Photoisomerisation
Action Spectroscopy

BRIAN DAVID ADAMSON

Submitted in total fulfilment of the requirements of the degree of Doctor of Philosophy

December, 2014

School of Chemistry
The University of Melbourne

Produced on archival quality paper
Abstract

A custom ion mobility mass spectrometer has been designed and built to investigate the photoisomerisation of molecular ions in the gas phase. The instrument differs from existing ion mobility mass spectrometers in that there is provision for optical access to the drift region to allow photo-excitation of the drifting ions as they drift. Photoisomerisation manifests as a change in the ions’ drift mobility, altering the time they take to drift through the instrument. By monitoring changes in the arrival time distribution as a function of laser wavelength it is possible to collect photoisomerisation action spectra. The instrument has been used to probe the photoisomerisation of selected cationic carbocyanine dyes. Comparison of the dyes’ laser-off and laser-on arrival time distributions reveals that these dyes have a multitude of isomers, that can be interconverted using laser light. The peak absorptions of these dyes are shown to be blue-shifted relative to their absorption spectra in solution by 30-50 nm. This work demonstrates that ion mobility can form the basis of a new spectroscopic technique for molecular ions that are not responsive to existing methods.
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.

Brian D. Adamson
Preface

Much of the work in this thesis has been, or will be, submitted for publication. Specifically, peer-reviewed articles based on the results described in chapters 4 and 5 have already been published:


Further experiments performed using the developed instrument, but not discussed in this thesis, have been published:


The instrument has also been described in an article that has recently been accepted by *Review of Scientific Instruments* (http://dx.doi.org/10.1063/1.4903753 - once published).

The 2D-NMR spectra of the (HITC)_2^2⁺ dimer, referred to in section 4, were recorded and interpreted by Neville Coughlan.

The master equation calculations referred to in section 5.3, and which appear in further detail in the second article mentioned above, were performed by Dr Gabriel da Silva.
Acknowledgements

I once read that laser laboratories can resemble dungeons, and the inhabitants - wretched inmates. But this would not be a fair description of my supervisor’s lab. Professor Evan Bieske has created a space within which young scientists have the freedom to pursue their goals, with the knowledge that their warden will have their back. Professor Bieske is acutely aware of the physical and mental wellbeing of his charges, is keenly insightful, and has an unparalleled sense of humour. In all, I cannot imagine a better person to work with.

I must acknowledge my fellow ‘inmates,’ both former and current. There are too many to list, but in particular I must thank those who welcomed me into the lab: Drs Berwyck Poad, Vik Dryza and Phil Wearne; and also those who have taken up the baton, and who have carried the work that is described here into new and exciting territory: Neville Coughlan, Katherine Catani and Peter Markworth.

This work would not have been possible without the assistance of the Science Faculty Workshop, in particular that of Richard Mathys, whose skill at turning half baked ideas into functioning parts never failed to impress. His ongoing assistance and advice has been invaluable.

Birds of a feather do flock together, and my dearest friends throughout the last few years have (generally!) been those working on a PhD of their own. At the risk of offending through omission, I must thank the following for being there, and for understanding that it is occasionally necessary to avoid talking shop: Paul, Ben, Andrew, Caitlin, Henry, Yasmina and Terry.

I must thank my family, for their love and support throughout.

Finally, I must thank my partner, Pat. For everything.
Contents

Abstract iii

Declaration v

Preface vii

Acknowledgements ix

1 Introduction 1
  1.1 Motivation for studying photoisomerisation . . . . . . . . . . . . . . 2
  1.2 History of ion mobility spectrometry . . . . . . . . . . . . . . . . 6
  1.3 Cyanine dyes . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 10

2 Background 15
  2.1 Determining mobility from drift time . . . . . . . . . . . . . . . . 17
  2.2 Resolution . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 19
  2.3 Predicting drift mobilities . . . . . . . . . . . . . . . . . . . . . . 21
  2.4 Changes in arrival time following photoexcitation . . . . . . . . . . 22

3 Experimental Setup 29
  3.1 Ion source . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 30
  3.2 Drift chamber . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 33
  3.3 First ion funnel . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 33
  3.4 Drift region . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 34
  3.5 Mass filter . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 39
  3.6 Ion detection and recording . . . . . . . . . . . . . . . . . . . . . . 41
  3.7 Light sources . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 41
  3.8 Software . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 42
  3.9 Instrument performance . . . . . . . . . . . . . . . . . . . . . . . . 43
    3.9.1 Resolution . . . . . . . . . . . . . . . . . . . . . . . . . . . . 44
    3.9.2 Mobility measurements . . . . . . . . . . . . . . . . . . . . . 46

4 Photoisomerisation of HITC+ and (HITC)2+ 49
  4.1 Photoisomerisation with continuous illumination . . . . . . . . . . . . 51
  4.2 Photoisomerisation with a pulsed light source . . . . . . . . . . . . 53
  4.3 Assignment of (HITC)2+ arrival time distribution . . . . . . . . . . . 59
  4.4 Photoisomerisation action spectra . . . . . . . . . . . . . . . . . . . 61
  4.5 Conclusion . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 65

5 Photoisomerisation of DTC+ 67
  5.1 Results . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 69
  5.2 Photoisomerisation of DTC+ . . . . . . . . . . . . . . . . . . . . . . 72
  5.3 Gas-phase photoisomerisation mechanism . . . . . . . . . . . . . . . 74
  5.4 DTC+ in N2 buffer gas . . . . . . . . . . . . . . . . . . . . . . . . . 76
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.5</td>
<td>Conclusions</td>
<td>78</td>
</tr>
<tr>
<td>6</td>
<td>Photoisomerisation of DTDC$^+$ and DODC$^+$</td>
<td>81</td>
</tr>
<tr>
<td>6.1</td>
<td>Assignment of the DODC$^+$ ATD</td>
<td>83</td>
</tr>
<tr>
<td>6.2</td>
<td>DODC$^+$ PISA spectra</td>
<td>88</td>
</tr>
<tr>
<td>6.3</td>
<td>Assignment of DTDC$^+$ ATD</td>
<td>90</td>
</tr>
<tr>
<td>6.4</td>
<td>DTDC$^+$ PISA spectra</td>
<td>93</td>
</tr>
<tr>
<td>6.5</td>
<td>Conclusions</td>
<td>95</td>
</tr>
<tr>
<td>7</td>
<td>Photoisomerisation of Pinacyanol</td>
<td>97</td>
</tr>
<tr>
<td>7.1</td>
<td>Calculations</td>
<td>99</td>
</tr>
<tr>
<td>7.2</td>
<td>Photoisomerisation of pinacyanol</td>
<td>101</td>
</tr>
<tr>
<td>7.3</td>
<td>Photofragmentation of pinacyanol</td>
<td>104</td>
</tr>
<tr>
<td>7.4</td>
<td>Conclusions</td>
<td>106</td>
</tr>
<tr>
<td>8</td>
<td>Summary and outlook</td>
<td>107</td>
</tr>
</tbody>
</table>
List of Tables

3.1 Reduced mobilities and collisional cross-sections for TBA and TPA 48
4.1 Calculated and experimental data for isomers of HITC\(^+\) & (HITC)\(^2+\) 56
5.1 Calculated data for isomers of DTC\(^+\) 70
6.1 Calculated data for isomers of DODC\(^+\) 84
7.1 Calculated data for isomers of pinacyanol 101
Chapter 1

Introduction

This thesis describes the development of an ion mobility mass spectrometer designed to study the photoisomerisation of molecular ions in the gas phase by observing changes in their drift mobility. In ion mobility spectrometry (IMS), ions are propelled through a buffer gas by an electric field, with a velocity that depends on the ions’ collision cross-section, which is sensitive to the molecular shape. In the new instrument, molecular ions are exposed to tunable light as they travel through the buffer gas. Photoinduced changes in molecular conformation are manifested as a change in the ions’ velocity and the time taken to travel from the source to the detector. By measuring the photoinduced change in the ions’ arrival time distribution (ATD) as a function of excitation wavelength, a photoisomerisation action (PISA) spectrum can be collected. This represents an entirely new way of recording electronic spectra of molecular ions in the gas phase.

Figure 1.1 A simplified schematic of a drift tube ion mobility spectrometer (DTIMS). An ion gate periodically allows bunches of ions to enter a gas filled drift region. An electric field ($E$) is provided by a series of electrodes and propels the ions through the gas with a velocity proportional to the ions’ mobility ($K$). Compact ions have a smaller collision cross-section than more extended ions, and therefore have a higher mobility and velocity. In DTIMS the mobility of an ion is determined from the time that it takes to travel the length of the drift region.
CHAPTER 1. INTRODUCTION

Following its design and construction, the new IMS instrument has been used to study the photoisomerisation of several carbocyanine dyes [1, 2]. The ATDs of the carbocyanine dyes reveal the existence of multiple isomers that can be interconverted by exposure to visible light. Isomers were identified on the basis of their relative energies, as calculated using density functional theory (DFT), as well as predicted collision cross-sections and mobilities.

Chapter 2 includes a more detailed explanation of IMS theory, covering the estimation of ion mobilities using computational methods, the relationship between collision cross section and drift mobility, the resolution of ion mobility mass spectrometers, and a discussion of the effect of photo-excitation on the ATDs of molecular ions. Chapter 3 describes the PISA instrument, including an overview of the design criteria and technical justifications, as well as performance tests. The remaining chapters detail the investigations of several carbocyanine dyes, and demonstrate the efficacy of the instrument to probe photoisomerisation of molecular ions, and as a means for obtaining photoisomerisation action spectra of molecular ions.

The remainder of the introduction elaborates on the importance of molecular photoisomerisation, discusses the history of ion mobility spectrometry, and introduces the carbocyanine dyes, which are the main molecular targets for the investigations described in this thesis.

1.1 Motivation for studying photoisomerisation

Photoisomerisation is a change in the structure or shape of a molecule initiated by the absorption of a photon (usually in the visible or ultraviolet range). Photoinduced structural rearrangements can occur via several different mechanisms, including electrocyclic ring opening or closing (for example, dithienylethenes, Figure 1.2a) or internal charge transfer (for example, spiropyrans, Figure 1.2b); \( cis \leftrightarrow trans \) isomerisation (for example, azobenzenes, Figure 1.2c) or via linkage isomerisation (for example, metal-nitrosyl complexes, Figure 1.2d [3]).
Molecules that undergo photoisomerisation, referred to as photochromic molecules, play a role in a wide variety of biological and technological processes. One prominent example is the detection of light in the eyes of all animals, which is triggered by photoisomerisation of retinal. The light sensitive rods and cones in the retina contain 11-cis-retinal bound, as a protonated Schiff base, to a lysine residue within the protein rhodopsin. Upon absorption of a visible photon, the 11-cis-retinal isomerises to the energetically favourable all-trans-retinal, distorting the rhodopsin and triggering a series of actions that result in a nervous signal being sent to the brain. The all-trans-retinal is then released from the rhodopsin and restored to the 11-cis form via an enzymatic process [4].

Retinal is also present in various channelrhodopsins, which are proteins that act as light-sensitive ion channels in various microorganisms. In this case, absorption of light by all-trans-retinal causes it to isomerise to 13-cis-retinal, opening the channel and allowing the flow of ions through the cellular membrane, in the direction of decreasing ion concentration [5, 6]. In the unicellular alga Chlamydomonas reinhardtii, where channelrhodopsin was first identified, the channelrhodopsin acts as a rudimentary visual photoreceptor, allowing the organism to determine the brightness and, roughly, the direction of origin of incident light [7].

Retinal is also used by some archaea, such as Halobacterium halobium, to harvest sunlight as an energy source. In this case, retinal is bound within halorhodopsin,
CHAPTER 1. INTRODUCTION

which acts as a chloride pump, and bacteriorhodopsin, a proton pump. In both cases the retinal resides in the all-trans conformation and converts to 13-cis-retinal following photoexcitation. The conversion back to the energetically preferable all-trans conformation pumps the ions through the cellular membrane. The resulting ion gradient provides the chemical potential to drive other cellular functions, including the formation of the ubiquitous biological fuel, adenosine triphosphate [8]. Other archaea, such as *Halobacterium Salinarum*, have both sensory and energy harvesting opsins [9].

In 2005, Deisseroth and coworkers succeeded in expressing channelrhodopsin in mammalian neurons, allowing the neurons to be reliably and selectively stimulated using pulses of blue light [10]. This was shortly followed by the expression of halorhodopsin in mammalian neurons, which allowed suppression of neural activity using yellow light [11]. In contrast to previous methods of neural stimulation and suppression, opsins can be genetically targeted to particular types of cells, and the stimulation can be more finely controlled, both temporally and spatially. The ability to stimulate and suppress neural activity, *in vivo*, with great specificity led to rapid development of the field of optogenetics [12]. Optogenetics was initially presented as a tool for probing the behaviour of neural networks, but potential future applications include the replacement of electrical pacemakers [13, 14], the restoration of vision to people with eyes that have damaged or degraded photoreceptors [15], and the selective suppression of the affected nerves during an epileptic seizure [16]. As a result, significant effort has gone towards development of genetically engineered opsin proteins. There are now dozens available, with a variety of wavelength responses and functionality, but the search for new opsins with improved or novel properties continues [17–19]. The search for new functionality could potentially be guided computationally by accurate theoretical models of the opsin proteins, and various groups have been working towards such models [20–23]. However, reliably modelling complex systems such as proteins is far from trivial. Computational modelling is more straightforward and reliable for isolated systems, which are amenable to accurate, high-level calculations that are currently impos-
1.1. MOTIVATION FOR STUDYING PHOTOISOMERISATION

Possible for systems that include a surrounding protein or solvent. An important goal of the approach developed in this thesis is to provide spectroscopic data for retinal (and other photoactive molecules) in the gas phase, against which various computational methods can be benchmarked. Andersen and coworkers have investigated isolated retinal protonated Schiff base (RPSB) by exposing mass-selected ions to tunable laser light in an ion storage ring and monitoring the neutral fragments released following photexcitation [24–27]. However their most recent spectrum for the dissociation of gas phase RPSB [26] differs from those they reported earlier [24, 25], prompting calls for further experimental investigations [28].

The search for optically controlled ion channels is not limited to retinal based switches. Considerable effort has been put towards the development of ion channels that can be optically controlled with other photochromic molecules such as azobenzenes and spiropyrans [29–31], including some that directly target specific biological receptors [32, 33]. Additionally, photochromic molecules, including the ones already mentioned and others such as azulenes, fulgides, diarylethenes and overcrowded alkenes, are not limited to applications in biological systems. They also play roles in existing and prospective technologies, such as optical data storage [34, 35], optical switches for molecular wires [36, 37], light driven molecular motors [38–40] and photoswitched organic light emitting diodes [41]. While many photochromic chromophores have been extensively studied in solution and attached to surfaces [42–45], for the most part they have not been investigated in the gas phase.

The goal of the work reported in this thesis was to develop a novel spectroscopic approach suitable for studying photochromic ions in the gas phase. The approach taken is an ‘action’ spectroscopy technique, whereby the absorption of light is detected indirectly by observing changes in ion drift mobility. Because the mobility of an ion depends on its shape, a change in mobility is a direct indicator of conformational change, as distinct to other observable actions such as photodissociation or fluorescence, which may occur in competition to isomerisation. By measuring the photoisomer yield as a function of laser wavelength (\(\lambda\)) one
can derive a spectrum that represents the molecule’s absorption spectrum $A(\lambda)$ convoluted with a wavelength-dependent isomerisation yield $\phi(\lambda)$. If $\phi$ is independent of $\lambda$, the photoisomerisation action spectrum mimics the absorption spectrum. This form of action spectroscopy, which we have termed photoisomerisation action (PISA) spectroscopy, complements existing spectroscopic techniques for probing molecular ions, including resonance enhanced photodissociation (REPD) spectroscopy [46–48], zero kinetic energy (ZEKE) photoelectron spectroscopy [49], mass analysed threshold ionisation (MATI) spectroscopy [50], and laser induced fluorescence (LIF) [51]. The approach described in this thesis differs from previous methods because the detectable “action” is a change in ion drift speed, rather than photodissociation, photoelectron ejection, or photon emission.

An important advantage of the technique is that it is possible to use IMS to separate isomers prior to irradiation and therefore measure PISA spectra for mobility-selected isomers, though this aspect is not explored in this thesis. Previously, isomer specific spectra for molecular ions have been measured using IR-UV double resonance REPD, or by REPD with preselection of the ions using field asymmetric ion mobility spectrometry (FAIMS) [52].

1.2 History of ion mobility spectrometry

The motion of ions through gas was first reported in 1896 by Rutherford and Thomson [53], who observed that various gases were able to conduct electricity following exposure to X-rays. By the turn of the century velocities had been measured for charged particles generated by ‘uranium rays’ [54], and for those arising from flames and electric arcs [55]. From these data Thomson began to develop a theory describing ions moving through a gas [56]. This theoretical treatment was elaborated by Langevin [57], whose kinetic theory of gases described the behaviour of gases at a molecular level. Lennard-Jones’ description of the interaction between ions and neutral atoms [58] was later used by Hassé and coworkers to predict the mobility of ions in the gas phase [59].
1.2. HISTORY OF ION MOBILITY SPECTROMETRY

Figure 1.3 Early drift measurement instrument built by Nolan and coworkers (reproduced from Reference 63). Sample molecules are introduced with the carrier gas, and ionised by the radioactive matter at X. The ions are carried longitudinally by the carrier gas and also propelled towards the far side of the tube by the electric field. Ions with the correct mobility reach the electrometer, whereas ions with higher/lower mobility reach the earthed plate before/after the electrometer. Varying either the drift potential or gas flow rate changes the mobility required to reach the electrometer.

The earliest ion mobility instruments were of a form that would now be referred to as a differential mobility analyzer. These devices consist of a rectangular tube through which a carrier gas flows. A potential difference applied to parallel metal plates on either side of the tube provides an electric field aligned perpendicular to the direction of gas flow. Ions are introduced (or formed) in the tube near one plate and are carried longitudinally by the carrier gas, and propelled transversally by the electric field. More mobile ions reach the plate on the other side of the tube early, whereas less mobile ions reach the other side later and further along the tube. By varying the field between the two plates and measuring the current arriving at a fixed point, the distribution of ion mobilities can be determined (see Figure 1.3). Variations on this approach are still used today and form the basis for aerosol droplet sizing instruments [60–62].

In the 1920s Tyndall and coworkers pioneered a different approach (see Figure 1.4) [64–66], in which the electric field is generated by a stack of ring electrodes.
Figure 1.4 An early DTIMS build by Tyndall and coworkers (reproduced from Reference 66). Ions produced by the polonium source, between grids F and G, are drawn towards the electrometer electrode by the electrodes between D and F. Grids A and C are held at constant potential, whereas the potential on grids B and D are cycled by an oscillator circuit. Ions are able to pass the two pairs of gate grids (A/B and C/D) when the potential on the varying electrodes is lower than the potential on the steady electrodes. Gate A/B allows a bunch of ions ions to enter the drift region, whereupon they drift towards the electrometer. If the period between gate opening times corresponds to the drift time of the ions, then the bunch will pass through gate C/D. By varying the oscillator frequency, an arrival time distribution can be measured.

Ions produced at one end of the drift region are propelled by the electric field towards an electrostatic gate part way along the drift region that periodically opens to allow a bunch of ions to drift through. This ion bunch continues to drift until it reaches a second gate at the end of the drift region. Ions that travel with an appropriate velocity pass through both gates and reach an electrometer. In Tyndall’s instruments the two gates were driven in parallel by an oscillator circuit; by varying the frequency of the oscillator, the period between gate openings could be varied. Techniques based on this approach are now referred to as drift tube ion mobility spectrometry (DTIMS). However with modern electronics it is possible to record an arrival time distribution directly, so the second gate is often not required, other than to isolate ions with a specific mobility for further interrogation.

Developments in vacuum technology, gas purity, electronics and ion detection allowed for incremental improvements in mobility measurements, but the approach remained fundamentally unchanged for some time, until in 1965, Saporoschenko combined an ion mobility drift cell with a magnetic sector mass spectrometer [67].
Prior to this there had been much controversy regarding the identity of the molecular ions arriving at the detector (for example, whether the ions forming in hydrogen gas following exposure to X-rays were $\text{H}^+$, $\text{H}_2^+$ or $\text{H}_3^+$ [68–71]). These ambiguities were addressed by McDaniel and coworkers who developed an instrument that combined a drift cell with a quadrupole mass filter, as shown in Figure 1.5 [72].

There were significant advances in IMS during the late 1960s and 1970s, with developments in the theory of ion mobility, experimental studies of a broad range of molecules, and development of commercial applications. Investigations of the interactions between ions and polar molecules by Bowers and coworkers ultimately led to the development of the angle-averaged ion dipole theory that describes the momentum transfer for collisions between ions and neutral molecules [73–76]. In 1975 Revercomb and Mason provided a rigorous treatment of the theory of ion mobility [77], establishing the relationship between ion mobility and the angle-averaged collision integral. These insights eventually allowed numerical prediction of ion mobilities based on molecular structures [78–80]. Commercial interest in ion mobility technology also began in the late 1960s, with Franklin GMO Cor-
poration developing and patenting several devices [81–83], including one similar to that of McDaniel and coworkers [84]. It was also around this time that defence researchers in the United States and the United Kingdom began to develop handheld ion mobility detectors for chemical warfare agents. Through the 1970s Karasek and coworkers demonstrated that ion mobility (under the title of plasma chromatography) could be used as a detection system for trace amounts of many compounds, including explosives and drugs of addiction [85–96]. In the meantime, various research groups systematically determined the drift mobility of a large number of atomic and molecular species, in a variety of gases, and over a broad range of temperatures and electric field strengths [97–99].

The invention of electrospray ionisation by Fenn and co-workers in the early 1980s had a dramatic effect on the field of mass spectrometry [100], and by 1989 it had been incorporated into ion mobility spectrometers [101], enabling the investigation of classes of molecules that had previously been too fragile to study intact, particularly biomolecules such as peptides [102–109], saccharides [110, 111] and lipids [112]. The millisecond timescale of ion mobility separations fits neatly between the timescales of chromatographic separations (minutes) and time of flight mass spectrometry (microseconds). This has allowed the use of ion mobility as an additional ‘nested’ technique for the separation and identification of complex mixtures [113–117]. There have been investigations of the mobilities of fragmented ions, ions formed by REMPI [118], and ions that have been annealed in the source region of the IMS (either by heating or by illumination with a fixed wavelength laser) [119].

Notwithstanding these extensive earlier investigations and developments, there have been no examples of using an IMS apparatus to probe molecular photoisomerisation, prior to the work described in this thesis.
1.3. CYANINE DYES

This thesis describes the use of ion mobility mass spectrometry to investigate the photoisomerisation of cyanine dyes, which consist of two nitrogen containing heterocycles linked by a chain of methine carbon atoms (generalised examples of which are shown in Figure 1.6). These dyes were studied because, despite their wide historical and current use, they had never been spectroscopically characterised in the gas phase, and because they are able to undergo $cis \leftrightarrow trans$ isomerisation following photoexcitation, making them amenable to PISA spectroscopy.

The first cyanine dye was reported by C. H. Greville Williams in 1856 [120, 121], who described it as having “a magnificent blue colour” (from which the class of molecules draws its name). Hopes to use these new dyes for colouring textiles were dashed by the dyes’ tendency to fade rapidly due to photo-oxidisation [122, 123], and it wasn’t until Vogel demonstrated that cyanine dyes could sensitisise silver halide photographic materials to a wider range of wavelengths that interest in them was restored [124, 125]. The overwhelming majority of colour photography sensitisers used since then have been dyes from the cyanine family [126]. While the initial interest in cyanine dyes derived from their use as photographic sensitisers, they have also been used in writeable CDs and DVDs [127, 128], where, due to their large optical absorption cross-sections, they efficiently convert laser light into heat, burning machine readable pits into the substrate of the disc. They have also been used in dye lasers, both as laser gain media and as saturable absorbers in pulsed lasers [129], and have recently found widespread use as fluorescent probes for biomolecular labelling [130–134].

Figure 1.6 Examples of generalised cyanine dyes, where $n=0$ corresponds to cyanine, $n=1$ to carbocyanine, $n=2$ to dicarbocyanine and so forth.
Despite their widespread importance there have been no previous spectroscopic studies of carbocyanine molecules in the gas phase. There are several reasons for this. First, the dyes are ionic systems which are difficult to introduce into the gas phase in sufficient concentrations for traditional fluorescence-based spectroscopic techniques. Second, the dyes exist as several different conformational isomers which have distinct absorption and emission spectra, which for any gas phase sample would overlap. In the work presented here, the dyes were introduced into the gas phase using electrospray ionisation and their electronic transitions probed by monitoring photoisomerisation in an IMS, demonstrating that the PISA approach provides the required sensitivity and selectivity to investigate carbocyanine dyes in the gas-phase for the first time.

A key characteristic of cyanine dyes is that there is unbroken conjugation between the two nitrogen atoms, resulting in the delocalisation of a positive charge along the length of the carbon chain which, in the ground state, locks each bond in the chain into either trans or cis configuration. As a result there are a number of possible isomers for each dye, but it is generally accepted that the lowest energy isomers are those with all-trans bonds, and that $S_1 \leftrightarrow S_0$ electronic excitation allows cis $\leftrightarrow$ trans isomerisation of the C-C bonds [136–138].

The accepted mechanism for photoisomerisation of cyanine dyes in solution is the Rullièere model [137], and is illustrated schematically in Figure 1.7, where the potential energy is plotted as a function of the torsion angle about one of the central C-C bonds [135, 138–141]. The barrier in the $S_0$ torsional curve at $\theta=90^\circ$ arises from a reduction in the magnitude of the conjugation energy, due to formation of
two decoupled $\pi$ subsystems. In the $S_1$ state the energy minimum is at $\theta=90^\circ$, at which point the highest occupied and lowest unoccupied $\pi$ molecular orbitals are localised on the odd numbered (polymethenic) and even numbered (polyenic) ends of the molecule, respectively [142].

In solution, cyanine dyes excited to the $S_1$ state either directly fluoresce, or alternatively, twist about one of the central C-C bonds in the linking carbon chain, surmounting a low energetic barrier, thereby accessing the potential energy minimum at $\theta=90^\circ$. Rapid, solvent-assisted vibrational relaxation quenches the molecules in this twisted configuration, before coupling through a conical intersection with the $S_0$ potential energy surface leads to some fraction $r$ becoming a cis conformer, and the remainder $(1 - r)$ returning to become the trans form. Again, rapid, solvent-assisted vibrational relaxation plays a role in stabilising the system in the trans or cis well.

Calculation of the $S_0$ potential energy curve for cyanine bond rotation via DFT methods is relatively straightforward, however the TDDFT methods commonly used to calculate excited state energies are notoriously unreliable when charge transfer is involved [143, 144], as it is in the case of cyanine dyes. Complete active space methods such as CASSCF or CASMP2 provide a more reliable view of the excited state potential energy surface, but the computation costs for large molecules are prohibitively high. Nevertheless, Schlegel and coworkers performed
CASCSF and CASMP2 for the $S_1$ surface of structurally similar streptocyanines (see Figure 1.8) [141]. Tri-methine streptocyanines display a barrierless transition from the trans configuration to the $90^\circ$ twisted form on the $S_1$ PES, whereas penta-methine and hepta-methine cyanines both display a barrier to isomerisation. This supports the Rullière model, but the barriers make it unlikely that longer cyanine ions follow this deactivation pathway in the gas phase. Rates of intersystem crossing for carbocyanines are low [145, 146], which leaves fluorescence and internal conversion as the primary deactivation pathways. But fluorescence to higher vibrational levels in the $S_0$ state would be unlikely to leave the ions with sufficient energy to overcome the ground state isomerisation barriers. Therefore it is likely that the primary pathway leading to isomerisation of cyanine dyes in the gas phase would be internal conversion followed by rearrangement on the $S_0$ potential energy surface.
Chapter 2

Background

This chapter briefly outlines the theory underlying IMS and describes how the technique can be combined with laser spectroscopy, including how photoisomerisation may affect an IMS ATD. Ion mobility spectrometry separates ions by using an electric field to propel them through a gas, in which their average velocity depends on their size and shape. Typically, ions are launched through an electrostatic gate with an initial packet width of $\Delta t_m$, travel through a drift tube, and are sensed by a charge sensitive detector that enables their flight time to be logged. The average drift velocity ($v_d$) of an ion travelling through a gas is proportional to the electric field ($E$):

$$v_d = K \times E,$$  \hspace{1cm} (2.1)

where the coefficient of proportionality ($K$) is the ion mobility. The mobility of an ion is related directly to the rate at which it collides with the bath gas. This varies linearly with the bath gas number density, which (following a rearrangement of the ideal gas equation) varies with pressure and inversely with temperature. For the sake of consistency, mobilities are often normalised to a reduced mobility ($K_0$) at a standardised temperature (273.15 K) and pressure (760 torr):

$$K_0 = K \left( \frac{P}{760 \text{ Torr}} \right) \left( \frac{273.15 \text{ K}}{T} \right),$$  \hspace{1cm} (2.2)

where $T$ is the temperature, $P$ the pressure and $K_0$ is the ion’s reduced mobility.

The mobility can be derived from the temperature dependent ion-neutral collision
integral \((\Omega(T))\), as described by the Mason-Schamp equation \[77\]:

\[
K = \frac{3ze}{16N} \sqrt{\frac{2\pi}{\mu k_B T}} \left( \frac{1}{\Omega(T)} \right),
\]

(2.3)

where \(ze\) is the charge of the ion, \(N\) is the number density of the bath gas, \(\mu\) is the reduced mass of the ion and the gas, \(k_B\) is the Boltzmann constant and \(\Omega(T)\) is the orientationally averaged collision integral, which depends on the potential energy surface describing the interaction of the molecular ion and the buffer gas molecule. It is \(\Omega(T)\) that encodes the shape of the molecule and which depends on the molecular structure. If the collisions are presumed to be between hard spheres, \(\Omega(T)\) is independent of temperature and is equal to the hard sphere collision cross-section.

Combining Equations 2.2 and 2.3 and substituting the number density using the ideal gas equation \((N = n/V = P/RT)\) gives

\[
K_0 \left( \frac{760T}{273.15P} \right) = \frac{3zeRT}{16P} \sqrt{\frac{2\pi}{\mu k_B T}} \left( \frac{1}{\Omega} \right),
\]

(2.4)

which leads to

\[
K_0 \times \Omega = \frac{C}{\sqrt{T}},
\]

(2.5)

where

\[
C = \frac{273.15 \times 3zeR}{760 \times 16} \sqrt{\frac{2\pi}{\mu k_B}}.
\]

(2.6)

This shows that for a given mass, charge and temperature, the product of the collision integral and the reduced mobility is constant, but that care needs to be taken when comparing measurements taken at different temperatures.

It is important to note that even at a fixed buffer gas temperature, the ion mobility is only constant for ions being driven by a low electric field. At low drift velocities, collisions between ions and neutrals are mostly thermal in nature. But as the ion drift velocity increases, the field-induced kinetic energy becomes more significant and the effective temperature of the ions becomes

\[
\frac{3}{2} k_B T_{\text{eff}} = \frac{1}{2} M v_d^2 + \frac{3}{2} k_B T,
\]

(2.7)
and the mobility is given by

\[ K = \frac{3ze}{16N} \sqrt{\frac{6\pi}{\mu(3k_B T + Mv_d^2)}} \left( \frac{1}{\Omega(T)} \right), \]  

(2.8)

where \( M \) is the mass of a neutral buffer gas molecule [77]. Providing the field-induced kinetic energy is small compared to the thermal energy, that is:

\[ \frac{Mv_d^2}{3kT} << 1, \]  

(2.9)

the ions will be drifting in the low field regime, and Equation 2.8 is sufficient to relate the mobility and cross-section of an ion. It will be shown later that the instrument developed in this project indeed operates within the low field regime.

2.1 Determining mobility from drift time

The time taken to travel through a drift tube of length \( l \) is

\[ t = \frac{l}{v_d}. \]  

(2.10)

Substituting Equation 2.1 and \( E = \frac{V}{l} \) (where \( V \) is the voltage drop across the drift tube) this becomes

\[ t = \frac{l^2}{KV}. \]  

(2.11)

If an ion mobility spectrometer is comprised of several sections with different lengths \( (l_i) \) and voltage drops \( (V_i) \), the total drift time \( (t_a) \) is the sum of the drift times in each section:

\[ t_a = \sum_i \frac{(l_i)^2}{KV_i}. \]  

(2.12)

Therefore, assuming the mobility of the ion is constant (with no changes in structure, buffer gas temperature/pressure or non-linearities due to high fields) and the length and voltage drop across each section is known, it is straightforward to
determine the mobility of an ion using Equation 2.13:

\[ K = \frac{1}{t_a} \sum_i \frac{(l_i)^2}{V_i}. \]  

(2.13)

In the new instrument there is a short section (the gate section), within which the ions travel against a significant flow of buffer gas. This means that the ions’ velocity in that region is no longer simply the product of their mobility and the drift field. Consequently, the relationship between ion arrival time and ion mobility is not described by Equation 2.13. This effect is usually relatively minor, but can become significant at higher buffer gas flow rates. For a buffer gas flow rate of \( v_{\text{ol}} \) and a gate area \( A \), the gas flow velocity in the gate region is

\[ v_{\text{gas}} = \frac{v_{\text{ol}}}{A}. \]  

(2.14)

The counterflow of gas reduces the ions’ velocity in the gate region to

\[ v_{\text{gate}} = \frac{KV_{\text{gate}}}{l_{\text{gate}}} - v_{\text{gas}}. \]  

(2.15)

As a result, the retention time in the gate region becomes

\[ t_{\text{gate}} = \frac{l_{\text{gate}}}{KV_{\text{gate}}/l_{\text{gate}} - v_{\text{gas}}}. \]  

(2.16)

So the total travel time through the whole instrument (which includes two other sections) is:

\[ t_a = \frac{(l_{\text{drift}})^2}{KV_{\text{drift}}} + \frac{(l_{IF2})^2}{KV_{IF2}} + \frac{(l_{\text{gate}})^2}{KV_{\text{gate}} - v_{\text{gas}}l_{\text{gate}}}, \]  

(2.17)

where \( V_{\text{drift}} \) is voltage drop across the main drift section and \( V_{IF2} \) is the voltage drop across the second ion funnel. After some rearrangements:

\[ Kt_a = \left( \frac{(l_{\text{drift}})^2}{V_{\text{drift}}} + \frac{(l_{IF2})^2}{V_{IF2}} \right) + \frac{K(l_{\text{gate}})^2}{KV_{\text{gate}} - v_{\text{gas}}l_{\text{gate}}}. \]  

(2.18)
one gets

$$Kt_a(KV_{gate} - v_{gas}l_{gate}) = (KV_{gate} - v_{gas}l_{gate})\left(\frac{(l_{drift})^2}{V_{drift}} + \frac{(l_{IF})^2}{V_{IF}}\right) + K(l_{gate})^2.$$  

(2.19)

Expanding Equation 2.19 and collecting like terms results in the quadratic equation:

$$- \left[ t_a v_{gas} l_{gate} - (l_{gate})^2 - V_{gate} \left( \frac{(l_{drift})^2}{V_{drift}} + \frac{(l_{IF})^2}{V_{IF}} \right) \right] K^2$$

$$+ \left[ v_{gas} l_{gate} \left( \frac{(l_{drift})^2}{V_{drift}} + \frac{(l_{IF})^2}{V_{IF}} \right) \right] K = 0,$$  

(2.20)

which can be solved to give $K$.

### 2.2 Resolution

As the ion bunch drifts through the instrument, the ions diffuse and the bunch spreads out. The spatial distribution of the ions is described by the diffusion equation, which for an ion bunch starting as a point has the solution

$$f(x, t) = \frac{A}{2(\pi Dt)^{1/2}} exp\left(\frac{-(x - x_t)^2}{4Dt}\right),$$  

(2.21)

where $A$ is the total number of ions, $t$ is the time that the ions have been drifting, $x_t$ is the location of the centre of the ion bunch at that time and $D$ is the diffusion constant. This is a Gaussian function such that the full-width at half-maximum of the ion bunch at time $t$ is

$$w = 4[Dt \ln(2)]^{1/2}.$$  

(2.22)

The Nernst-Townsend-Einstein relation relates $D$ and $K$ for systems in the low field regime [77]:

$$K = \frac{qD}{kT} = \frac{zeD}{kT},$$  

(2.23)
which leads to

\[ w = 4 \left( \frac{KkT \ln(2)}{ze} \right)^{1/2}. \]  

(2.24)

The temporal width \( (w_t) \) of the ion bunch as it moves through a plane perpendicular to the direction of travel is the spatial width divided by the average velocity:

\[ w_t = \Delta t = 4 \left( \frac{KkT \ln(2)}{ze} \right)^{1/2} \left( \frac{1}{v_d} \right). \]  

(2.25)

Combining \( v_d = \frac{L}{t} \) and \( v_d = KE = \frac{KV}{t} \) gives \( v_d = \left( \frac{KV}{t} \right)^{1/2} \), which, when substituted into Equation 2.25, leads to:

\[ \Delta t = 4 \left( \frac{kT \ln(2)}{zeV} \right)^{1/2} t. \]  

(2.26)

It is important to note that as the drift field can be different in three distinct sections in our instrument, it is necessary to determine the contribution to the ion packet width for each section individually. The three terms in Equation 2.17 correspond to the time spent within each section. Substituting each of these, along with the voltage drop over the corresponding section, into Equation 2.26 gives that section’s contribution to the overall packet width. There may also be a significant contribution to the packet width due to the initial width of the ion packet at launch. The total packet width is then given by:

\[ \Delta t_f = \sqrt{\Delta t_{in}^2 + \Delta t_{gate}^2 + \Delta t_{drift}^2 + \Delta t_{IF2}^2} \]  

(2.27)

where \( \Delta t_{in} \) is the initial FWHM of the ion bunch, and \( \Delta t_{gate}, \Delta t_{drift} \& \Delta t_{IF2} \) are the contributions to the packet width due to diffusion in the section immediately after the ion gate, the main drift region and the second ion funnel, respectively. Therefore, we can predict a diffusion limited resolution \( (R_d) \) for the instrument:

\[ R_d = \frac{t_a}{\Delta t_f} = \frac{t_{gate} + t_{drift} + t_{IF2}}{\sqrt{\Delta t_{in}^2 + \Delta t_{gate}^2 + \Delta t_{drift}^2 + \Delta t_{IF2}^2}} \]  

(2.28)

Under ideal conditions, assuming the initial ion packet width is insignificant rel-
2.3. PREDICTING DRIFT MOBILITIES

...ative to the width due to diffusional spreading, the diffusion-limited resolution should vary linearly with respect to the square root of the ionic charge and drift voltage and with the inverse of the square root of temperature.

\[ R_d \propto \left( \frac{Vz}{T} \right)^{1/2} \]  

(2.29)

It is apparent from Equation 2.28 that the resolving power of an ideal instrument is constant under given conditions, and that the width of each ion bunch is proportional to its arrival time (assuming short \( \Delta t_{in} \)). For an instrument with resolution \( R_d \), the temporal width of arrival peak will be:

\[ R_d = \frac{t}{\Delta t} \rightarrow \Delta t = \frac{t}{R_d}. \]  

(2.30)

By combining this with a time shifted Gaussian function, one gets:

\[ f(t) = \frac{2AR_d}{t_a} \sqrt{\ln(2)} \exp\left[ -4\ln(2) \left( \frac{R_d(t - t_a)}{t_a} \right)^2 \right]. \]  

(2.31)

2.3 Predicting drift mobilities

To assist with identifying arrival time peaks, it is useful to calculate a predicted mobility for each of the isomers that may be present. In this work, this was done using MOBCAL, a computer program developed by Jarrold and coworkers \[147\]. MOBCAL estimates the mobility of an ion based on its chemical structure, using three different methods. First, the projection approximation (PA) method assumes hard sphere collisions and averages the projected cross-section over randomly selected orientations of the collision partners. Second, the exact hard sphere scattering (EHSS) method calculates an average of the momentum transfer for hard-sphere collisions for multiple randomly selected approach angles and takes into account multiple collisions, which are important for molecules with convex structures \[78\]. Third, the trajectory approximation (TJ) method calculates an average of the momentum transfer occurring from collisions between the molecular ion and a
neutral gas molecule \[79, 80\], where the intermolecular interaction is represented as the sum of atom-atom Lennard-Jones (LJ) interaction terms supplemented by charge-induced dipole induction terms.

The original parameters (such as atomic hard sphere radii and LJ potential parameters) used in this code were based on data from carbon and silicon clusters drifting in helium gas. The values determined for carbon were also used for nitrogen and oxygen atoms, and the values for silicon used for sulphur and iron. This led to inaccurate predictions of mobility for molecular ions that included these elements. Subsequently, optimised parameters for hydrogen, carbon, oxygen and nitrogen, in helium bath gas, were empirically determined by Siu and coworkers \[148\]. Optimised parameters for the above elements plus fluorine were determined for the trajectory approximation method in both helium and nitrogen buffer gases by Kim and coworkers \[149\].

In this work MOBCAL was used to predict the mobilities of different configurational isomers using structures optimised using density functional theory (DFT) calculations with the B3LYP functional \[150, 151\] and Pople type \[152\] basis sets (6-31G(d), unless noted otherwise). Calculations were performed using the Gaussian09 software package \[153\]. The mobilities reported in this work were calculated by the EHSS method, using the original parameters.

\subsection{Changes in arrival time following photoexcitation}

In this project we sought to discern photo-induced changes in arrival time distributions, so it was necessary to develop an understanding of how the drift velocity is affected by molecular photoisomerisation. What follows is a treatment of expected photo-induced changes for single laser pulse excitation and for continuous laser excitation.
2.4. CHANGES IN ARRIVAL TIME FOLLOWING PHOTOEXCITATION

Single laser pulse excitation

Following exposure to light, electronically excited ions will return to the ground electronic state through several competing processes. Rapid relaxation via fluorescence or internal conversion returns the ions to the ground state ($S_0$) from the excited state ($S_1$) on timescales short enough to be effectively instantaneous compared to the time taken to traverse the drift region. In the case of fluorescent decay back down the ground vibrational state, there will be no appreciable impact on the mobility of the ion. Internal conversion, however, results in an ion that is in a highly excited vibrational state of the ground electronic state manifold, which may have sufficient energy to surmount an isomerisation barrier. Alternatively, the ions may undergo intersystem crossing to a long lived excited state of higher multiplicity, again with liberation of significant vibrational energy.

If a bunch of ions (of isomer A) is exposed to a laser pulse at some point, resulting in some of the ions permanently photoisomerising, or entering an excited state with a lifetime longer than the remaining drift time (isomer/state B), then (following from Equation 2.12) the total drift time for the altered ions is the sum of the drift times over the lengths of the drift region before ($l_{pre}$) and after ($l_{post}$) excitation:

$$t_{a,B} = \frac{l_{pre}}{K_A E} + \frac{l_{post}}{K_B E}, \quad (2.32)$$

where $K_A$ and $K_B$ are the mobilities of isomer A and B respectively. Or alternatively:

$$t_{a,B} = \frac{l_{post}}{K_B E} + t_{ex}, \quad (2.33)$$

where $t_{ex}$ is the time of laser pulse. This arrival peak will take a form described by Equation 2.31. If the photoisomer (or excited state) decays back to the parent isomer (or ground state) on a time scale similar to the flight time (for example, via a thermally driven back-isomerisation, or decay from a triplet state), then there will be a distribution of ions with arrival times lying between the arrival time of the parent ions ($t_{a,A}$) and the arrival time of the altered ions that do not decay
before arriving at the detector \((t_{a,B})\). If we assume that the altered ions decay back to the parent ion as a first order process, then the rate is proportional to the number of ions in the altered state \((N_B)\):

\[
\frac{d[N_B]}{dt} = -k[N_B], \quad (2.34)
\]

where \(k\) is the decay rate constant. Therefore the number of altered ions still present \(t\) seconds after the time of excitation is

\[
[N_B] = [N_{B,0}]e^{-kt}, \quad (2.35)
\]

where \(N_{B,0}\) is the number of ions initially altered by the excitation laser pulse. Substituting Equations 2.35 into 2.34 gives the relaxation rate as a function of relaxation time \((t_r)\):

\[
\frac{d[N_B]}{dt} = [N_{B,0}]ke^{-kt}. \quad (2.36)
\]

The distance travelled by the altered ions before they relax is \(t_r \times K_B E\). Therefore the distance remaining after they relax is

\[
l_{post} - t_r K_B E, \quad (2.37)
\]

their remaining travel time is

\[
l_{post} - t_r K_B E \quad \frac{K_A E}{K_A E}, \quad (2.38)
\]

and their final arrival time will be

\[
t_{a,(B\rightarrow A)} = t_{ex} + t_r + \frac{l_{post} - t_r K_B E}{K_A E}. \quad (2.39)
\]

Rearranging Equation 2.39 we can determine the relaxation time distribution from the arrival time distribution, as long as the mobility of both forms of the ion are
2.4. CHANGES IN ARRIVAL TIME FOLLOWING PHOTOEXCITATION

Figure 2.1 Predicted arrival time distributions (neglecting diffusion) for isomers that return to their original form on timescales similar to their flight time through the instrument. (a) shows a case where the decay rate is slow enough that there is still an appreciable number of ions in the altered state. (b) shows a case with a decay rate high enough that all the ions have returned to the original state by the end of the drift section.

known:

\[ t_r = \frac{K_A E (t_{a,B \rightarrow A} - t_{ex}) - l_{post}}{(K_A - K_B) E} \]  \hspace{1cm} (2.40)

Equation 2.40 acts to transform an arrival time distribution into a relaxation time distribution. This means that, for well resolved isomers that convert from one form to the other on a timescale comparable to the flight time through the instrument, it should be possible to determine the conversion rate constant. Note that the preceding determination of arrival time distribution neglects diffusion effects, so the predicted arrival time distributions would need to be convoluted with a Gaussian function (with a width proportional to arrival time) to give an accurate prediction. The Arrhenius equation has been used throughout this work to estimate the isomerisation rates based on isomerisation barrier heights calculated by DFT methods:

\[ k = f \times \exp \left( -\frac{E_A}{k_B T_{eff}} \right) \]  \hspace{1cm} (2.41)

where \( f \) is the average frequency of collisions between the ion and the bath gas, \( E_A \) is the activation energy for the isomerisation, \( k_B \) is the Boltzmann constant and \( T_{eff} \) is the effective temperature, as determined by Equation 2.7. For metastable isomers isolated in the gas phase, with first order isomerisation rates, the isomer
half-life would be

\[
t\frac{1}{2} = \frac{\ln(2)}{k} = \ln(2) \left[ f \times \exp\left( -\frac{E_A}{k_B T_{eff}} \right) \right]^{-1}. \tag{2.42}
\]

\(t_{a,A}\) and \(t_{a,B}\) respectively indicate arrival times for ions that spend the entire drift flight in the original and altered states.

**Figure 2.2** Predicted arrival time distributions (neglecting diffusion) for ions that gradually convert to a long lived altered state over the course of the entire drift section (a) or over the course of an illuminated region in the central section of the drift tube (b). Constant illumination presents another scenario, in which ions could be gradually transformed into another form over time. If this new form is long lived on the time scale of the mobility experiments then this would result in arrival time distributions such as those shown in Figure 2.2. On the other hand, if the altered state is short lived, then the ions may undergo rapid cycling from the ground state, to the excited state, then back to the ground state, with some fraction of the ions spending some time in the altered state. If this cycling is rapid enough,
then the populations of ions in each of the states would reach equilibrium, and the mobility would be an average of the mobility of each state, weighted by the proportion of time spent in each state. What follows is a calculation of this average mobility. The rate of change in the number of ions in each of three states (shown in Figure 2.3) is described by the rate equations below:

\begin{align*}
\frac{dS_1}{dt} &= k_1[S_0] - (k_2 + k_4)[S_1], \\
\frac{dB}{dt} &= k_2[S_1] - k_3[B], \\
\frac{dS_0}{dt} &= k_3[B] - k_1[I][S_0] + k_4[S_1].
\end{align*}

Assuming the system rapidly reaches equilibrium, the rates of change reduce to zero:

\begin{align*}
0 &= k_1[I][S_0] - (k_2 + k_4)[S_1], \\
0 &= k_2[S_1] - k_3[B], \\
0 &= k_3[B] - k_1[I][S_0] + k_4[S_1].
\end{align*}

These equations can be rearranged to give

\begin{align*}
(k_2 + k_4)[S_1] &= k_1[I][S_0], \\
k_3[B] &= k_2[S_1], \\
k_1[I][S_0] &= k_3[B] + k_4[S_1].
\end{align*}

From Equation 2.49, we get

\[ [S_1] = \frac{k_1}{k_2 + k_4} I[S_0]. \]
Substituting Equation 2.52 into Equation 2.50 leads to

\[ k_3[B] = \frac{k_1k_2}{k_2 + k_4} I[S_0], \quad (2.53) \]

\[ [B] = \frac{k_1k_2}{k_3(k_2 + k_4)} I[S_0]. \quad (2.54) \]

By setting \([S_0]\) to 1, the relative populations of ions in each state at equilibrium become:

\[ [S_0] = 1, \quad (2.55) \]

\[ [S_1] = \frac{k_1}{k_2 + k_4} I, \quad (2.56) \]

\[ [B] = \frac{k_1k_2}{k_3(k_2 + k_4)} I, \quad (2.57) \]

with the total number of ions \((N)\) given by

\[ N = 1 + \frac{k_1}{k_2 + k_4} I + \frac{k_1k_2}{k_3(k_2 + k_4)} I, \quad (2.58) \]

and the average mobility of the ion given by

\[ K_{\text{average}} = \frac{K_{S_0} + K_{S_1}I^{k_1/k_2} + K_BI^{k_1k_2/k_3(k_2+k_4)}}{1 + \frac{k_1k_0I^{k_1k_2}}{k_3(k_2+k_4)}}. \quad (2.59) \]

If there is no intersystem crossing, then \(k_2 = 0\) and Equation 2.59 reduces to

\[ K_{\text{average}} = \frac{K_{S_0}k_4 + K_{S_1}Ik_1}{k_4 + Ik_1}. \quad (2.60) \]
Chapter 3

Experimental Setup

Figure 3.1 Section view of the IMS apparatus, showing the electrospray ion source (A), transfer capillary (B), first ion funnel (C), drift region (D), second ion funnel (E), differential pumping stage with octopole ion guide (F), lens stack (G), quadrupole mass filter (H) and ion detector (I).

Although commercial ion mobility spectrometers are available, they are expensive and are not readily adaptable for use with lasers. Therefore this project was largely dedicated to the design, construction, and validation of a purpose built ion mobility spectrometer, capable of separating ions based on their gas phase mobility, but importantly also having optical access to the drift region to allow laser excitation of the drifting ions. This chapter covers of the design of the instrument, as well as descriptions of the lasers, optics, pumping, and signal collection systems, as well as some measures of the performance of the instrument.

The instrument shown in Figures 3.1 and 3.2 works as follows: Electrosprayed ions pass through a heated transfer capillary and accumulate in the first ion funnel. An electrostatic ion gate periodically injects ion bunches into the drift section, where they are either immediately irradiated by a transverse pulse of laser light, or alternatively exposed to a coaxial light beam from a continuous or pulsed laser in the straight section of the drift region. A photo-induced change in ion conformation
Figure 3.2 Schematic diagram of the ion mobility apparatus shown in Figure 3.1. and drift speed results in the separation of isomers over the remainder of the drift region. After the drift region a second ion funnel gathers the ions towards a 0.35 mm orifice leading to an octopole ion guide which carries them through a differentially pumped chamber to a quadrupole mass filter and ion detector.

3.1 Ion source

The ion source for the instrument is an electrospray unit [100]. The analyte is dissolved in a volatile solvent (either acetonitrile or 50:50 methanol:water) and delivered via syringe pump (Kent Scientific, Genie Plus) to a fine stainless steel capillary. The electrospray capillary tip is typically held 3-6 mm from the transfer capillary entrance, and at a potential of 3-5 kV relative to the transfer capillary entrance. The electrospray is housed within a glass tube, which is filled with flowing nitrogen gas at slightly above atmospheric pressure. The electrospray was aimed downwards, past the entrance of a 24 cm long, 0.8 mm I.D. glass capillary, so that heavier droplets would overshoot the capillary entrance,
3.1. ION SOURCE

carried by momentum and gravity (see Figure 3.3).

The electrospray has been operated in two ways. In the first mode of operation (used for most experiments described in this thesis), the ends of the transfer capillary were coated with conductive epoxy, and the inside of the capillary coated with a thin film of graphite to prevent the build up of charge [while still maintaining a high resistance (>100 MΩ) between the two ends]. The entrance of the transfer capillary was held at ground via a resistor (∼1 MΩ), while the exit was held at the potential of the entrance of the ion funnel. The electrospray tip was biased by a ±5 kV power supply (Applied Kilovolt HPR5), allowing for the generation of both positive and negative ions. The first few centimetres of the transfer capillary was heated by wire-wound resistors attached to an aluminium block (see Figure 3.4). The temperature of the aluminium block was typically ∼160 °C. In this mode, the ions were carried into a region at higher potential than at the start of the capillary. The potential gradient was relatively gentle, and the viscous flow of gas was sufficient to carry the ions through the capillary (see Figure 3.5a).

In the second mode of operation, a length of Nichrome wire was wound around the transfer capillary, inside the instrument. Alternating current is passed through this wire via an isolating 10:1 step down transformer, and the heater wire biased to the same potential as the start of the ion funnel. The amplitude of the AC voltage is controlled with a Variac. The presence of the heater wire flattens out the potential along the length of the capillary, resulting in a steeper potential gradient near the capillary entrance (see Figure 3.5b). This increased gradient is too steep to allow the passage of ions. To overcome this, the glass capillary was replaced with a stainless steel capillary of the same length and I.D., which was insulated in a glass tube. Replacing the glass capillary with a metal capillary and raising the maximum potential of the ESI source (from 5 kV to 10 kV (Applied Kilovolt HP10)) eliminated the need to push ions into a region of higher potential (see Figure 3.5c). These changes resulted in a marked increase in ion current, and dramatically improved stability.
CHAPTER 3. EXPERIMENTAL SETUP

Figure 3.4 Schematic diagram of electrospray and transfer capillary.

Figure 3.5 Variation in the electrical potential from electrospray tip to start of drift region. (a) Glass capillary without second heater element. (b) Glass capillary with second heater element. (c) With metal capillary and higher voltage potential applied to electrospray tip.
3.2 Drift chamber

The first ion funnel, drift region and second ion funnel are contained in a purpose-built box, built from 25 mm thick poly(methyl methacrylate) (PMMA, commonly called perspex), with internal dimensions $l = 1130$ mm, $w = 350$ mm, $h = 220$ mm and a removable lid sealed by an O-ring. Three interior PMMA baffles support the box, reducing mechanical deformation when it is pumped down to normal operating pressure (5-15 Torr). The drift region is pumped by a $28$ m$^3$/hr dual-vane rotary pump (Edwards E2M28), connected via a foreline trap to the source side of the first ion funnel. Buffer gas (either He or N$_2$) is supplied to the chamber towards the exit end via a mass flow controller (Sevenstar D08-1F). The flow rate is typically 0.2-1 SLM. This results in a counterflow of buffer gas back through the first ion funnel, preventing neutral molecules (particularly solvent vapour from the electrospray) entering the drift region. The pressure in the drift chamber is controlled by a combination of adjusting the buffer gas flow rate and choking the outlet flow with a valve.

3.3 First ion funnel

Upon emerging from the ESI transfer capillary, the ions enter the first of two ion funnels (shown in Figure 3.6). This funnel consists of 50 nickel plated brass electrodes, each 1 mm thick and separated by 1 mm thick PTFE washers. Each electrode has a circular opening, the first 10 of which are of 34 mm diameter. The diameter then decreases linearly to 3 mm. The first and last electrodes have only DC potentials ap-

Figure 3.6 Section view of the first ion funnel.
plied to them, whereas the potential of the intervening electrodes consists of a superposition of a radio frequency (RF) potential, with opposite phases applied to alternating electrodes, and a DC potential that is set by a voltage divider along the length (see Figure 3.7). The RF field confines the ions radially, pushing them towards the centre of the funnel as they are driven through by the DC potential gradient. The RF voltage for the funnel is generated by a dedicated power supply (CGC Instruments [154]) running at 500 kHz and capable of supplying up to 720 Vp-p (although electrical breakdown of the gas in the chamber typically occurs at much lower amplitudes), and capacitively coupled to the ion funnel. The DC potential gradient across the funnel is a fraction of the total voltage across the instrument (set by a resistive voltage divider). The DC potential on the final electrode can be switched, allowing it to act as a gate, accumulating ions in the funnel when held at a high potential and allowing the passage of ions when dropped to a lower potential. The gate could originally be switched up by to 40 V, but the power supply was later modified to allow it to switch 65 V. Timing of the gate is controlled by a delay generator (Stanford Research Systems DG535) usually set to trigger at 20 Hz, with a gate opening time of 50-500 µs.

3.4 Drift region

The drift region of the instrument consists of 82 electrodes made from 1 mm thick stainless steel. The first 5 electrodes, immediately following the ion funnel have 5 mm diameter openings and are spaced 5 mm apart, as shown in Figure 3.8. This section is built directly into one of the PMMA baffles which ensures that all of the buffer gas must pass through the apertures of these electrodes. This forms a gate region with a significant counterflow of gas that prevents neutral molecules, including solvent from the electrospray, passing from the first ion funnel into the main drift region. The closer spacing of the electrodes creates a stronger field, ensuring that the ions are able to overcome the counterflow of gas. The remaining
3.4. DRIFT REGION

Figure 3.7 A wiring diagram for the first ion funnel. The DC field is provided by the high voltage DC power supply, and divided by two chains of 1 MΩ resistors (the first resistor in one chain, and the last resistor in the other are 0.5 MΩ to ensure that the field decreases evenly, rather than stepping down after every second electrode), which are in parallel to two variable resistors. The overall potential across the entire funnel is determined by the effective total resistance of the ion funnel relative to the total resistance through the entire instrument. The RF potential is capacitively coupled onto alternating electrodes, excluding the first and last. The first electrode is DC only, the last has a ±20 V switchable potential, superimposed on a reference potential provided by the voltage divider.

Drift electrodes have 34 mm openings, and are spread 12 mm apart. The electrodes are connected in series with 1 MΩ resistors to establish a potential gradient that drives the ions through the drift region.

A crucial feature of this instrument is provision for a tunable laser beam to overlap the ion bunch, in order to modify their electronic state or isomeric form, and hence alter their drift mobilities. This has been achieved by two means. First, light from a pulsed or CW laser can enter through openings cut into selected drift electrodes (see Figure 3.9A) and coaxially overlap the central section of the drift region. This necessitated introducing curved sections into the drift region. While curved sections have been employed in ion mobility spectrometers previously [155], they
Figure 3.8 Source region of the apparatus. Ions that pass through the electrospray transfer capillary (A) are confined radially and focussed by the first ion funnel (B), the last electrode of which acts as an electrostatic gate. Bunches of ions that are released by the gate initially travel through a gate region (C) in which the electrode openings are 5 mm diameter and there is a significant counterflow of buffer gas to prevent neutral molecules entering the main drift region (D). The path of the transverse laser beam pulse is also shown (E).

have always been followed by an ion funnel to regather the ions in the centre of the drift tube.

To assess whether it was feasible to use a curved drift tube without an ion funnel, the setup was modelled using SIMION software combined with a statistical diffusion simulation program [156, 157]. SIMION is an ion optics simulation program, which calculates the paths taken by ions through electric and magnetic fields [158, 159]. The electrode geometry is defined by the user, then SIMION calculates the electric field between electrodes by numerical solution of the Laplace equation. Each electrode’s contribution to the total field is solved individually, and the total field calculated as a linear combination of the individual contributions. Ion trajectories are calculated numerically over a number of time steps (which vary in size depending on ion velocity and conditions of the field around the ions). At each step, the total field is recalculated to reflect changes in the potential of
any of the electrodes. The force on each ion is determined from the gradient of the electrical potential at the ion’s location, and the ion is accelerated along that vector.

Two approaches are available to simulate the effect of neutral buffer gas on the motion of the ion. The first approach is suited to ions in the molecular flow regime, whereas the second is more suited to the diffusive flow regimes. The first approach models individual collisions between the ions and the buffer gas molecules [160]. Whether a collision occurs during a given time step is determined randomly with the probability of a collision determined by comparison of the mean free path of the ion and the distance that the ion has travelled during that time step. If a collision occurs the ion changes course in a fashion determined by hard sphere collision dynamics [161]. The approach works best if the number of collisions is low, and the mean free path of the ions is much longer than the distance travelled by the ion during each time step. The other approach takes a statistical diffusion approach [156, 157]. The distance travelled by the ions with each time step is much

Figure 3.9 (A) Coaxial optical access to the drift region is via 8 mm diameter holes cut in the electrodes that form the curved sections. (B) Optical access is also available for MALDI or laser-ablation type sources.
longer than the ions’ mean free path. With each time step, SIMION moves the ion as it would move normally, then moves the ion a random distance (based on the ions’ diffusion constant) in a random direction, thus simulating the behaviour of an ion that collides many times during each time step of the program. For the buffer gas pressures in the ion drift tube (∼10 Torr), the first approach would require very short time steps, resulting in prohibitive computation times. Consequently the second approach was used for modelling the behaviour of ions under typical drift conditions. The SIMION results showed that for a curved drift tube, ions towards the inside of the curve are dragged ahead of ions on the outside due to the shorter path length as well as a steeper effective potential gradient. Simulations suggested that this longitudinal spreading could be countered by using an S-bend arrangement (see Figure 3.10); ions with a shorter path in the first curve have a longer path in the second curve and vice versa, although there is some over-correction. It is worth noting that the SIMION model appears to overestimate the degree of diffusion. This is partly due to the relatively large size of the ion markers, which results in the relatively few ions towards the edge of the packet appearing as a solid mass. Typical ion packet arrival time widths are on the order of 0.1−0.3 ms which, for ions travelling at ∼50 m/s, corresponds to a spacial width of 5−15 mm for the ion packets at the end of the drift tube. The packet size at the time of laser excitation would be smaller again, and is smaller than the laser spot size typically used.

The second means of irradiating the ion bunch is with a transverse laser beam. Windows in the side of the chamber allow a pulse of light from a tunable laser to cross the drift region perpendicular to the ions’ direction of travel. This can occur either shortly after the gate region (as shown in Figure 3.8E), or roughly halfway through the main drift section.

The drift region ends with a second ion funnel, consisting of 40 electrodes similar to those in the first ion funnel. The second ion funnel differs from the first funnel in two ways. First, the diameter of the ion funnel starts decreasing immediately,
3.5. MASS FILTER

Figure 3.10 SIMION modelling of packet of ions drifting through the S-bend section. Red markers indicate ion distributions at regular intervals. Ions initially travel in a spherical packet (A), but as they traverse the first bend, ions towards the inside of the bend move ahead of ions towards the outside (B). With a double bend this distortion is partially corrected, returning the ion packet to a rough sphere (C), however there is a degree of overcorrection (D).

without an initial section of constant diameter. Second, the final electrode does not have an independently switchable potential. The funnel is followed by a 1 mm thick stainless steel plate with a 0.35 mm orifice leading into a differential pumping section. The funnel is mounted on a PMMA base, which in turn is mounted onto the inside of a stainless steel vacuum chamber adaptor that connects the PMMA drift chamber to the stainless steel vacuum chamber containing the remainder of the instrument. One side of the adaptor seals onto the outer face of the drift chamber with an o-ring set in a groove cut into chamber wall. The other side attaches to the rest of the instrument via a 2.75 inch CF flange (see Figure 3.11).

3.5 Mass filter

Following the IMS drift section, the ions enter an octopole ion guide, which confines the ions radially, but allows neutral gas to be pumped away by a 330 L/s
Figure 3.11 The second ion funnel (A), mounted in a stainless steel adaptor (B), which seals onto the wall of the drift region chamber (C) with an o-ring (not shown), and connected to the remainder of the instrument via a 2.75 inch CF flange (D). The differential pumping stage that follows contains an octopole ion guide (E).

turbomolecular pump (Pfeiffer Vacuum TPU330) backed by a 12 m$^3$/hour rotary pump (Edwards RV12). From there the ions pass through another orifice (5 mm diameter) into the final chamber, which is pumped by a 230 L/s turbomolecular pump (Pfeiffer Vacuum TPH240) backed by a 3 m$^3$/hour rotary pump (Edwards RV3), and contains a lens stack that focuses the ions into the quadrupole mass filter (Extrel C50). The mass filter consists of 3/4 inch (19 mm) rods driven by a 300 W, 1.2 MHz power supply, allowing for mass selection up to 500 Da. It would be feasible to increase the mass range by switching to narrower rods (up to 2000 Da with 3/8 inch (9.5 mm) diameter rods) at the cost of reduced mass resolution and transmission.
3.6 Ion detection and recording

Following the mass filter is an electron multiplier (Photonis Channeltron 4870E) which is used to detect the ions in a single ion counting mode. The arrival of each ion triggers a cascade of electrons that is further amplified and detected by a pulse amplifier/discriminator [MIT Inc. (now Advanced Research Instruments Corp.) F-100T]. The pulse discriminator sends a TTL pulse to a multichannel scaler (FAST ComTec P7882), that logs each pulse in one of two histograms (one for laser-on arrivals, and another for laser-off arrivals), to progressively collect laser-on and laser-off arrival time distributions. Successive ATDs are collected at each wavelength and the difference is calculated to determine any change resulting from exposure to laser light.

3.7 Light sources

Two light sources have been used for the experiments described in this thesis. Initially, a CW source (Time Bandwidth Tiger-PS Ti:sapphire, with the saturable absorber replaced with an IR mirror - wavelength range of 745 nm to 850 nm) was directed axially along the length of the central portion of the drift region. A mechanical shutter was used to periodically block the laser beam at a rate of 0.2 Hz (collecting 50 laser-off and 50 laser-on ATDs each cycle). This laser was initially used to demonstrate the efficacy of the instrument, but the limited wavelength range precluded extensive use of this light source. Consequently, most experiments were performed using a tunable optical parametric oscillator (OPO, Coherent Scientific Opotek Vibrant), which delivers short (~5 ns) pulses of light in the range of 210-2400 nm, at a repetition rate of 10 Hz. This laser was aligned perpendicularly to the drift path of the ions, shortly (~30 mm) after the gate, as shown in Figure 3.8E. It could also cross the ion path roughly halfway along the drift region in order to trigger photoisomerisation further into the drift region. It could also be aligned coaxially, but doing so results in a much longer span between
the inlet and outlet windows and requires a relatively well collimated beam; passing the light through perpendicularly makes it straightforward to adjust the beam size to control the power density (an aspect that is not necessary for CW beams, due to their relatively low instantaneous power). The timing of the laser is controlled using a second output on the delay generator that controls the ion gate timing. This second output is passed through a D type flip-flop configured as a frequency divider, resulting in trigger pulse being sent to the laser at half the frequency of the ion gate, so that the laser only fires for every second bunch of ions. When operated in a transverse fashion, the timing of the laser is critical to ensure that the beam overlaps the ion bunch. The timing depends on where the laser crosses the path of the ions, and varies linearly with the ion arrival time. As such, once the timing for one ion has been determined, the timing for other isomers can easily be predicted. It is worth noting that the total delay between the gate and the laser pulse is the sum of the delay on the trigger pulse and the laser’s internal delay between the flash lamp and the Q-switch ($\text{delay}_{\text{FL-QS}} - 185 \mu s$ at full power, longer for lower laser powers). We found that, for a beam crossing immediately after the gate, the following formula was a reliable predictor for the required delay, as $760 \mu s$ was the total required delay for an ion bunch with an arrival time of $22 \text{ ms}$.

\[
\text{delay}_{\text{trigger}} (\mu s) = \frac{760 \times t_a (\text{ms})}{22 (\text{ms})} - \text{delay}_{\text{FL-QS}} (\mu s) \tag{3.1}
\]

### 3.8 Software

The instrument is controlled by a LabView (National Instruments) Virtual Instrument (VI), that controls the mass filter and the laser, and reads the ATD data from the multichannel scaler. The data are saved in ASCII format. For each wavelength (or mass) the VI writes one line that describes the current operational parameters, followed by two columns for the binned arrival counts for laser-on and laser-off respectively. The data is then processed using Matlab (Mathworks). Matlab scripts take the data from the recorded files and plots surfaces (or colour maps)
of the data with respect to arrival time and either mass or wavelength. Laser-off, laser-on and difference data can all be plotted. Further processing was performed by integrating over selected arrival time ranges (to give either the mass distribution of the ions arriving at that time, or the wavelength dependence of those arrivals), or by integrating over selected wavelength or mass ranges (to give the arrival time distribution (or change in ATD) for that mass or wavelength range). Integrated arrival time distributions were fitted with Gaussian functions to extract arrival times, which were then used to calculate ion mobilities. Integrated mass distributions of selected arrival time ranges were used to check whether ions with different arrival times had the same mass or not. Integrated wavelength data gave the wavelength dependence of selected changes in arrival time.

3.9 Instrument performance

The performance of the instrument was tested under a range of conditions, using tetrabutylammonium (TBA) and tetrapropylammonium (TPA). An example arrival time distribution for TBA drifting in nitrogen is shown in Figure 3.12.

![Figure 3.12](image)

**Figure 3.12** ATD of tetrabutylammonium. Inset is a close up of the arrival peak, with the FWHM width labelled. This width corresponds to a resolving power of \( \sim 82 \).
3.9.1 Resolution

An important measure of the performance of an IMMS apparatus is the resolving power. Higher resolving powers allow bunches of ions with similar mobilities to be separated. In our case this is particularly important, as we need to discern relatively small changes in mobility that follow photoisomerisation.

The resolution of our ion mobility spectrometer under a range of operating conditions is illustrated in Figure 3.13. Data were collected with the drift region filled with 8, 11.5 and 12.5 Torr of both nitrogen and helium, and the resolution determined for various injection gate widths and drift voltages. The maximum drift voltage with helium buffer gas is limited by electrical breakdown (to \( \sim 2.5 \text{kV} \) at 12 Torr), whereas with a nitrogen buffer gas the drift voltage is limited to the maximum voltage of the power supply (5 kV). The best resolution with helium buffer gas was 65, with a drift voltage of 2.5 kV. In nitrogen a resolution of 95 was achieved at the maximum drift potential. The resolution for small gate opening times (50 \( \mu \text{s} \)) consistently corresponded to roughly 80% of the diffusion limited expected resolution (described by Equation 2.27). Increasing the gate opening time reduces the resolution, with the degradation being most significant at higher fields (i.e. for shorter drift times).

In terms of resolution, the instrument compares favourably with commercially available instruments but it has a lower performance than the best custom built devices. There are currently 2 broad categories of drift tube ion mobility spectrometer. First, there are small, bench-top (or hand-held), ion mobility spectrometers, used primarily for security purposes such as detection of hazardous substances, such as explosives or drugs. Second, there are larger laboratory devices that include a mass selection stage. The majority of commercially available devices fall into the first category, and have resolving powers in the range of 20-60 [162]. Until recently, the only commercially available laboratory instruments were the first and second generation Waters Synapt Travelling Wave Ion Mobility (TWIM) spectrom-
Figure 3.13 (a) Effect of field strength on resolving power at various pressures (red: 8 Torr, blue: 11.5 Torr, green: 12.5 Torr) of $N_2$ (triangles) and He (circles) bath gases. The diffusion limited resolving powers predicted by Equation 2.28 are denoted by black squares. Vertical columns of data show degradation of resolution with increasing gate opening time (from 50 $\mu$s to 500 $\mu$s). (b) Resolution as percentage of the diffusion limited resolving power.
eters [163]. These instruments perform mass selection, trapping and fragmentation prior to the ion mobility stage, and TOF mass spectrometry post mobility separation. As such, they are powerful tools for the identification of compounds, able to determine the mass and collision cross-section of the parent ion and any fragment ions. But the nature of TWIM spectrometers limits their resolving power; the first generation Waters Synapt had a resolving power of 10, whereas the second generation instrument has a resolving power of 40 for 2+ ions [164]. Because resolving power increases with the square root of the ion’s charge, this corresponds to an equivalent resolving power of \( \sim 28 \) for singly charged ions. In 2013 the Agilent 6560 IM-QTOF system became available. This instrument is a DT-IMS instrument with a constant field through the drift region, allowing the device to achieve a resolving power exceeding 60 for singly charged ions. The drift region is followed by a quadrupole mass filter, a collision induced dissociation cell and a time of flight mass spectrometer [165].

The other instruments in this category are custom instruments, built in-house by particular research laboratories [119, 155]. Some of these instruments achieve resolving powers significantly higher than the commercial instruments, primarily by running at higher drift potentials. For example, an instrument built by Bowers and coworkers achieved a resolution of 110 with a drift voltage of \( \sim 5 \) kV [166]. An instrument built by Jarrold and coworkers demonstrated a resolution of 172, using a drift voltage of 10 kV [119]. Clemmer and coworkers have developed an instrument that has achieved a resolution exceeding 300 (for a 3+ ion) by looping the ion path back on itself and switching the voltage gradient to give a very long effective ion path (\( >20 \) m) and a total drift voltage of \( >14 \) kV [155].

### 3.9.2 Mobility measurements

Another measure of an IMMS instrument’s performance is linearity and predictability of arrival times. Figure 3.14 shows the arrival times of (TBA) in He buffer gas and (TPA) in \( \text{N}_2 \) buffer gas for a range of buffer gas pressures and elec-
tric fields. In both cases the arrival time varies linearly with respect to both the inverse electric field strength and number density of the buffer gas. The lack of any deviation from linear behaviour indicates that the instrument is operating in the ‘low field’ regime for ion mobility.

![Graph showing peak arrival time vs. (E/N)^-1 (Td^-1)](image)

**Figure 3.14** Ion bunch arrival times for TBA in He (Circles) and TPA in N\textsubscript{2} (Triangles), for a range of pressures and voltages.

The reduced mobilities and collisional cross-sections for TBA and TPA measured with our instrument are summarised in table 3.1. There is no entry in table 3.1 for the mobility of TPA drifting through helium because the data on TPA were collected after the change to using nitrogen as the drift gas in the instrument. Kotiaho and coworkers showed that the reduced mobilities of tetraalkylammoniums do not vary with temperature between 295 K and 360 K [167], so according to equation 2.5 it is the collision cross-section that must vary with \( T^{-1/2} \). Consequently, for the sake of comparison, the tabulated values for the collision cross-section have been normalised to 273K. The reduced mobilities measured on the new instrument lie close to the values reported in the literature. Particularly good agreement is found between our measured reduced mobilities in N\textsubscript{2} and those re-
ported by Hill and coworkers [168], but while our measured cross-section for TBA in helium agrees with the cross-section reported by Kim and coworkers [149], while the collision cross-sections measured on the new instrument for TBA and TPA drifting in nitrogen differ by 1% and 3%, respectively.

### Table 3.1

<table>
<thead>
<tr>
<th>Ion / buffer gas</th>
<th>$K_0$ (cm²V⁻¹s⁻¹)</th>
<th>$Ω_0$ (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TBA / He</td>
<td>4.82</td>
<td>116.7</td>
</tr>
<tr>
<td></td>
<td>(exp)</td>
<td>(lit)</td>
</tr>
<tr>
<td>TBA / N₂</td>
<td>1.22 1.18–1.40 [102, 107, 167–169]</td>
<td>176.0 174.3-174.6 [149, 165]</td>
</tr>
<tr>
<td></td>
<td>(exp)</td>
<td>(lit)</td>
</tr>
<tr>
<td>TPA / N₂</td>
<td>1.41 1.43 [168]</td>
<td>155.4 150.9-151.0 [149, 165]</td>
</tr>
<tr>
<td></td>
<td>(exp)</td>
<td>(lit)</td>
</tr>
</tbody>
</table>

*Mobilities ($K_0$) and collisional cross-sections ($Ω_0$) for TBA and TPA compared with literature values. All values have been reduced to STP.*
Chapter 4

Photoisomerisation of HITC\(^+\) and \((\text{HITC})_{2}^{2+}\)

![Diagram](image.png)

Figure 4.1 (a) The all-trans form of HITC\(^+\) (b) one of the cis forms of HITC\(^+\) (c) the dicationic dimer \((\text{HITC})_{2}^{2+}\) with a 10-10' interchain bond.

This chapter focuses on the photoisomerisation of the polymethine dye HITC\(^+\) (1,1',3,3',3'-hexamethylindotricarbocyanine), a symmetric tricarbocyanine dye consisting of two methyl substituted indole groups linked by a conjugated chain of 7 methine carbon atoms.

The photo-physical properties of HITC\(^+\) have been extensively studied in solution by various methods including transient absorption and Raman spectroscopy [135, 170, 171]. It has been established that the lowest energy isomer has a chain with all bonds in the \(\text{trans}\) configuration and that upon \(S_1\leftarrow S_0\) electronic excitation, \(\text{trans}\rightarrow\text{cis}\) isomerisation occurs to form photoisomers that are higher in energy, but separated from the all-\(\text{trans}\) isomer by energetic barriers [136–138]. The predominant photo-isomer has an absorption spectrum that is red-shifted relative to the all-\(\text{trans}\) isomer [172], and has a lifetime in solution of \(\sim 300\ \mu\text{s}\).
This chapter also examines the photoisomerisation behaviour of the (HITC)$_2^{2+}$ dimer (Figure 4.1c). When carbocyanine dyes lose an electron, whether by chemical oxidation or by electron injection from the $S_1$ excited state into some substrate (such as the silver halides in photographic media), they form radical dications, with the radical site delocalised across every second carbon. Radical recombination leads to bond formation between carbon atoms on two separate radicals to form a tetracationic dimer. Loss of H$^+$ from each of the newly bonded carbon atoms results in the final, stable dicationic dimer [173]. Figure 4.2 shows the dimerisation mechanism of HITC$^+$.  

For many dicarbocyanines, the bond occurs between the 8th carbon (2 carbons removed from the nitrogen) of one monomer, and the 10th carbon (4 removed from the nitrogen) forming an 8-10′ linked dimer. But for hexamethylindoledicarbocyanine (HIDC$^+$) it forms between the 10th carbon on both monomers, due to steric hinderance from the gem-dimethyl groups [174]. 2D-NMR studies of (HITC)$_2^{2+}$,
4.1. PHOTOISOMERISATION WITH CONTINUOUS ILLUMINATION

produced by oxidation of HITC$^+$ with ferric chloride, indicate that the same occurs for the tricarbocyanine studied in the work. The (HITC)$_2^{2+}$ dimer has not been examined previously, however studies on other cyanine dye dimers suggest that the absorption spectrum of the dimer is likely to be broader and slightly blue shifted relative to the monomer [174].

4.1 Photoisomerisation with continuous illumination

The first results demonstrating evidence for photoisomerisation in the drift tube are shown in Figure 4.3a. The ATD shows that the drifting ion population contains three distinct species (peaks A, C and D). Preliminary mass scans demonstrated that the earlier peaks (A & C in Figure 4.3a) have a lower $m/z$ ratio than the slower peak D, indicating that they may be the (HITC)$_2^{2+}$ dimer. This was confirmed using a higher resolution mass scan (spectrum shown in Figure 4.3b), which displayed ions with $m/z = 408.3$ Da (1 Da lighter than the mass of HITC$^+$) and an isotope distribution with a spacing of 0.5 Da, suggesting a 2+ charged dimer with an overall loss of 2 Da, consistent with dimerisation. Assignment of the peaks is further supported by the following evidence: (1) The peak (peak D) dominates when freshly prepared solution is electrosprayed, whereas, as the solution ages, or is exposed to an oxidising agent such as ferric chloride, the earlier peaks (A & C) grow in relative intensity. (2) When the ions are launched with initial bunch widths sufficiently short to have no impact on resolution, the resolution of the earlier peaks (A & C) is greater than the resolution of the later peak (D) by a factor of about $\sqrt{2}$, indicating that ions associated with the earlier peaks have twice the charge of those associated with peak D, in accordance with Equation 2.29. (3) The ratio of the measured mobility of peaks C and D (1.143) roughly match that predicted by DFT and MOBCAL calculations (1.166).

Irradiation of the ions by a coaxially aligned Ti-Saph laser light results in a depletion in the ion count of peak C and a corresponding increase in the ion count in the
Figure 4.3 (a) ATD with no laser, ATD with ions exposed to 747 nm CW laser light and the difference between the two. (b) Mass spectrum of the electrosprayed ions from an HITC⁺ solution.
valley B. The appearance of ions in valley B suggests that isomers associated with peak C are transformed to the isomer associated with peak A, since the apparent mobility is the weighted average of the mobilities of the conformers before and after isomerisation, and in this instance the laser overlaps the central section of the drift region.

Counting the fraction of ions that change mobility as a function of laser wavelength ($N_B$) produced the action spectrum shown in Figure 4.4. It is clear that the wavelength range of the Ti-Saph laser only overlaps the red edge of the HITC dimer absorption. Although the spectrum is incomplete, it demonstrates that coaxial excitation with a continuous wave light source would be an effective approach for monitoring the photoisomerisation of molecular ions in the gas phase.

4.2 Photoisomerisation with a pulsed light source

All the data presented henceforth were collected with illumination provided by a pulsed OPO, with the light beam crossing perpendicular to the ion path shortly after the ion gate (as per the transverse laser beam indicated in Figure 3.2). Figure 4.5a shows the ion count of a HITC$^+$/HITC$^2_2$ mixture as functions of mass and arrival time, whereas Figure 4.5b shows the change in the ion count distribution resulting from exposure to laser light with wavelength 650 nm. It is apparent that both species are affected by light at this wavelength and, importantly, that the change in mobility is not accompanied by a change in mass, indicating that this
Figure 4.5 (a) Arrival time distribution as a function of m/z plot for electrosprayed HITC solution. The faster two peaks are associated with the dicaticonic (HITC$^{2+}$) dimer (m/z=408.3 amu), whereas the slower peak is due to the HITC$^+$ monocation (m/z=409.3 amu). (b) Photoinduced signal as function of m/z and ion arrival time with laser tuned to $\lambda$=650 nm. Laser enhanced signal is indicated by yellow/orange, whereas laser depleted signal is indicated by blue. The earlier peaks are associated with photoisomerisation of (HITC)$^{2+}$ whereas the later peaks are associated with photoisomerisation of trans-HITC$^+$ into cis-HITC$^+$. 
4.2. PHOTOISOMERISATION WITH A PULSED LIGHT SOURCE

A: all-trans (0 kJ/mol)
B: 2-cis (8.0 kJ/mol)
C: 9-cis (15.6 kJ/mol)
D: 10-cis (14.8 kJ/mol)
E: 8-cis (31.4 kJ/mol)

**Figure 4.6** Low energy isomers of HITC$^+$ optimised by DFT B3LYP/6-31G(d) calculations, with zero point corrected energies, relative to the all-trans isomer.

is a photoisomerisation process, rather than photofragmentation. To help identify relevant HITC$^+$ photo-isomers, the drift mobilities were estimated for the more stable forms of HITC$^+$, using structures calculated by DFT [B3LYP/6-31G(d)], using the Gaussian 09 package [153]. Reduced mobilities were estimated using the exact hard sphere (EHS) model as implemented in the MOBCAL program (see Section 2.3).

The five lowest energy HITC$^+$ isomers are shown in Figure 4.6. Energies, collision cross-sections and mobilities are summarised in Table 4.1. As expected, the all-trans isomer (isomer A) is predicted to lie lowest in energy (Figure 4.6A). The next 4 most energetically favourable isomers differ from the all-trans isomer by trans $\rightarrow$ cis isomerisation about a single polymethine C-C bond. Isomer B (rotation about the C$_2$-C$_8$ bond, Figure 4.6B) lies 8.0 kJ/mol higher in energy than isomer A. Isomer C (rotation about the C$_9$-C$_{10}$ bond, Figure 4.6C) lies 15.6 kJ/mol above
isomer A, while isomer D (rotation about the C_{10}-C_{11} bond, Figure 4.6D), lies 14.8 kJ/mol above isomer A. Isomer E (rotation about the C_{8}-C_{9} bond, Figure 4.6E) lies significantly higher in energy than isomer A, by 31.5 kJ/mol. Other isomers with 2 or more cis linkages in the polymethine chain are calculated to lie yet higher in energy.

**Table 4.1** Data for low energy conformers of HITC\(^+\) (Figure 4.6), 10-10’-linked-(HITC)\(_2\)\(^2+\) (Figure 4.8) and the HITC\(^++\) radical formed by cleaving the interchain bond in (HITC)\(_2\)\(^2+\). Data include energies (corrected for vibrational zero point energy) relative to that of the lowest energy isomer, collision cross-section (\(\Omega\)) and reduced drift mobility in He (\(K_0\)).

<table>
<thead>
<tr>
<th>Isomer</th>
<th>(\Delta E) (kJ/mol)</th>
<th>(\Omega) ((A^2))</th>
<th>(K_0) (cm(^2)/s/V) (calc)</th>
<th>(K_0) (cm(^2)/s/V) (exp)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HITC(^+)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A (trans)</td>
<td>0</td>
<td>171.8</td>
<td>3.135</td>
<td>3.164</td>
</tr>
<tr>
<td>B (2-cis)</td>
<td>8.0</td>
<td>172.5</td>
<td>3.123</td>
<td></td>
</tr>
<tr>
<td>C (9-cis)</td>
<td>15.6</td>
<td>170.0</td>
<td>3.168</td>
<td></td>
</tr>
<tr>
<td>D (10-cis)</td>
<td>14.8</td>
<td>170.7</td>
<td>3.156</td>
<td></td>
</tr>
<tr>
<td>E (8-cis)</td>
<td>31.4</td>
<td>169.8</td>
<td>3.172</td>
<td></td>
</tr>
<tr>
<td>HITC(^++)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{trans})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(HITC)(_2)(^2+)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A (trans 10-10’)</td>
<td>0</td>
<td>294.0</td>
<td>3.656</td>
<td>3.617</td>
</tr>
<tr>
<td>B (2-cis)</td>
<td>9.1</td>
<td>293.1</td>
<td>3.665</td>
<td></td>
</tr>
<tr>
<td>– (8-cis) (\text{(Unstable)})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C (9-cis)</td>
<td>14.0</td>
<td>295.0</td>
<td>3.641</td>
<td></td>
</tr>
<tr>
<td>D (10-cis)</td>
<td>12.6</td>
<td>295.6</td>
<td>3.632</td>
<td></td>
</tr>
<tr>
<td>E (11-cis)</td>
<td>29.5</td>
<td>283.7</td>
<td>3.789</td>
<td></td>
</tr>
<tr>
<td>F (12-cis)</td>
<td>16.1</td>
<td>293.1</td>
<td>3.665</td>
<td></td>
</tr>
<tr>
<td>G (13-cis)</td>
<td>35.2</td>
<td>287.0</td>
<td>3.738</td>
<td></td>
</tr>
<tr>
<td>H (14-cis)</td>
<td>8.8</td>
<td>290.8</td>
<td>3.694</td>
<td></td>
</tr>
</tbody>
</table>

Figure 4.7a shows the predicted arrival times for the isomers of HITC\(^+\) scaled such that the mobility of the all-trans isomer (isomer A) aligns with the centre of the HITC\(^+\) peak in the laser-off arrival time distribution in Figure 4.7b. Isomers A and B are predicted to have very similar mobilities and arrival times (within 0.3%) and are the slowest forms of HITC\(^+\). Isomers C, D and E are predicted
Figure 4.7 (a) Predicted arrival times for isomers of HITC$^+$ (Figure 4.6) and (HITC)$_2^{2+}$ (Figure 4.8). Calculated arrival times are scaled so that the trans HITC$^+$ peak corresponds to the measured HITC$^+$ peak at 22.9 ms. (b) Arrival time distribution for ions from electrosprayed HITC solution drifting in helium buffer gas. Peaks at 20.0 and 22.9 ms are due to the (HITC)$_2^{2+}$ dimer and HITC$^+$ monomer, respectively. (c) Photoinduced signal with $\lambda=755$ nm laser pulse intercepting HITC$^+$ ions. (d) Photoinduced signal with $\lambda=650$ nm laser pulse intercepting HITC$^+$ ions. (e) Photoinduced signal integrated over $\lambda=660-700$ nm with laser pulse intercepting (HITC)$_2^{2+}$ ions. (f) Laser-on-laser-off signal integrated over $\lambda=620-650$ nm with laser pulse intercepting (HITC)$_2^{2+}$ ions.
to have higher mobilities than isomer A (by 1.0%, 0.7%, and 1.2%, respectively). Figures 4.7c and 4.7d show the change in arrival time distribution for HITC\(^+\) resulting from illumination at two different wavelengths. Figure 4.7c shows that illumination at 650 nm results in a shift to earlier arrival time, whereas Figure 4.7d shows that illumination at 755 nm results in a shift to later arrival times. This suggests the presence of a mix of isomers, with isomerisation occurring from the all-trans isomer to one or more of isomers C, D or E at shorter wavelengths, and isomerisation back to the all-trans isomer occurring at longer wavelengths. This interpretation is compatible with transient absorption studies of HITC\(^+\) in solution which show that the photo-isomer absorbs at longer wavelengths compared to the all-trans isomer [175].

The question arises as to why the ion population contains cis-form(s) of HITC\(^+\) given that trans-HITC\(^+\) is clearly the lowest energy isomer and dominates in the solution. Based on calculated free energies, one expects that at 295 K trans-HITC\(^+\) will be at least 100 times more abundant than the next most stable forms (isomers B, C and D in Figure 4.6). One possibility is that cis-HITC\(^+\) cations are generated in the electrospray process and are transported through the desolvation capillary, the ion funnel, and into the drift tube, a journey requiring several milliseconds. It is also feasible that the ions are subject to RF heating in the first ion funnel. Transient absorption studies show that in DMSO and acetonitrile solutions the HITC\(^+\) photo-isomer is relatively long-lived, taking around 300 \(\mu\)s to back-convert to the trans-isomer [142, 176, 177]. In acetonitrile, the back reaction rate constant is typically described by an Arrhenius type expression with pre-exponential factor \(3 \times 10^{11} \text{s}^{-1}\) and activation energy 42.9 kJ/mol [178]. The presence of cis forms of HITC\(^+\) in the drift tube prior to irradiation implies that the lifetime is considerably longer in the gas phase, possibly because the collision rate is orders of magnitude lower than in solution. In this regard, it is relevant to note that the detection of a photo-induced mobility change for HITC\(^+\) ions in the drift tube proves that different isomers can exist in the gas phase for timescales comparable to the flight time (\(~\)20 ms).
4.3 Assignment of \((\text{HITC})_2^{2+}\) arrival time distribution

A similar approach to the one described above for HITC\(^+\) was taken for interpreting the behaviour of the \((\text{HITC})_2^{2+}\) dimer (Figures 4.1c and 4.8). The conformational landscape of \((\text{HITC})_2^{2+}\) is inherently more complicated than that of the HITC\(^+\) monomer, because the two polymethine chains can be linked at different positions, and because \textit{trans-cis} isomerisation can occur around C-C bonds in either or both chains.

DFT B3LYP/6-31G(d) calculations predict that the minimum energy structure of \((\text{HITC})_2^{2+}\) is such that planar HITC\(^*\) subunits with all-\textit{trans} bonds are linked through a single interchain bond at the 10-10\(^\prime\) C atom positions (Figures 4.1c and 4.8A). The two polymethine chains are disposed at 90\(^\circ\) to one another, an arrangement that minimises the Coulomb repulsion between the positive charges on the two sub-units (Figure 4.8a). Structures in which the interchain linkage occurs through other even C atoms (e.g. 8-10\(^\prime\), 8-8\(^\prime\) links) lie higher in energy, as do structures in which the odd C atoms are linked.

In analogy with the HITC\(^+\) monomer, one might expect that the most likely \((\text{HITC})_2^{2+}\) photo-isomers correspond to twisting about a single C-C bond in one of the two monomer subunits. Results from the DFT and MOBCAL calculations for the isomers with a single \textit{cis} configured bond are summarised in table 4.1 and the corresponding structures shown in Figure 4.8. At first glance there are 8 possible photoisomers with a single \textit{cis} configured bond, due to the interlinking bond breaking the symmetry of the HITC\(^+\) monomer.

Typically, twisting around a C-C bond to move an end group towards the remainder of the molecule produces a more compact, scissored structure with a larger drift mobility than the all-\textit{trans} form. For example, isomers E and G in Figure 4.8, are predicted, respectively, to have mobilities 3.5\% and 2.5\% greater than the all-\textit{trans} isomer. Twisting around the C\(_8\)-C\(_9\) bond results in the end group moving too close to the other monomer, and as a result the structure is unstable and reverts to the
CHAPTER 4. HITC$^+$ AND $(HITC)_2^{2+}$

![Diagrams of different isomers of HITC$_2^{2+}$ with energies and structures](image)

**Figure 4.8** B3LYP/6-31G(d) optimised structures for the all-trans (HITC)$_2^{2+}$ dimer, and for dimers with a single cis bond (hydrogen atoms not shown for clarity). Vibrational zero point corrected energies relative to the all-trans isomer. The dimer with a cis C$_8$-C$_9$ bond was unstable and returned to the all-trans form.

all-trans form. It is also possible that trans-cis isomerisation moves one end group away from the other half of the dimer, as for isomers C and D in Figure 4.8. In this case the structure becomes less compact and the mobility decreases slightly (by 0.4% and 0.6% respectively). The small change in mobility may mean that ATD peaks for these photo-isomers are virtually indistinguishable from that of the all-trans form of (HITC)$_2^{2+}$.
4.4 PHOTOISOMERISATION ACTION SPECTRA

Figure 4.7a shows the predicted arrival times for the (HITC)$_2^{2+}$ isomers, scaled so that the all-trans isomer matches the main (HITC)$_2^{2+}$ peak in figure 4.7b. Figure 4.7e shows the change in arrival time over a range of longer wavelengths (660-700 nm) whereas Figure 4.7f shows the change over a range of shorter wavelengths (620-650 nm). Inspection of Figure 4.7e and Figure 4.7f reveals that there are possibly 3 photo-isomer peaks produced from (HITC)$_2^{2+}$. The dominant photo-isomer (peak i) is formed over the 580-740 nm wavelength range and is associated with ions having $\sim$5% larger mobility than the parent (HITC)$_2^{2+}$ ions. A much weaker, slightly slower photo-isomer (peak ii in Figure 4.7e) is generated mainly at longer wavelengths (660-740 nm). Finally, a very weak peak appears at arrival times slightly later than the region where the ion count has been depleted. The relatively narrow width suggests that this peak overlaps with and is mostly cancelled out by the depletion of the parent isomer (peak iii in Figure 4.7).

It is surmised that peaks i and ii in Figure 4.7 correspond to isomers E and G for which the large mobility change arises because part of one monomer is more effectively shadowed by the other monomer. On the other hand, peak iii corresponds to an isomer, or mix of isomers with an outwards turning end group, such as isomer C or D.

4.4 Photoisomerisation action spectra

The wavelength dependence of the laser induced change in drift speed is illustrated in Figure 4.9, which shows a two dimensional plot of (laser-on)−(laser-off) counts as a function of wavelength and drift time. There is an obvious conversion of a slower HITC$^+$ isomer to a faster isomer over the 560-710 nm range, whereas between 730 and 770 nm faster HITC$^+$ ions are converted to a slower form. The two dimensional wavelength response data (Figure 4.9) can be analysed to extract a one dimensional photoisomerisation action spectrum (PISA spectrum). When irradiation results in an appreciable mobility change (such that parent and daugh-
CHAPTER 4. HITC+ AND (HITC)$_2^{2+}$

Figure 4.9 Difference in laser-on and laser-off signals as a function of wavelength and ion arrival time. Laser enhancement is indicated by yellow/orange, whereas laser depletion is indicated by blue. Earlier peaks are associated with photoisomerisation of (HITC)$_2^{2+}$ whereas later peaks are connected with photoisomerisation of HITC$^+$. Later ion arrival peaks are fully resolved, determining the action spectrum simply involves integrating the total count of the daughter arrival peak. This approach is less practicable when the arrival peaks of the parent and daughter isomers are not fully resolved as is the case for HITC$^+$ (Figure 4.7). Therefore, to extract the one dimensional action spectrum, the difference between the laser-on and laser-off ATDs at each wavelength is fitted with a double Gaussian function,

$$f(t) = A \times [e^{-\frac{(t-t_a-\Delta t/2)^2}{2\sigma^2}} - e^{-\frac{(t-t_a+\Delta t/2)^2}{2\sigma^2}}]$$

where the two Gaussians have equal and opposite amplitudes ($\pm A$), and are separated by time ($\Delta t$). The mean arrival time ($t_a$), separation ($\Delta t$) and width ($\sigma$) are determined from the mean (laser-on)–(laser-off) difference ATD and are fixed across all wavelengths. The PISA spectrum then corresponds to the fitted amplitude $A$ plotted against wavelength. For HITC$^+$, acceptable fits to the experimental (laser-on)–(laser-off) ATDs were obtained with $\sigma=160-170\mu$s and $\Delta t=40-100\mu$s. Importantly, the form of the PISA spectrum was relatively insensitive to variation.
of $\sigma$ and $\Delta t$ over these ranges. Here, it is worth remarking that the peak separation for the two HITC$^+$ isomers (40-100 $\mu$s) is much less than the ATD peak widths (FWHM=400 $\mu$s) and that without laser excitation it would be impossible to separate the two forms using our instrument.

Figure 4.10 (a) Absorption spectrum of $10^{-6}$ M HITC perchlorate in methanol. The absorption spectrum of the HITC$^+$ photo-isomer in DMSO solution, reproduced from Reference [175], is shown as a dotted line. (b) PISA spectrum for HITC$^+$ drifting in He buffer gas. (c) Absorption spectrum of (HITC)$_2^{2+}$ dication in methanol. (d) PISA spectrum for (HITC)$_2^{2+}$ dication. Black points indicate data collected with CW Ti-Saph laser.

The resulting PISA spectrum for HITC$^+$ is plotted in Figure 4.10b along with the absorption spectrum of HITC dissolved in methanol (Figure 4.10a) which corresponds to the accepted absorption curve of trans-HITC$^+$ [175]. The positive signal for HITC$^+$ (Figure 4.10b), peaking at $\sim$695 nm, is connected primarily to $\text{trans} \rightarrow \text{cis}$ photoisomerisation, whereas the weaker negative signal, extending from 730 to 770 nm, is associated mainly with $\text{cis} \rightarrow \text{trans}$ photoisomerisation. These
assignments are consistent with previous condensed phase transient absorption measurements which show that the HITC$^+$ photo-isomer absorbs mainly over the 790-850 nm range with a peak at 805 nm (Figure 4.10a) [175].

The PISA spectrum of (HITC)$_2^{2+}$ (Figure 4.10d), obtained by plotting the intensity of the main photoproduct peak as a function of wavelength has a maximum at 700 nm, and is very similar to the solution-phase spectrum of (HITC)$_2^{2+}$ but is shifted by 15 nm to the blue (Figure 4.10c). The electronic absorption spectra of (HITC)$_2^{2+}$ in methanol is very similar to the one of the HITC$^+$ monomer (Figure 4.10a and c), with the dimer peak shifted slightly to shorter wavelength by 5 nm. This confirms that the single bond between the two HITC$^+$ subunits has little effect on the energy for electronic excitation. Such similarities have also been noted for the monomer and dimer spectra of other polymethine dyes [174].

Finally, it should be noted that even at higher laser intensities, there is no evidence for photo-induced cleavage of the single interchain bond to give two singly charged HITC$^+$ radical fragments, which would have the same $m/z$ value as the parent ions. The cleavage is calculated to require 361 kJ/mol and would entail absorption of two 660 nm photons. Calculations using the DFT B3LYP/6-31G(d) structure and NBO charge distributions predict that the HITC$^+$ radical has a $\sim$7% lower mobility than the (HITC)$_2^{2+}$ parent ion and should arrive later, roughly halfway between the HITC$^+$ monomer and the (HITC)$_2^{2+}$ dimer parent.

Extracting separate spectra for the trans and cis forms of HITC$^+$ from the PISA spectrum shown in Figure 4.10b is not possible at this stage. The main difficulties are that the spectra of the isomeric forms overlap, there is no way to estimate their relative initial populations or the absorption cross-sections, and the ATD peaks are overlapped. Nonetheless, comparison of the PISA spectrum and the solution phase spectra of the trans and cis forms (Figures 4.10a and b) suggests that the gas-phase bands are blue-shifted by 40-50 nm from the solution-phase bands. Using PISA spectroscopy to determine the absorption spectra of individual isomeric forms would be more straightforward if the ATD peaks for the different
isomeric forms were completely resolved.

4.5 Conclusion

The material presented in this chapter unambiguously demonstrates that photoisomerisation of HITC$^+$ and (HITC)$_2^{2+}$cations occurs in the gas phase and that photoisomerisation is not necessarily mediated through rapid solvent-induced vibrational relaxation, although collisions with He buffer gas, which, under the prevailing conditions occur at a rate $k_c \approx 10^9 \text{s}^{-1}$, presumably play a role in stabilising the final isomeric form(s).

The target HITC$^+$ and (HITC)$_2^{2+}$ ions represent a relatively complicated photochemical systems due to the possibility for isomerisation about one or more of the bonds in the polymethine chain. And as will be shown in the following chapters, shorter chain carbocyanine dyes possessing just a few energetically accessible isomers, which absorb in the visible region and which also undergo photoisomerisation, represent simpler targets for gas-phase photoisomerisation studies.
Chapter 5

Photoisomerisation of DTC$^+$

Figure 5.1 The all-trans 3,3’-diethylthiacarbocyanine cation (DTC$^+$) described in this chapter.

This chapter focuses on photoisomerisation of the 3,3’-diethylthiacarbocyanine cation (DTC$^+$), a symmetric carbocyanine dye, consisting of 2 benzothiazole units linked by a conjugated chain of 3 methine carbon atoms. NMR studies show that the trans-DTC$^+$ isomer (Figure 5.1 and 5.2A) predominates in solution [179, 180]. Following $S_1 \leftarrow S_0$ electronic excitation over the 460-580 nm range, trans-DTC$^+$ isomerises about one or more of the chain’s C-C bonds to form one or more of the isomers shown in Figure 5.2. On the basis of calculated absorption cross-sections and transition energies [181], and NMR spectra of cooled, irradiated samples [180], it has been proposed that the 2-cis isomer (shown in Figure 5.2B) is the main photoproduct, although this assignment might be questioned given the much stronger evidence for the formation of the 8-cis photo-isomer of DOC$^+$ (DTC$^+$ with S atoms replaced by O atoms) [180]. Once formed, the photo-isomer back-isomerises over a barrier on the $S_0$ surface to form the trans isomer, with a temperature dependent rate described by an Arrhenius expression with activation energy and pre-exponential factor that depend on solvent viscosity, and which in the case of DTC$^+$ range from 58 to 71 kJ/mol and $10^{12.3}$ to $10^{14.3}$, respectively [139].

This chapter explores the photodynamics of DTC$^+$ in the gas phase using a combi-
Figure 5.2 The 10 possible cis/trans isomers of DTC$^+$. For clarity, hydrogen atoms are not shown.
nation of ion mobility spectrometry and laser photoisomerisation, delivering information on the photo-isomer branching ratios, and a gas-phase photoisomerisation action spectrum. The experimental results are interpreted with the aid of quantum chemical calculations of energies and structures, from which collision cross-sections and mobilities are predicted.

5.1 Results

To identify the relevant DTC\textsuperscript{+} isomers, the structures and energies were calculated for each isomer using DFT [B3LYP/6-31G(d)]. The optimised structures are shown in Figure 5.2, along with their energies relative to the all-\textit{trans} isomer. The optimised structure for each isomer was used to estimate its mobility, using the exact hard sphere (EHS) scattering model as implemented in the MOBCAL program\cite{78–80}. Structures and energies were also determined for the transition states that separate the isomers. Measured and calculated data for isomers of DTC\textsuperscript{+} are summarised in Table 5.1. The calculations predict that 8-\textit{cis}-DTC\textsuperscript{+} lies 13.7 kJ/mol higher in energy than \textit{trans}-DTC\textsuperscript{+}, with the two forms separated by a 103.4 kJ/mol barrier. These relative energies and barrier heights are consistent with previous DFT calculations\cite{182}. On the other hand, the 2-\textit{cis} isomer lies slightly higher in energy (18.3 kJ/mol) but is separated from \textit{trans}-DTC\textsuperscript{+} by a substantially lower isomerisation barrier (61.9 kJ/mol). The other isomers lie yet higher in energy. It is important to note that the calculated energy and collision cross section are both relatively insensitive to which side of the molecular plane the ethyl chains lie.

The measured ATD for DTC\textsuperscript{+} cations without laser irradiation is shown in figure 5.3b. The ATD is fit extremely well by the sum of two Gaussian curves, evidence that the ion population is mainly composed of two isomers. Comparison of the calculated and measured arrival times (5.3a and b) suggests that the more intense peak (at $t_d=20.44$ ms) is associated with \textit{trans}-DTC\textsuperscript{+}, whereas the faster peak is
CHAPTER 5. PHOTOISOMERISATION OF DTC$^+$

Table 5.1 Data for conformers of DTC$^+$ (5.2). Included are zero-point corrected energies and free energies relative to that of the lowest energy isomer, collision cross-sections ($\Omega$) and reduced mobilities ($K_0$) in helium.

<table>
<thead>
<tr>
<th></th>
<th>$\Delta E$</th>
<th>$\Delta G$</th>
<th>$\Omega$</th>
<th>$K_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kJ/mol</td>
<td>kJ/mol</td>
<td>A$^2$ (calc)</td>
<td>cm$^2$/s/V (calc)</td>
</tr>
<tr>
<td>trans (A)</td>
<td>0</td>
<td>0</td>
<td>145.3</td>
<td>3.706</td>
</tr>
<tr>
<td>2-cis (B)</td>
<td>18.3</td>
<td>19.5</td>
<td>143.5</td>
<td>3.752</td>
</tr>
<tr>
<td>8-cis (C)</td>
<td>13.7</td>
<td>13.9</td>
<td>141.7</td>
<td>3.800</td>
</tr>
<tr>
<td>2,8-cis (D)</td>
<td>42.8</td>
<td>43.7</td>
<td>143.5</td>
<td>3.752</td>
</tr>
<tr>
<td>2,9-cis (E)</td>
<td>30.2</td>
<td>32.8</td>
<td>143.2</td>
<td>3.760</td>
</tr>
<tr>
<td>2,10-cis (F)</td>
<td>42.0</td>
<td>44.7</td>
<td>140.8</td>
<td>3.824</td>
</tr>
<tr>
<td>8,9-cis (G)</td>
<td>49.2</td>
<td>51.6</td>
<td>138.0</td>
<td>3.902</td>
</tr>
<tr>
<td>2,8,10-cis (H)</td>
<td>57.8</td>
<td>60.8</td>
<td>144.0</td>
<td>3.739</td>
</tr>
<tr>
<td>2,8,9-cis (J)</td>
<td>63.8</td>
<td>68.1</td>
<td>136.6</td>
<td>3.942</td>
</tr>
<tr>
<td>all-cis (K)</td>
<td>89.1</td>
<td>94.1</td>
<td>134.2</td>
<td>4.012</td>
</tr>
</tbody>
</table>

associated with the 8-cis form (isomer C). This is consistent with the 8-cis-DTC$^+$ being the next lowest energy structure after the all-trans isomer.

It is somewhat surprising that the peak associated with the 8-cis isomer has relative intensity of 0.22 compared to the trans-DTC$^+$ peak given that the 8-cis isomer lies 13.9 kJ/mol higher in energy than the trans isomer. At equilibrium, the population ratio would correspond to a temperature of 1110 K, far higher than the effective collision temperature in the drift region ($\sim$296 K (according to Equation 2.7)]. The most likely explanation is that 8-cis-DTC$^+$ is produced in the electrospray ion source or first ion funnel where the electric field is stronger and collision energy higher, and that the back isomerisation, which entails surmounting a substantial barrier (89.7 kJ/mol), occurs very slowly in the drift tube. The fact that a sharp, undistorted 8-cis-DTC$^+$ peak is apparent in the ATD proves that the back conversion rate is $< 2 \times 10^1$ s$^{-1}$. On the other hand, the 2-cis-DTC$^+$ isomer, which is formed through photoisomerisation in solution [181] but which does not seem to manifest in the ATD of DTC$^+$, is separated from the trans isomer by a much lower barrier (43.6 kJ/mol) and may relax more efficiently to trans-DTC$^+$ than 8-cis-DTC$^+$ as the ions cool in the desolvation capillary, first ion funnel, and drift region.
5.1. RESULTS

Figure 5.3  (a) Predicted arrival times and relative Gibbs free energies for isomers of DTC\(^+\) (see figure 5.2 and table 5.1). Calculated arrival times are scaled so that the trans-DTC\(^+\) arrival time (A) corresponds to the measured DTC\(^+\) peak at 20.44 ms. (b) Experimental arrival time distribution for electrosprayed DTC\(^+\) ions drifting in helium buffer gas. (c) Difference between laser-on and laser-off ATDs with λ=535 nm laser pulses intercepting alternate DTC\(^+\) ion packets. The fitted form of Equation 5.1 is shown in red. It is apparent that the depletion of the peak at \(t_a=20.44\) ms is greater than the increase in signal at \(t_a=19.93\) ms, indicating that some fragmentation occurs.

Thermal isomerisation rates calculated using the Arrhenius equation, assuming \(10^9\) collisions per second (roughly the rate of collisions between the DTC\(^+\) ion and helium atoms in the drift region), an effective temperature of 296 K, and barrier heights of 43.6 kJ/mol and 89.7 kJ/mol gives rate constants of 20 and \(1.5 \times 10^{-7}\) for the back isomerisation of 2-cis-DTC\(^+\) and 8-cis-DTC\(^+\), respectively. This corresponds to half-lives of \(~34\) ms and \(~2\) months for the two isomers, respectively. This suggests that a significant fraction of any 2-cis isomer present would isomerise back to the all-trans isomer during the drift flight, whereas the 8-cis isomer would likely survive the entire journey through the drift region.
Figure 5.4 Schematic potential energy curves for photoisomerisation of DTC\(^+\). The curves on the left side correspond to torsion around the C2-C8 bond (\(\theta'\)) and the right curves to torsion around the C8-C9 bond (\(\theta\)). Energies (in kJ/mol) for stationary points on the \(S_0\) curve are from B3LYP/6-31G(d) DFT calculations, whereas the \(S_1\) PES is adapted from References 137 and 141.

5.2 Photoisomerisation of DTC\(^+\)

The effect of irradiating the DTC\(^+\) cations with light at a wavelength of at 535 nm is apparent in the ATD shown in Figure 5.3c. Depletion of the trans-DTC\(^+\) peak by \(\sim 5\%\) is matched by a corresponding enhancement of the 8-cis-DTC\(^+\) peak. The (laser-on)–(laser-off) difference ATD (5.3c) is fitted with the function,

\[
f_\lambda(t) = A(\lambda) \times \left[ e^{-\frac{(t-t_{a,C})^2}{2\sigma_w^2}} - e^{-\frac{(t-t_{a,A})^2}{2\sigma_w^2}} \right] \tag{5.1}\]

assuming that the only photophysical process is photoisomerisation from trans-DTC\(^+\) to 8-cis-DTC\(^+\). Here, \(t_{a,C}\) and \(t_{a,A}\) are the mean arrival times of the 8-cis and trans isomers, \(\sigma_w\) describes the peak width, and \(A(\lambda)\) is the wavelength-dependent amplitude of the photoresponse. Although the fit to the experimental data indicates that a minor fraction of the DTC\(^+\) cations (\(< 20\%\)) was photodissociated (see 5.3), there is no indication of the presence of more than a single
5.2. PHOTOISOMERISATION OF DTC⁺

photo-isomer.

Figure 5.5 Difference in laser-on and laser-off ATDs as a function of wavelength and ion arrival time. The blue region corresponds to laser induced depletion of trans-DTC⁺, and the orange region to enhancement of the faster cis-DTC⁺. The mass spectrometer is set to m/z=366 amu.

Figure 5.6 PISA spectrum for DTC⁺ drifting in He buffer gas (upper curve). Absorption spectrum of trans-DTC⁺ and photo isomer DTC⁺ in methanol solution (lower curves - taken from References 170 and 183).

The wavelength dependence of the difference ATD is plotted in Figure 5.5 where it is apparent that the photoresponse extends from 440 to 560 nm. Figure 5.6
shows the photoisomerisation action spectrum (PISA spectrum) obtained by fitting the difference ATD at each wavelength to Eqn. 5.1 and plotting the amplitude \( A(\lambda) \) against wavelength. Overall, the gas-phase PISA spectrum of DTC\(^+\) resembles the spectrum of \( \text{trans-DTC}^+ \) in solution but is blue-shifted by 25 nm (\( \sim 800 \text{ cm}^{-1} \)), with the respective spectral maxima occurring at 535 and 560 nm (see Section 5.6).

Significantly, there is a net conversion of \( \text{trans-DTC}^+ \) ions to faster \( \text{8-cis-DTC}^+ \) ions over the entire wavelength range, with no sign of the reverse \( \text{cis} \rightarrow \text{trans} \) process. In solution, the \( S_1 \rightarrow S_0 \) absorption curves of \( \text{trans-DTC}^+ \) and the photo-isomer are overlapped (Figure 5.6, lower), with the photo-isomer maximum being slightly blue-shifted compared to the \( \text{trans-DTC}^+ \) maximum (550 and 560 nm, respectively) [170, 183, 184]. Because the electrosprayed ion population is dominated by \( \text{trans-DTC}^+ \), with a much smaller fraction of \( \text{cis-DTC}^+ \), and because the absorption spectra of the two forms are overlapped, the PISA spectrum reflects a net \( \text{trans} \rightarrow \text{cis} \) photoisomerisation.

The behaviour of DTC\(^+\) can be contrasted with that of HITC\(^+\), for which net \( \text{trans} \rightarrow \text{cis} \) isomerisation was observed at short wavelength and \( \text{cis} \rightarrow \text{trans} \) isomerisation at longer wavelengths [1]. The difference is that the \( \text{cis} \) HITC\(^+\) isomers absorb well to the red of the dominant \( \text{trans-HITC}^+ \) isomer (maxima at 805 and 750 nm, respectively, in methanol) [175], and in contrast to DTC\(^+\), the spectra are not overlapped.

### 5.3 Gas-phase photoisomerisation mechanism

The accepted photochemical processes accompanying \( S_1 \rightarrow S_0 \) excitation for DTC\(^+\) in solution, first proposed by Rullière [137], are illustrated in figure 5.4 where the potential energy is plotted as a function of the torsion coordinates \( \theta \) and \( \theta' \), corresponding to twisting about the C\(_8\)-C\(_9\) and C\(_2\)-C\(_8\) bonds, respectively (right and left sides of Figure 5.4) [137, 139, 183, 184]. The \( S_1 \) (upper) curve is based on an analy-
sis of the temperature dependence of photo-isomer yield and fluorescence quantum efficiency [183], and on the CI-INDO calculations of Baraldi et al. [184]

In solution, DTC$^+$ ions photoexcited to the $S_1$ state traverse a small barrier (17 to 30 kJ/mol depending on solvent [139]) before twisting into the deep minimum at $\theta=90^\circ$, corresponding to a conical intersection with the $S_0$ state. The twisted state $t'$ is coupled to a region of the $S_0$ surface where either the 2-cis isomer or the trans isomer is accessed. The right side of Figure 5.4 illustrates the corresponding process, in which torsion about the C$_8$-C$_9$ bond leads to the $t$ conical intersection which couples to a region of the $S_0$ surface where either the 8-cis isomer or the trans isomer is formed. The presence of torsional barriers on the $S_1$ surface is consistent with the temperature dependence of the quantum yield for $trans\rightarrow cis$ isomerisation, which is 0.070 at 190 K and 0.250 at 293 K [183].

For isolated trans-DTC$^+$ ions, the barriers for C$_2$-C$_8$ and C$_8$-C$_9$ torsions in the $S_1$ state, have been calculated using the CI-INDO method, as 13 and 10 kJ/mol, respectively [184], presumably sufficiently high to prohibit access to the twisted states ($t'$ and $t$), and confine the system to the trans Franck-Condon region, at least at the prevailing effective temperature in the drift section of the apparatus (296 K). Therefore, in the gas phase, the excited DTC$^+$ molecules can probably only be deactivated through fluorescence, intersystem crossing (ISC), or internal conversion (IC). As in the case of HITC$^+$, fluorescence to higher vibrational levels in the $S_0$ manifold is unlikely to provide sufficient energy to surmount isomerisation barriers, particularly given the modest Stokes shift for DTC$^+$ (~600 cm$^{-1}$) [170]. Involvement of ISC in photoisomerisation is also improbable given that ISC rates are very low for DTC$^+$, even in the presence of solvents containing heavy atoms [145]. On the other hand, IC from the Franck-Condon state is known to occur for DTC$^+$. In solution, estimates for the IC quantum yield ($\phi_{IC}$) range from 0 to 0.3 [139]. Note that even if the DTC$^+$ molecules manage to surmount the $S_1$ torsional barriers and access the conical intersections $t'$ and $t$, they will be transferred into highly vibrationally energised levels of the $S_0$ manifold. Ultimately, access to highly vibrationally excited levels of the $S_0$ manifold, either through direct IC from the
Franck-Condon region or through the conical intersections, will be followed by exploration of the conformational landscape of the $S_0$ potential energy surface, as the molecules cool through collisions with the He buffer gas.

The conformational exploration of the $S_0$ PES following excitation and subsequent internal conversion was investigated using time-dependent energy grained master equations, as implemented in a modified version of Multiwell [185–187]. This approach uses stochastic methods to model the changes in configuration that occur as an ion collides with neutral gas molecules, while the ion also cools from a state with a single photon’s worth of excess energy. The results of the calculations are consistent with the experimental results above, in that the thermal isomerisation of DTC$^+$ after internal conversion of an absorbed photon favours the formation of 8-$\text{cis}$-DTC$^+$ over the formation of 2-$\text{cis}$-DTC$^+$, and does so for the entire range of absorption wavelengths, as well as for a variety of cooling rates. These calculations are explained in further detail in the journal article based on this chapter [2].

### 5.4 DTC$^+$ in N$_2$ buffer gas

The experiments described above were repeated with N$_2$ as the bath gas. As predicted by Equation 2.3, the larger collision cross-section and heavier mass of the N$_2$ molecule, compared to helium, reduced the mobility of the drifting ions. However it also resulted in the appearance of two new, very weak peaks, unseen in the helium ATDs, at earlier arrival times than the all-$\text{trans}$ and 8-$\text{cis}$ isomer peaks (see figure 5.7). Neither of the two new peaks appear to be affected by exposure to laser light.

The mobilities of these peaks, relative to the all-$\text{trans}$ and 8-$\text{cis}$ peaks, match the relative mobilities of all-$\text{cis}$-DTC$^+$ (isomer K) and 8,9-di$\text{cis}$-DTC$^+$ (isomer G) as calculated by MOBCAL. As in the case of the 8-$\text{cis}$ isomer discussed above, the arrival count of each of these isomers is significantly higher than expected at temperatures present in the instrument. Additionally, there is no sign of any
ions arriving at the predicted arrival time for isomer J, which is lower in energy than isomer K by $\sim 25$ kJ/mol. But it is possible that a wide variety of isomers is generated by collisional activation in the electrospray or in the first ion funnel. The isomers that are generated would then relax to lower energy isomers at rates determined by the isomerisation barrier heights. For fully thermalised ions in
the drift region the effective temperature is 296 K and the rate of collision with buffer gas molecules is \( \sim 10^9 \) per second. Under these conditions an isomerisation pathway with a barrier height of 40 kJ/mol would be expected to have a half-life of 8 ms (less than the typical drift time), whereas a barrier height of 45 kJ/mol would lead to a half-life of 60 ms (significantly longer than the typical drift time).

Figure 5.8 shows barrier heights for all possible relaxation pathways, as calculated by DFT [B3LYP/6-31G(d)], with the dominant pathway (with lowest barrier) for each isomer shown in bold. The most stable isomer after the all-trans isomer (isomer A) is isomer C, with a barrier height of 89.7 kJ/mol. The next most stable is isomer G, with a barrier height of 46.0 kJ/mol, then isomers B, F, K and E, with isomerisation barriers in the range of 40 to 45 kJ/mol. The remaining isomers (H, J and D) have barrier heights less than 40 kJ/mol. The dominant isomerisation relaxation pathways are also shown in Figure 5.7, along with the predicted arrival times of each isomer. It is clear that three of the four discernible arrival time peaks correspond to the three most stable isomers (A, C and G), and the fourth peak corresponds to isomer K. The other isomers with barrier heights higher than isomer K (isomers B and F) are predicted to arrival at similar times to isomers A and C, so they would not be resolvable.

5.5 Conclusions

The photoisomerisation of the polymethine dye DTC\(^+\) has been probed by monitoring the change in its drift speed in He buffer gas. Photoexcitation over the 450-570 nm range causes net conversion of trans-DTC\(^+\) to 8-cis-DTC\(^+\), which is manifested in a modification of the ions’ arrival time distribution. The gas-phase photoisomerisation action spectrum of DTC\(^+\) has a maximum at 535 nm and is shifted by 25 nm to shorter wavelength compared to the maximum of the absorption spectrum for DTC\(^+\) in methanol solution. Intriguingly, we fail to observe the 2-cis isomer, which is deemed the primary photo-isomer in studies of DTC\(^+\) in solution [179, 180]. In the gas phase, barriers in S\(_1\) torsional potential energy curves
presumably confine the excited trans-DTC\(^{+}\) molecule to the Franck-Condon region such that internal conversion to the S\(_0\) manifold and fluorescence are the dominant deactivation processes. The theoretical results support the experimental observations and demonstrate that the 8-cis isomer is preferred over the 2-cis isomer because it lies lower in energy and because it is separated from the trans isomer by a substantially higher barrier.
CHAPTER 5. PHOTOISOMERISATION OF DTC$^+$
Chapter 6

Photoisomerisation of DTDC$^+$ and DODC$^+$

This chapter focuses on the gas-phase photoisomerisation of two structurally similar dyes, 3,3'-diethylthiadicarbocyanine (DTDC$^+$, Figure 6.1, left) and 3,3'-diethyloxydicarbocyanine (DODC$^+$, Figure 6.1, right). DTDC$^+$ is similar to the DTC$^+$ dye studied in Chapter 5, but with a longer polymethine chain. DODCI and DTDCI have both been extensively studied in solution [188–212]. Significantly, DODCI was the subject of the study that led Rullière to the model that is now accepted to describe the photoisomerisation of carbocyanine dyes in solution [137]. One early investigation examining the rotational diffusion of DODCI suggested that the normal form in solution is the relatively compact 8,11-di-cis isomer [192] (shown in Figure 6.2 as isomer F). However, following subsequent experiments [205], the consensus is that the stable conformer is all-trans-DODCI, as shown in Figure 6.1 [213–215]. The visible absorption band of DODCI in ethylene glycol solution has a peak at 585 nm. Excitation of the normal isomer leads to the formation of a photoisomer with an absorption spectrum that is red-shifted relative to the normal isomer, peaking at 620 nm [199]. Like other carbocyanine dyes, DODCI does not readily undergo intersystem crossing to the T$_1$ state from
**Figure 6.2** Selected isomers of DODC$^+$. For clarity, hydrogen atoms have been omitted. Gibbs free energies, collision cross-sections, mobilities & isomerisation barriers are listed in table 6.1.
the $S_1$ state, but can populate triplet states from higher $S_n$ states, in parallel with increased photofragmentation [209, 210].

In solution, DTDCI has a visible absorption band with a maximum at 650 nm. Tarnovskii and coworkers determined that DTDCI forms at least two photoisomers, in a stepwise fashion, in ethanol solution [211]. Excitation of the normal isomer leads to the formation of the first photoisomer, which has an absorption spectrum that is red-shifted relative to the absorption of normal isomer, peaking at 656 nm. In turn, excitation of the first photoisomer produces a second photoisomer with an absorption that is blue-shifted relative to absorption of the normal isomer, peaking at 635 nm. They propose that the first photoisomer could be either 8-cis or 9-cis-DTDCI (the DTDCI analogues of isomers C & D in Figure 6.2), and that the second photoisomer is 8,10-cis-DTDCI (analogous to isomer E in Figure 6.2). In the same study, Tarnovskii and coworkers reported that they did not observe any evidence of a second photoisomer for DODCI. Spectroscopic studies of DTDCI and DODCI in the gas phase should help with the identification of photoactive isomers and provide information on their absorption spectra.

6.1 Assignment of the DODC$^+$ ATD

To help identify the relevant DODC$^+$ isomers, their structures and energies were calculated using DFT [B3LYP/6-31G(d)] [153]. The mobilities for the optimised structures were calculated using the exact hard sphere collision model, as implemented in MOBCAL [78–80]. The transition state structures and the corresponding barrier heights were calculated for transformation between selected isomers of DODC$^+$. The optimised structures for several isomers of DODC$^+$ are shown in Figure 6.2, and the the Gibbs free energies, relative to the all-trans isomer, collision cross-sections, mobilities and lowest barrier height (corresponding to what is expected to be the dominant relaxation pathway) for isomers of DODC$^+$ are summarised in Table 6.1. The relative Gibbs free energies and scaled, predicted
Table 6.1 Calculated data for isomers of DODC\(^+\), including Gibbs free energies (relative to the all-trans isomer), collision cross-sections (\(\Omega\)) and reduced mobilities (\(K_\theta\)) in helium and barrier heights for selected isomers. The barrier height listed for each isomer is for the relaxation pathway that has the lowest barrier and is given relative to the respective isomer energy.

<table>
<thead>
<tr>
<th>Label</th>
<th>Isomer</th>
<th>(\Delta G) (kJ/mol)</th>
<th>(\Omega) ((\text{Å}^2))</th>
<th>(K_\theta) ((\text{cm}^2/\text{s}/\text{V}))</th>
<th>Lowest Barrier (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A)</td>
<td>all-trans</td>
<td>0</td>
<td>150.9</td>
<td>3.572</td>
<td>N/A</td>
</tr>
<tr>
<td>(B)</td>
<td>2-cis</td>
<td>18.3</td>
<td>148.8</td>
<td>3.622</td>
<td>59.5</td>
</tr>
<tr>
<td>(C)</td>
<td>8-cis</td>
<td>12.3</td>
<td>148.6</td>
<td>3.626</td>
<td>97.3</td>
</tr>
<tr>
<td></td>
<td>9-cis</td>
<td>15.5</td>
<td>148.2</td>
<td>3.637</td>
<td>97.8</td>
</tr>
<tr>
<td></td>
<td>2,8-cis</td>
<td>45.0</td>
<td>148.3</td>
<td>3.633</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>2,9-cis</td>
<td>32.0</td>
<td>148.5</td>
<td>3.630</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>2,10-cis</td>
<td>36.5</td>
<td>145.3</td>
<td>3.709</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>2,11-cis</td>
<td>30.1</td>
<td>147.6</td>
<td>3.650</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>2,12-cis</td>
<td>39.8</td>
<td>145.7</td>
<td>3.700</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>8,9-cis</td>
<td>43.2</td>
<td>142.8</td>
<td>3.774</td>
<td>-</td>
</tr>
<tr>
<td>(E)</td>
<td>8,10-cis</td>
<td>25.4</td>
<td>148.6</td>
<td>3.628</td>
<td>96.9</td>
</tr>
<tr>
<td>(F)</td>
<td>8,11-cis</td>
<td>24.7</td>
<td>143.3</td>
<td>3.760</td>
<td>95.1</td>
</tr>
<tr>
<td></td>
<td>9,10-cis</td>
<td>50.7</td>
<td>145.7</td>
<td>3.699</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>2,8,9-cis</td>
<td>64.6</td>
<td>143.0</td>
<td>3.777</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>2,8,10-cis</td>
<td>60.4</td>
<td>146.0</td>
<td>3.690</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>2,8,11-cis</td>
<td>56.9</td>
<td>143.6</td>
<td>3.752</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>2,8,12-cis</td>
<td>66.6</td>
<td>144.8</td>
<td>3.722</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>2,9,10-cis</td>
<td>50.7</td>
<td>145.9</td>
<td>3.694</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>2,9,11-cis</td>
<td>43.1</td>
<td>146.9</td>
<td>3.670</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>2,9,12-cis</td>
<td>51.6</td>
<td>146.0</td>
<td>3.691</td>
<td>-</td>
</tr>
<tr>
<td>(G)</td>
<td>8,9,10-cis</td>
<td>69.3</td>
<td>140.4</td>
<td>3.838</td>
<td>55.1</td>
</tr>
<tr>
<td></td>
<td>8,9,11-cis</td>
<td>85.6</td>
<td>143.2</td>
<td>3.763</td>
<td>-</td>
</tr>
<tr>
<td>(H)</td>
<td>8,9,12-cis</td>
<td>66.0</td>
<td>140.7</td>
<td>3.830</td>
<td>48.6</td>
</tr>
<tr>
<td>(J)</td>
<td>2,8-trans</td>
<td>83.7</td>
<td>138.4</td>
<td>3.893</td>
<td>50.7</td>
</tr>
<tr>
<td></td>
<td>2,9-trans</td>
<td>86.5</td>
<td>141.6</td>
<td>3.806</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>2,10-trans</td>
<td>85.6</td>
<td>143.2</td>
<td>3.764</td>
<td>-</td>
</tr>
<tr>
<td>(K)</td>
<td>2,11-trans</td>
<td>85.3</td>
<td>138.5</td>
<td>3.892</td>
<td>53.2</td>
</tr>
<tr>
<td>(L)</td>
<td>2,12-trans</td>
<td>97.8</td>
<td>129.7</td>
<td>4.155</td>
<td>43.5</td>
</tr>
<tr>
<td>(M)</td>
<td>8,9-trans</td>
<td>87.9</td>
<td>139.8</td>
<td>3.856</td>
<td>44.3</td>
</tr>
<tr>
<td></td>
<td>8,10-trans</td>
<td>79.0</td>
<td>143.9</td>
<td>3.744</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>8,11-trans</td>
<td>64.7</td>
<td>146.1</td>
<td>3.688</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>9,10-trans</td>
<td>89.3</td>
<td>143.4</td>
<td>3.759</td>
<td>-</td>
</tr>
<tr>
<td>(N)</td>
<td>2-trans</td>
<td>112.9</td>
<td>131.8</td>
<td>4.089</td>
<td>44.1</td>
</tr>
<tr>
<td>(O)</td>
<td>8-trans</td>
<td>110.8</td>
<td>137.0</td>
<td>3.934</td>
<td>32.6</td>
</tr>
<tr>
<td>(P)</td>
<td>9-trans</td>
<td>122.7</td>
<td>140.0</td>
<td>3.849</td>
<td>25.8</td>
</tr>
<tr>
<td>(Q)</td>
<td>all-cis</td>
<td>156.3</td>
<td>126.2</td>
<td>4.271</td>
<td>18.1</td>
</tr>
</tbody>
</table>
arrival times for isomers of DODC$^+$ are shown in Figure 6.3a.

The lowest energy isomer is all-trans-DODC$^+$, followed by the isomers with a single cis bond. 8-cis-DODC$^+$ (isomer C) lies next lowest in energy (12.3 kJ/mol above all-trans-DODC$^+$), followed by 9-cis-DODC$^+$ (isomer D: 15.5 kJ/mol) and 2-cis-DODC$^+$ (isomer B: 18.3 kJ/mol). Thermal isomerisation from isomers C and D to the all-trans isomer is predicted to occur very slowly because the isomerisation pathways must cross transition state barriers of 97.3 kJ/mol and 97.8 kJ/mol, relative to isomers C and D, respectively. The barrier to isomerisation from isomer B to all-trans-DODC$^+$ is lower, at 59.5 kJ/mol relative to isomer B, but this is sufficient for isomer B to have a lifetime significantly longer than the drift time (22 s, as estimated using Equation 2.42 with an effective temperature of 296 K and a collision rate of $\sim 10^9$ s$^{-1}$). The remaining isomers lie higher in energy and although many of them are predicted to have mobilities similar to that of lower energy isomers, there are some that are predicted to be significantly more mobile. Of these faster isomers, some have calculated isomerisation barriers that correspond to lifetimes similar to that of the drift time (isomers L, M and N have barriers in the range of 43.5 – 44.3 kJ/mol, corresponding to half-lives of 33 – 46 ms, as calculated using Equation 2.42). Some of the other faster isomers have barriers to isomerisation that are high enough to suggest that they would persist through the drift region (isomers F, G, H, J and K, with isomerisation barriers of at least 48 kJ/mol, corresponding to predicted lifetimes exceeding 260 ms), while others have barriers to isomerisation that are too low for them to endure the drift region (isomers O, P and Q, each with at least one barrier less than 32.6 kJ/mol, corresponding to predicted lifetimes of less than 0.4 ms).

The ATD for DODC$^+$ without irradiation is shown in Figure 6.3b. There is one major peak, preceded by three faster, smaller peaks. The peaks are all associated with ions with the same mass, indicating that they are isomers of DODC$^+$.

Comparison of the ATD in Figure 6.3b to the scaled predicted arrival times in Figure 6.3a suggests that the major peak is comprised of the all-trans isomer and one
Figure 6.3 (a) Predicted arrival times and calculated relative isomer energies for DODC$^+$ isomers. The calculated arrival times are scaled so that the predicted arrival time for the all-trans isomer matches the arrival time for the major observed peak. Icons indicate the number of cis bonds in the ion as follows: all-trans; $\times$1 cis bond; $\bullet$2 cis bonds; $\bullet$3 cis bonds; $\triangleleft$4 cis bonds; $\triangle$5 cis bonds; $\blacklozenge$all-cis. The labels indicate isomers as per Table 6.1. (b) Laser-off ATD for ions electrosprayed from DODCI solution, drifting in helium buffer gas. (c) Photoinduced differences between laser-on and laser-off ATDs. Irradiation by 465-655 nm light causes a depletion of ions at the slower edge of the major peak (1), and an increase in ions at the faster edge of the major peak (2), whereas irradiation by 565-605 nm light has the reverse effect. Light in both ranges causes an increase in ions in the earlier peaks (3-5).
or more single cis or double cis isomers. The next slowest peak (with an arrival times of 20.5 ms) is likely to include isomer F, as it is the lowest energy isomer with an appropriate calculated mobility, and isomerisation barriers high enough to endure through the drift region (but this does not necessarily preclude the possibility that this peak includes other, higher energy isomers). It appears likely that the two fastest ion bunches are composed of isomers N and L, because the only other isomer calculated to be sufficiently mobile to arrive that early (isomer Q) has a relaxation pathway barrier of 18.1 kJ/mol. Significantly, the presence of the two fastest peaks appears to depend on conditions within the drift tube. The ATD in Figure 6.4a was collected with the ions drifting through helium and a total drift voltage of 2 kV, whereas the ATDs in Figures 6.4b and 6.4c were collected with nitrogen as the buffer gas, at pressures of 7.8 Torr and 9.7 Torr, respectively, and with a higher total drift voltage of 4.5 kV. The various drift gases, pressures and voltages resulted in different arrival times, so the ATDs have been plotted such
that the peaks in each ATD are aligned vertically. Isomer L is only present in the ATD collected using helium buffer gas and neither isomer L or N is present in the ATD collected using a higher pressure of nitrogen buffer gas. These two isomers were predicted to have lifetimes similar to the drift time, with isomer N predicted to be slightly more stable than isomer L. It is possible that the barrier heights for the relaxation of these two isomers mark the lower bound required for an isomer to survive the drift region, and that the slight increase in effective temperature associated with the change to nitrogen buffer gas (due to the mass term in Equation 2.7) combined with the longer drift times is sufficient to eliminate them. On the other hand, isomers G through M are all calculated to lie lower in energy than isomers L and N, all have isomerisation barriers that are higher than those for isomers L and N, and all have predicted arrival times that should lie between peaks 3 and 4 in the DODC\textsuperscript{+} ATDs. At this stage, the reason for the absence of isomers that are expected to be more stable than isomers that are observed is unknown.

### 6.2 DODC\textsuperscript{+} PISA spectra

The change in the DODC\textsuperscript{+} ion count as a function of arrival time and wavelength is shown in Figure 6.5. It is apparent that in the wavelength range of 450 to 570 nm there is depletion of the ion account arriving at 21.5 ms, corresponding to a decrease in the number of all-\textit{trans}-DODC\textsuperscript{+} ions, and an increase in the number of ions arriving in 4 distinct regions of the ATD, as indicated by the brackets. At longer wavelengths there is a depletion of the ion count at \(\sim 21\) ms and an increase in the ion count at \(\sim 21.5\) ms, indicating isomerisation from a faster isomer to the all-\textit{trans} isomer and confirming the presence of multiple isomers in the laser-off ATD peak. For the fastest three photoisomers, the wavelength dependence was determined by integrating the change in ion count over the arrival time range indicated by the brackets. The wavelength dependence for the formation of the photoisomer that arrives at 21 ms was determined by first fitting a double Gaus-
6.2. DODC\textsuperscript{+} PISA SPECTRA

Figure 6.5 Difference in laser-on and laser-off DODC\textsuperscript{+} ATDs as a function of wavelength and ion arrival time. The blue region corresponds to the laser induced depletion of the parent isomer, whereas the yellow and red regions indicate the regions of increased ion count. Four regions of photoisomers are indicated with brackets.

Figure 6.6 (a) Spectra for DODC\textsuperscript{+} photoisomer formation and photofragmentation. The style and colour of the photoisomer formation spectra match those of the indicator brackets in Figure 6.5. As a result of the different method used to determine the spectrum for the formation of the slowest photoisomer (solid black line plot), its vertical scale is not in proportion to the other spectra. The solid purple curve indicating the photofragmentation spectrum has been reduced by a factor of 10. (b) Absorption spectra of the normal isomer and photoisomers of DODCI in ethylene glycol solution, as measured by Penzkofer and coworkers [199].
sian function to the data in Figure 6.3c, then fixing the fitted peak arrival times and widths constant and fitting the amplitude of the two Gaussian functions to the ATD at each wavelength. The fragmentation spectrum was determined by taking difference between the total number of ions with the laser-on and with the laser-off at each wavelength. The most abundant product was the isomer(s) that is only slightly faster than the parent isomer (indicated by the solid black curve in Figure 6.6). Formation of this photoisomer occurs over the 450–570 nm range. The PISA spectrum for this process has a broad, flat top, suggesting that the absorption may be saturated. For longer wavelengths (570–610 nm) the PISA response curve became negative, indicating that isomerisation from the photoisomer to the all-trans isomer predominates. The formation of the next slowest photoisomer (the dashed blue curve) follows similar a wavelength dependence, except that the response curve does not become negative at longer wavelengths. The formation of the fastest two isomers (shown by the red dot and green dot-dash curves) have a different wavelength dependence. The PISA spectra for these isomers follow a similar wavelength dependence to the photofragmentation spectrum (the thinner purple curve), and occur in the wavelength range where the PISA spectra for the other isomers appear to be saturated, suggesting that the formation of the two fastest photoisomers requires absorption of multiple photons.

6.3 Assignment of DTDC\(^+\) ATD

Optimised structures, relative energies and mobilities were calculated for the isomers of DTDC\(^+\). The calculated relative energies for DTDC\(^+\) are similar to those for DODC\(^+\) and while the mobility of DTDC\(^+\) isomers were found to be typically around 5% lower than the corresponding DODC\(^+\) isomers, they follow a similar trend (see Figure 6.7). Transition state structures and energies were not calculated for DTDC\(^+\), but are expected to follow a similar pattern to those of DODC\(^+\).

The arrival time distribution for DTDC\(^+\) (Figure 6.8b) is remarkably similar to
6.3. ASSIGNMENT OF DTDC$^+$ ATD

![Figure 6.7](image)

**Figure 6.7** Comparison of calculated Gibbs free energies, at 298 K, and calculated collision cross-sections for isomers of DODC$^+$ and DTDC$^+$, relative to the respective all-trans isomer. Linked pairs of points indicate similarly configured isomers.

that for DODC$^+$ (Figure 6.8a). Both ATDs were collected under similar conditions (12.3 Torr of helium and drift voltage of 2 kV), so the difference in arrival times is due to the difference in the mobility. Given the similarity of the DODC$^+$ and DTDC$^+$ structures and ATDs, it is likely that the same isomers were present for both dyes. The calculated cross-section for all-trans-DTDC$^+$ (159.4 Å) is 5.7% larger than the cross-section for all-trans-DODC$^+$ (150.9 Å). This corresponds well with the major peak of DTDC$^+$ arriving later than the major peak of DODC$^+$ by a factor of 4.4% (22.31 ms versus 21.36 ms), under similar drift conditions. The three minor peaks that precede the major peak in the DODC$^+$ ATD are also present in the DTDC$^+$ ATD, with arrival times that are scaled by very similar factors to the major peak (compare Figures 6.8a and 6.8b).

A significant difference between the two arrival time distributions is that the major peak is more asymmetric for DTDC$^+$ than for DODC$^+$. The dotted curves in Figures 6.8a & 6.8b are Gaussian functions that were fitted to the major peak in each the laser-off ATD. It is clear that there is a more pronounced shoulder on the faster edge of the major peak for DTDC$^+$ than for DODC$^+$. It is possible
Figure 6.8 (a) Laser-off ATD for DODC$^+$ (isomer A). (b) Laser-off ATD for DTDC$^+$ (isomer A). (c) Photoinduced changes in arrival time distribution for DTDC$^+$. Excitation by light with wavelengths less than 640 nm causes a depletion of the slow edge of the slowest peak, and an increased population of faster isomers. Excitation by longer wavelength light causes a depletion in the faster edge of the main peak, and an increase in the slower edge. Dashed lines have been scaled by a factor of 50. Dotted curves are Gaussian functions fitted to the dominant peak in each laser-off ATD.

that this is partly due to the presence of 2,10-cis-DTDC$^+$ (isomer E), which is the second photo-isomer that Tarnovskyi and coworkers suggest is observed in solution for DTDCI, but not for DODCI. It is also possible that the mobilities of the single cis isomers are closer to the mobility of the all-trans isomer for DODC$^+$ than they are for DTDC$^+$, resulting in a better overlap of the arrival peaks.
Figure 6.8c shows the change in the ATD for DTDC\textsuperscript{+} following exposure to light, averaged over two wavelength ranges. At wavelengths shorter than 640 nm, there is a depletion of ions arriving in the slower edge of the major peak and an increase in the number of ions arriving in the faster edge of the peak, as well in the faster peaks, indicating that some all-\textit{trans}-DTDC\textsuperscript{+} ions are photoisomerised to faster \textit{cis} isomers. Following exposure to light with wavelengths longer than 640 nm there is a depletion of ions arriving in the faster edge of the main peak and an increase in the number of ions arriving in the slower edge of the peak, indicating that some \textit{cis}-DTDC\textsuperscript{+} ions photoisomerise to the all-\textit{trans} form. There is no apparent change in the faster peaks following excitation by light in the longer wavelength range, although this may be due to low signal to noise ratio.

The change in the DTDC\textsuperscript{+} ion count plotted, as a function of arrival time and wavelength, is shown in Figure 6.9. Over the range of 500 nm to 640 nm there is a depletion of all-\textit{trans}-DTDC\textsuperscript{+} (at an arrival time of 22.4 ms), and an increase in the other isomers (arriving at 19.0, 19.6, 21.3 and 22.0 ms). At longer wavelengths there is a depletion of the slowest and most abundant photoisomer (at 22.0 ms) and an increase in all-\textit{trans}-DTDC\textsuperscript{+}.

The wavelength dependence for the formation of each photoisomer, as well as for fragmentation, was determined in the same manner as for DODC\textsuperscript{+}. The resulting spectra are shown in Figure 6.10a, with the style of each spectrum matching that of the brackets in Figure 6.9, and photofragmentation yield indicated with a solid purple plot. Figure 6.10b shows the absorption spectra of DTDC\textsuperscript{+} in ethanol solution, as measured by Tarnovskii and coworkers [211]. The spectra for the formation of the two most abundant isomers both peak at 570 nm (blue shifted from the absorption of DTDC\textsuperscript{+} in solution by 80 nm). But since a significant amount of fragmentation occurs, with the photofragmentation spectrum peaking at 600 nm, it is likely that these PISA spectra do not reflect the gas-phase absorption spec-
Figure 6.9 Difference between laser-on and laser-off DTDC$^+$ ATDs as a function of wavelength and ion arrival time. The blue region corresponds to the laser induced depletion of the parent isomers, whereas the yellow and red regions indicate regions of increased ion count. Four distinct photoisomers are indicated with brackets.

Figure 6.10 (a) PISA spectra for DTDC$^+$ photoisomer formation and photofragmentation. The style and colour of the photoisomer formation spectra match those of the indicator brackets in Figure 6.9. The plot showing the PISA spectrum for the formation of the two fastest photoisomers have been multiplied by a factor of 30, and the photofragmentation spectra (solid purple line) reduced by a factor of 10. (b) Absorption spectra of the normal isomer and first (P1) and second (P2) photoisomers of DTDCI in ethanol solution, as measured by Tarnovskii and coworkers [211].
6.5. CONCLUSIONS

The spectrum for all-trans-DTDC\textsuperscript{+}. The fragmentation is likely due to the absorption of multiple photons, and would reduce the photoisomerisation yield at the absorption maximum. The PISA spectrum for the formation of the slowest photoisomer becomes negative over the range of 640-700 nm, indicating that photoisomerisation away from this isomer predominates at these wavelengths. Figure 6.10a also shows the PISA spectra for the formation of the two most mobile isomers. The yield for the formation of these isomers is very low but, despite the relatively weak signal, it is apparent that their formation follows the photofragmentation spectrum. This suggests that the formation of these faster isomers may also be multiple-photon process.

6.5 Conclusions

When electrosprayed into the gas phase and analysed by ion mobility spectrometry, both DODC\textsuperscript{+} and DTDC\textsuperscript{+} exhibit evidence for at least five isomers. Three of these isomers are clearly separated in the ATD, whereas the slowest and most abundant peak is composed of at least two isomers that have mobilities that are too similar to be resolved. The slowest arrival peak is probably the all-trans isomer (isomer A), overlapping a slightly faster bunch of ions that is likely a mixture of isomers, particularly the single-cis isomers (isomers B, C & D), but also possibly some double-cis isomers. The fastest three isomers are proposed to consist primarily of isomers F, N and L.

Exposing the ions to pulses of tunable light results in both fragmentation and isomerisation. Both DODC\textsuperscript{+} and DTDC\textsuperscript{+} undergo isomerisation from the all-trans conformation to the other isomers following exposure to light with shorter wavelength (450-570 nm for DODC\textsuperscript{+} and 500-640 nm for DTDC\textsuperscript{+}), whereas following exposure to longer wavelength light (570-610 nm for DODC\textsuperscript{+} and 640-700 nm for DTDC\textsuperscript{+}) there is a net change from the most abundant photoisomer to the all-trans isomers. The formation of two most mobile isomers of both DODC\textsuperscript{+} and DTDC\textsuperscript{+} follow the spectrum for the photofragmentation of the all-trans isomer,
so it is likely that the formation of these isomers requires absorption of multiple photons.
Chapter 7

Photoisomerisation of Pinacyanol

This chapter focuses on the dye 1,1’-Diethyl-2,2’-carbocyanine, commonly referred to as pinacyanol. The central polymethine carbon chain in pinacyanol is similar to DTC$^+$ discussed in Chapter 5, however pinacyanol has quinoline moieties at either end, rather than benzothiazole units. Pinacyanol was first synthesised in 1905 [216], and was the first dye used to sensitise silver halides to red light [217]. More recently it has proven useful as a mode-locking dye for rhodamine 6G and rhodamine B dye lasers [218].

Due to the importance of pinacyanol, there have been many investigations of its photophysics and photochemistry. The fluorescence lifetime and ground state recovery rates of pinacyanol have previously been measured in solution and found to depend strongly on solvent viscosity [219–221]. Arvis and Mialocq measured the lifetimes of triplet pinacyanol formed by triplet transfer from naphthalene [222]. The triplet state decay rates were found to be in the range of of $2 \times 10^3 \text{s}^{-1}$, depending on the solvent. The same work also established that, in the absence of a triplet state donor, the quantum yield of triplet formation following $S_1 \leftarrow S_0$ excitation is $< 1\%$. Rentsch and coworkers demonstrated that pinacyanol in ethanol, when excited with 550 nm light, and probed at 640 nm, initially shows photobleaching (with a lifetime of $16 \pm 2 \text{ps}$), followed by a period of enhanced absorption, with two lifetime components [223]. The faster of the two components of the enhanced
absorption has a lifetime of $381 \pm 62$ ps, whereas the longer component has a lifetime on the order of nanoseconds. Sundström and Gillbro measured transient absorptions for pinacyanol in methanol with a lifetime of 16 ns - faster than the microsecond lifetimes of pinacyanol triplet states, but much slower than the picosecond pinacyanol $S_1$ decay [224]. It is believed that this transient is due to absorption by the photoisomer. By measuring the magnitude of the nanosecond transient as a function of wavelength Sundström and Gillbro were able to acquire its absorption spectrum (shown in Figure 7.2B), and demonstrate that it is red-shifted relative to that of the normal isomer [225].

![Figure 7.2](image_url)

**Figure 7.2** Absorption spectra of the normal isomer of pinacyanol (A) and photoisomer (B) dissolved in methanol. Reproduced from Reference 225.

Park and coworkers calculated the absorption wavelengths for various pinacyanol isomers by the semi-empirical Pariser–Parr–Pople molecular orbital (PPP MO) method [226]. Of the isomers calculated, only one conformer (the 9-cis isomer) had an absorption maximum red-shifted relative to the calculated all-trans isomer maximum, suggesting that the 9-cis isomer may be the photoisomer observed in the transient absorption studies.

This chapter describes the application of ion mobility mass spectrometry and laser excitation to the characterisation of pinacyanol in the gas phase. The methods
are similar to those used for the HITC$^+$, DTC$^+$, DODC$^+$, and DTDC$^+$ ions described in the preceding chapters, except for the following modifications. First, the switchable potential on the ion gate that follows the first ion funnel was increased from 40 V to 65 V, improving transmission with the gate open while still stopping ions completely with the gate closed. Second, in contrast to most of the data presented for the other cyanine dyes, pinacyanol was studied in nitrogen buffer gas, rather than helium, allowing a higher drift potential to be applied without electrical breakdown and consequently improving the mobility resolution of the instrument. Third, the Matlab data processing script was modified to scale the arrival time axis for the ATD at each wavelength, based on the observed arrival time of the dominant laser-off ATD peak, eliminating the effect of variations in arrival time, such as those resulting from changes in the buffer gas pressure. Finally, the pinacyanol ion was also studied at higher laser intensities, to deliberately induce photo-fragmentation and to demonstrate that structural information on photofragments can be derived from their drift mobilities.

7.1 Calculations

Optimised structures for pinacyanol were calculated using DFT [B3LYP/6-31G(d)], and are shown in Figure 7.3. The mobilities and collision cross-sections for each isomer were calculated using the exact hard sphere (EHS) scattering model, as implemented in MOBCAL [78–80]. Structures and energies for isomerisation transition states were also calculated. The zero point corrected energies, Gibbs free energies at 298K, dominant isomerisation pathway barrier heights, collision cross-sections and mobilities for each isomer are summarised in Table 7.1. The energies and predicted arrival times for each isomer are shown in Figure 7.4a; the lines that join the isomers show the most likely isomerisation pathways.

The relative energies of the pinacyanol isomers follow a similar pattern to that of the other carbocyanines, with the energy increasing with the number of cis
bonds. In particular, the lowest lying isomers are the all-trans isomer (Figure 7.3A), the 2-cis isomer, which lies 25.0 kJ/mol higher in energy (Figure 7.3B), followed by the 9-cis isomer, lying 27.4 kJ/mol above the all-trans isomer (Figure 7.3C). Although the 9-cis isomer lies higher in energy than the 2-cis isomer, the barrier for isomerisation back to the all-trans isomer is significantly higher for the 9-cis isomer (75.3 kJ/mol) than for 2-cis-pinacyanol (40.9 kJ/mol), in accordance
with the proposal that it is the preferred photoisomer \cite{226}.

The predicted range of mobilities for pinacyanol isomers is generally smaller than for isomers of DTC\(^+\). For example, the difference in mobility between all-\textit{trans}-pinacyanol and 9-\textit{cis}-pinacyanol is 1.5\%, whereas the difference between the mobilities of the corresponding isomers of DTC\(^+\) is 2.5\%. The mobilities of 2-\textit{cis}-pinacyanol (isomer B) and 2,10-\textit{dicis}-pinacyanol (isomer F) are lower than the mobility of the all-\textit{trans} isomer. This is in contrast to DTC\(^+\) for which the all-\textit{trans} isomer is the slowest form.

### 7.2 Photoisomerisation of pinacyanol

The arrival time distribution for pinacyanol (propelled through 8.9 Torr of nitrogen gas by a total drift potential of 4.72 kV) with the laser off displays only a single peak (shown in Figure 7.4b), corresponding to a reduced mobility of 1.18 cm\(^2\)(Vs\(^{-1}\)). When exposed to light in the 450-600 nm range the mobility of some pinacyanol

<table>
<thead>
<tr>
<th>Table 7.1</th>
<th>Calculated data for conformers of pinacyanol (shown in Figure 7.3). Included are zero-point corrected energies and Gibbs free energies relative to that of the lowest energy isomer, barrier heights (for the isomerisation pathway with the lowest barrier), collision cross-sections ((\Omega)) and drift mobilities ((K_0)) (calculated for drifting in in helium).</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Delta E) (kJ/mol)</td>
<td>(\Delta G) (kJ/mol)</td>
</tr>
<tr>
<td>all-\textit{trans} (A)</td>
<td>0</td>
</tr>
<tr>
<td>2-\textit{cis} (B)</td>
<td>24.2</td>
</tr>
<tr>
<td>9-\textit{cis} (C)</td>
<td>26.9</td>
</tr>
<tr>
<td>2,9-\textit{cis} (D)</td>
<td>39.0</td>
</tr>
<tr>
<td>2,10-\textit{cis} (E)</td>
<td>47.5</td>
</tr>
<tr>
<td>2,11-\textit{cis} (F)</td>
<td>47.2</td>
</tr>
<tr>
<td>10,11-\textit{cis} (G)</td>
<td>55.6</td>
</tr>
<tr>
<td>2,9,11-\textit{cis} (H)</td>
<td>58.8</td>
</tr>
<tr>
<td>2,9,10-\textit{cis} (J)</td>
<td>62.6</td>
</tr>
<tr>
<td>all-\textit{cis} (K)</td>
<td>81.3</td>
</tr>
</tbody>
</table>
Figure 7.4 (a) B3LYP/6-31G(d) calculated relative Gibbs free energy plotted against predicted arrival time for pinacyanol isomers. Calculated arrival times are scaled to match the arrival time for the all-trans isomer with the arrival time of the main peak in the laser-off ATD. Lines joining isomer data points indicate the barrier height for expected isomerisation pathways. The barriers to isomerisation from isomer K to isomers J and H are similar in energy, so both are shown. For all other isomers there is one isomerisation pathway with a barrier that is significantly lower than the others. (b) Laser-off ATD for pinacyanol. (c) Summed change in the ATD following excitation by light with a wavelength in the range of 450-600 nm. (d) Summed change in the ATD following excitation by light in the range of 610-650 nm.
ions increased (see Figure 7.4c), whereas at longer wavelengths, in the 610-650 nm range, the reverse occurred, although the effect is small (see Figure 7.4d).

The wavelength dependent change in the arrival time distribution is shown in Figure 7.5. It can be seen that over the 450-600 nm range there is a shift in ion intensity to earlier arrival times. But there is also significant noise, caused by fluctuations in the ion count of the parent peak, that is independent of laser irradiation. The wavelength dependence for isomerisation was determined by summing, at each wavelength, the change in ion count between the arrival times of 20.85 and 21.40 ms. The total change at each wavelength was normalised by the laser power. The resulting PISA spectrum is shown in Figure 7.6a. The photoisomerisation action spectrum shows a net conversion from the all-trans isomer to a more mobile cis-isomer between 450 and 610 nm. The PISA spectrum, which
displays signs of vibronic structure, is similar to the absorption spectrum of pinacyanol in methanol solution, but is shifted by 30 nm to shorter wavelength. The PISA signal becomes negative at longer wavelengths (610-660 nm), corresponding to photoisomerisation from a faster cis isomer to the slower all-trans isomer. This response occurs in the expected spectral region for the photoisomer identified by Sundström and Gillbro [225].

### 7.3 Photofragmentation of pinacyanol

Pinacyanol was used to investigate the use of the instrument to probe photofragmentation processes. To induce photofragmentation, the laser beam was focused to \( \sim 3 \) mm diameter at the point it intersected the ion packet. This gave an intensity of \( \sim 60 \text{ mJ/cm}^2/\text{pulse} \), 20-50 times higher than was typically used for photoi-
7.3. PHOTOFRAGMENTATION OF PINACYANOL

Figure 7.7 Difference between laser-on and laser-off ion count, as function of mass and arrival time, when electrosprayed pinacyanol ions were exposed to intense 570 nm light. Circles denote masses and predicted arrival times based on DFT and MOBCAL calculations for the indicated structures.

Isomerisation studies of pinacyanol and other carbocyanine ions described in the preceding chapters. Under these conditions, a significant fraction (~30%) of the ions underwent photofragmentation when the light was tuned to the band maximum (570 nm). The dominant fragments are indicated in Figure 7.7, which shows the difference in the laser-on and laser-off signal plotted as a function of arrival time and mass. The main fragments correspond to loss of ethyl radicals from either end of the pinacyanol molecule. Optimised structures for the all-trans isomers of the parent ion and ions resulting from the loss of ethyl radicals from one or both ends are inset in Figure 7.7 along with their masses and predicted arrival times. There are also charged fragments corresponding to the loss of one or two ethane molecules. Structures for these fragments have not been calculated, but there is little doubt about the assignment of the signals in Figure 7.7. Interestingly, the fragment corresponding to the loss of both ethyl groups (−C_2H_{10}) has a long tail, a situation that may arise if an impurity molecule becomes attached to the fragment ion in the drift region (slowing the ion down), but which subsequently detaches.
in the drift region or octopole ion guide prior to mass selection. By tuning the quadrupole mass filter to the appropriate mass it may be possible to identify the adduct, however this is difficult because of the limited mass range of the instrument (≤440 Da).

7.4 Conclusions

The photoisomerisation of the dye pinacyanol has been probed by monitoring changes in its mobility in nitrogen. Based on the calculated energies and heights of the barriers to conformational relaxation for the various cis-isomers it is likely that the photo-isomer formed in the gas phase is the 9-cis isomer. The \( \text{trans} \rightarrow \text{cis} \) isomerisation occurs over the range of 450-600 nm, with a peak blue-shifted \( \sim 30 \) nm relative to the absorption of the dye in methanol solution. There is also some \( \text{cis} \rightarrow \text{trans} \) isomerisation occurring at longer wavelengths. Pinacyanol also undergoes fragmentation when illuminated with intense light, showing loss of ethyl radical(s) or ethane.
Chapter 8

Summary and outlook

The PISA apparatus provides a new means for studying photoisomerisation and photofragmentation of molecular ions in the gas phase. The results presented in the preceding chapters clearly demonstrate the instrument’s ability to collect photoisomeriation action spectra and to assist with the identification of isomers. Several of the spectra, such as those for DODC$^+$ and DTDC$^+$, are distorted due to saturation and photofragmentation, but other spectra, particularly that for pinacyanol, demonstrate the instrument’s utility. Furthermore, it is evident from the results for HITC$^+$, DODC$^+$ and DTDC$^+$ that is possible to observe $\text{cis} \leftrightarrow \text{trans}$ isomerisation in both directions, although in the instrument as reported here it is the net change between isomers that is observed.

The instrument has continued to evolve during the preparation of this thesis. In particular, the addition of a Bradbury-Nielsen gate halfway along the drift section has allowed the instrument to select isomers based on mobility, prior to irradiation. This has enabled the collection PISA spectra for specific isomers, which is a significant improvement compared to simply observing the net change. An article discussing this aspect has been accepted [227].

Finally, the PISA instrument has been used to study the photoisomerisation and photofragmentation of various molecular ions, including the protonated Schiff-base retinal chromophore and the spiropyran-merocyanine system [228, 229]. This is just the beginning, and it is expected that the PISA approach will generate spectroscopic and structural insights for a broad range of photoactive molecular ions.
Bibliography


[31] A. Mourot, M. A. Kienzler, M. R. Banghart, T. Fehrentz, F. M. E. Huber,


118


