

1 **An Ion Mobility Mass Spectrometer for Investigating Photoisomerization and**
2 **Photodissociation of Molecular Ions**

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An ion mobility mass spectrometry apparatus for investigating the photoisomerization and photodissociation of electrosprayed molecular ions in the gas phase is described. The device consists of a drift tube mobility spectrometer, with access for a laser beam that intercepts the drifting ion packet either coaxially or transversely, followed by a quadrupole mass filter. An ion gate halfway along the drift region allows the instrument to be used as a tandem ion mobility spectrometer, enabling mobility selection of ions prior to irradiation, with the photoisomer ions being separated over the second half of the drift tube. The utility of the device is illustrated with photoisomerization and photodissociation action spectra of carbocyanine molecular cations. The mobility resolution of the device for singly charged ions is typically 80 and it has a mass range of 100-440 Da, with the lower limit determined by the drive frequency for the ion funnels, and the upper limit by the quadrupole mass filter.

10 Keywords: ion mobility spectrometry, photoisomerization, ion spectroscopy, mass
11 spectrometry

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12 I. INTRODUCTION

13 Molecular isomerization plays a key role in many natural and man-made photochemical
14 processes. For example, the retinal protonated Schiff base is the key photoactive unit
15 in the visual transduction cycle and in bacterial photosynthesis, where in both cases its
16 action involves isomerization about C=C bonds along the polyene chain. Chemists and
17 material scientists are currently attempting to harness photoisomerizing molecules such
18 as azobenzenes, diarylethenes and spiropyrans as light-activated engines in molecular
19 machines.¹⁻³ In order to understand and model photoactive systems there are significant
20 advantages in examining the core molecules in the gas phase, due to the relative ease with
21 which gas-phase data can be compared with accurate calculations for isolated molecules.
22 Here we describe an instrument for probing the photoisomerization of biologically and
23 technologically important molecular ions in the gas phase based on photo-induced changes
24 in the molecules' drift velocity as they pass through a gas cell. The technique's foundation
25 is ion mobility mass spectrometry (IMMS), a method whereby charged molecules are
26 separated on the basis of both mass and shape. Typically, a packet of molecular ions,
27 formed through either electrospray ionization or laser desorption, is propelled by an
28 electric field through a drift tube containing a buffer gas (normally He or N₂). Extended or
29 uncoiled molecules tend to travel more slowly through the buffer gas than folded, compact
30 molecules, allowing spatial and temporal separation of a structurally heterogeneous
31 population of molecular ions into packets of its constituent isomers. The ions pass from
32 the drift tube into a mass spectrometer in order to measure their mass distribution. IMMS
33 has been used to examine isomers for an enormous range of molecules including peptides,
34 proteins, carbohydrates, and clusters.⁴⁻¹¹

35 The IMMS apparatus described in this paper has been developed to accommodate
36 laser excitation of drifting charged molecules in order to probe their photoisomerization
37 behaviour. Previously, the transformation from one configurational isomer to another in
38 IMMS devices has been promoted using collisional heating in a short section of the drift
39 region,¹² or by heating the gas in the drift region.^{13,14} Laser excitation provides a potentially
40 more selective means for activating molecular ions, with control over both excitation
41 wavelength and beam intensity. Molecular ions typically have electronic transitions in the
42 visible or ultraviolet range, permitting straightforward energisation using photoexcitation.

43 For many molecules, rapid non-radiative deactivation (internal conversion, intersystem
44 crossing) transforms electronic energy into vibrational energy allowing isomerization
45 barriers to be overcome, leading to changes in molecular geometry and collision cross
46 section. Alternatively, for some molecules photoisomerization can be initiated through
47 dynamics on the excited state potential energy surface (PES), proceeding through a conical
48 intersection to the isomer region of the ground state PES.¹⁵

49 Significantly, by measuring the photo-isomer yield as a function of laser wavelength
50 one can derive an action spectrum that represents the molecule's absorption spectrum
51 $A(\lambda)$ convoluted with a wavelength-dependent isomerization yield $\phi(\lambda)$. If $\phi(\lambda)$ is
52 independent of λ , the photoisomerization action spectrum mimics the absorption spec-
53 trum. This form of photoisomerization action (PISA) spectroscopy complements exist-
54 ing spectroscopic techniques for probing molecular ions, including resonance enhanced
55 photodissociation,¹⁶⁻¹⁸ zero kinetic energy (ZEKE) photoelectron spectroscopy,¹⁹ mass
56 analysed threshold ionisation (MATI) spectroscopy,²⁰ and laser induced fluorescence
57 (LIF).²¹ The approach described in this paper differs from previous methods because the
58 detectable "action" is a change in ion drift speed, rather than photodissociation, photo-
59 electron ejection, or photon emission. An important advantage of our machine is that it is
60 possible to measure PISA spectra for mobility-selected isomers. Previously isomer specific
61 spectra for molecular ions have been measured using IR-UV double resonance REPD, or
62 by REPD with preselection of the ions using field asymmetric ion mobility spectrometry
63 (FAIMS).²²

64 The new IMMS machine has been employed to investigate photoisomerization of
65 molecules containing conjugated carbon chains including carbocyanine dyes HITC⁺ and
66 DTC⁺,^{23,24} and the retinal protonated Schiff base.²⁵ The apparatus has also been used to
67 structurally characterise charged fragments from retinal protonated Schiff base, helping to
68 unravel the photodissociation mechanism.²⁶ In this paper we provide a comprehensive de-
69 scription of the apparatus, illustrating its capacity to characterize photoisomerization and
70 photofragmentation processes using the positively charged carbocyanine dye molecules
71 DTC⁺ and DCY4⁺ as examples.

72 II. BACKGROUND

73 In its simplest form, ion mobility mass spectrometry involves injecting a packet of ions
74 into a drift cell filled with buffer gas where they are subject to an electric field. For low
75 electric fields the ions' drift velocity v_d is proportional to the electric field E and is given
76 by,²⁷

$$v_d = K \times E \quad (1)$$

77 where K is the ion mobility. The mobility is in turn related to the collision integral,
78 $\Omega^{(1,1)}(T)$, through the Mason-Schamp equation,^{27,28}

$$K = \frac{3ze}{16N} \left(\frac{2\pi}{\mu k_B T} \right)^{1/2} \frac{1}{\Omega^{(1,1)}(T)}. \quad (2)$$

79 In Eqn. 2, z is the number of elementary charges on the ion, e is the electronic charge,
80 N is the number density of buffer gas molecules, k_B is the Boltzmann constant, and
81 $\mu = Mm/(M + m)$ is the reduced mass (m and M are the masses of the drifting ion and
82 buffer gas molecule, respectively). The collision integral, $\Omega^{(1,1)}(T)$, which for hard spheres
83 is the collision cross section, is related to the deflection angle of the collision partners
84 averaged over impact parameter, collision orientation and velocity. Because $\Omega^{(1,1)}(T)$
85 depends on the intermolecular potential energy surface (PES) describing the interaction of
86 the molecular ion and the buffer gas atom, it is sensitive to the molecular conformation
87 and therefore changes following photoisomerization.

88 The drift region is normally operated in the low field regime such that the mobility is
89 independent of field strength and the field-induced collision energy is much less than the
90 thermal energy. The regime is defined by the relationship,²⁷

$$\frac{Mv_d^2}{3kT} \ll 1 \quad (3)$$

92 Under these conditions the effective temperature of the drifting ions is close to that of the
93 buffer gas (300 K). The collision rate for the molecular ions drifting in He or N₂ at 10 Torr,
94 estimated from the Langevin rate, is $\approx 3 \times 10^8 \text{ s}^{-1}$.

95 To establish contact between the measured ion mobility (K) and the molecular structure,
96 the mobility is normally predicted using the MOBICAL program developed by Jarrold
97 and coworkers.²⁹⁻³¹ Three methods are commonly used. First, the simple projection
98 approximation (PA) assumes hard sphere collisions and averages the projected cross

99 section over collision orientations. Second, the exact hard sphere scattering (EHSS) method
 100 is similar to the PA method but accounts for multiple scattering collisions, important for
 101 molecules with convexities. Third, the trajectory method (TM) uses classical trajectory
 102 simulations to determine the average momentum transfer occurring from interactions
 103 between the molecular ion and a neutral gas molecule, with the intermolecular interaction
 104 represented as the sum of atom-atom Lennard-Jones interaction terms supplemented by
 105 charge-induced dipole induction terms. The necessary isomer geometries for the mobility
 106 calculations are obtained using *ab initio* or density functional theory (DFT) calculations.

107 III. INSTRUMENT CONSTRUCTION

108 A. Overview

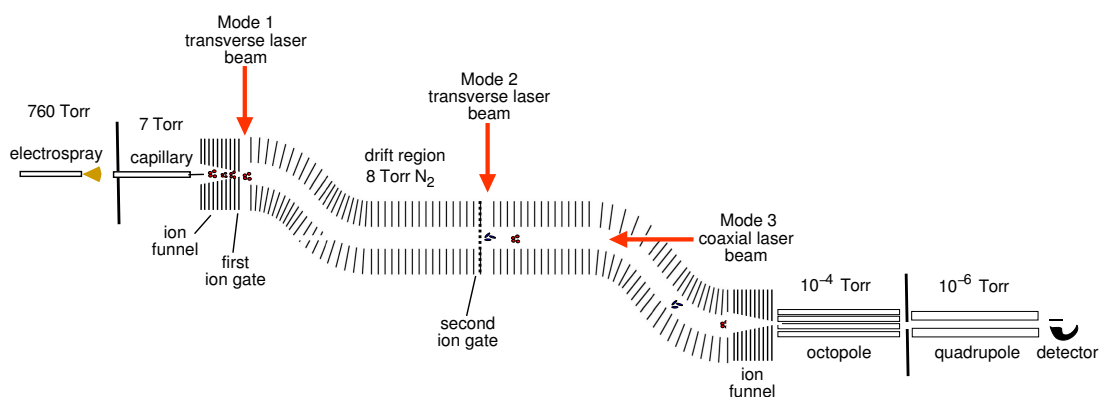


FIG. 1. Schematic view of the ion mobility mass spectrometer. Ions from an electrospray ion source pass through a heated desolvation capillary, and into an ion funnel (IF1). Ions are injected from IF1 through an ion gate into the drift region filled with N_2 gas ($P \approx 8$ torr) and subjected to an electric field of ≈ 40 V/cm. After passing through the drift tube, ions are collected by a second ion funnel, travel through an octopole ion guide, are mass selected by a quadrupole mass filter, and sensed by an ion detector. Ions can be irradiated by a transverse laser beam after the first ion gate (**Mode 1**), by a transverse laser beam halfway along the drift region after the second ion gate (**Mode 2**), or coaxially in the middle section of the drift region (**Mode 3**).

109 The machine is essentially a conventional ion mobility spectrometer with provision
 110 for a laser beam to overlap the drifting ions coaxially or transversely. As shown in Fig. 1,
 111 electrosprayed ions pass through a heated transfer capillary and accumulate in the first

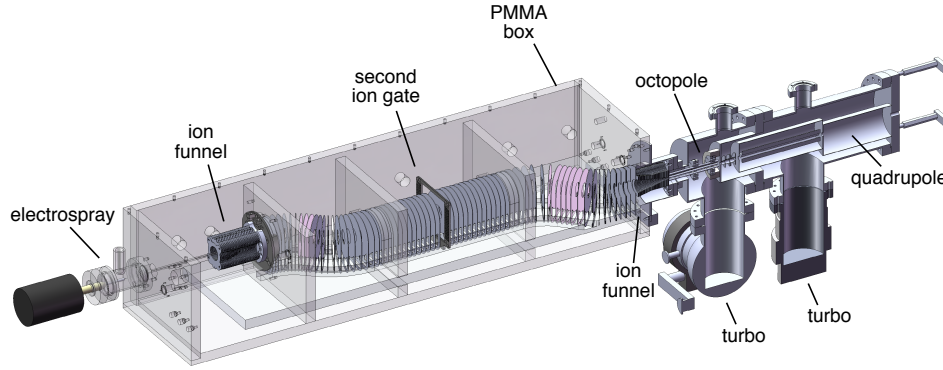


FIG. 2. A section of the IMMS apparatus, showing electro spray ion source, first ion funnel, second ion gate, second ion funnel, octopole ion guide, quadrupole mass filter.

112 ion funnel. An electrostatic ion gate periodically injects ion bunches into the drift section
 113 filled with low pressure N_2 or He gas ($P=5-15$ Torr) where the ions are subjected to a drift
 114 field of ≈ 40 V/cm. Following the drift region the ions are collected by a second ion funnel,
 115 before passing through a small orifice, an octopole ion guide, quadrupole mass filter, and
 116 finally being sensed by an ion detector. The ions can either be irradiated by a transverse
 117 laser beam immediately after the first ion gate or halfway through the drift region after a
 118 second ion gate (used to mobility-select bunches of ions), or coaxially in the middle section
 119 of the drift region. These different excitation modes are described below (Section III I).
 120 Irrespective of where photoexcitation occurs, a photo-induced change in ion conformation
 121 and drift mobility results in spatial and temporal separation of the photo-isomer ions from
 122 the parent ions over the remaining section of the drift region.

123 B. Housing

124 The first ion funnel, drift region and second ion funnel are contained in a purpose-
 125 built poly(methyl methacrylate) (PMMA) box, with internal dimensions $l = 1130$ mm,
 126 $w = 350$ mm, $h = 220$ mm (wall thickness 25 mm) and a removable lid sealed by an O-ring.
 127 Three interior PMMA baffles support the box, reducing mechanical deformation when it
 128 is pumped down to normal operating pressure (5-15 Torr). The octopole ion guide and
 129 quadrupole mass filter are housed in a tubular stainless steel chamber (150 mm diameter)
 130 divided into two differentially pumped chambers, and which has ports for connecting

131 turbo molecular pumps, electrical feedthroughs, and vacuum gauges.

132 C. Gas Flow and Pumping

133 The drift region is pumped by a 28 m³/hr dual-vane rotary pump (Edwards E2M28),
134 connected via a foreline trap to the source side of the first ion funnel. Buffer gas (either He
135 or N₂) is supplied to the chamber towards the exit end via a mass flow controller (Sevenstar
136 D08-1F). The flow rate is normally 0.2 SLM. This results in a counterflow of buffer gas back
137 through the first ion funnel, preventing neutral molecules (particularly solvent vapour
138 from the electrospray) entering the drift region. The pressure in the drift chamber is
139 controlled by a combination of adjusting the buffer gas flow rate and choking the outlet
140 flow with a valve. The octopole chamber is pumped by a 330 L/s turbo molecular pump
141 and typically has a pressure of 10⁻³ Torr, while the quadrupole chamber is evacuated by a
142 230 L/s turbo molecular pump and has an operational pressure of $\leq 4 \times 10^{-6}$ Torr.

143 D. Electrospray Ion Source

144 The ion source is a homebuilt electrospray unit. Typically, the analyte is dissolved
145 in either acetonitrile or 50:50 methanol:water and delivered at 5-20 μ L/min using a sy-
146 ringe pump to a stainless steel capillary. The capillary tip is positioned 3-6 mm from the
147 desolvation capillary entrance, and at a potential of 3-5 kV relative to the desolvation
148 capillary. The electrospray assembly is contained in a glass tube (50 mm diameter), filled
149 with flowing N₂ gas at atmospheric pressure. The ions enter a stainless steel desolvation
150 capillary (ID 0.8 mm) sealed within a glass tube that passes into the PMMA box through
151 a 1/4" Cajon fitting. Inside the PMMA box, the desolvation capillary is wrapped with
152 nichrome wire carrying AC current from a step-down isolation transformer, heating it to
153 150-250 C.

154 E. First Ion Funnel

155 After emerging from the transfer capillary, the ions enter an ion funnel, based on the
156 design of Smith and coworkers,³² consisting of 50 nickel-plated brass electrodes, each 1mm
157 thick and separated by 1mm thick PTFE washers. Each electrode has a circular opening,

158 the first 10 of which are 34 mm diameter. Thereafter, the diameter decreases linearly to
159 3 mm. The first and last electrodes have only DC potentials applied to them, whereas
160 the potentials of the intervening electrodes are a superposition of a radio frequency (RF)
161 potential, with opposite phases applied to alternating electrodes, and a DC potential that is
162 set by a voltage divider along the length. The RF field confines the ions radially as they are
163 driven through the funnel by the DC potential gradient. The RF potential for the funnel
164 ($f=500$ kHz) is generated by a dedicated power supply the output of which is capacitively
165 coupled to the ion funnel and is capable of supplying up to $720 V_{pp}$ (although electrical
166 breakdown of the gas typically occurs at much lower amplitudes). The DC potentials to
167 the electrodes are set by a resistive voltage divider, with the total potential drop across
168 the funnel normally being 180 V. The aperture of the final electrode of the ion funnel is
169 covered by fine Ni mesh, and can be switched by up to 65 V with respect to the adjacent
170 electrodes. This allows it to act as an ion gate; ions accumulate in the funnel when the gate
171 potential is high, and are released when the potential is dropped. The gate is normally
172 triggered at 20 Hz with an opening time of 50-500 μs .

173 F. Drift Region

174 The electric field in the drift region is sustained by 82 stainless steel electrodes (1 mm
175 thick, laser cut) with 34 mm apertures. These electrodes are mounted into slots in a
176 PMMA bed, which, if necessary, can be removed from the main PMMA housing. The drift
177 electrodes are arranged so that a 38.5 cm long straight section is preceded and followed
178 by two S-bends (see Figs. 1 &2). Appropriately positioned holes (9 mm diameter) cut
179 into the S-bend electrodes allow a laser beam to coaxially overlap ions travelling through
180 the straight section of the drift tube. The first 5 electrodes (immediately following the
181 ion funnel) have 5 mm diameter openings and are separated by 5 mm. The remaining
182 electrodes have 34 mm openings, and are 12 mm apart. The electrodes are connected in
183 series by 1 M Ω resistors to make a voltage divider such that the electrode potentials are
184 provided by a single high voltage power supply.

185 Halfway along the drift region is a second ion gate that can be opened briefly to select
186 a packet of isomers that have separated from other isomers in the first part of the drift
187 region. The gate, based on the design of Bradbury and Nielsen,³³ consists of two 0.1 mm

188 Nichrome wires loomed on a 3D-printed RGD840 polymer former, such that in the central
189 region the wires alternate and are spaced by 0.6 mm. To block ions the potential of one
190 wire is raised by 18 V with respect to the other, whereas to pass ions the wires are set to
191 the same potential.

192 A crucial feature of the instrument is provision for a tunable laser beam to overlap the
193 ion bunch, modifying their isomeric form, and hence alter their drift mobilities. Provision
194 has been made for both coaxial and transverse excitation of the drifting ions. The machine
195 was designed so that the drifting ions could be overlapped coaxially with the output beam
196 of a continuous laser, necessitating introduction of two S-bend sections into the drift region
197 (see Fig. 1). Although curved drift sections have been employed in other ion mobility
198 spectrometers,³⁴ they have normally been followed by an ion funnel to regather the ions
199 to the centre of the drift tube. Modelling of the S-bend sections using ion optics simulation
200 software (SIMION 3D v8.0.5) and a statistical diffusion simulation program,^{35,36} shows
201 that as the ion bunch moves around the first curve, ions on the inside move ahead of ions
202 on the outside, due to the shorter path length and higher electric field (see Figure 3). This
203 longitudinal spreading is countered in the second part of the curve where ions with a
204 shorter path in the first curve have a longer path and vice versa, although because the ion
205 packet has spread radially there is some overcompensation.

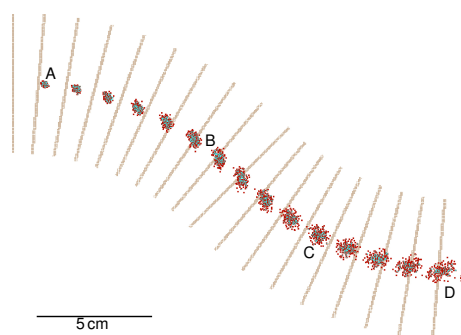


FIG. 3. Simulation of 200 Da ions drifting through 15 Torr of N₂ propelled by an electric field that is 50 V/cm along the centreline. Ion packet snapshots are shown for 400 μ s time intervals. The initial spherical ion packet (A) is distorted as it traverses the first bend with ions on the inside moving ahead of ions on the outside (B). The deformation is corrected in the second bend (C), although the ion packet still ends up being slightly distorted (D). Simulation details are given in the text.

206 **G. Second Ion Funnel**

207 The drift region ends with a second ion funnel, consisting of 40 electrodes with the
208 aperture diameter decreasing linearly, from 34 mm to 3 mm, which operates with an RF
209 drive frequency of 500 kHz. The funnel is followed by a 1 mm thick stainless steel plate
210 with a 0.35 mm orifice leading into a differentially pumped section containing an octopole
211 ion guide, which confines the ions radially, while allowing neutral gas to be evacuated. The
212 ions then pass through another orifice (3 mm diameter) into a final chamber, containing a
213 lens stack that focuses the ions into the quadrupole mass filter (Extrel C50, 19 mm rods,
214 $f=1.2$ MHz).

215 **H. Ion Detection, Signal Processing and Equipment Control**

216 The ions are detected by an electron multiplier (Photonis Channeltron 4870E) oper-
217 ating in single ion counting mode. The output of the detector is sent to a pulse am-
218 plifier/discriminator (MIT Inc. Model F-100T), the TTL output of which is passed to a
219 multichannel scaler (FAST ComTec P7882, bin width 10 μ s) that logs each pulse in one
220 of two histograms (one for laser-on arrivals and the other for laser-off arrivals), to pro-
221 gressively collect laser-on and laser-off arrival time distributions (ATDs); the difference
222 between the two ATDs reflects the change resulting from exposing the ions to laser light.
223 Synchronization of the two ion gates and the pulsed laser is accomplished using digital
224 delay generators (Stanford Research Systems Model DG535 and Berkerley Nucleonics
225 Corporation Model 575). The instrument is controlled by a Labview (National Instruments)
226 Virtual Instrument (VI), that sets the quadrupole mass filter and OPO wavelength, and
227 reads the arrival time distribution data from the multichannel scaler.

228 **I. Photoexcitation**

229 The light source for most investigations has been a pulsed optical parametric oscillator
230 with a scan range of 220-2500 nm (5 cm^{-1} bandwidth, 5 ns pulse width).²³⁻²⁵ Normally,
231 ions are injected into the drift region at 20 Hz with the laser fired at 10 Hz so that laser-on
232 and laser-off ATDs are recorded. The photo-signal corresponds to the difference between
233 laser-on and laser-off ATDs. Photoisomerization has also been accomplished using the

234 output of a quasi-continuous Titanium:Sapphire laser with mechanical chopping of the
235 light beam to record laser-on and laser-off ATDs and discern the laser-induced signal.²³

236 As shown in Figure 1, the drifting ions can either be excited at the beginning of the
237 drift region (Mode 1), after a second ion gate halfway along the drift region (Mode 2), or
238 coaxially in the central part of the drift region (Mode 3). The three excitation modes are
239 described in more detail below.

240 **Mode 1:**

241 Ions are irradiated 30-40 mm after the first ion gate by a transverse burst of light from a
242 pulsed laser. Parent, photo-isomer and photofragment ions are spatially and temporally
243 separated after passage through the drift tube. The advantage of this operational mode is
244 that the entire ion packet, which at this stage has a diameter of ≈ 3 mm, can be irradiated
245 with a relatively intense laser beam before appreciable diffusional spreading. A drawback
246 is that one measures the net effect of laser excitation. For example, if the ion packet
247 contains 2 isomers (I_1 and I_2), then the laser beam potentially causes $I_1 \rightarrow I_2$ and $I_2 \rightarrow I_1$
248 photoisomerizations with the I_1 and I_2 photo-isomer ions arriving at practically the same
249 time as ions produced directly by the ion source. Therefore, any photo-isomerization
250 signal is observed against a background.

251 **Mode 2:**

252 Packets of ions are irradiated halfway along the drift region after being mobility-selected
253 by the second ion gate. For this mode, the second ion gate is opened for $\approx 100 \mu\text{s}$ at an
254 appropriate delay after opening the first gate to transmit a packet of the desired target
255 ions. A short time later a transverse laser pulse intercepts the selected ions ≈ 15 mm
256 downstream from the ion gate. Mode 2 has the considerable advantage that a packet of
257 mobility-selected isomers is excited with spatial and temporal separation of the photo-
258 isomers over the remainder of the drift region. Consequently, the photo-isomer signal
259 can often be observed against a zero background. Normally, the laser beam is expanded
260 to have a relatively large cross section ($\approx 4 \text{ mm} \times 10 \text{ mm}$) to ensure that the entire ion
261 packet is exposed to light. This IMS-photoexcitation-IMS-MS arrangement is analogous
262 to the IMS-collision-IMS-MS approach of Clemmer and co-workers, where ions selected
263 by the first IMS stage are subjected to a collisional excitation in a region with enhanced
264 electric field strength with separation of the collisionally produced isomers in a second
265 IMS stage.¹²

266 **Mode 3:**

267 The ions are irradiated coaxially in the straight section of the drift region by the beam from
268 a pulsed or continuous laser passing through holes cut into the S-bend drift electrodes.
269 This excitation mode was employed in our original investigations of the carbocyanine
270 dye HITC,²³ using light from a continuous Ti-Sapphire laser ($\lambda=740\text{-}860\text{ nm}$, intensity
271 $\sim 1\text{ W/cm}^2$) chopped with a mechanical shutter to record laser-on and laser-off arrival
272 time distributions (ATDs). Mode 3 is potentially useful for molecular ions that are optically
273 pumped from the ground state to an excited state, and which rapidly relax to the ground
274 state. Under these circumstances, laser excitation can potentially be used to establish a
275 light-driven equilibrium between the ground and excited states, which, assuming the
276 ground and excited state ions have different drift mobilities, should induce a change in
277 the ions' arrival time distribution.

278 Although, our photoisomerization studies have mainly employed Mode 1 or Mode
279 3,²³⁻²⁶ as explained below in Section IV B there are significant advantages in using Mode 2,
280 with preselection of the target isomers based on their mobilities. Future studies are likely
281 to use this approach.

282 One disadvantage of the current IMMS machine is that laser light with wavelengths
283 shorter than 310 nm tends to produce background ions in the drift tube region, presumably
284 through multiphoton ionization of organic contaminants. Background ionisation is not a
285 problem for light with $\lambda \geq 310\text{ nm}$.

286 **IV. INSTRUMENT PERFORMANCE**

287 In the following section we summarise the performance of the IMMS instrument and
288 present examples of its use to characterise the photoisomerization and photodissociation
289 of molecular ions.

290 **A. IMMS Performance**

291 With the first and second ion gates fully open, the ion count rate for electrosprayed
292 tetrabutylammonium (TBA) cations ($m/z=242\text{ Da}$) is $\approx 10^6\text{ s}^{-1}$, dropping to $5 \times 10^3\text{ s}^{-1}$ if
293 the first ion gate is pulsed at 20 Hz with 100 μs opening time (with the second ion gate

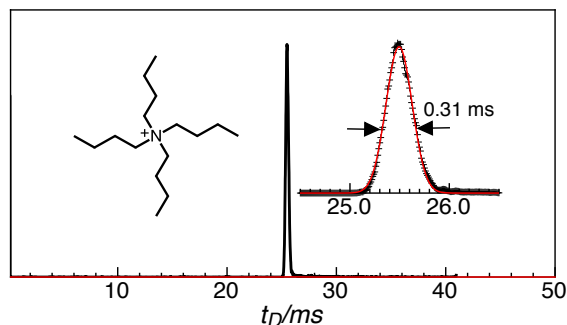


FIG. 4. Arrival time distribution (ATD) for electro sprayed TBA ions propelled through 10.8 Torr of N_2 gas. Inset is an expanded view of the peak fitted by a Gaussian function. The peak width corresponds to a mobility resolution of 82.

open). The instrument has an effective mass range of 100-440 amu with the lower limit determined by the 500 kHz drive frequency for the ion funnels, and upper limit by the quadrupole mass filter.

An important measure for an ion mobility spectrometer's performance is the resolving power, which for an ideal drift tube IMS instrument, R , is given by,²⁷

$$R = \frac{t_d}{\Delta t} = \left[\frac{16 kT \ln 2}{Vze} + \left(\frac{\Delta t_0}{t_d} \right)^2 \right]^{-1/2} \quad (4)$$

where, t_d is the drift time, Δt is the width of the detected pulse, V is the potential drop across the drift region, and Δt_0 is the temporal width of the ion packet at launch (presumed to have a Gaussian profile).²⁷ The first term in Eqn. 4 corresponds to diffusional spreading of the ion packet whereas the second term accounts for the finite temporal width of the injected ion pulse. The instrument's performance is illustrated in Fig. 4, which shows an arrival time distribution (ATD) for tetrabutylammonium cations with a potential drop of 4.57 kV across the drift region and a gate opening time of $100 \mu s$, demonstrating a mobility resolution of 82. This compares with a diffusion limited resolution of 101 predicted using Eqn. 4 and taking into account the ions' passage through the drift region and the second ion funnel (where the drift field is lower). The instrument routinely achieves a mobility resolution of 75-85 for singly charged ions. Employing the second electrostatic gate halfway along the drift region gives the machine an IMS-IMS capacity (Mode 2, see Fig. 1), with each stage having a mobility resolution of ≈ 50 for singly charged ions.

312 B. Photoisomerization of Molecular Ions

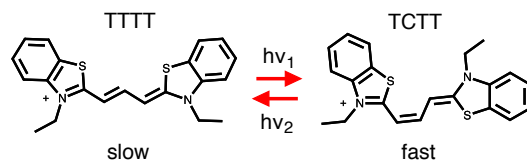


FIG. 5. Photoisomerization of DTC⁺ molecules.

313 The machine's capacity to probe photoisomerization of molecular ions is conveniently
314 illustrated for carbocyanine dyes, which consist of a polymethine chain terminated at
315 each end by an aromatic group (Fig. 5). Carbocyanines, which have been extensively
316 studied in solution,³⁷⁻⁴⁰ absorb light strongly in the visible region, with photo-excitation
317 causing *trans-cis* photoisomerization about one of the C-C bonds in the polymethine chain.
318 Specifically, we consider the carbocyanine molecule DTC⁺, comprising two aromatic
319 groups linked by a conjugated chain of 3 carbon atoms. Each of the C-C bonds can
320 have either a *trans* (T) or *cis* (C) conformation, giving 10 distinguishable isomers (TTTT,
321 CTTT, TCTT, CCTT, CTCT, CTTC, TCCT, CCCT, CTCC, CCCC). The ATD collected for an
322 electrosprayed DTC⁺ sample, with no laser radiation and with the second ion gate opened
323 to pass all ions [Fig. 6(a)], displays clear evidence for two isomers with arrival times of
324 $t_D=26.2$ and 25.6 ms. The two peaks can be assigned as the TTTT and TCTT isomers on
325 the basis of density functional theory (DFT) calculations and computed drift mobilities
326 (based classical trajectory calculations using the DFT equilibrium geometries).²⁴ The TTTT
327 and TCTT isomers lie lowest in energy (relative energies of 0 and 13.7 kJ/mol) and are
328 expected to dominate the drifting ion population, with the more compact TCTT isomer
329 having a 2.5% higher mobility than the extended TTTT isomer.²⁴

330 By opening the second ion gate for $100 \mu\text{s}$ at an appropriate delay with respect to the first
331 gate, either the TTTT or TCTT isomer can be selected [Figures 6(b) and (c)]. Photoexcitation
332 of the mobility-selected TTTT or TCTT isomers with a laser pulse ($\lambda=532$ nm, $I=1-2$
333 mJ/pulse/cm²) immediately after the second gate causes photoisomerization - TTTT
334 isomers are transformed to TCTT isomers and vice versa. In both cases, the depletion
335 of one isomer is balanced to within 1% by formation of the other isomer, proving that
336 photofragmentation and other loss mechanisms are negligible. The data presented in
337 Figure 6 show that by using the second ion gate one can cleanly separate and irradiate

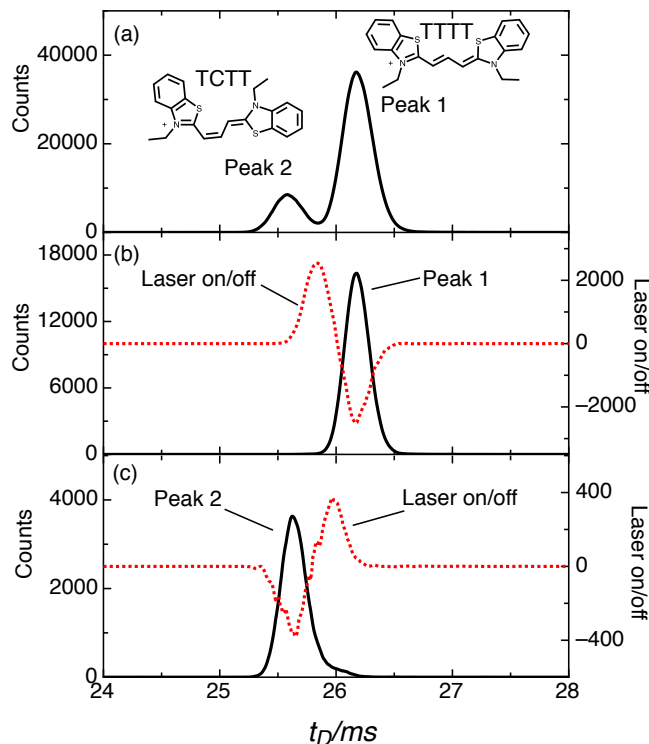


FIG. 6. (a) Laser-off ATD for DTC^+ with second ion gate open. The two peaks correspond to the TTTT and TCTT isomers. (b) ATD with second ion gate selecting TTTT DTC^+ (Peak 1). The red dotted trace shows the laser on-laser off signal at $\lambda=532$ nm, which causes TTTT \rightarrow TCTT isomerization. (c) ATD with second ion gate selecting TCTT DTC^+ (Peak 2). Radiation at 532 nm causes TCTT \rightarrow TTTT isomerization.

338 isomers whose collision cross sections differ by 2%.

339 Through measuring the photo-isomer signal as a function of the laser wavelength, it
 340 is possible to obtain a photoisomerization action (PISA) spectrum corresponding to the
 341 molecule's absorption spectrum $[A(\lambda)]$ convoluted with the photoisomerization yield
 342 $[\phi(\lambda)]$. As shown in Fig. 7(b), the PISA spectra for the two isomers are different; the
 343 spectrum for the TTTT isomer has a peak ≈ 10 nm to longer wavelength than that for
 344 the TCTT isomer. This is consistent with spectra for DTC^+ in methanol solution [Fig-
 345 ure 7(c)], where the absorption spectrum for all-*trans* DTC^+ has a peak 10 nm to longer
 346 wavelength than that of the photo-isomer. Also noteworthy is that the bands for DTC^+ in
 347 solution are shifted 25 nm to longer wavelength compared to the maxima of the gas-phase
 348 spectra. The similarity with the solution spectra suggests that the PISA spectra of the
 349 TTTT and TCTT isomers actually mimic their absorption spectra and that in this case the

350 isomerization yield $\phi(\lambda)$ is independent of wavelength. Previously, we have modelled
 351 the DTC^+ photoisomerization as a process in which the electronically excited molecules
 352 undergo internal conversion to the electronic ground state followed by isomerization, with
 353 stabilisation of the vibrationally energised isomers through collisional quenching by buffer
 354 gas molecules.²⁴ Under these circumstances, because the photon energy (200-260 kJ/mol)
 355 is much larger than the isomerization barriers (40-90 kJ/mol), one would expect that the
 356 isomerization yield should be almost independent of wavelength.

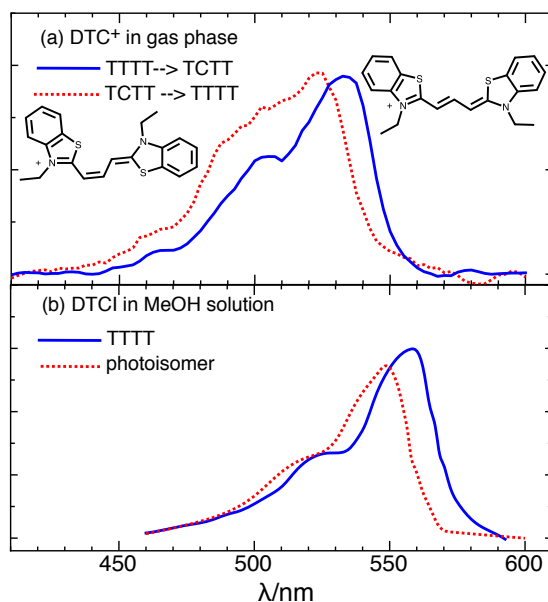


FIG. 7. (a) PISA spectra for isomers of DTC^+ , showing wavelength dependence for the $\text{TTTT} \rightarrow \text{TCTT}$ isomerization (solid blue curve) and $\text{TCTT} \rightarrow \text{TTTT}$ isomerization (dashed red curve). (b) Absorption spectra of all-*trans* DTC^+ and DTC^+ photoisomer in methanol solution.^{37,41}

357 C. Photodissociation of Molecular Ions

358 At higher laser intensities molecular ions in the drift region undergo resonance en-
 359 hanced photofragmentation so that the apparatus can also be used to measure photofrag-
 360 mentation action spectra. Although photodissociation studies of molecular ions are
 361 conveniently conducted using tandem mass spectrometers or ion traps, with many dif-
 362 ferent arrangements already described in the literature,^{16,18,22,42,43} the IMMS device has
 363 the advantage that structural information for the fragment ions can be derived from their

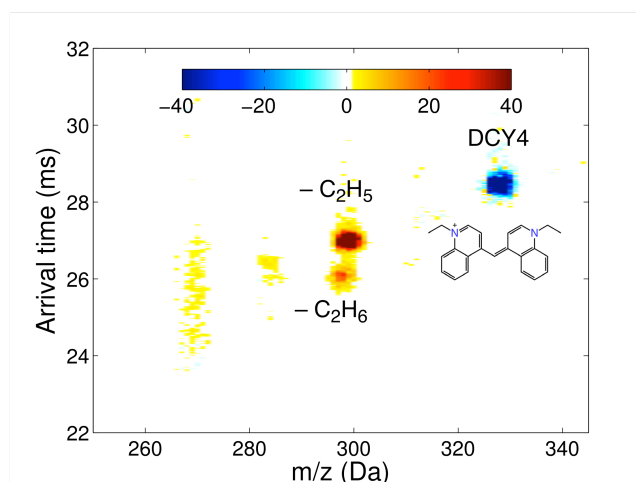


FIG. 8. Photofragment signal from DCY4⁺ as a function of mass and arrival time with OPO wavelength set to 570 nm. Laser induced depletion of the DCY4 ions at 328 Da is matched by enhancement of ions corresponding to loss of C₂H₅ and C₂H₆.

364 collision cross sections. We have exploited this feature to deduce that the $m/z=248$ Da
 365 photofragment from the retinal protonated Schiff base is the protonated Schiff base of
 366 β -ionone rather than a previously postulated bicyclic structure.^{26,44}

367 As an example of the IMMS machine's capacity for photodissociation spectroscopy,
 368 Fig. 8 plots the photo-signal for the polymethine dye 1,1'-diethyl-4,4'-cyanine (DCY4⁺) as
 369 a function of arrival time and mass, with the ions irradiated at the beginning of the drift
 370 tube (Mode 1) with light at a wavelength of 570 nm ($I \approx 10$ mJ/pulse/cm²). Depletion
 371 of the parent DCY4⁺ ions ($m/z=327$ Da, $t_d=28.3$ ms) is accompanied by production of
 372 fragments with masses of 298, 297, 267, 268, 269 Da, corresponding to loss of one or two
 373 ethyl radicals or ethane molecules from the terminal aromatic heterocycles. The lower
 374 panel of Fig. 9 shows the difference between the laser-off and laser-on ion signals as a
 375 function of arrival time and laser wavelength for DCY4⁺ and photofragments. Here, the
 376 second quadrupole is run in RF-only mode to transmit all ions. Photofragments arriving
 377 at 27 and 26 ms correspond to DCY4⁺ cations that have shed an ethyl radical or ethane
 378 molecule, respectively. The resonance enhanced photodissociation spectrum for DCY4⁺,
 379 obtained by plotting the photofragment yield as a function of wavelength, overlaps the
 380 absorption band of DCY4⁺ in aqueous solution (Fig. 9, upper panel), showing that in this
 381 case there is minimal shift in the absorption band caused by the solvent.

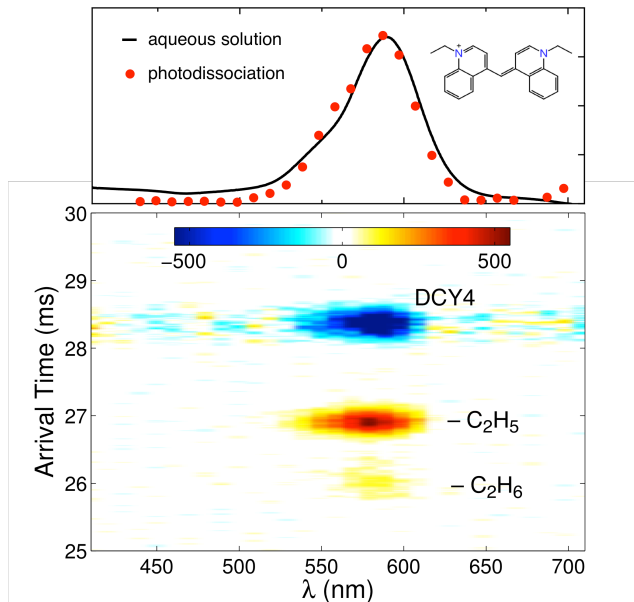


FIG. 9. Lower panel: Photofragment signal for DCY4^+ cations as a function of wavelength and arrival time. The quadrupole mass filter was operated in RF-only mode to transmit all ions. Upper panel: Resonance enhanced photodissociation action spectrum of DCY4^+ cations recorded by plotting the $-\text{C}_2\text{H}_5$ photofragment signal as a function of laser wavelength.

382 V. SUMMARY AND OUTLOOK

383 The IMMS apparatus provides a new means for investigating photoisomerization of
 384 molecular ions in the gas phase, with the advantages of isomer selection prior to the
 385 spectroscopy stage and identification of the product isomer(s). The apparatus can also be
 386 used for photodissociation studies, with the advantage that the charged product's can be
 387 identified from both its drift mobility and mass. Although most previous studies have
 388 involved photo-exciting molecular ions at the beginning of the drift tube (Mode 1),^{23–26}
 389 there are significant advantages in separating the target isomer before irradiation (Mode 2).
 390 There are numerous molecular ions suitable for the new approach, including systems that
 391 are important in biology (protein chromophores, retinal, carotenoids) or in light-activated
 392 devices (spiropyrans, diarylethenes, fulgides, azobenzenes). The main drawback of the
 393 approach for obtaining spectra of molecular ions is that it is only suitable for species that
 394 photoisomerize. Although this may seem like a severe restriction limiting the technique
 395 to larger molecules, in fact many small charged molecules have several isomeric forms.

396 For example, even a small molecular ion like $C_3H_3^+$ exists as both the cyclopropenyl and
397 propargyl cations which will have significantly different collision cross sections and which
398 may be interconvertible through photo excitation.

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