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Photodissociation of trapped ions

Robert C. Dunbar*

Chemistry Department, Case Western Reserve University, Cleveland, OH 44106, USA

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Abstract

The ion-trapping ion cyclotron resonance spectrometer, or Fourier transform mass spectrometer, provides a powerful and convenient environment for the study of photodissociation of gas-phase ions. This capability has been explored for about 30 years in a number of laboratories including our own. A variety of developments and applications, historical and current, are organized here under five broad headings: (1) optical spectroscopy of ions; (2) kinetics of the dissociation process; (3) dynamics of the dissociation process; (4) thermochemistry of dissociation; and (5) probing the structure and energy of the ions. (Int J Mass Spectrom 200 (2000) 571–589) © 2000 Elsevier Science B.V.

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1. Introduction

Much of the research of our group has centered around the study of photodissociation of gas-phase ions, which has led us to a remarkable variety of rich, often unexpected science. This is a fine occasion to survey from a personal perspective the spectroscopy, photophysics and photochemistry that this theme has given us keys to enter. Just about thirty years ago have passed since the first photodissociation of gas-phase ions trapped in the ion cyclotron resonance (ICR) cell, using the rudimentary light-source technology of a slide projector, with wavelength selection by coarse cutoff filters [1]. A few photodissociation studies in other types of mass spectrometers [2,3] preceded our application of the still-novel ICR instrument to this chemistry, and innumerable other instrumental approaches have followed. However, the particularly favorable combination of the ICR instrument's capabilities for unraveling ion chemistry, and its convenience for providing a trapped-ion photolysis target in an environment giving few or no collisions with neutrals, has led to enduring popularity of this approach and has led to a wide and varied range of experiments in ours and many other laboratories. Many of the ideas and methods are still powerful and timely, and are being applied in various laboratories to contemporary problems.

The present account is a personal perspective on the evolution and scope of trapped ion photodissociation methods and applications. It is not a history, nor a review. No attempt to be comprehensive or balanced in the presentation or the references is intended; for a more comprehensive survey, one may refer to a number of reviews, for instance [4–20].

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* Corresponding author. E-mail: rdc@po.cwru.edu

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2. Experimental aspects

The first photodissociation study of trapped ions was the investigation of H_2^+ in the low-pressure quadrupole ion trap [2], but it was the application of the ICR ion trap that opened up the field to study by chemists. Initial ICR studies used some technologies now considered old-fashioned, including marginal-oscillator ion detection, in situ ion production, electromagnets, and arc-lamp light sources, but Fourier-transform ICR ion detection, external ion sources, superconducting magnet instruments, and laser light sources were adopted as these technological advances matured, and are now commonly used.

Photodissociation studies tend to be experimentally straightforward. Ions are prepared by some means (electron impact ionization, photoionization, ion–molecule reactions, electrospray ionization, matrix-assisted laser desorption ionization, fast-atom bombardment ionization, etc.) and trapped in the ICR cell. Irradiation of the trapped ions by a light source leads to dissociation. The rate or extent of dissociation is detected using the ICR detection machinery by monitoring the decrease in parent ion signal, and/or the appearance of fragment-ion signals.

We will not describe the instrumental aspects in more detail. A large number of reviews of the ICR and Fourier transform ICR (FTICR) techniques are available, including several books [21–24]. As for other techniques, [12] gave a survey of other instruments then in use for photodissociation studies, including ion beams, drift tube mass spectrometers, and tandem quadrupoles. More recently, high-pressure quadrupole ion traps and reflectron time-of-flight instruments have proven very useful in various applications involving photodissociation.

3. The science

It seems useful to classify the scientific targets addressed by photodissociation experiments into five more or less distinct subjects, which will form a framework for this survey. (1) Optical spectroscopy of ions, (2) kinetics of the dissociation process, (3) dynamics of the dissociation process, (4) thermochemistry of dissociation, (5) probing the structure and energy of the ions.

4. Spectroscopy

Direct investigation of gas-phase ions by optical absorption spectroscopy remains a challenging endeavor, because typical experimental conditions offer only miniscule concentrations of the absorbing species. Only a few laboratories, working with a few small ionic species, have been able to make progress in this direct way. A highly fruitful way around this barrier is the indirect approach using photodissociation, which we have termed photodissociation spectroscopy (PDS). The principle is that an ion will dissociate only if it absorbs a photon, and at the same time (with various caveats) dissociation is the normal consequence of a photon absorption event. Thus a plot of photodissociation probability (or cross section) versus wavelength is a more or less faithful mirror of the optical absorption spectrum of the ion. Fig. 1 shows early, representative spectra of organic ions [25]. We termed this approach PDS, and it has found wide application in ours and other laboratories.

For two reasons, many of the contributions of PDS to spectroscopic knowledge have been concerned with radical ions (odd-electron ions). For one thing, even-electron ions, which are typically closed shell species, have sufficiently low reactivity that they can be and have been studied spectroscopically in solution, whereas radical ions tend to be disastrously reactive under solution conditions. For another thing, the optical spectroscopy of radical ions is more interesting: There is a rich spectroscopy of radical ions in the visible and near-ultraviolet regions, because the half-empty highest occupied molecular orbital is available for promotion of electrons from the lower-lying occupied molecular orbitals: such inner-orbital promotions are not available to closed shell ions, which are therefore less commonly colored in the visible spectral region. The observation of spectra of a variety of organic radical cations was thus a natural development when it became convenient to work with them in

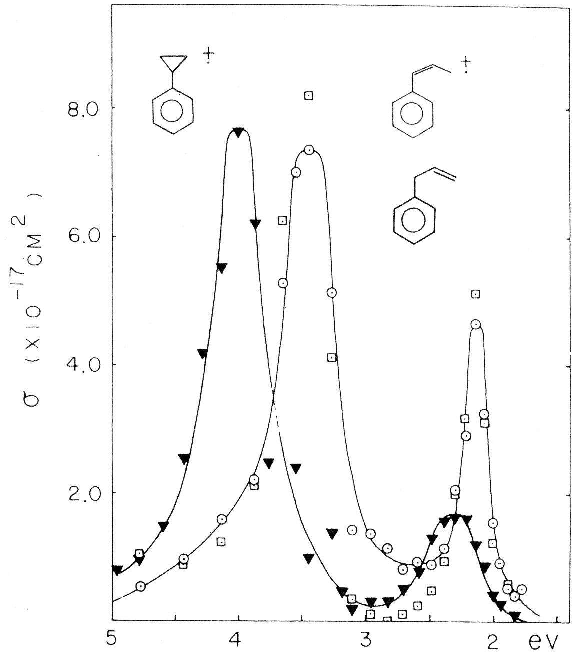

Fig. 1. Photodissociation spectra of three isomeric $C_9H_{12}^+$ ions (arc-lamp source with interference filter wavelength selection). The identical spectra from 1-phenylpropene (open square with dot) and 3-phenylpropene (open circle with dot) indicate rearrangement to a common structure upon ionization, whereas cyclopropyl benzene ion (closed inverted triangle) retains a distinct structure ([25]).

a vacuum environment. PDS in the ICR ion trap, where radical ions are easily generated, thermalized and trapped, provided a timely approach which turned out to be widely applicable and fruitful. Another sensible approach to obtaining spectra of highly reactive radical ions is to stabilize and characterize them at low temperatures in frozen glassy matrices [26,27], and in fact this spectroscopic approach flourished in the same period as the first gas-phase studies.

Many of the inner orbitals which give rise to spectroscopic peaks were actually identified by the technique of ultraviolet photoelectron spectroscopy (UVPES), which developed in the same era and provided a nice complement to the optical spectroscopic studies. The complementarity of these two approaches is illustrated in Fig. 2, which displays the PDS peak and the UVPES peak belonging to the same pi orbital of 2-methyl-1-penten-3-yne, showing that the peaks match up properly when plotted on appropriately matched energy scales [28].

The spectra shown in Fig. 3 illustrate a spectroscopic trick whose applicability to ionic systems was first pointed out by Freiser and Beauchamp [29]. In this illustration from our work [30], the PDS spectrum of a protonated unsaturated ketone (phorone) is compared with the UV absorption spectrum of the corresponding neutral, and is seen to exhibit a large red shift in this $\pi \rightarrow \pi^*$ transition. Analysis shows that this redshift gives an interesting quantity, the difference in proton affinities ΔPA^* between the molecule in its ground state and in its π^* excited electronic state. Since the ground state proton affinity is well known, this is thus a route to measuring the proton affinities of excited electronic states.

The spectroscopy of transition-metal-containing ions is another rich field for gas phase PDS, but in general observation and interpretation of these spectra has been slower to develop than organic systems. The group of the late Ben Freiser obtained spectra of many organometallic ions (see [31] for one example). They did not emphasize interpretation of the spectroscopic transitions, however, since their main interest was in locating thermochemical thresholds, as discussed in the following. In a promising new development, Posey's group reported the PDS observation and interpretation of well understood metal–ligand charge transfer transitions in gas-phase coordination complexes of transition metals, as for example in methanol-solvated tris(2,2′-bipyridyl)iron(II) [32].

4.1. Vibrational resolution

The spectra shown in Figs. 1 and 3 were taken at a rather low wavelength resolution, which shows the location and intensity of the electronic transitions nicely. Going to higher resolution should be able to resolve vibrational substructure (as is seen in Fig. 2). A striking confirmation of this hope was the tunable-laser spectrum shown in Fig. 4, for 1,3,5-hexatriene radical ion [33]. It does indeed show clearly resolved vibrational progressions, which can be assigned to two vibrational normal modes of the parent cation. There was initial optimism that spectra like this would

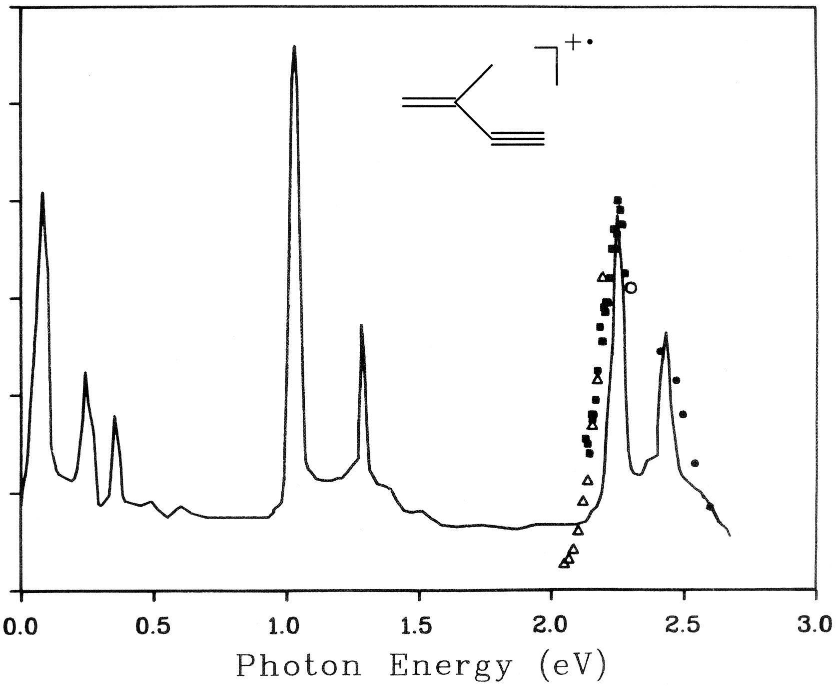

Fig. 2. Tunable dye laser photodissociation spectrum (points) of 2-methyl-1-penten-3-yne ion, and UVPES spectrum of the neutral ([28]).

open up a systematic way to characterize normal mode frequencies of a whole catalog of molecular ions; this hope was encouraged by the contemporary observation of PDS spectra of extraordinary vibra-

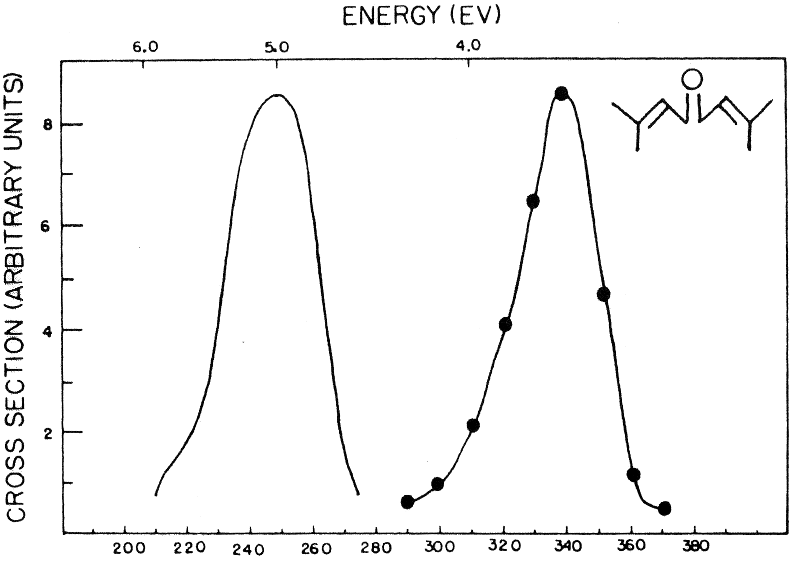

Fig. 3. Photodissociation spectrum of protonated phorone and UV absorption spectrum of the neutral ([30]).

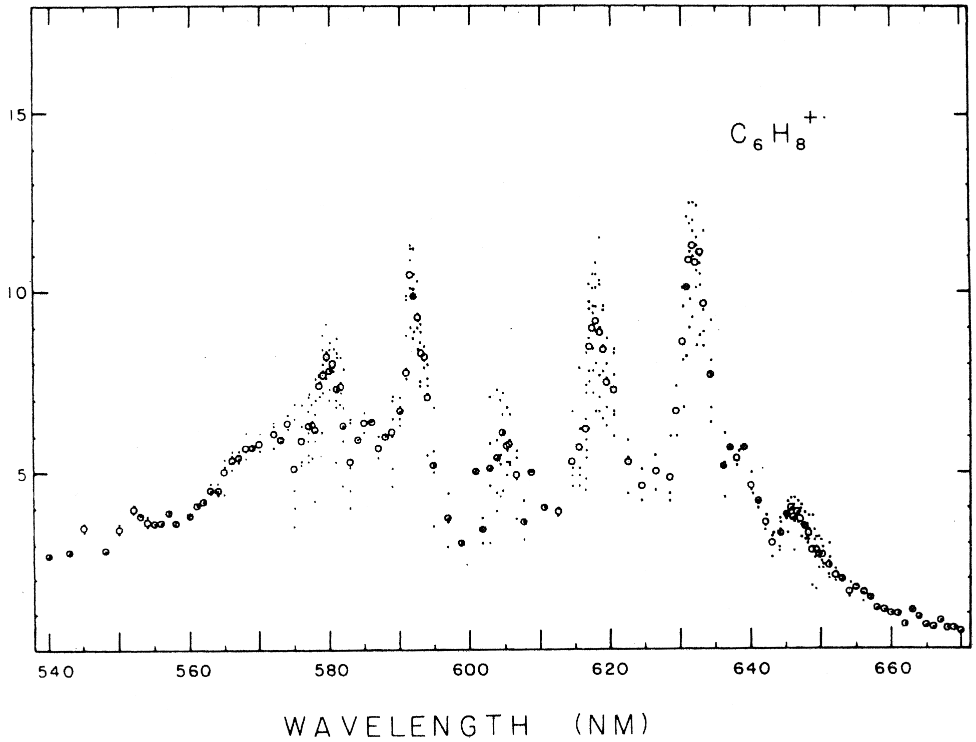

Fig. 4. Tunable dye laser photodissociation spectrum of 1,3,5-hexatriene ion (open circles represent means of grouped data points) ([33]).

tional/rotational resolution for small ions in beam-type mass spectrometer instruments (for example, CH_3I^+ [34], N_2O^+ [35], CO_3^- [36]). Our group achieved some further success in this respect, notably the spectra of isomeric chloropropene ions (discussed in the following) [37], as well as the enyne ion spectrum already shown in Fig. 2. However, it turned out to be uncommon for the PDS peaks to show such clear vibrational structure as Fig. 4, probably due to the spectral congestion typical of ions at room temperature. Referring back to Fig. 2, the comparison of the high-resolution PDS spectrum of 2-methyl-1-penten-3-yne ion with the corresponding UVPES vibrational structure showed the expected vibrational structure in the PDS spectrum, but with peak broadening by about a factor of 3 relative to the UVPES spectrum [28]. Some barely resolved structure was also found in the ferrocinium ion spectrum, but the interpretation was uncertain [38]. Most of the high-resolution vibrational characterization of radical ions has actually been achieved with either variations of UVPES [and its more recent relative zero electron kinetic energy (ZEKE) spectroscopy], or with low-temperature spectroscopy in solid matrices. In addition, some radical ions exhibit observable visible/UV fluorescence, and for many of these Maier's group in particular has obtained fluorescence or laser-induced fluorescence spectra of extremely high resolution using cooled ions [39].

4.2. Infrared spectroscopy

Photodissociation with a tunable infrared light source gives another spectroscopic attack on gas-phase ions. Multiphoton infrared dissociation (IRMPD) is commonly observable for trapped ions, and the wavelength dependence of the process gives a view of the infrared absorption spectrum of the ion in just the same way as the visible/UV PDS experiments discussed above. Limitations here have been technological, since broadband, continuously tunable IR lasers of sufficient intensity to bring about IRMPD have not been available. Most work has been done with the available wavelength regions of line-tunable CO_2 lasers. This gives tantalizing views of portions of the IR spectrum in the 900–1100 cm^{-1} region, but is far from being the equivalent of a conventional IR spectrometer. A number of illustrations of this approach have been reported over the years from various labs notably those of Eyler and co-workers [40,41] and Beauchamp and co-workers [7,42,43].

An intrinsic limitation of using IRMPD as an IR spectroscopic tool is that as the ion absorbs successive photons, its internal energy increases, and the wavelengths of the individual normal modes shift due to anharmonic couplings. This broadens the spectral feature corresponding to a particular vibration, and limits the spectroscopic usefulness of the approach. Some concepts to get past this problem use IR/visible [44–46] or IR/IR [47] two-laser dissociation schemes, in which one or a few IR photons are contributed by a low-power IR laser, whereas energy pumping up to the dissociation limit is achieved with a second laser of fixed wavelength. Since the tunable IR laser acts only on the un-excited initial state of the ion, the spectrum created by sweeping the IR wavelength is unaffected by IRMPD broadening, and should be able to give IR spectra of high resolution.

Another new approach of great promise uses a weakly attached rare gas (Ar) atom in a van der Waals complex with the molecular ion of interest. The Ar atom does not greatly perturb the vibrational spectroscopy, but is readily detached by an infrared photon, giving an ingenious way of doing one-photon IR spectroscopy on the ion. Meijer’s group has combined this trick with the use of a free-electron tunable IR laser source and a supersonic beam mass spectrometer to obtain IR spectroscopy of a growing set of interesting molecular cations, such as benzene [48] and naphthalene [49].

The emergence of novel experimental approaches like these, combined with the broadband tunability of synchrotron or free-electron-laser light sources, promises accelerating progress in the IR photodissociation spectroscopy of ions.

5. Dissociation kinetics

An enduring theme of physical chemistry, and notably of mass spectrometry, has been the development of understanding of the kinetics of unimolecular dissociation of an excited molecule. Trapped-ion photodissociation offers an avenue to this with some nice characteristics: (1) the trapped ions are thermalized, and thus have a very well characterized and fairly narrow distribution of internal energies. This is not quite as nice as experiments, like many using supersonic molecular beam expansion cooling techniques and/or state-selective laser selection approaches, where the target molecules have essentially zero or precisely fixed internal energy; but a well thermalized population of ions gives results which can often be thermally deconvoluted in data workup, and are just as good for many purposes. (2) Excitation of the target ions by photon impact gives the ions a precisely known increment of excitation energy, so that the dissociation kinetics correspond to ions of well known energy above the dissociation threshold energy. (3) The ion trap lets one extend the time scale for the dissociation event to arbitrarily long times, giving a kinetic window extending from $\sim 10^6\ s^{-1}$ out to rate constants in principle slower than $1\ s^{-1}$. (4) The marvelous ion production, manipulation and mass-resolved detection capabilities of the FTICR spectrometer open a great array of chemical species and unimolecular reactions to quantitative kinetic study.

The time-resolved photodissociation experiment [50], which we termed TRPD, is fundamentally simple. Following production, trapping and thermalization of the target ions, a laser pulse excites ions above the dissociation threshold. Following a variable delay time during which dissociation proceeds, the ICR detection sequence is initiated to sample the extent to which precursor ions have dissociated to fragments. It was recognized that the relatively slow nature of cyclotron resonance detection places a lower limit on the usable delay times, and thus sets an upper limit to the observable dissociation rate constant, but pushing the limits of the experiment allows dissociation rates up to the order of $10^6\ s^{-1}$ to be observed.

The accessibility of extraordinarily slow unimo-

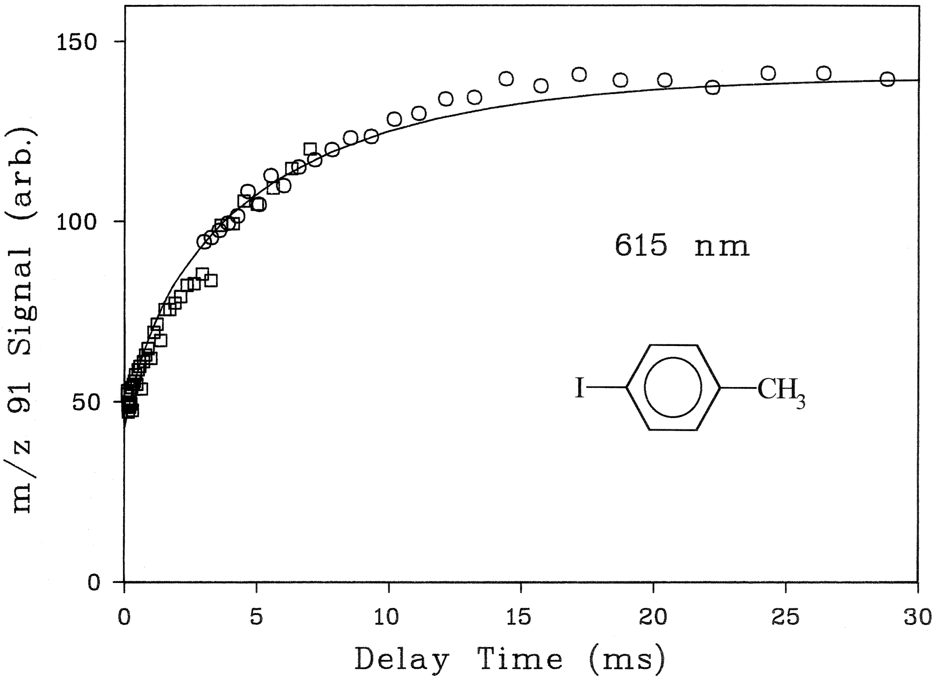

Fig. 5. TRPD spectrum of *p*-iodotoluene ion at 615 nm ([51]).

lecular processes to this technique has led to some of the most fascinating applications of this approach. A nice example is the dissociation of iodotoluene shown in Fig. 5, having a time scale of longer than 5 ms for breakup of the photoexcited ion [51]. Note that this means that after the target ion absorbs the excitation photon, the excess energy is stored in the isolated ion for 5 ms or more before the energy finds its way into the bond-breaking process. Direct observation of such slow dissociation events is difficult or impossible using other, nontrapping, approaches. This has allowed testing and confirmation of theories of unimolecular dissociation into previously little-explored slow regimes (see [4] for a review).

It might seem interesting to follow this intriguing direction to the ultimate limits of slow dissociation, in which the ions would dissociate minutes, perhaps days, following the excitation laser pulse. However, a physical limitation crops up [52], which is that any ion excited with internal energy greater than the temperature of its surroundings radiates away its internal energy as infrared photons on a time scale which is seldom as long as 1 s, and normally much shorter than this. So even under ideal ion trapping conditions where no collisions occur to disturb the photoexcited ion, it still makes no sense to look for unimolecular dissociations involving internal excitation energy storage times of many seconds or longer.

Going in the other direction toward observation of faster dissociation processes, the ICR detection process itself imposes a limit. In order to mass resolve the parent and fragment ions involved in the dissociation, the system must be observed for a time not less than a significant fraction of one cyclotron orbit, which sets a natural limit roughly of the order of 1 μs (depending on the magnetic field strength used and on the masses involved) on the shortest lifetime of the parent ion that can be time resolved by cyclotron detection. A study of styrene ion [53] pushed close to the limits of our instrument, as shown in Fig. 6. Here TRPD curves are displayed for three different internal energies: the fastest case, labeled 0.5 s, corresponded to a dissociation rate constant of about $3 \times 10^{-5}\ s^{-1}$. The different dissociation rates exhibited in Fig. 6 are

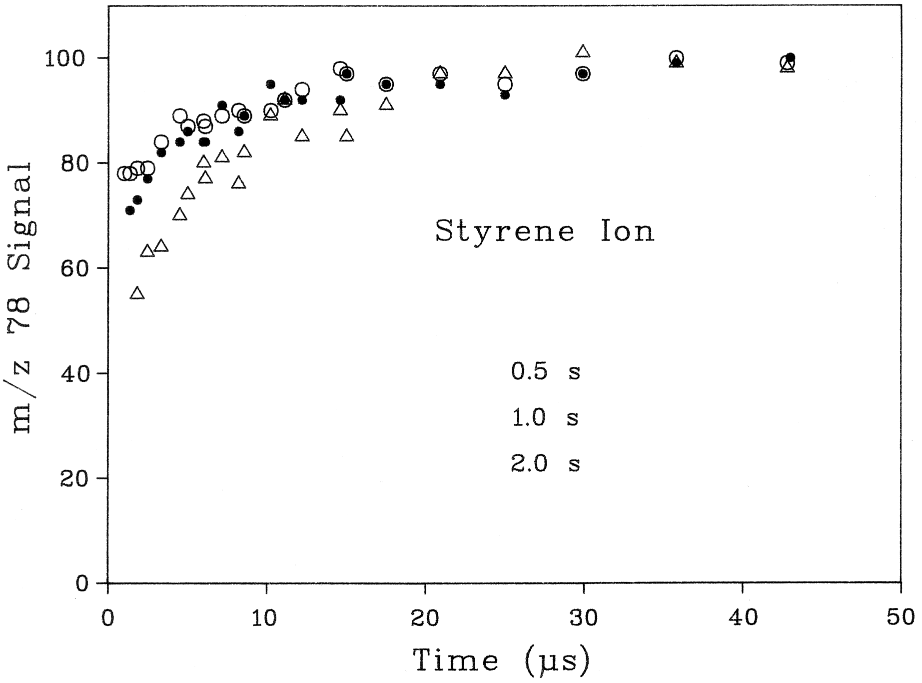

Fig. 6. TRPD spectra (*m/z* 78 photoappearance curves) of styrene ion at 308 nm. Three delay times after electron impact ionization are displayed, representing ions with three different levels of internal excitation prior to photon impact. The ions with the shortest cooling period before photon impact, 0.5 s (circle), evidently retain the largest amount of internal energy and exhibit the fastest dissociation rate, whereas the ions with the longest cooling period, 2.0 s (triangle), give the slowest dissociation rate ([53]).

a natural consequence of the fact that unimolecular dissociation normally has a rate constant that increases with increasing internal energy. In this study, the highly energetic ions were those recently ionized by the energetic electron beam. As the delay between the electron beam ionization and the photodissociation was lengthened, the ions cooled off, allowing us to measure dissociation rate constants for ion populations having several different average internal energies.

6. Dynamics of dissociation

The ion-trap photodissociation experiment has useful possibilities for determining the velocities and directions of the fragments. Fragment velocities can be determined in at least two experimental approaches, the trap-escape approach and the time-of-flight approach. The first relies on the fact that ion escape from the trap along the magnetic field direction (the *z* axis for our purposes) is prevented by the electrostatic trapping well, whose depth is well known. (Ions are prevented from escaping in the *x*/*y* directions by the magnetic field.) Thus if a cloud of ions in the center of the cell is photodissociated, the fragments will escape from the trap, and be lost to subsequent detection, only if their kinetic energy along the *z* direction exceeds the depth of the trapping well. A plot of fragment ion signal intensity as a function of voltage on the trapping plates, as in Fig. 7, can accordingly be analyzed to find the kinetic energy of the fragments [54,55]. This approach has been developed for ion–molecule reaction applications by various groups including those of Bowers and Rincon [56] and Marx [57]. It was applied by Freiser's group to particularly good effect in reactions of metal dications, where the kinetic energy releases can be

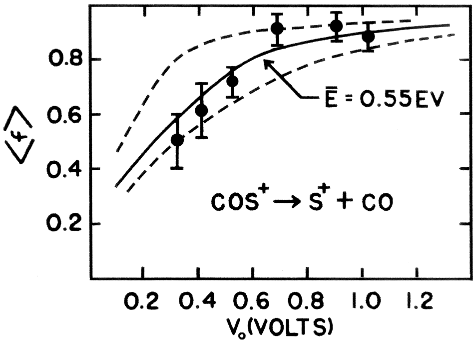

Fig. 7. Ion retention plot for S^+ from OCS^+ photodissociation at 310 nm as a function of voltage on the trapping plates. The $\langle f\rangle$ symbol represents the fraction of photodissociation fragment ions whose kinetic energy is insufficient to allow escape from the trap. The fitted value of kinetic energy release was 0.55 ± 0.2 eV ([55]).

large, and are mechanistically revealing (see [58], for example).

In the second approach, using time-of-flight ideas, the trapping well is set at a value large compared with the kinetic energy of the fragments, but the voltage on the trapping plates is dropped to zero at the moment of the excitation laser pulse. After a delay of typically tens of microseconds, the trap-plate voltage is switched back on, and all the fragment ions still remaining in the cell are trapped and subsequently detected. Thus those fragment ions are lost from the cell whose z velocity is large enough to escape from the cell during the delay interval between the laser pulse and the switching back on of the trapping voltage. This approach was demonstrated for iodotoluene dissociation [59], but it has been found to be difficult to use, and has not been popular.

Finding the direction of dissociation is a particularly pleasing capability of ICR-PD [54,55,60,61]. Of course photodissociation with ordinary light gives fragments which fly off isotropically in space, but if the light is linearly polarized, then the fragmentation may show a nonisotropic distribution with respect to the direction of polarization of the light. Observing this anisotropy in the ICR-PD experiment takes advantage of the fact that the magnetic field provides a preferred direction for ion loss from the cell (as we saw in the previous paragraphs). Assume that the fragments from the photodissociation always fly apart with velocity sufficient to surmount the trapping well and escape from the cell along the z direction. Assume also that the light polarization direction is along the magnetic field direction. Then if the dissociation process favors fragmentation along the polarization direction (parallel dissociation) fragments will be lost extensively from the cell; whereas, if the opposite case, where dissociation is perpendicular to the light polarization, the fragments will be mostly retained and subsequently detected. This works well in practice, as was first demonstrated for CH_3Cl^+ [54,60], and was subsequently applied to OCS^+ [55] and to at least one interesting larger-ion case, that of $Fe(CO)_4^-$ [62]. Fig. 8 shows the observed anisotropy for CH_3Cl^+, compared with the predictions for parallel and perpendicular polarization of the transition moment.

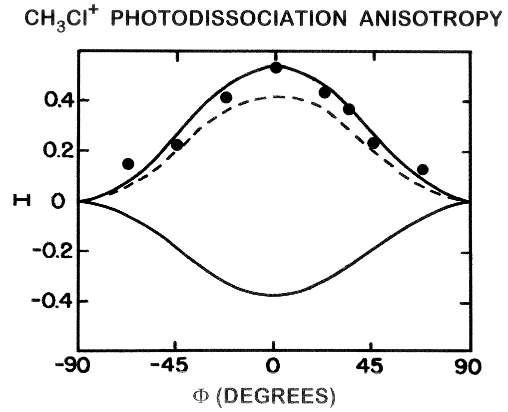

Fig. 8. Anisotropy parameter (labeled I in this work, although β would now be the conventional label) of the observed CH_3^+ photoproduct signal vs. polarization angle of the light at 366 nm. The solid lines represent ideal curves for parallel (upper curve) and perpendicular (lower curve) orientations of the transition moment. The dashed curve shows the reduction in predicted anisotropy when the anisotropy parameter is reduced from 2.0 (pure parallel) to 1.5 ([54]).

This technique is interesting for two reasons: first, determining the direction of dissociation tells us about the orientation in the ion of the electronic transition (or direction of the transition dipole moment) involved in the photon absorption. Second, if substantial anisotropy is observed for the photodissociation, as was true for CH_3Cl^+ [54,60] and for $Fe(CO_4)^-$ [62], but not for COS^+ [55], it shows that the dissociation process is fast compared with the time it takes for the ion to reorient (rotate) in space, which is of the order of picosec. In more recent times, ion-beam photodissociation instruments have been found (by the Bowers group in particular [63]) to allow convenient and precise observation of photodissociation anisotropies for many ions, and this approach has largely superseded trapped ion techniques for this purpose.

7. Dissociation thermochemistry

Finding the energies needed to break bonds in ionic molecules, i.e. bond strengths, is one of the central goals of physical mass spectrometry. It is natural to look to photodissociation approaches in doing this, since the highly precise energy input offered by photoexcitation gives a big step toward the needed control over energy conservation inherent in quantitative bond-strength determinations. Three strategies are common: (a) we can do a threshold measurement, looking to determine the smallest photon energy (longest wavelength) capable of dissociating the ion; (b) we can do a kinetic analysis by inserting a known photon energy into the molecule and analyzing the resulting rate of dissociation to find the corresponding bond strength; (c) finally, we can dissociate with thermal radiation and derive a thermal activation energy for dissociation.

7.1. Threshold methods

The most prolific and fruitful applications of this first approach have been those of the Freiser group to metal-containing ions. As an example, the long-wavelength cutoff of the spectrum shown in Fig. 9 was used to assign a bond strength of 65 kcal mol^{-1} to the V^+–C_6H_6 bond. Such transition metal systems are particularly favorable for avoiding one of the pitfalls of threshold determinations, which is the possibility that the ion does not happen to absorb photons in the threshold wavelength region. Freiser's group has argued [18] that the multiplicity of spectroscopic transitions in typical transition metal-containing ions makes it very likely that optical absorption will span the threshold wavelength and give a valid threshold observation.

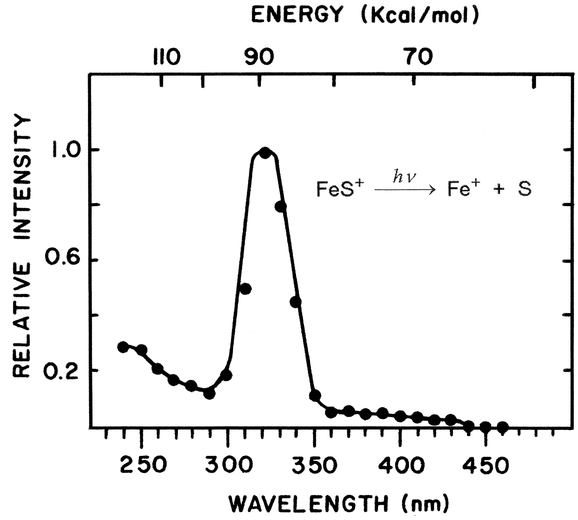

Fig. 9. Photodissociation spectrum from Freiser's group of $V(C_6H_6)^+$ showing the well defined threshold at 440 nm (65 kcal mol^{-1}) ([31]).

There are some other hazards with threshold PDS measurements. As with all threshold fragmentation techniques, a kinetic shift can shift the apparent threshold to higher energy, if the ion photoexcited in the near-threshold region does not have time to dissociate before it is detected or deactivated. This problem persists even at low pressure and long trapping times, since an "intrinsic kinetic shift" is always present due to deactivation of the metastable photoexcited parent ion by infrared photon emission. The analysis of TRPD kinetics results for methylnaphthalene ions illustrated this, showing a kinetic shift of 1–2 eV, depending on the detection method [64]. Kinetic shifts are particularly severe for large ions with high thresholds, and must ultimately be addressed by theoretically guided corrections or data fitting. This has not been done extensively in threshold photodissociation, but it has been developed to a high degree for the analogous threshold collision-induced dissociation experiment [65].

Further sources of error include the presence of thermal internal energy in the target ion, which shifts the threshold to lower energy; and the possibility of

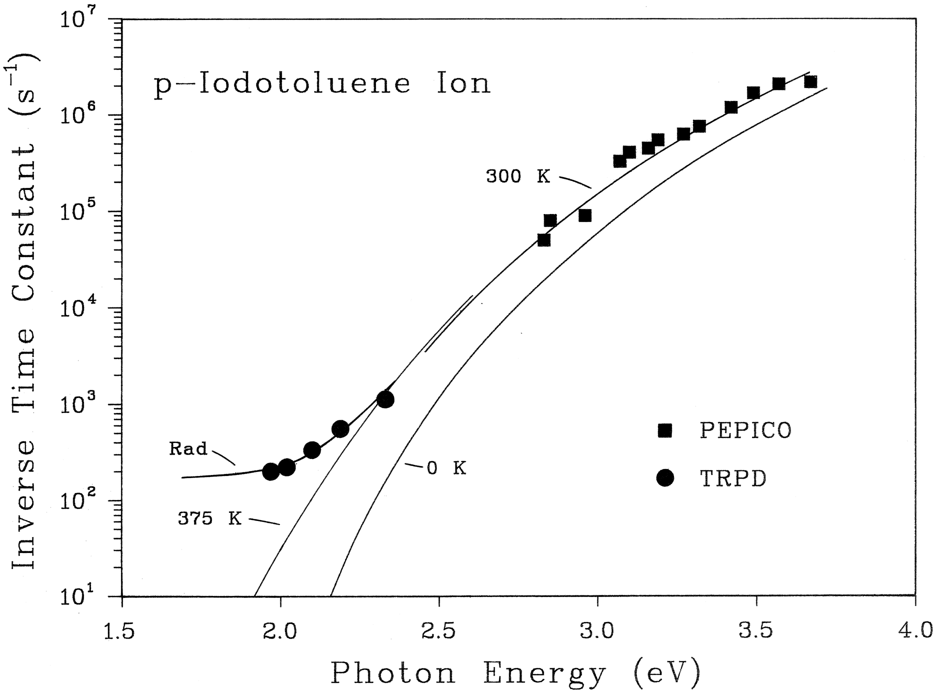

Fig. 10. Dissociation rate constants from TRPD and PEPICO for iodotoluene ion. The curve marked "300 K," which gives a good fit to the PEPICO points, is the predicted RRKM rate-energy curve assuming a dissociation energy of 1.9 eV, corrected for the 300 K thermal internal energy appropriate to the PEPICO experiment. The curve marked "375 K" is the corresponding predicted RRKM curve for a dissociation experiment at 375 K, which is the temperature appropriate to the TRPD experiment. The variant of the 375 K curve marked "rad" is further corrected for IR radiative relaxation of the slowly dissociating ions, giving a curve which fits the observed TRPD points. The curve marked "0 K" is the calculated RRKM rate-energy curve assuming zero thermal internal energy, which is displayed here to show the ideal dissociation kinetics undistorted by thermal energy and radiative relaxation effects ([51]).

absorption of two photons, again shifting the threshold to lower energy.

7.2. Kinetic determinations of dissociation energies

The theory of dissociation kinetics in energized molecules is highly developed, and abundantly supported by quantitative agreement with experiment in many systems. This is worked out in various approaches which can generally be termed statistical dissociation theories. Most common is transition state theory, which encompasses Rice-Ramsperger-Kassel-Marcus (RRKM) theory, variational transition state theory, and phase space theory. Other approaches such as statistical adiabatic channel theory are also receiving current attention. All of these approaches have in common the assumption that the internal excitation energy in the molecule (the photon energy in this case) flows randomly and statistically among internal degrees of freedom, notably vibrational degrees of freedom, of the dissociating molecule. For photodissociating ions that have been investigated this turns out to be a broadly valid assumption, because the photon energy, initially inserted in the form of electronic excitation, commonly degrades into vibrational excitation before anything else happens.

Having in hand the ability to predict dissociation kinetics with confidence, we can then observe the dissociation rate as a function of (known) photon energies, and deduce the binding energy which reproduces the observed kinetics. For example, Fig. 10 shows the kinetic characteristics of the iodotoluene ion dissociation [51], whose TRPD behavior was illustrated in Fig. 5. After making corrections to the

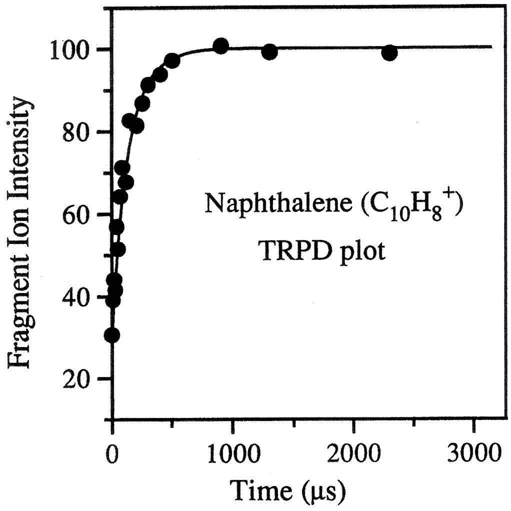

Fig. 11. Naphthalene ion two-photon TRPD plot at 355 nm ([66]).

dissociation rate for the competing relaxation by emission of infrared photons, the four low-energy TRPD points could be combined with the higher-energy photoelectron photoion coincidence (PEPICO) observations and fitted to the RRKM predicted curve, giving a very precise dissociation energy of 1.9 eV, as well as a transition-state entropy (at 1000 K) of −4 cal mol^{-1} K^{-1}. Another example [66], that of naphthalene ion, was interesting, because in this case the high threshold and large kinetic shift made it necessary to photoexcite the ions by absorption of two visible-laser photons to reach internal excitations near 7 eV. The TRPD spectrum shown in Fig. 11, along with a corresponding one for $C_{10}D_8^+$, could be fitted to yield energies for loss of H and C_2H_2 of 4.48 and 4.41 eV, respectively.

In the kinetics approach to thermochemistry, the observed kinetics of dissociation are fitted to theoretical predictions, with the dissociation thermochemical parameters being treated as adjustable. It is very desirable to have kinetic data over a very wide range of rates in order to get a well constrained fit. TRPD gives data points extending to very slow dissociation rates, and is thus uniquely valuable in combination with other techniques which characterize faster regions of the kinetics. This was illustrated above in Fig. 10, where the simultaneous use of TRPD and PEPICO data gave an excellent fit. Another example of this is shown in Fig. 12, where the TRPD results for benzene ion dissociation were combined with Neusser's dissociative resonance-enhanced multiphoton ionization results, to give a tightly constrained fit to a high-quality variational RRKM calculated curve [67].

7.3. Thermal dissociation by blackbody radiation

Thermal kinetics gives a powerful and traditional route to the determination of activation energies and thermochemistry for dissociation (as well as other reaction processes). The essential idea is that if the dissociating population of molecules can be established in thermal equilibrium at a known temperature T, and if T is sufficiently high so that the dissociation occurs at a measurable rate, then the activation energy E_a can be measured with high confidence from the temperature dependence of the observed rate constant,

$$E_a = -Rd(\ln k)/d(1/T) \qquad (1)$$

where R is the gas constant, and k is the rate constant. For barrierless processes, which includes many ionic dissociations, E_a is readily interpreted in terms of the enthalpy of dissociation.

Some work has been done toward making use of thermal dissociation kinetics in this sense in high-pressure mass spectrometer situations [68–72]. It is not necessarily easy to achieve the high-pressure limit at which thermal equilibrium is assured. The problem is that the exchange of energy with the surroundings must be very fast compared with rate at which energized molecules are leaving the population by dissociation; otherwise the high-energy tail of the Boltzmann population becomes depleted, and Eq. (1) loses its validity. This is the problem of reactive depletion, also known as the fall-off phenomenon in pressure-dependent unimolecular reaction kinetics.

Our understanding of this problem, and of ways to address it, evolved out of our work on the laser intensity dependence of low-power IR laser-induced multiphoton dissociation at near-zero pressure [73–75]. We realized that the laser could be considered as effectively equivalent to a thermal (blackbody) radi-

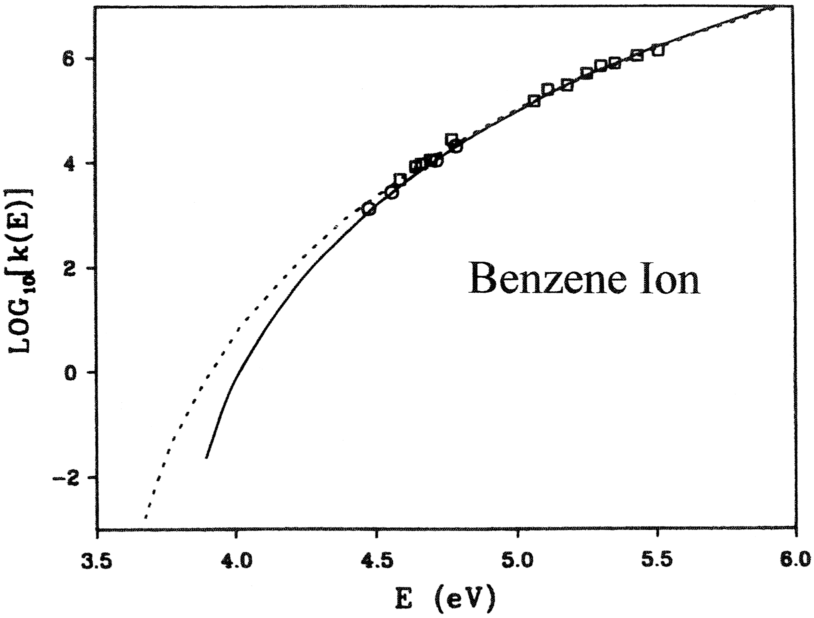

Fig. 12. TRPD (circle) and REMPI (square) data for benzene ion dissociation. The solid fitted line is our best variational RRKM fit with a D_0 of 3.88 eV. The dashed curve is the calculated curve of Neusser's group ([106]) employing a simpler RRKM model and a D_0 of 3.65 eV ([67]).

ation source, and that the dependence of k_{diss} could be analyzed in terms of an equivalent temperature which varied with the laser intensity in a well understood way. Starting with activation energies obtained by means of Eq. (1), an approach was worked out, using a truncated Boltzmann model and a modified Tolman theorem, to correct for the effect of reactive depletion [76]. Alternatively, the intensity-dependence data could be analyzed directly by master equation modeling [73] or random-walk kinetics modeling [74] using E_a as a fitting parameter.

At the same time, similar infrared-radiation-induced dissociations were being observed by the Waterloo group without the benefit of an IR laser, that is by the unaided action of the IR radiation coming from the thermal cell walls (a zero-cost light source) [77]. Applied to these data, master equation and activation energy analyses were entirely successful in interpreting the temperature dependence of this thermal-radiative dissociation, which we termed zero-pressure thermal radiatively induced dissociation [78,79].

One of the features quickly evident in the radiative analysis was that the larger the ion (in terms of the number of internal degrees of freedom) the more nearly it approached the ideal situation in which the exchange of radiation with the walls is fast compared with the dissociation rate of energized ions, which is the limit in which true thermal equilibrium is maintained [80]. Williams' group, recognizing this, looked at low-pressure thermal dissociation of increasingly large ions, and quickly found that for ions of the size of oligopeptides and small proteins, this limit is very well satisfied. They used the now-current term blackbody infrared radiative dissociation for such larger-ion dissociations, and have proceeded with an extensive series of studies of activation energies for dissociation reactions in various larger ions. Activation energy analysis via Eq. (1) is often completely appropriate, as for bradykinin [81], ubiquitin [82] or oligonucleotide duplexes [83]. They have also worked out fairly routine and reliable master-equation procedures for analyzing the temperature dependence in systems which are not quite large enough for Eq. (1) to be valid [84].

8. Probing ion properties

The previous sections have hinted at various ways in which photodissociation observations can give us information about the target ion. Here we will focus on some approaches in which photodissociation observations function more explicitly as a probe of the structure or the energetic state of the ion. Under this general heading, we can identify three distinct kinds of ion-probing ideas made possible by suitable PD techniques: (1) thermometric probes of the time-evolving energetic state of the ion, (2) spectroscopic probes of isomers and rearrangements, and (3) fragmentation probes of the ion structure.

8.1. Photodissociation can probe the ion's internal energy

An ion isolated in space can store internal energy E^0_{int} which it acquires either during the process which forms it, or as a result of some subsequent excitation procedure. This internal energy gradually drains out of the ion by collisions with background neutrals, or by radiating IR (or sometimes visible-wavelength) photons. Our group has worked quite extensively to develop photodissociation-based probes of this stored internal energy, and to measure the rates of radiative and collisional energy relaxation.

Most of what is known experimentally about both radiative and collisional cooling rates of ions has come from studies of this nature, now amounting to quite a substantial body of experience. The state of understanding of radiative cooling, in particular, was comprehensively reviewed not long ago [5]. Taking a different viewpoint, such studies of radiative ion cooling also provide nearly the only experimental information about vibrational normal mode infrared absorption intensities in polyatomic ions. This has proven useful in thinking about interstellar ion light-emission characteristics, as for example in the case of naphthalene ion [85], where two strongly conflicting pictures in the astronomy literature of the ion's radiative emission properties were resolved by comparison with our measured value of the ion's radiative cooling rate.

Given the challenge of finding tools to measure the instantaneous internal energy of a trapped ion, our group has worked with three strategies, exploiting features of (1) TRPD kinetics, (2) competitive photofragment formation, and (3) two-photon dissociation kinetics. We will note examples of each of these.

8.1.1. TRPD approach

The most generally applicable, most straightforward, and most satisfactory, internal energy probe approach makes use of the dissociation kinetics and TRPD [50]. The rate of unimolecular dissociation of the photoexcited ion is a strong function of the total internal energy E^* of the dissociating ion. In turn, E^* is equal to the sum of the original energy plus the photodissociation photon, $E^* = E^0_{\mathrm{int}} + h\nu$. A measurement of the dissociation unimolecular rate constant thus leads directly to a determination of the instantaneous value of E_{int} at the moment when the probe laser pulse strikes the target ion (see Fig. 6, for example, showing the evolution of the TRPD curves as a function of the decaying ion internal energy). Carrying this analysis further, measuring E_{int} as a function of time after ion formation yields a decay plot showing the dissipation of the ion's initial energy as time passes. Fig. 13 shows an example of such an energy decay plot. In this case the cyanophenanthrene ion is initially formed with approximately 1.6 eV of excess internal energy when it is created by multiphoton ionization at 193 nm. The cooling plot of Fig. 13 shows the dissipation of this excess energy by infrared radiative emission, with a radiative cooling time constant of 0.31 s^{-1}.

This TRPD-thermometry approach turned out to be so convenient and generally applicable that it was used to characterize the radiative and collisional cooling properties of a considerable number of molecular cations, including chlorobenzene [50], styrene [53], thiophenol [86], naphthalene [85], tri-t-butylbenzene [87], ferrocene [88], and nickelocene [89].

8.1.2. Fragment-ratio approach

Another approach to internal energy probing, using competitive fragmentation, works out in an analogous way. In the example of *n*-butylbenzene ion, the ratio

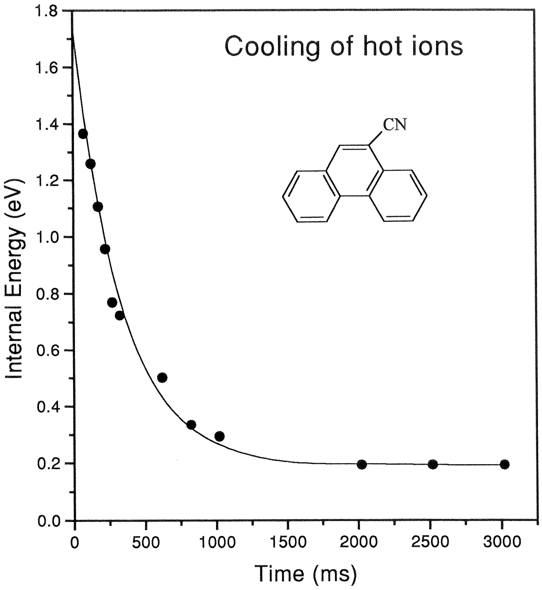

Fig. 13. Cooling curve for cyanophenanthrene ion showing the internal energy vs. time following the initial formation of the ions, as determined by TRPD thermometry ([107]).

of the photofragmentation products *m/z* 91 to 92 is very sensitive to internal energy, and this E_{int} dependence could be well quantified [90]. So it was possible to measure the 91/92 ratio at a fixed photodissociation wavelength, as a function of time, and construct a plot of internal energy versus time. The cooling kinetics of hot *n*-butylbenzene ions were thus characterized, as were those of dioxane ions in a similar successful application of this thermometric approach [91].

Extending our study of the *n*-butylbenzene ion system beyond this ion cooling work, we were able to carry out an ion-heating study [75]. The *n*-butylbenzene ions were subjected to laser heating by irradiation with an IR laser, while the internal energy of the target ions was monitored thermometrically using a 440 nm probe laser. The resulting plot of internal energy as a function of time as the ions heated up and began to undergo dissociation gave an unprecedented view of the intramolecular details of the IRMPD process.

8.1.3. Two-photon approach

A slightly different approach to probing the time dependence of ion internal energy is provided by exploiting the sequential two-photon photodissociation process, which was first pointed out by Freiser and Beauchamp [92]. Because of the ability of isolated ions to store excess internal energy for long times, it is easy to achieve photodissociation by irradiation using photons whose individual energy $h\nu$ is inadequate to break the target bond. The energy of two (or more) photons is pooled together by successive absorption of photons, with the energy being stored in the ion, until the accumulated internal energy is sufficient to bring about fragmentation. This two-photon dissociation mechanism is often observed, even at rather low laser intensities, but it becomes useful as a probe of the energy relaxation behavior when the conditions are arranged so that the time between absorption of the successive photons is comparable to the time it takes for the stored energy in the ion to dissipate. Then analyzing the kinetics can lead to a value for the rate of dissipation of E_{int}. To carry this out it is necessary to vary some parameter which controls the time interval between absorption of the successive photons. This has been achieved (1) by varying the intensity of the irradiating laser [92,93], (2) by chopping the irradiating laser beam at a variable chopping rate [94,95], or (3) by delivering the two photons in separate light pulses with a variable delay between the two pulses [96,97]. All of these approaches are successful, and all have been used as internal-energy probes in various studies of energy dissipation from internally energetic ions by way of collisional and/or radiative processes. All three approaches were applied and compared in one study of thiophenol ions [98].

The two-photon thermometric techniques just described, and indeed all of the thermometric probes described in this section, can be used equally well to determine the energy dissipation from hot ions by IR radiative cooling or by collisional energy removal involving collisions with a bath gas. However, for the particular case of collisional cooling, a simpler and faster approach can be used, in which the laser two-photon photodissociation parameters are unvarying, while the pressure of bath gas is varied. This pressure dependence approach was used from the very first [92], and was the first used in our laboratory when we began our study of collisional quenching by various bath gases [99]. We made systematic comparisons of quenching efficiencies as a function of the complexity, state of deuteration, and other properties of the bath gas (for instance, [100,101]).

8.2. Nature of the PD fragments can indicate ion structure

It is of course a fundamental principle of mass spectrometry that the chemical structure of an ionic molecule is reflected in the nature and relative abundances of its fragmentation products. Photodissociation by visible/UV light is a good way to induce fragmentation, and is in fact a particularly clean approach since the energy deposited in the fragmenting ion is well controlled and well known. However, in spite of these attractive features, if we look for specific advantages to be gained from PD fragmentation patterns in comparison with other ion dissociation methods, there seem to have been few cases where PD offers distinctively different ion-structure information. The literature describes many PD studies that draw structural conclusions about the parent ion from the fragmentation pattern. With few exceptions, however, PD fragment patterns have not been found to be highly distinctive compared with depositing the same amount of energy in other ways, such as above-threshold ionization by electron-impact, photon absorption or charge transfer; or ion activation by collisions, surface impact, electron impact, and so forth. Thus PD fragmentation does not seem to stand out from other fragmentation techniques as a way of obtaining structure-sensitive fragment information, and this aspect of probing ion structures will not be pursued here.

Photodissociation by IRMPD with a low-power continuous-wave laser has been considered more promising. It has been argued that the incremental, slow input of energy by a series of IR photons is particularly favorable for picking out the lowest energy decomposition pathway(s), and this characteristic has proven useful for distinguishing isomeric ions [102–104]. At least in favorable cases, the IRMPD fragmentation patterns can differ among isomers in informative and useful ways [105].

8.3. PD spectra can differentiate isomeric ions

Isomeric ions have the same mass and may well be similar in their fragmentation patterns, reactivities, and even their mobilities, but their spectroscopic properties will always differ (at a sufficient degree of resolution). Early applications of PDS, and many further ones over the years, have been aimed at such isomer distinctions. As an early illustration, Fig. 1 showed PDS results for isomeric $C_9H_{12}^+$ ions, where the isomer containing the double bond in conjugation with the benzene π system is clearly differentiated by its red shift from the cyclopropylbenzene structure. Further, the spectra of the ions from the two phenylpropene neutral molecules are identical, showing rearrangement into conjugation upon ionization, while the phenylcylopropane neutral clearly gives a unique ion structure. There has been much work devoted to characterizing some distinctive chromophoric groups in organic radical ions, such as conjugated double bonds, with the idea of recognizing such structural features in a convenient spectroscopic way, and exploiting this spectroscopy to recognize ion isomers and rearrangements.

When resolved vibrational structure is present in the visible/UV PDS spectrum, isomer recognition becomes much more incisive than with low-resolution electronic spectra. An early success was the clear distinction of chloropropene ion isomers by their distinctive vibrational structure, as shown in Fig. 14 [37]. More recently, IRMPD spectra have begun to suggest the power of using direct vibrational-spectroscopic information to characterize ion structures. For example, Shin and Beauchamp obtained IRMPD spectra in the 900–1100 cm^{-1} region of $Mn(CO)_4CF_3^-$ from different precursors, and found the match of vibrationally resolved spectral structure to be so close as to give convincing proof of the structural similarity of the different ions [42].

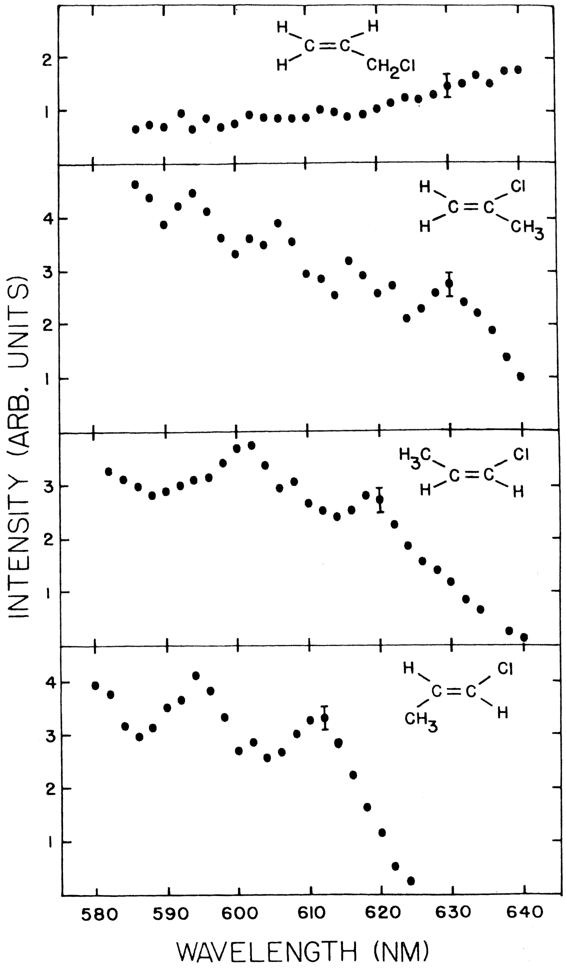

Fig. 14. Tunable dye laser photodissociation spectra (extent of disappearance of the $C_3H_5Cl^+$ ion as a function of laser wavelength) for four isomeric chloropropene molecular ions. The photodissociation product ion was $C_3H_5^+$ in all cases. At this wavelength resolution the differing vibrational fine structure is clearly distinguishable for the different isomers ([37]).

The continuing evolution of imaginative and powerful photodissociation-based approaches to such spectroscopic problems, combined with the increasing availability of high-power, tunable light sources (synchrotrons, free electron lasers, OPO lasers, for instance) has bright promise. It may not be far fetched to envision a future in which the infrared spectrum of an ion in a mass spectrometer may be a standard and routine part of its characterization, just as has been the case for molecules in solution for over half a century.

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