision cross section 139 ± 1 Å²), which dominates at high IF1 RF drive voltage, is therefore likely to be the *trans*-ABH⁺ isomer, with the faster isomer being the *cis*-isomer (measured collision cross section 137 ± 1 Å²). Calculated cross sections for the *trans*- and *cis*-ABH⁺ isomers were both 142 ± 1 Å², where the uncertainty reflects the range of calculated values delivered by the Trajectory Method of MOBCAL.^{45–47} The presence of both *trans*- and *cis*-ABH⁺ peaks in the ATD obtained with low IF1 drive voltage demonstrates that the two isomers are separated by a substantial energy barrier; otherwise, they would interconvert in the drift tube. The barrier for *trans* to *cis* conversion is estimated to be at least 80 kJ/mol (from RI-MP2/cc-pVDZ calculations), significantly larger than the thermal energy of the drifting ions at 300 K.

Exposing *trans*-ABH⁺ to light over the 370–500 nm range causes isomerization to *cis*-ABH⁺. This behavior is apparent in [Figure 5a](#), which shows a light-off ATD and a light-on/off difference ATD obtained with 440 nm irradiation of *trans*-ABH⁺. There is clear depletion of the *trans* peak and appearance of the *cis* isomer peak at shorter arrival time. Note that because the ions are irradiated halfway along the drift region, the *cis* isomer photoappearance peak is situated approximately halfway between the parent *trans* peak and the

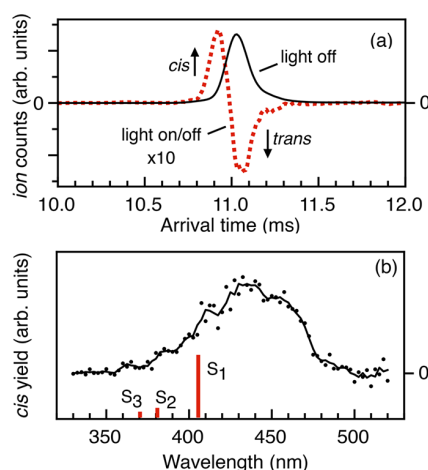


Figure 5. (a) Arrival time distribution with high RF drive voltage for *trans*-ABH⁺ with the light off (solid black curve) and the difference in the light on and light off arrival time distributions at 440 nm (dashed red curve). The enhancement and depletion signals differ in area by $\approx 15\%$ due to photodissociation. (b) PISA spectrum of *trans*-ABH⁺, normalized for total ion count and light fluence. Red lines indicate wavelengths and intensities of vertical electronic excitations calculated at the EOM-CC2/def2-TZVP level of theory.

cis peak in Figure 5a. The collision cross section of the photoisomer corresponds to the cross section for *cis*-ABH⁺ (both 137 Å²). Although photoisomerization is the dominant process, the depletion signal exceeds the enhancement signal by around 15% due to photodissociation.

Plotting the integrated *cis*-ABH⁺ photoappearance signal as a function of wavelength gives the *trans* to *cis* PISA spectrum shown in Figure 5b. The PISA spectrum exhibits a single band spanning the 480–370 nm range with a maximum at ≈ 435 nm, which is assigned to the S₁ $\leftarrow$ S₀ transition on the basis of electronic structure calculations and its similarity to the band in the photodissociation (PD) action spectrum of Féraud et al.²⁰ The PD action spectrum, which was recorded under cryogenic conditions at ≈ 40 K, displays a resolved vibrational progression with 41 cm^{−1} spacing near the band onset that was assigned to a low-frequency torsional mode around the azo bond, corresponding to the isomerization coordinate. Our results clearly demonstrate that excitation of the S₁ $\leftarrow$ S₀ band leads to isomerization in the gas phase.

Calculated vertical excitation energies (VEEs) and oscillator strengths for ABH⁺, which are summarized in Table 1, are consistent with the calculations of Féraud et al.²⁰ In contrast to *trans*-azobenzene in which the S₁ state is optically dark with $n\pi^*$ character and the S₂ state is optically bright with $\pi\pi^*$ character, the S₁ state of the protonated azobenzene cation is bright with $\pi\pi^*$ character, whereas the S₂ and S₃ states are

approximately degenerate and are associated with charge transfer from the phenyl rings to the azo group. The S₁ VEE predicted by EOM-CC2 agrees with the PISA spectrum band maximum, whereas there is poorer correspondence with the TDDFT values. We note that TDDFT provides an inadequate description of vertical excitations in heteroarene systems due to considering only singles excitations,⁵¹ whereas EOM-CC2 includes approximate treatment of double excitations.⁴⁰ A rigorous treatment of the excited states requires inclusion of both static and dynamic electron correlation effects using multireference methods.^{40,52–54}

The EOM-CC2 calculations suggest that the S₂ $\leftarrow$ S₀ and S₃ $\leftarrow$ S₀ transitions should be very weak with oscillator strengths of 0.02–0.04 (a factor of 25–50 weaker than the S₁ $\leftarrow$ S₀ transition). The PISA spectrum shows only a weak photoisomerization response associated with these transitions and an even lower photodissociation yield (less than 15% of the photoisomerization response). In contrast, the PD spectrum of ABH⁺ reported by Féraud et al. shows a strong photodissociation signal for the S₂ and S₃ excited states with prominent peaks at 405 and 390 nm.²⁰ The difference in the ABH⁺ photodissociation response for the S₂ and S₃ excited states for the two experiments may be linked to differences in laser intensity and buffer gas pressure, which will affect respectively the probability for multiphoton absorption and rate of collisional deactivation.

Unfortunately, due to low signal levels, it was not possible to record a corresponding PISA spectrum of the *cis*-ABH⁺ isomer. As shown in Figure 4, at low RF drive voltage to IF1, the *cis* isomer constitutes $\approx 30\%$ of the signal. However, the total ion count is very low due to poor ion collection. At high RF drive voltage to IF1 the total ion count is much higher, but the *cis*-ABH⁺ isomer ions are almost completely converted to *trans*-ABH⁺ isomer ions before their injection into the drift region.

In summary, protonation of the azo group significantly red-shifts the $\pi\pi^*$ transition compared to the corresponding transition in neutral *trans*-azobenzene (435 nm compared to 365 nm). Facile photoisomerization is observed for the S₁ $\leftarrow$ S₀ transition, demonstrating that protonation is an effective way to red-shift the azobenzene photoisomerization response for practical applications.

Protonated 4-Aminoazobenzene (NH₂ABH⁺) Cation.

We turn now to consider the protonated 4-aminoazobenzene (NH₂ABH⁺) cation, in which a single phenyl ring is *para*-substituted with an electron-donating amino group. The NH₂ABH⁺ molecule has three likely protomers, with the proton either attached to one of the two azo N atoms or to the amino group (Figure 6). The ATD for NH₂ABH⁺, shown in Figure 7a, exhibits a single peak irrespective of the RF drive voltage to IF1, suggesting either a single isomer is present or there are several isomers with very similar collision cross sections. As shown in Figure 7a and b, exposing the NH₂ABH⁺

Table 1. Calculated Vertical Excitation Energies [eV (nm)] and Oscillator Strengths for ABH⁺ Compared with Experimental Values^a

method	LUMO $\leftarrow$ HOMO		LUMO $\leftarrow$ HOMO−1		LUMO $\leftarrow$ HOMO−2	
	S ₁ $\leftarrow$ S ₀	<i>f</i>	S ₂ $\leftarrow$ S ₀	<i>f</i>	S ₃ $\leftarrow$ S ₀	<i>f</i>
EOM-CC2	3.0 (406)	1.00	3.4 (364)	0.04	3.5 (359)	0.02
CAM-B3LYP	3.2 (382)	0.80	3.6 (345)	0.07	3.6 (341)	0.04
Exp	2.85 (435)					

^aAll calculations were performed using the def2-TZVP basis set.

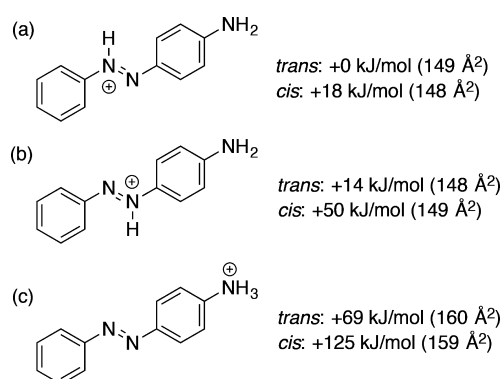


Figure 6. Structures of $\text{trans-NH}_2\text{ABH}^+$ protomers. Energies calculated at the DLPNO-CCSD(T)/cc-pVTZ// ω B97X-D/6-311+G(2df,p) level of theory are given relative to the energy of the trans-(a) protomer. Calculated collision cross sections with N_2 are given in parentheses.

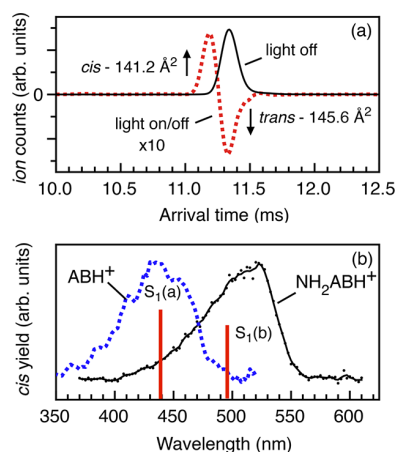


Figure 7. (a) ATDs of $\text{trans-NH}_2\text{ABH}^+$ with the light-off ATD (black) and the difference in the light-on and light-off arrival time distributions at 515 nm (dashed red curve). Collision cross sections are given with an uncertainty of $\pm 1 \text{ \AA}^2$ (trans) and $\pm 1.5 \text{ \AA}^2$ (cis). The depletion and enhancement signals balance to within 5%, proving that photoisomerization is the dominant process at this wavelength. (b) PISA spectrum of $\text{trans-NH}_2\text{ABH}^+$. Red lines indicate wavelengths and intensities of vertical $S_1 \leftarrow S_0$ transitions of protomers (a) and (b) (see Figure 6) calculated at the EOM-CC2/aug-cc-pVDZ level. For comparison, the PISA spectrum of ABH^+ is shown as a blue dotted curve.

isomer to light of wavelengths between 410 and 540 nm causes isomerization to a faster species with a maximum response at 525 nm. The transformation presumably corresponds to a trans to cis photoisomerization.

Calculations conducted at the DLPNO-CCSD(T)/cc-pVTZ// ω B97X-D/6-311+G(2df,p) level of theory identified the isomers shown in Figure 6. For the trans isomers, protonation on the azo N atom most distant from the amino-substituted ring (trans-(a)) is preferred over protonation on the other azo N atom (trans-(b)) by 14 kJ/mol, whereas the isomer with the proton located on the amino nitrogen atom (trans-(c)) lies 69 kJ/mol higher in energy. The energetic ordering of the cis protomers parallels that of the trans protomers. The cis-(a) protomer is more stable than the cis-(b) and cis-(c) protomers by 32 and 107 kJ/mol, respectively, and is 18 kJ/mol less stable than the trans-(a) protomer. Given the relative energies of the various isomers, one might expect that trans-(a) should be the predominant gas-phase protomer. On the basis of calculated collision cross sections, given in Figure 6, one would predict only a small difference between the arrival times of the four cis- and trans- isomers of protomers (a) and (b), with the trans and cis isomers of protomer (c) having significantly longer arrival times. As for ABH^+ , the calculated collision cross sections for the azo-protonated NH_2ABH^+ isomers are slightly larger than the measured cross sections, suggesting that an azo-protonated $\text{trans-NH}_2\text{ABH}^+$ protomer is the observed species.

To connect the PISA spectrum shown in Figure 7b to one of the two azo-protomers of $\text{trans-NH}_2\text{ABH}^+$, we consider the vertical excitation energies for each protomer calculated at the EOM-CC2/aug-cc-pVDZ level of theory (Table 2). First, the anilinium-like protomer (c) can be excluded, as only the optically dark S_1 state lies in the visible, with the bright S_2 state occurring in the UV as for neutral azobenzene.¹ Protomers (a) and (b) are both predicted to have bright $S_1 \leftarrow S_0$ transitions in the visible centered at 441 and 498 nm, respectively. Protomer (a) is calculated to be 14 kJ/mol more stable than protomer (b) and should therefore be the dominant form. However, the vertical excitation energy for protomer (b) better matches the experimental band maximum. Given that the CC2 method has a mean absolute deviation of 0.32 eV for VEEs in typical heteroarene compounds with a maximum deviation of 1.5 eV,⁴⁰ the calculated vertical excitation energies do not provide grounds for a definite spectral assignment. It is of course possible that protomers (a) and (b) both contribute to the PISA spectrum, in which case their relative contributions could possibly be distinguished through hole burning experiments.

The main band in the PISA spectrum of NH_2ABH^+ is red-shifted by 90 nm with respect to the corresponding band of ABH^+ (525 nm versus 435 nm) and has a steeper band onset (Figure 5). The spectral shift can be attributed to the *para* electron-donating amino group in NH_2ABH^+ increasing electron density in the delocalized π -system relative to ABH^+ and consequently increasing the energy of the HOMO and reducing the HOMO–LUMO gap. These differences are

Table 2. Vertical Excitation Energies [eV (nm)] and Oscillator Strengths for $\text{trans-NH}_2\text{ABH}^+$ Protomers Calculated at the EOM-CC2/aug-cc-pVDZ Level of Theory^a

protomer	LUMO $\leftarrow$ HOMO		LUMO $\leftarrow$ HOMO-1		LUMO $\leftarrow$ HOMO-2	
	$S_1 \leftarrow S_0$	f	$S_2 \leftarrow S_0$	f	$S_3 \leftarrow S_0$	f
(a)	2.8 (441)	1.31	3.8 (330)	0.01	4.2 (298)	0.01
(b)	2.5 (498)	1.18	3.7 (338)	0.01	3.9 (316)	0.02
(c)	2.7 (460)	0.00	3.8 (324)	0.82	4.0 (313)	0.06
Exp	2.36 (525)					

^aThe experimental value is listed at the bottom.

consistent with trends derived from the PD spectra for ABH^+ and NMe_2ABH^+ reported by Feráud et al.²⁰ In summary, the PISA spectra show that a combination of protonation and *para*-substitution with an electron-donating group shifts the absorption of the *trans*- NH_2ABH^+ cation into the green region of the spectrum, while the molecule still retains the *trans*-to-*cis* isomerization required for its use as a molecular photoswitch.

CONCLUSIONS

Photoisomerization action (PISA) spectra measured for *trans*- ABH^+ and *trans*- NH_2ABH^+ in the visible region exhibit a single photoisomerization band assigned in both cases as the $\pi\pi^*$ $\text{S}_1 \leftarrow \text{S}_0$ transition. The NH_2ABH^+ spectrum has a maximum at 525 nm, which is red-shifted from the ABH^+ spectrum maximum at 435 nm due to stabilization of the HOMO by the electron-donating amino group. No photoisomerization response was discernible for the $\text{S}_2 \leftarrow \text{S}_0$ or $\text{S}_3 \leftarrow \text{S}_0$ transitions of ABH^+ or NH_2ABH^+ , similar to the situation for the higher $\pi\pi^*$ transitions of neutral *trans*-azobenzene.¹ Overall, the PISA spectra are consistent with previously reported PD spectra of ABH^+ and NMe_2ABH^+ , although the bands are broader due to the higher temperature in the drift tube (close to 300 K) compared to the cryogenic ion trap used for the PD measurements (40 K).²⁰ Perhaps most significantly we have shown that protonation of azobenzenes leads to a significant red-shift in their absorption maxima in the gas phase while retaining the *trans* to *cis* isomerization response required for their application as photoswitch molecules. Ultimately, the results demonstrate that ion mobility spectrometry coupled with laser spectroscopy is a useful strategy for investigating the photoswitching behavior of isolated protonated azobenzenes.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.7b05902.

Calculated geometric parameters for the ABH^+ and NH_2ABH^+ protomers and isomers, a RI-MP2/cc-pVTZ potential energy curve describing the conversion between the planar and twisted *trans*- ABH^+ structures (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: evanj@unimelb.edu.au (E.J.B.).

ORCID

Michael S. Scholz: 0000-0003-3290-2722

James N. Bull: 0000-0003-0953-1716

Eduardo Carrascosa: 0000-0003-4338-8669

Evan J. Bieske: 0000-0003-1848-507X

Notes

The authors declare no competing financial interest.

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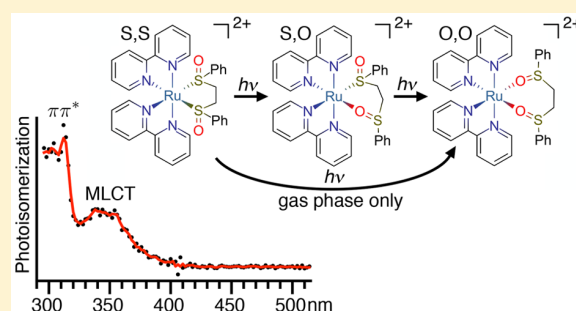
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Linkage Photoisomerization of an Isolated Ruthenium Sulfoxide Complex: Sequential versus Concerted Rearrangement

Michael S. Scholz,[†] James N. Bull,[†] Eduardo Carrascosa,[†] Brian D. Adamson,^{†,‡} Gilbert K. Kosgei,[§] Jeffrey J. Rack,[§] and Evan J. Bieske^{*,†}[†]School of Chemistry, University of Melbourne, Parkville, Victoria 3010, Australia[‡]Sandia National Laboratories, Livermore, California 94550, United States[§]Department of Chemistry and Chemical Biology, University of New Mexico, Albuquerque, New Mexico 87131, United States

Supporting Information

ABSTRACT: Ruthenium sulfoxide complexes undergo thermally reversible linkage isomerization of sulfoxide ligands from S- to O-bound in response to light. Here, we report photoisomerization action spectra for a ruthenium bis-sulfoxide molecular photo-switch, $[\text{Ru}(\text{bpy})_2(\text{bpSO})]^{2+}$, providing the first direct evidence for photoisomerization of a transition metal complex in the gas phase. The linkage isomers are separated and isolated in a tandem drift tube ion mobility spectrometer and exposed to tunable laser radiation provoking photoisomerization. Direct switching of the S,S-isomer to the O,O-isomer following absorption of a single photon is the predominant isomerization pathway in the gas phase, unlike in solution, where stepwise isomerization is observed with each sulfoxide ligand switching in turn. The change in isomerization dynamics is attributed to rapid vibrational quenching that suppresses isomerization in solution. Supporting electronic structure calculations predict the wavelengths and intensities of the peaks in the photoisomerization action spectra of the S,S- and S,O-isomers, indicating that they correspond to metal-to-ligand charge transfer (MLCT) and ligand-centered $\pi\pi^*$ transitions.



INTRODUCTION

Photochromic molecules reversibly switch from one state to another in response to light, converting photonic energy into the internal molecular energy required for molecular rearrangement.¹ Photochromic molecules have been proposed for use as light-activated molecular switches for applications that include photopharmacology, light harvesting, energy storage, and for nonlinear optical materials.^{2–6}

Over the past two decades, a range of photochromic ruthenium complexes have been developed, exploiting light-induced linkage isomerization of sulfoxide ligands on a ruthenium polypyridyl core.^{7–10} In solution, these complexes have photoisomerization quantum yields up to 0.79 with thermal half-lives extending to several hours or longer.^{11,12} Density functional theory (DFT) calculations suggest isomerization is initiated on an excited ³MLCT (metal-to-ligand charge transfer) surface and then proceeds along surfaces with predominantly MC (metal centered) character in a non-adiabatic manner.^{13,14} Spectroscopic measurements show that the ³MLCT surface is present throughout the isomerization and imply strong mixing between this surface and the MC surface, which is formally $\text{Ru}-\text{S } \sigma^*$ (antibonding) in nature.^{11,12} Direct comparison of theoretical predictions with experimental data is often difficult due to strong solvent perturbation of excited state energy levels in ruthenium polypyridyl complexes.¹⁵ Moreover,

even simple ruthenium polypyridyls display complex photochemistry which underpins their roles as photosensitizers in dye-sensitized solar cells and as photopharmacological agents.^{16,17}

In a step toward characterizing the inherent (solvent-free) photochemistry of a ruthenium-based photoswitch molecule, we have probed the photoisomerization of the ruthenium bis-sulfoxide complex $[\text{Ru}(\text{bpy})_2(\text{bpSO})]^{2+}$ ($\text{Ru}(\text{bpSO})$), where bpy = 2,2'-bipyridine and bpSO = 1,2-bis(phenylsulfinyl)ethane) in the gas phase. As shown in Figure 1, the $\text{Ru}(\text{bpSO})$ complex has three stable linkage isomers, as each of the two sulfoxide groups can be either S- or O-bound, giving S,S-, S,O-, and O,O- $\text{Ru}(\text{bpSO})$ isomers. Earlier studies on the S,S-isomer in solution have shown two photons are required to reach the O,O-isomer; exposing the S,S-isomer solution to 355 nm light produces the S,O-isomer, and subsequent 400 nm irradiation yields the O,O-isomer.¹² No direct isomerization from the S,S- to O,O-isomer occurs. In contrast, we demonstrate that in the gas phase a single photon can generate the O,O-isomer directly from the S,S-isomer with minor formation of the S,O-isomer. This direct conversion has been previously observed in the related $[\text{Ru}(\text{bpy})_2(\text{OSSO})]^{2+}$ ($\text{Ru}(\text{OSSO})$), OSSO =

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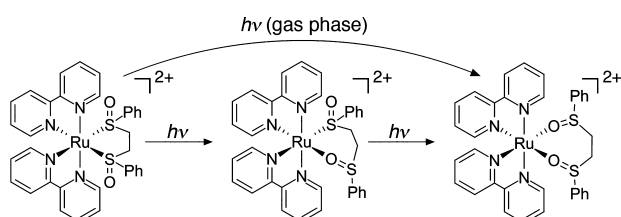


Figure 1. Photoinduced linkage isomerization in the Ru(bpSO) complex. Stepwise isomerization from the S,S- to the S,O- and O,O-isomers is observed in solution, whereas direct isomerization from the S,S- to the O,O-bound-isomer is the predominant process in the gas phase.

dimethylbis(methylsulfinylmethyl)silane) and $[\text{Ru}(\text{bpy})_2(\text{F-bpSO})]^{2+}$ ($\text{Ru}(\text{F-bpSO})$, $\text{F-bpSO} = 1,2\text{-bis}(2\text{-fluorophenyl-sulfinyl})\text{ethane}$) complexes in solution, where double isomerization was proposed to be facilitated by low barriers on the excited state triplet manifold leading to rapid quasi-statistical equilibration before nonadiabatic relaxation to the ground state.¹⁸ Results from the present study suggest that solvation affects isomerization dynamics in these systems and that gas phase investigations can provide key insight into the intrinsic photochemistry of transition metal complexes.

The present investigation complements previous gas phase spectroscopic investigations of ruthenium complexes, which have mainly focused on ruthenium polypyridyl complexes such as the prototypical photosensitizer $[\text{Ru}(\text{bpy})_3]^{2+}$, which has been extensively studied in solution.^{19,20} In pioneering work, Posey and co-workers obtained an electronic spectrum of $[\text{Ru}(\text{bpy})_3]^{2+}$ in the gas phase observing a progressive red shift in MLCT bands with increasing microsolvation.^{15,21,22} More recently, photodissociation action spectra have been recorded for ruthenium bipyridyl complexes in a range of oxidation states.^{23–25} However, these earlier studies employed techniques that were not suited to following structural changes such as isomerization. To our knowledge, the present study reports the first observation of the photoisomerization of a transition metal complex in the gas phase.

METHODS

Experimental Procedure. The photoisomerization of Ru(bpSO) was investigated using a purpose-built tandem ion mobility–mass spectrometer coupled with a tunable optical parametric oscillator (OPO) system. The experimental apparatus has been described previously.^{26,27} Electrosprayed ions from a 10^{-4} M solution of S,S-Ru(bpSO) in acetonitrile were injected as 100 μs pulses at 40 Hz into a drift tube ion mobility stage, where the ions were separated spatially and temporally on the basis of their drift mobility in 6 Torr of N_2 buffer gas with an applied electric field of ≈ 40 V/cm. The separated isomers then passed through a quadrupole mass filter and were detected using a channeltron electron multiplier. The arrival time distribution (ATD) of the ions was built up by plotting the ion signal as a function of arrival time at the detector. In order to measure photoisomerization action (PISA) spectra, the isomer of interest was selected using a pulsed electrostatic ion gate halfway along the drift tube. Immediately after the ion gate, alternate ion packets were exposed to the output of a pulsed UV–vis OPO (EKSPLA NT342B, 20 Hz, <0.35 mJ/cm² per pulse), generating laser-off and laser-on ATDs. The effect of light on the ions is manifested in the difference between the laser-on and laser-off ATDs. The photoisomerization action spectrum was generated by plotting the photoisomer yield as a function of OPO wavelength.

Isomerically pure S,S-Ru(bpSO) was synthesized according to a previously published procedure and its isomeric purity confirmed

using UV–vis and NMR spectroscopy.¹² The S,O-Ru(bpSO) and O,O-Ru(bpSO) ions were generated by either UV irradiation of the S,S-isomer in solution or by ion activation in the first RF ion funnel, as described below. Experiments were performed in the dark to avoid isomerization in solution prior to electrospraying.

Computational Procedure. Supporting electronic structure calculations were performed using a combined density functional theory (DFT) and ab initio approach. Geometries and harmonic frequencies were optimized at the TPSS-D3(BJ)/def2-TZVP level of theory.^{28–31} Single point energies were then calculated at the DLPNO-CCSD(T)/def2-TZVP level.^{32,33} Vertical excitation energy calculations to simulate absorption spectra were performed at the PBE0/def2-TZVP and NEVPT2(14,13)/def2-TZVP levels of theory; further details are given in the Supporting Information.^{28,29,34} All electronic structure calculations were performed using the ORCA 4.0 program package.^{35,36}

RESULTS AND DISCUSSION

First, arrival time distributions (ATDs) of electrosprayed Ru(bpSO) were gathered operating the instrument as a single ion mobility drift tube under different ion source conditions; resulting ATDs are shown in Figure 2. A clear dependence on

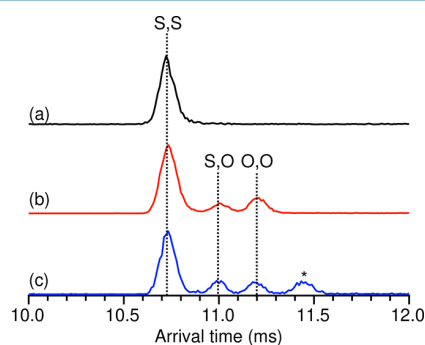


Figure 2. Arrival time distributions for electrosprayed solutions of pure S,S-Ru(bpSO). (a) Low RF drive voltage for the source ion funnel. (b) High RF drive voltage for the source ion funnel. (c) Exposure of the solution to 360 nm light and low RF drive voltage on the source ion funnel. The peak labeled with an asterisk corresponds to a Ru(bpSO)–MeCN adduct that traverses the drift region intact and then dissociates to yield bare Ru(bpSO) in the exit region of the drift region prior to mass selection.

the source conditions was found: a single peak with an arrival time of 10.72 ms was observed with a low radio frequency (RF) drive voltage on the source ion funnel (Figure 2a), whereas two additional slower peaks with arrival times of 10.99 and 11.20 ms were observed when the RF drive voltage was increased (Figure 2b). As the electrosprayed solution consisted purely of the S,S-isomer, the fastest isomer can be confidently assigned to S,S-Ru(bpSO). Exposure of the S,S-Ru(bpSO) isomers in solution to UV light prior to electrospraying and with a low RF drive voltage yielded the ATD shown in Figure 2c, where three later peaks are observed, in addition to the S,S-Ru(bpSO) peak. The slower two isomers in Figure 2b with arrival times of 10.99 and 11.20 ms are assigned to the S,O-Ru(bpSO) and O,O-Ru(bpSO) isomers, respectively, on the basis of prior studies¹² which found that upon exposure to UV light S,S-Ru(bpSO) in solution yields S,O-Ru(bpSO) and O,O-Ru(bpSO) isomers. These assignments are also consistent with the appearance of S,O-Ru(bpSO) and O,O-Ru(bpSO) at higher RF drive voltages, as electronic structure calculations indicate that these isomers lie significantly higher in energy than the S,S-

Ru(bpSO) isomer (by 1800–2500 and 4200–4400 cm^{-1} for S,O-Ru(bpSO) and O,O-Ru(bpSO), respectively; Table S2).^{32,33,36} As discussed below, PISA spectra of the S,S- and S,O-isomers are consistent with their condensed phase absorption spectra, further supporting the ATD peak assignments.

Next, the effect of light on the gas phase S,S-Ru(bpSO) ions was investigated by exposing them to tunable radiation from the OPO (following selection with the electrostatic ion gate). As shown in Figure 3a, two slower isomers are formed from

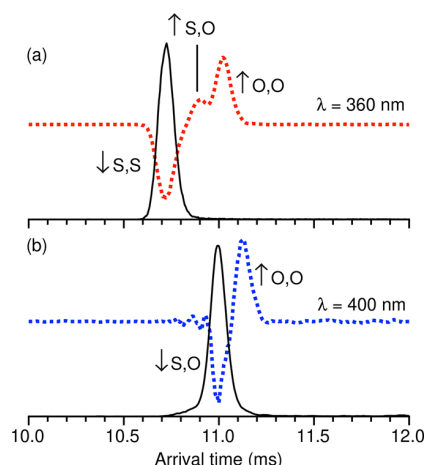


Figure 3. Example light-on/light-off difference ATDs for (a) S,S-Ru(bpSO) gathered at 360 nm (red) and (b) S,O-Ru(bpSO) at 400 nm (blue) superimposed over the light-off ATDs (black). In each case, the difference ATD was generated by subtracting the light-off ATD from the light-on ATD.

S,S-Ru(bpSO) at 360 nm (near the band maximum of the condensed phase MLCT transition). Plotting the yield of these photoproducts as a function of wavelength produced the PISA spectrum shown in Figure 4. Two distinct bands are apparent with maxima at 345 nm (29 400 cm^{-1}) and at 310 nm (32 350 cm^{-1}). No wavelength or power dependence was observed in the photoisomerization branching ratio (Figures S1 and S2), and so the PISA spectrum corresponds to the sum of the S,O- and O,O-Ru(bpSO) isomer yields. The lower energy band

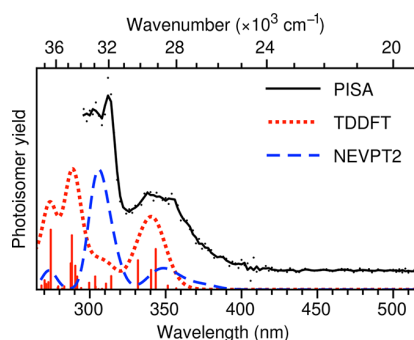


Figure 4. Gas phase PISA spectrum for S,S-Ru(bpSO) corresponding to aggregate S,O- and O,O-Ru(bpSO) yields as a function of wavelength (black) and calculated TDDFT absorption spectrum (red dotted). The calculated NEVPT2 absorption spectrum is plotted for reference (blue dashed, further details in the Supporting Information, Section 1.1).

peaking at 345 nm is close to the analogous band maximum in solution at 335 nm (29 850 cm^{-1}), which has been assigned to a MLCT transition from the ruthenium center to the bipyridyl ligands.¹² Similarly, the higher energy band peaking at 310 nm is close to the band assigned to bipyridyl-localized $\pi\pi^*$ transitions for S,S-Ru(bpSO) in solution (319 nm, 31 350 cm^{-1}).¹² It was not possible to measure below 290 nm due to background signal caused by photoionization of trace contaminants in the drift region. Overall, the gas phase PISA spectrum is similar to the absorption spectrum of S,S-Ru(bpSO) in solution,¹² reinforcing assignment of the earliest ATD peak in Figure 2 to the S,S-Ru(bpSO) isomer.

In order to confirm band assignments, excited state calculations were performed using time-dependent density functional theory (TDDFT, details in the Supporting Information).^{28–30,37} The TDDFT-simulated spectrum is shown below the experimental PISA spectrum in Figure 4, along with a spectrum generated using multireference NEVPT2 theory to confirm that TDDFT provides at least a qualitatively correct description for the present system (see the Supporting Information for computational details).³⁴ As shown in Figure 4, the TDDFT calculations predict two major absorption bands for S,S-Ru(bpSO) at 340 nm (29 440 cm^{-1}) and 290 nm (34 640 cm^{-1}). The calculated electronic character of the transitions agrees well with previous assignments,¹² with the low-energy transition at 340 nm corresponding to MLCT associated mainly with the bipyridyl ligands with a minor component connected with the bpSO phenyl rings and the higher energy transition at 290 nm corresponding to bipyridyl-centered $\pi\pi^*$ transitions. Kohn–Sham orbitals responsible for the calculated transitions are depicted in Table S4.

The NEVPT2 calculations are able to treat MLCT excited states accurately.³⁸ The discrepancy of <1000 cm^{-1} between the TDDFT and NEVPT2 calculations for the MLCT bands suggests that TDDFT performs reasonably at least for this system (vertical excitation energies are tabulated along with a quantitative discussion of relative performances in the Supporting Information). There is poorer agreement between TDDFT and NEVPT2 calculations for the higher energy band, with a difference of around 30 nm ($\sim 3000 \text{ cm}^{-1}$). For reasons of economy, and because the TDDFT approach provides a reasonable qualitative description of the excited state character, for the S,O-Ru(bpSO) isomer only the TDDFT approach was used.

Given that $\pi\pi^*$ excitation leads to isomerization, there must be efficient conversion from the initial $^1\pi\pi^*$ state to the $^3\text{MLCT}$ state from which photoisomerization occurs.¹³ However, it is unclear whether internal conversion (IC) to a $^1\text{MLCT}$ state precedes intersystem crossing (ISC), which is known to occur on a femtosecond time scale in ruthenium polypyridyls,^{19,20} or whether rapid ISC yields a $^3\pi\pi^*$ state before internal conversion to the $^3\text{MLCT}$ manifold. To elucidate the mechanism, we are presently performing wavelength-dependent transient absorption studies to probe the dynamics following $\pi\pi^*$ excitation.

Significantly, whereas direct isomerization is observed from the S,S-isomer to the O,O-isomer in the gas phase, stepwise isomerization via the S,O-isomer was observed in solution.¹² Power dependence studies (Figure S1) indicate that in the gas phase the branching ratio between the S,O- and O,O-Ru(bpSO) photoproducts does not depend on light fluence at both band maxima, and therefore both single and double isomerizations are triggered by absorption of a single photon.

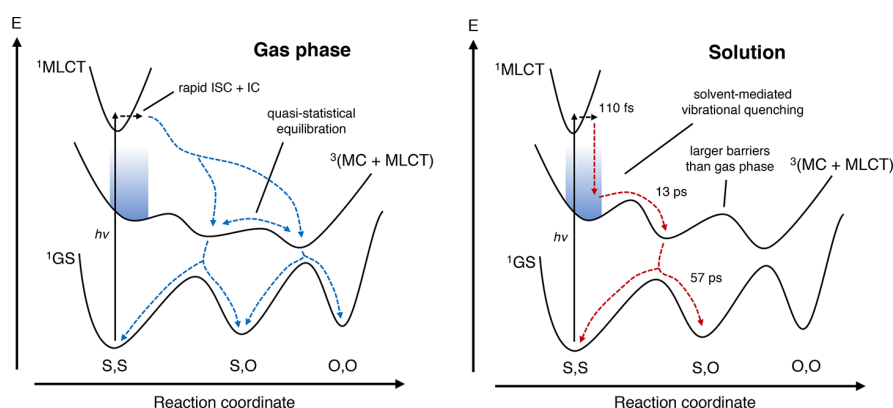


Figure 5. Schematic potential energy surfaces for S,S-Ru(bpSO) isomerization in the gas phase (left) and in solution (right). Relaxation time scales in solution are taken from King et al.¹²

Likewise, the branching ratio for formation of S,O-Ru(bpSO) and O,O-Ru(bpSO) does not vary with wavelength (Figure S2). Together, these results suggest that the thermal reversion barriers are sufficiently high on the ground state potential energy surface to prevent back-isomerization of the S,O- and O,O-isomers under the present experimental conditions.³⁹ Support for this interpretation comes from DFT calculations on the closely related [Ru(bpy)₂(dmsO)₂]²⁺ complex (dmsO = dimethyl sulfoxide), which predict that barriers to thermal reversion on the ground state potential energy surface are ≥ 85 kJ/mol compared to barriers on the triplet MC and MLCT surfaces of ≈ 20 kJ/mol.¹⁴ Although the present system differs from this model system through presence of a chelating linker between the sulfoxides, the electronic character of the triplet state surfaces should be comparable.

Schematic potential energy surfaces (PESs) shown in Figure 5 illustrate the proposed mechanisms for isomerization dynamics for S,S-Ru(bpSO) in the gas phase and in solution. They are based on the experimental results from the present study and from King et al.¹² as well as DFT calculations of Boggio-Pasqua and co-workers on the closely related [Ru(bpy)₂(dmsO)₂]²⁺ complex.^{13,14} Although the previous theoretical work considered the MC and MLCT states to be distinct, we discuss the lowest triplet surface in Ru(bpSO) as a mixed surface with varying MC and MLCT character for the following reasons: the two states are similar in energy,¹⁴ multiconfigurational character has been predicted in low-lying triplet states of ruthenium coordination complexes,⁴⁰ and Kohn–Sham density functional theory has difficulty describing such mixed states.⁴¹ Future computational studies using appropriate multireference methods may be able to elucidate the electronic character of the triplet surface. Note that for simplicity the reaction coordinate is depicted as being one-dimensional, whereas in reality a multidimensional reaction coordinate likely exists along which direct S,S- to O,O-isomerization can occur.

The different rates of vibrational quenching in solution and in the gas phase are probably responsible for the difference in isomerization dynamics. Specifically, vibrational energy transfer to the solvent (i.e., thermalization) is usually complete on a sub-200 ps time scale, although the rate is solvent dependent. This time scale is on the same order as the time scale for isomerization of the present system in solution,¹² as illustrated in Figure 5. Assuming S,S- to O,O-Ru(bpSO) photoisomerization occurs on the excited state surface in a sequential manner,

vibrational energy transfer to solvent causes excited state molecules in the S,O geometry to be trapped before they can further isomerize to O,O-Ru(bpSO). In contrast, vibrational energy quenching in the present gas phase experiment is much slower, taking place through ion–molecule collisions occurring every few nanoseconds, with hundreds of collisions required to thermalize the ions. Gas phase ions therefore remain vibrationally energized on the excited state surface, allowing the excited state population to sequentially propagate through the transient S,O-isomer to form O,O-Ru(bpSO). This is consistent with studies on Ru(OSSO) and Ru(F-bpSO) in solution, which suggested a mixture of S,O- and O,O-isomers results from a quasi-statistical equilibrium on the ³MLCT surface, where interconversion between excited state isomers is rapid compared to deactivation to the singlet electronic ground state.¹⁸

The direct S,S- to O,O-Ru(bpSO) isomerization in the gas phase might also be related to the strength of the Ru–S bond on the triplet surface. As discussed above and illustrated in Figure 5, the triplet states of Ru(bpSO) are thought to have mixed MC and MLCT character. MC character is formally antibonding toward the sulfoxide ligands and should induce weaker Ru–S bonds, while MLCT character should have no significant impact on the Ru–S bond strength. One might expect that the MC character of the lowest triplet state should be enhanced relative to MLCT character in the gas phase because there is no solvent to stabilize the separated charges associated with MLCT.⁴² For these reasons we hypothesize that weaker Ru–S bonds on the isomerizing triplet surface in the gas phase should promote formation of the S,O- and O,O-Ru(bpSO) isomers, while suppressing recovery of S,S-Ru(bpSO). We note that this hypothesis is consistent with previous solution studies considering changes in Ru–S bond strengths following incorporation of electron-withdrawing groups (EWGs) into the bpSO ligand, such as fluorination of the phenyl groups or insertion of a silane group in the alkyl linker.¹⁸ EWGs decrease the electron donating character of the sulfur atoms, leading to longer, weaker Ru–S bonds, allowing direct S,S- to O,O-Ru(bpSO) conversion.¹⁸

The S,O-isomer also undergoes photoisomerization in the gas phase. As shown in Figure 3b, irradiation of isolated S,O-Ru(bpSO) yields a light-on/light-off difference ATD in which depletion of the S,O-Ru(bpSO) peak is matched by growth in a later peak with an arrival time consistent with O,O-Ru(bpSO). Notably, formation of the S,S-isomer was not observed. The

lack of reverse photoisomerization is consistent with the PES presented in Figure 5, as the S,S-Ru(bpSO) isomer lies energetically uphill on the excited triplet surface, while barriers on ground state singlet surface are sufficiently large to prevent thermal reversion before thermalization by buffer gas. The PISA spectrum, generated by monitoring the O,O-isomer yield as a function of wavelength, is plotted in Figure 6 along with a

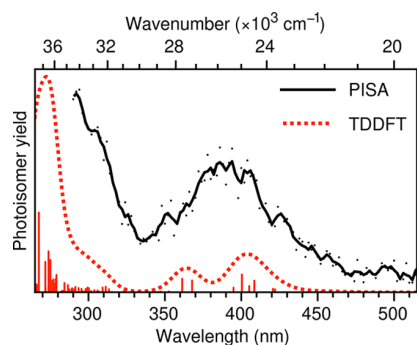


Figure 6. Gas phase PISA spectrum of S,O-Ru(bpSO) corresponding to O,O-Ru(bpSO) yield as a function of wavelength (black) and the TDDFT-simulated absorption spectrum (red). Further details of the calculation are given in the Supporting Information.

TDDFT-simulated spectrum. The PISA spectrum exhibits a lower energy band with a maximum at ≈ 395 nm (MLCT) and another band with an onset at 330 nm and increasing in intensity to shorter wavelength (bpy-centered $\pi\pi^*$ transition). Over the measured region, the gas phase PISA spectrum is again very similar to the solution absorption spectrum.¹²

Finally, no photoisomerization was observed for O,O-Ru(bpSO) over the 295–600 nm range, and hence no PISA spectrum could be measured. This is consistent with solution studies that demonstrated thermal but not photochemical reversion from O,O-Ru(bpSO) to S,O-Ru(bpSO) and S,S-Ru(bpSO).¹² Although we have no estimate for the barrier height for reversion in this system, the barriers must be sufficiently large that thermal isomerization rate following return to the ground electronic state is much less than 10^8 – 10^9 s⁻¹, the collision rate of ions with the buffer gas molecules in our experiment. As with S,O-Ru(bpSO), these observations are consistent with the proposed potential energy surfaces.

CONCLUSIONS

We report gas phase photoisomerization action spectra for the S,S- and S,O-Ru(bpSO) photoswitching complexes. The two isomers display ligand-centered electronic transitions in the UV and MLCT transitions in the visible, which both lead to photoisomerization via a triplet surface. In the gas phase, absorption of a single photon induces isomerization directly from the S,S- to the O,O-bound isomer, whereas in solution double linkage isomerization is likely suppressed by a combination of solvent-mediated vibrational quenching and increased Ru–S bond strength in the excited state. We aim to continue these gas phase studies by examining the roles of the chelate linker and of metal-centered excited states in the photoisomerization of metal–sulfoxide complexes, in similar ruthenium complexes and in analogous osmium compounds.^{18,43,44} Comparison of condensed and gas phase PISA spectra should allow us to directly assess the effect of solvation on photoisomerization.⁴⁵ Additionally, studies of osmium

polypyridyl complexes, which, due to strong spin–orbit coupling, have bright $T_1 \leftarrow S_0$ transitions, may allow direct optical access to the 3 MLCT surface and provide an alternative route to initiating photoisomerization.⁴⁶

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.8b00871.

Full details of the computational methods used in this study, a description of the reference NEVPT2 calculation, a listing of relative energies and collision cross sections for each isomer, and a discussion of the branching ratio dependence on light fluence and wavelength (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: evanj@unimelb.edu.au (E.J.B.).

ORCID

Michael S. Scholz: 0000-0003-3290-2722

James N. Bull: 0000-0003-0953-1716

Eduardo Carrascosa: 0000-0003-4338-8669

Brian D. Adamson: 0000-0002-8948-0228

Jeffrey J. Rack: 0000-0001-6121-879X

Evan J. Bieske: 0000-0003-1848-507X

Notes

The authors declare no competing financial interest.

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