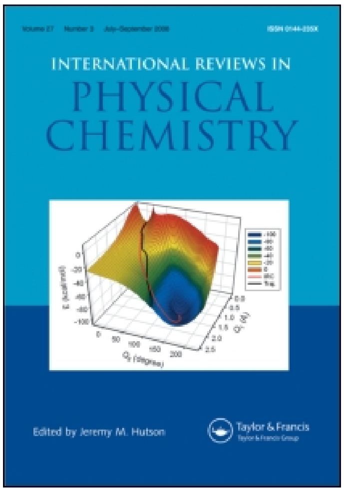

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Recent progress in gas-phase ion chemistry

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Recent progress in gas-phase ion chemistry

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Recent advances in gas-phase ion chemistry are discussed. These include theoretical and experimental approaches to ion structure determinations, ion spectroscopy and photodissociation, unimolecular dissociation reactions of polyatomic cations and ion-molecule reactions. Considerable progress in many of these areas of research has come through the experimental use of tandem (MS/MS) mass spectrometers. From the theoretical viewpoint, *ab initio* calculations have demonstrated predictive capabilities for ion structure determinations and statistical theories—quasiequilibrium theory (QET) and variational transition state theory (VTST)—are still of great value in treating the dynamics of ionic systems.

1. Introduction

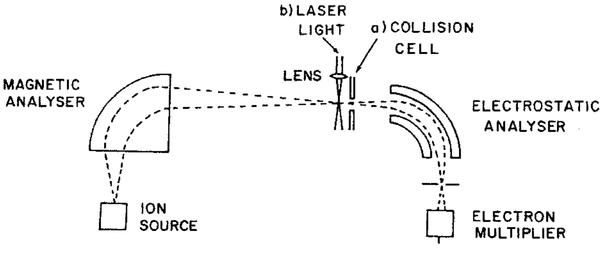
Gas-phase ion chemistry has advanced rapidly in recent years, in several directions. These include ion structure determinations, spectroscopy, unimolecular dissociations, ion–molecule reactions, ion photodissociation and related areas. There has been a strong interplay between experiment and theory in all of these areas. The monograph series edited by Bowers (1979, 1984) has been valuable in providing up-to-date reviews with emphasis on the chemical physics aspect of gas-phase ion chemistry. Several additional recent books and reviews are pertinent (Almoster-Ferreira 1984, Baer 1981, 1985, Berkowitz and Groeneveld 1983, Comita and Brauman 1985, Dannacher 1984, Holmes 1985, Lorquet 1981, 1984, McLafferty 1983, Miller and Bondybey 1983, Powis 1984). Rather than give a general overview, I have chosen specific examples which seem to me to be significant turning points and exemplify the methods, experimental and theoretical, which are employed. These obviously reflect my own taste and preference.

A most valuable set-up for ion beam experiments has been a commercially available, double focusing mass spectrometer of reversed geometry, the VG-Analytical ZAB-2F which has been described in detail (Morgan *et al.* 1978) (figure 1). It belongs to the new generation of tandem mass spectrometers. It has produced remarkable results concerning the spectroscopy (Carrington and Kennedy 1984), photodissociation dynamics (Jarrold *et al.* 1983), structures (Holmes *et al.* 1982), unimolecular reactions (Illies *et al.* 1982), and collisionally induced reactions (Burgers *et al.* 1983, Rabrenovic *et al.* 1983) of gas-phase ions.

A very successful theoretical approach for ion structures and energetics has been that of *ab initio* molecular orbital calculations using the Gaussian 80 system of programs (Binkley *et al.* 1981). This approach has demonstrated remarkable predictive capabilities (Bouma *et al.* 1982 a, b).

2. Interesting new ion structures; the methylenoxonium radical cation, $[CH_2OH_2]^{+\cdot}$ and related ylidions

The discovery of the methylenoxonium radical cation, $[CH_2OH_2]^{+\cdot}$, was a triumph of theory. This radical cation was predicted on the basis of *ab initio* calculations



THE ZAB-2F

Figure 1. Schematic diagram of a tandem mass spectrometer, a so-called 'MS/MS'—the ZAB-2F. Reactant ions are mass selected by the magnetic analyser. They can undergo collisionally activated dissociations (CAD) in the field-free region between the two analysers, if a collision gas is introduced into the collision cell. Alternatively, they can undergo photodissociation if a laser beam is allowed to intersect the ion beam. The ionic products of the CAD or of the photodissociation are analysed by the electrostatic analyser. The dashed lines indicate that the ions come to an intermediate focus in the field-free region close to, or at the crossing point with, the laser light or with the collision gas.

(Bouma *et al.* 1982 a) and verified experimentally to be a stable, observable gas-phase species (Bouma *et al.* 1982 b, Holmes *et al.* 1982). CH_2OH^+ lies in a deep potential well, 45 kJ/mol lower than that of the methanol radical cation, CH_3OH^+, and separated from it by a 112-kJ/mol barrier (figure 2). *Ab initio* molecular orbital calculations with a large basis set and incorporating electron correlation were carried out for the two CH_4O^+ isomers and for the 1,2-hydrogen-shift transition structure converting one to the other.

The neutral counterpart of the methylenoxonium radical cation is unstable and indirect ways of producing the ion experimentally had to be devised. A suitable precursor molecule is ethylene glycol ($HOCH_2CH_2OH$) which upon ionization and dissociative rearrangement loses formaldehyde to produce the desired ion, $[CH_2OH_2]^+$. The fact that an ion having a structure different from methanol has indeed been formed, was unequivocally proved by Collisionally Activated Dissociation

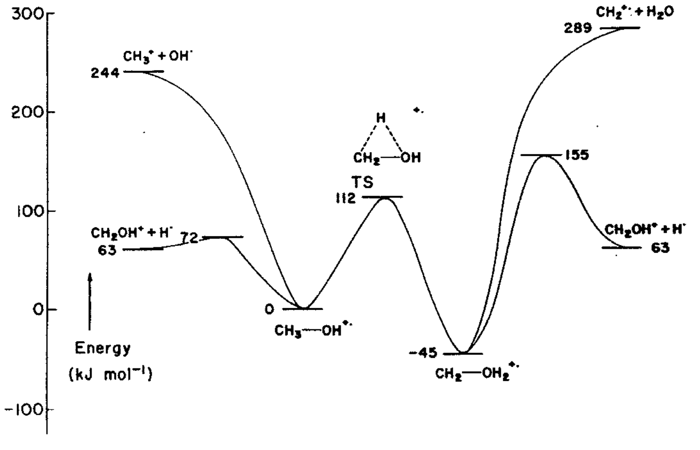


Figure 2. Schematic potential energy profile connecting the methanol ($CH_3OH^{+\cdot}$) and methylenoxonium ($CH_2OH_2^{+\cdot}$) radical cations, including the intramolecular and dissociative rearrangements (Bouma *et al.* 1982 a).

(CAD). Early developments of this method for ion structure elucidation are largely due to McLafferty and co-workers (McLafferty *et al.* 1973) and it has recently been reviewed (Levsen and Schwarz 1983, McLafferty 1983). The basic principle is as follows. A high-energy ion (>keV) collides with a neutral target atom or molecule. As a result, the colliding ion is excited internally and dissociates in a fashion which reflects its original structure, that is, the atomic connectivity. While there has been some criticism of the CAD method in the past, it has emerged as the method of choice in numerous cases, demonstrating the existence of isomeric ionic structures in the gas phase. Its success is easily demonstrated when comparing the Collisional Activation (CA) mass spectra of the two $[CH_4O]^{+\cdot}$ isomers (figure 3) (Holmes *et al.* 1982). The CA mass spectrum of $[CH_3OH]^{+\cdot}$, which has been obtained in the gas phase by the ionization of methanol, demonstrates a large peak at an ion mass-to-charge ratio, $m/z = 15$. This demonstrates the existence of a methyl group in the methanol radical-cation. The CAD mass spectrum of $[CH_2OH_2]^{+\cdot}$ shows two strong peaks, at $m/z = 14$ and $m/z = 18$, due to the pre-existing methylene and water groups, respectively, in the ion. It shows an additional peak which is absent in the methanol spectrum: a very narrow one at $m/z = 16$ which is due to charge stripping and formation of the doubly charged ion

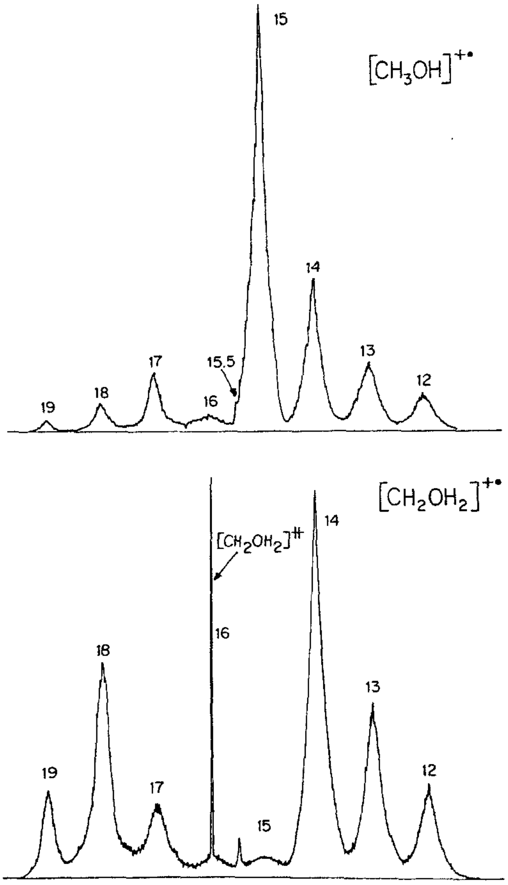


Figure 3. Partial collisional activation (CA) mass spectra of $[CH_4O]^{+\cdot}$ (methanol and methylenoxonium) isomers (Holmes *et al.* 1982).

$[CH_2OH_2]^{++}$, isoelectronic with ethylene. Clearly, the two spectra are not only distinguishable, but also give clear indications of the ion structure backbone, the connectivity of the atoms. This is easily understood in the following way. The collisional activation step deposits a relatively large amount of internal energy into the ion in a 'vertical' type process. It is well known that simple bond cleavages are preferred over isomerizations and rearrangements of polyatomic ions as the internal energy of these ions increases. Simple bond cleavages normally require high critical energies but also have high activation entropies, while dissociative rearrangements have low activation energies but also low activation entropies ('tight' transition states in the terminology of unimolecular reaction rate theory (Robinson and Holbrook 1972)). The microcanonical rate coefficients $k(E)$ for simple bond cleavages are much more steeply rising functions of the internal energy E, than are the $k(E)$ values for parallel reactions involving isomerizations. As a result, the collisionally activated ion dissociates in a fashion which 'remembers' the way the atoms were connected without, or with very little, concomitant isomerization taking place. Thus, while the isomerization barrier between the methanol radical cation and the methylenoxonium radical cation is lower than their respective dissociation limits to the methyl cation and methylene cation (figure 2), the structure-specific dissociations prevail over the isomerization reaction.

The methylenoxonium radical-cation is just one member of a class of radical-cations, the so-called 'ylidions', which can be considered as complexes of a radical-cation ($CH_2^{\dot{+}}$, $CHCH^{\dot{+}}$, $CH_2CH_2^{\dot{+}}$ or $CH_3CH^{\dot{+}}$) and an electron-rich polar neutral molecule (e.g., H_2O, NH_3, HF, HCl, CH_3OH, $CH_2=O$) (Heerma *et al.* 1981, Bouma *et al.* 1983 a, b, c, Apeloig *et al.* 1983, Schwarz 1983, Holmes *et al.* 1983, Weiske *et al.* 1984, Burgers *et al.* 1985). The ylidions in turn are just one group of ions among many other groups, originally unexpected, surprising, exotic and extremely interesting, which the gas-phase ion-chemists have encountered. Many of these, including the ylidions, may be of importance in interstellar chemistry (Schwarz 1983). Their study has demonstrated the power of the combination of *ab initio* calculations with CA mass spectra.

3. Ion spectroscopy through photodissociation; the methyl iodide radical cation $CH_3I^{\dot{+}}$

Structure elucidation by collisional activation spectra of ions discussed in the previous section does not imply that proper ionic structures—internuclear distances, angles, etc.—are obtained. Vibrational and rotational spectroscopy of molecular ions is required and has been developed in recent years. The problem originally was one of intensity. If sample densities are increased to increase intensities, a whole new ion–molecule reaction chemistry is initiated—for example, through the striking of a gas discharge—but the spectra of required ionic species are rarely obtained. An elegant way to obtain absorption spectra results if the absorption process leads to a photodissociation product. This requires production of an excited state of the ion above a dissociation threshold. However, experiments of this type no longer require a high pressure gas where the desired ion is contaminated by other species; a mass-selected ion beam—the desired ionic species in a high degree of purity—is instead illuminated with radiation, mostly with lasers in recent years. Photodissociation of polyatomic cations has been pioneered by Dunbar and co-workers (Bowers 1979, 1984) who employed ICR spectrometers. The introduction of tandem mass spectrometers—double quadrupole (Vestal and Futrell 1974), double magnetic sector (Carrington *et al.* 1979), magnetic plus electric (Carrington and Kennedy 1984) instruments and tunable lasers have opened the way for high-resolution, laser-induced photodissociation spectroscopy of polyatomic cations. The common principle of operation of these instruments is that they have a selector sector in which the desired ion beam is formed, a reaction region in which the ion beam is crossed with a laser beam or the two beams overlap in a collinear fashion, and an analyser sector in which the photodissociation products are mass analysed and detected.

Morrison and co-workers (McGilvery and Morrison 1977, Goss *et al.* 1981) have studied the photodissociation of CH_3I^+ and CD_3I^+. The instrument they employed, a triple quadrupole mass spectrometer, is shown schematically in figure 4. The methyl iodide ion is formed by electron impact in the spin-orbit split ground electronic state ($\tilde{X}$ state), $^2E_{3/2}$ and $^2E_{1/2}$. Absorption of light, in the photon energy range 1·8–2·8 eV, leads to the electronically excited $\tilde{A}$ $E_{1/2}$ state with various degrees of vibrational excitation. This state is able to predissociate into the vibrational continuum of the $\tilde{X}$ state, producing CH_3^+ fragment ions. The earlier results (figure 5 (McGilvery and Morrison 1977)) demonstrate two band maxima, due to transitions from the doublet ground state, exhibiting strong vibrational progressions. The more advanced study (Goss *et al.* 1981), with a resolution better than 0·3 cm^{-1}, allowed partial resolution of rotational structure (figure 6). The combined studies gave numerical information on vibrational frequencies and rotational constants of the $\tilde{A}$ state. The quality of the spectra is comparable to that of neutral species, although the effective pressure of the absorbing sample is only 10^{-9} Pa. Doppler tuning (Carrington and Kennedy 1984)

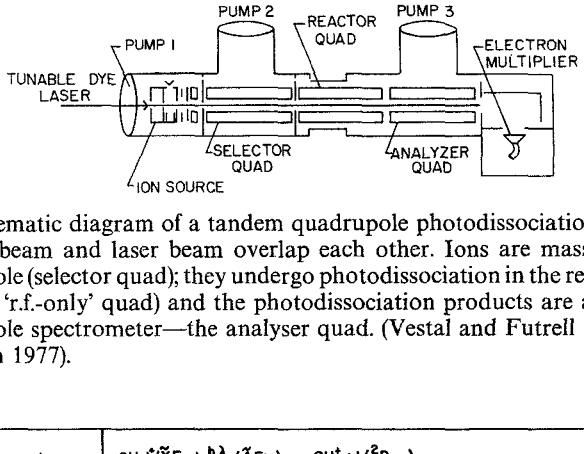


Figure 4. Schematic diagram of a tandem quadrupole photodissociation mass spectrometer. The ion beam and laser beam overlap each other. Ions are mass selected in the first quadrupole (selector quad); they undergo photodissociation in the reactor quad (which is a so-called 'r.f.-only' quad) and the photodissociation products are analysed by the third quadrupole spectrometer—the analyser quad. (Vestal and Futrell 1974, McGilvery and Morrison 1977).

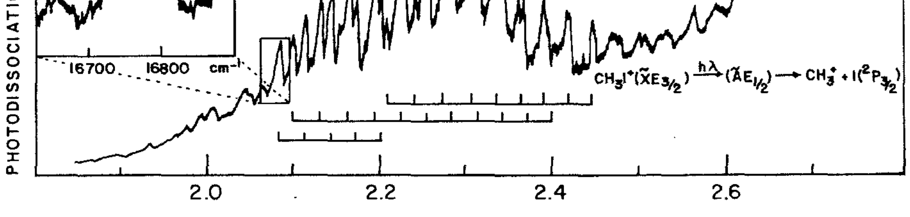


Figure 5. Photodissociation spectrum of the methyl fragment from the methyl iodide ion. Several C–I stretch vibrational series are evident (McGilvery and Morrison 1977).

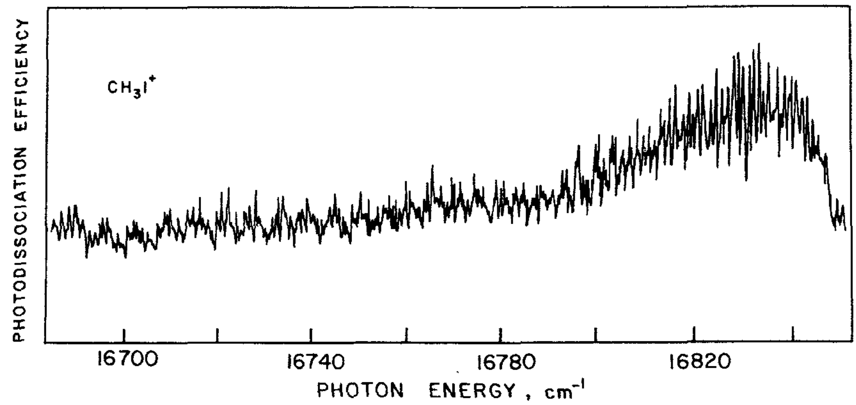


Figure 6. The photodissociation spectrum of the (0, 0, 11) band of CH_3I^+: $CH_3I^+(\tilde{X}E_{1/2};\ 0,0,0)\xrightarrow{h\nu}CH_3I^+(\tilde{A}E_{1/2};\ 0,0,11)\rightarrow CH_3^+ + I(^2P_{3/2})$; ν_1, CH stretch; ν_2, CH deformation; ν_3, CI stretch. The resolution is 0·3 cm^{-1} (37 μeV) and the energy range corresponds roughly to the inset of figure 5 which was obtained at a resolution of ~0·4 meV (Goss *et al.* 1981).

furnishes even higher resolving powers and the linewidths measured for H_3^+ were limited only by the lifetimes of the predissociating states. The infrared spectrum of H_3^+ in the region 872 to 1094 cm^{-1} exhibits an average line density of over 100 lines per cm^{-1} (Carrington and Kennedy 1984).

Recently, the relatively new area of multiphoton ionization photoelectron spectroscopy (MPI PES) has begun to yield information on vibrational frequencies of medium-sized molecular ions such as benzene and substituted benzenes (Meek *et al.* 1982, Long *et al.* 1983, Anderson *et al.* 1982, 1984, 1985, Durant *et al.* 1984), although the detailed interpretation of these spectra in terms of fundamental frequencies and mode forms is still a very difficult task.

The spectroscopy of molecular ions has clearly come of age and new and exciting data are to be expected.

4. Photodissociation dynamics of small ion clusters; $(NO)_2^+$ and related species

The combination of ions and light is a very powerful one as has already been shown in the previous section. Bowers and co-workers (Jarrold *et al.* 1983, 1984 a, b) have employed in recent years an experiment in which a high-energy ion beam is crossed with a laser beam (figure 1). They have extended the capability of the instrumentation in two major ways: (*a*) the laser light is polarized; (*b*) the electric sector is employed as a kinetic-energy analyser. This has allowed the study of the dynamics of photodissociation of small cluster ions. Product kinetic energy distributions were derived together with information about the angular distribution of the products. Similar results were obtained for the dimers $(NO)_2^+$ and $(N_2)_2^+$. Figure 7 shows typical results for laboratory energy distributions, for angles of 0° and 90°, respectively, between the laser beam polarization and the ion beam direction. The conclusions for the $(NO)_2^+$ cluster were as follows. (i) Photodissociation of the $(NO)_2^+$ cluster to $NO^+ + NO^{\cdot}$ occurs by a transition to an excited state with a lifetime negligible compared to a rotational period. It occurs by a direct transition to a repulsive surface; (ii) the polarization of the transition is predominantly parallel with the $NO^{\cdot}-NO^+$ axis in the cluster. These conclusions are in accord with the results of figure 7, for the following reason. Suppose the polarization of

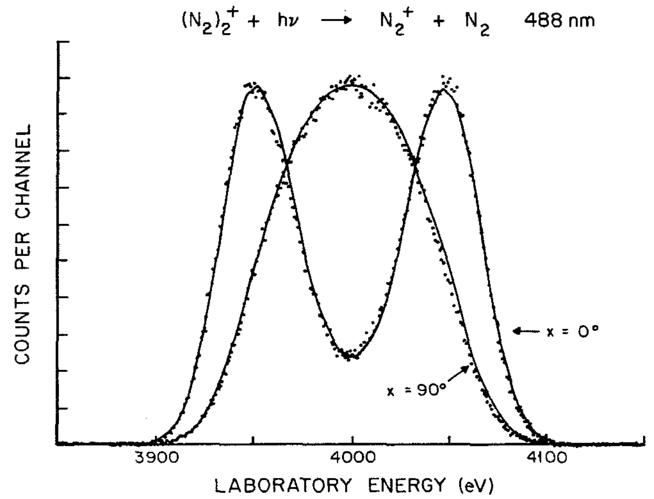


Figure 7. Peak shapes for N_2^+ from the photodissociation of $(N_2)_2^+$ at 488 nm. The data are for angles of 0° and 90° between the laser beam polarization and the ion beam direction. Similar data were observed for NO^+ from $(NO)_2^+$. The points are the experimental data and the line is a simulation with an assumed angular distribution (Jarrold *et al.* 1983, 1984 a).

the electric vector of the light is in the ion beam direction (0° case). Clusters which will be excited are those whose intermolecular axis happens to lie parallel to the ion beam direction. If dissociation occurs along the axis of the breaking bond, the photofragments will recoil in the direction of the ion beam and in the opposite direction. The ion velocities and energies in the laboratory frame will therefore demonstrate a doubly peaked distribution (figure 7). If the polarization of the electric vector is perpendicular to the ion beam direction, clusters whose intermolecular axis happens to lie perpendicular to the ion beam direction will be sampled. The photo-fragments will recoil perpendicularly to the ion beam direction and the kinetic energy distribution in the laboratory frame will be singly peaked, slightly broadened (figure 7). The data were simulated by calculations and anisotropy parameters β were deduced (Jarrold *et al.* 1983, 1984 a, b). The photon energy was also varied allowing the determination of the partitioning of available energy into kinetic energy and internal energy. The dissociation of $(NO)_2^+$ is accounted for by a simple impulsive model, whereby the two nitrogen atoms recoil from each other and the oxygens are 'spectators'. This is in agreement with the experimental observation that 51% of the available energy appears as kinetic energy of the products. The $(NO)_2^+$ ion has presumably a nearly *cis* rectangular structure and as a result the model predicts that most of the internal energy of the products will appear as rotational excitation.

5. Unimolecular dissociations of polyatomic cations

5.1. *Structures of neutral fragments; the dissociation of aniline*

Unimolecular fragmentations of polyatomic cations form the basis of mass spectroscopy. Organic mass spectrometry is a highly developed field and has been around since the late fifties and early sixties. Until recently however, the structures of neutral fragments of ionic dissociations were usually only inferred indirectly, for example, through thermochemical calculations. An interesting case occurred in our own work (Lifshitz *et al.* 1983). We have carried out measurements of appearance energies (AEs) of fragment ions as a function of ion source residence time. On the basis of the AE limit for long-lived (~1 ms) aniline cations we came to the conclusion that at threshold the dissociation,

$$C_6H_5NH_2^{+\cdot} \rightarrow c-C_5H_6^{+\cdot} + HNC \tag{1}$$

produces HNC and not the more stable isomeric structure HCN. This induced the development by Holmes, Terlouw and co-workers (Burgers *et al.* 1983) of a very elegant method of identifying neutral products of ion fragmentations by means of collisionally induced dissociative ionization. The experiments employed the ZAB-2F instrument (figure 1). Reactant and product ions of reaction (1) were prevented from entering the collision chamber in the field-free region between the magnetic and electric sector by a positive voltage on the collision gas cell. The neutral fragments, which were not prevented from entering the cell were dissociatively ionized by an inert gas in the collision cell. This ionization occurred by virtue of their high (~keV) kinetic energy, originally acquired by the reactant ion in the acceleration region of the ion source. The spectrum due to the dissociative ionization of the neutral fragment was mass analysed by the electric sector. It was clearly distinguishable as HNC and differed from that of HCN which can be ionized in the ion source or produced as a fragment of other unimolecular decompositions, for example, of pyridine

$$C_5H_5N^{+\cdot} \rightarrow C_4H_4^{+\cdot} + HCN \tag{2}$$

The method of collisional re-ionization of neutral fragments has been developed further and the placement of a deflecting electrode in front of the collision chamber (figure 8) was found to be more effective than the retarding potential on the chamber, and to give better mass resolutions (Holmes and Mommers 1984). This method is in its development stages and new and exciting results are constantly being obtained (Burgers *et al.* 1984, Clair *et al.* 1985).

5.2. *Reaction kinetics and dynamics; the dissociation of bromobenzene*

Kinetic data on gas-phase unimolecular reactions of neutral reactions (activation energies, pre-exponential factors and activation entropies) are quite well known (Benson and O'Neal 1970). There is little information of this kind concerning ionic reactions, the main reason being that these reactions are normally run at very low

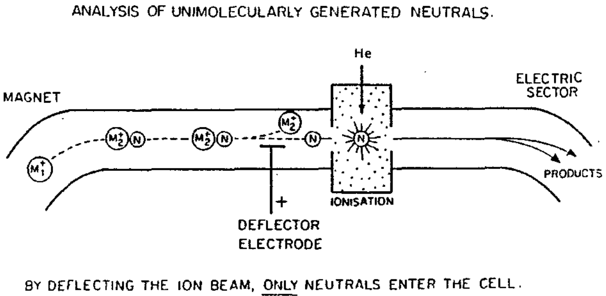


Figure 8. Collision-induced dissociative ionization of unimolecularly generated neutrals. The instrument is a ZAB-2F, as in figure 1. By deflecting the ion beam, only neutrals enter the collision cell (adapted from the Ph.D. thesis of A.A. Mommers, University of Utrecht, 1985).

pressures and measurements are made on a nonthermal system. Rosenstock has demonstrated the usefulness of calculating equivalent activation entropies, $\Delta S^{\ddagger}$, and pre-exponential factors, A_{∞}, in spite of the fact that these pertain to the canonical system. This was commented upon previously (Lifshitz 1983). One reaction for which activation parameters have been obtained and compared with those of neutral analogues, is the simple bond cleavage in the bromobenzene radical-cation (Rosenstock *et al.* 1980)

$$\mathrm{C_6H_5Br^{+\cdot} \rightarrow C_6H_5^{+} + Br^{\cdot}} \tag{3}$$

This reaction has been recently studied by us (Malinovich *et al.* 1985) over a fairly wide time range (from microseconds to milliseconds) using an ion trapping device. The method which we have employed is time-resolved photoionization mass spectrometry (TPIMS). Photoionization is induced by a pulsed vacuum U.V. light source, a Hinteregger discharge in hydrogen producing the many-line spectrum. Photoions are trapped in a cylindrical ion trap, CIT (Mather *et al.* 1980) (figures 9 and 10). They are ejected into the quadrupole mass filter by a drawout pulse, following a variable delay time. Experimental photoionization efficiency (PIE) curves were fitted with a quasiequilibrium theory (QET) model calculation (figure 11) by assuming a critical energy $E_0 = 2{\cdot}76\,\mathrm{eV}$ and an equivalent 1000 K entropy of activation $\Delta S^{\ddagger} = 8{\cdot}07$ e.u. This activation entropy corresponds to the totally loose, so-called 'orbiting' transition state (OTS), well known from Langevin's theory of ion–molecule reactions, where the long-range ion-induced dipole potential governs the kinetics.

Ultra-slow unimolecular dissociations, having microcanonical rate coefficients $k(E) \leqslant 10\,\mathrm{s^{-1}}$, at near threshold energies, can be sampled by TPIMS, in spite of competing I.R.-radiative decay of the parent ion. This method has allowed, for the first time, observation of very slow unimolecular dissociations at near threshold energies with good energy resolutions ($\sim 0{\cdot}05\,\mathrm{eV}$).

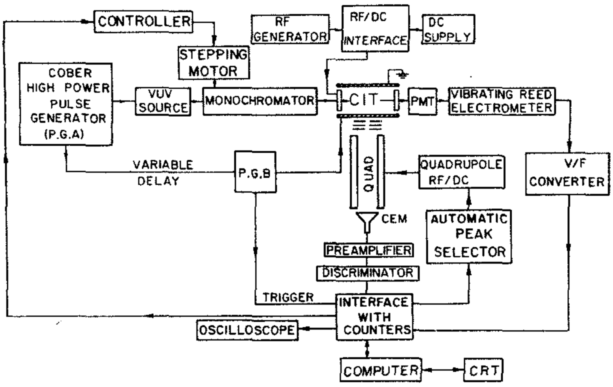


Figure 9. Time-resolved photoionization mass spectrometer (TPIMS). CIT, Cylindrical Ion Trap; PMT, photomultiplier; CEM, channeltron electron multiplier; PG, pulse generator; QUAD, quadrupole mass spectrometer. The vacuum U.V. source is a Hinteregger hydrogen discharge lamp; the monochromator is a McPherson Model 225 1-m, normal-incidence instrument; the computer is an Industrial Micro Systems, IMS 5000, microcomputer. A radio frequency (r.f.) potential is applied to the cylindrical barrel electrode of the CIT and causes ion trapping (Malinovich *et al.* 1985).

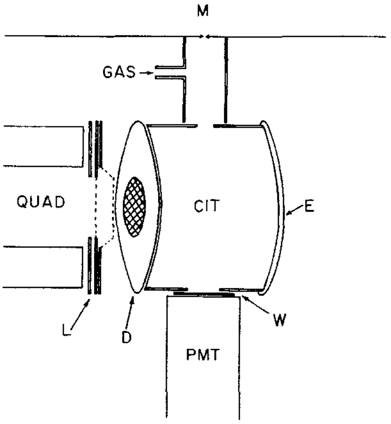


Figure 10. Schematic drawing of the Cylindrical Ion Trap (CIT) and its connections to the monochromator (M), to the photomultiplier (PMT), and to the quadrupole mass filter (QUAD). E, earthed end-cap electrode; D, drawout end-cap electrode; W, sodium salicylate coated window; L, ion lens. At present, the gas enters the cell through the side arm connecting the monochromator and the CIT. In a new cell design, the gas enters through the top of the cylindrical electrode (Malinovich and Lifshitz, unpublished).

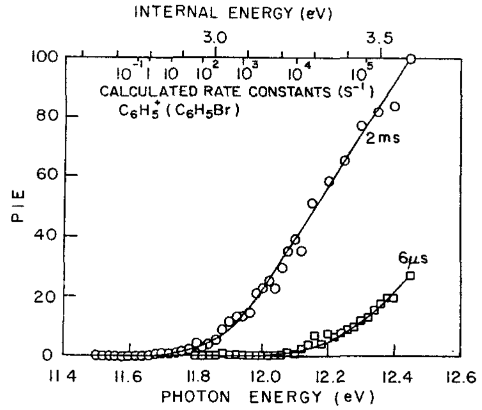


Figure 11. Time-resolved experimental (circles and squares) and calculated (smooth lines) daughter ($C_6H_5^+$) PIE curves. The maximum possible internal energy in the ion (upper scale) for a zero kinetic energy electron was calculated from the photon energy, $h\nu$ (lower scale) and from the known ionization energy of bromobenzene, $IE(C_6H_5Br) = 8{\cdot}97$ eV: internal energy (eV) $= h\nu - 8{\cdot}97 + 0{\cdot}12$, where the 0·12 eV correction stands for the average thermal energy of neutral bromobenzene at the temperature of the experiment (303 K). The calculated bromobenzene ion dissociation rates at these internal energies are also shown on the upper scale. The PIE curves were exactly calculated from the QET model (Malinovich *et al.* 1985).

5.3. *Special effects; quantum mechanical tunnelling in the dissociation of methane radical-cations*

The methane radical-cation undergoes a slow unimolecular decomposition

$$CH_4^{+\cdot} \rightarrow CH_3^+ + H^\cdot \qquad (4)$$

having a lifetime of the order of $\sim 10^{-6}$–10^{-5} s which is quite unusual for such a small ion. Rosenstock (1967) and Klots (1971) first implicated tunnelling through a centrifugal barrier as the source of metastable decompositions (in the microsecond range) occurring in methane. This was verified experimentally, through the study of the reaction in methane and deuterated methanes, by the effect of temperature on intensities and on kinetic energy release distributions (Solka *et al.* 1975, Illies *et al.* 1982). The latter study is a very detailed one employing the ZAB-2F spectrometer (figure 1). Both metastable ion intensities and average kinetic energy releases were observed to increase with ion source temperatures. A statistical model was derived for the tunnelling process which gave remarkably good agreement with the experimental results. The increase in kinetic energy release arises, because, as the temperature is raised, levels with higher total angular momentum are populated, the centrifugal barrier is higher, and tunnelling occurs at a higher energy above threshold. The effect of temperature on intensities is more subtle and may be understood by referring to figure 12. The methane radical-cation is produced by electron impact ionization with a wide distribution of internal energies. A narrow slice of this distribution contributes to rate coefficients $1\times10^3<k<2\times10^6\,\mathrm{s}^{-1}$. The wider is this slice (the so-called 'metastable window'), the higher is the fractional abundance of metastable ions. Furthermore, if $k(E)$—the microcanonical rate coefficient—rises slowly with E, the metastable window will be wider, and vice versa. Calculations show (figure 12) that as the orbital angular momentum is raised, the centrifugal barrier changes shape from low and wide to high and narrow. This change is shape results in an increase in the metastable tunnelling window—and therefore in an increase in metastable intensity. The mass dependence of tunnelling through the polarization centrifugal barrier results from the interplay of several factors. The intensities for $CH_4^{\ddagger}$ and $CD_4^{\ddagger}$ are about similar while that for CD_3H^+ is about a factor of two higher over the whole range of temperatures studied. The barrier maximum is,

$$V_{\mathrm{eff}}^{\max}=\frac{L^4}{8\mu^2\alpha e^2} \tag{5}$$

where:

L orbital angular momentum
α polarizability
μ reduced mass
e electron charge

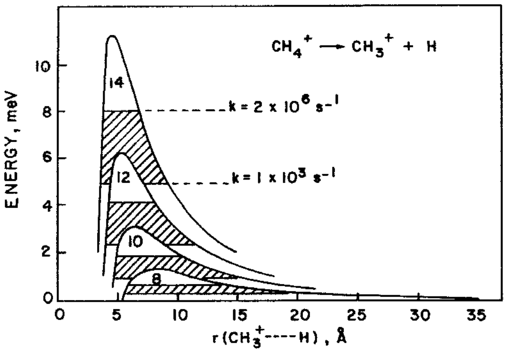


Figure 12. Variation of position and size of metastable tunnelling window with orbital angular momentum. Barriers are shown for product orbital angular momenta, $L=8$, 10, 12 and 14 and with product rotational angular momentum $J=0$. The shaded areas on the barriers show the size of the metastable tunnelling windows (rate constants in the range 2×10^6–$1\times10^3\,\mathrm{s}^{-1}$) (Illies *et al.* 1982).

CD_3H^+ leads to H˙ loss, preferentially over D˙ loss, because of the zero-point energy difference. The kinetic energy releases and intensities for CD_4^+ are lower than those for CD_3H^+ mainly because of the lower centrifugal barriers for CD_4^+, resulting from the larger reduced mass (equation (5)). The differences between the results for CD_3H^+ and CH_4^+ fragmentations are twofold. (i) There is a much faster rate of barrier encounter, $\omega(E, J_0)$, in CH_4^+

$$\omega(E, J_0) = \frac{1}{h\rho(E, J_0)} \tag{6}$$

where:

E internal energy
J_0 total angular momentum
$\omega(E, J_0)$ the number of times the barrier is encountered per second
$\rho(E, J_0)$ the density of states of the reactant ion
h Planck's constant

because of the lower density of states (equation (6); see also Miller (1979), Osamura *et al.* (1981)). (ii) The distribution of J levels populated in CH_4^+ is lower than in CD_3H^+, leading to lower centrifugal barriers for CH_4^+.

The methane molecule ion case provides a very clear-cut experimental verification (and perhaps the only one) for quantum mechanical tunnelling effects on unimolecular reactions.

6. Unimolecular dissociations and ion–molecule reactions; Variational Transition State Theory (VTST)

Many ionic dissociations, for example reaction (3), have negligible reverse activation energies. As a result there is no pronounced maximum in the potential energy surface between reactants and products (save for a rotational (centrifugal) barrier) and the location of the transition state is not well defined. Lifshitz (1978) has suggested that a variational criterion for the location of the transition state may be particularly well suited for these systems. In Variational Transition State Theory (VTST) one chooses the transition state at the dividing surface between reactants and products that produces the smallest transition state theory rate constant (Chesnavich and Bowers 1979). This corresponds to a local minimum in the sum of quantum mechanical states W of the $s-1$ degrees of freedom perpendicular to the reaction coordinate r at energy less than or equal to $E-V(r)$, where $V(r)$ is the potential energy at r

$$\frac{\partial}{\partial r} W_{s-1}(E-V(r); r) = 0 \tag{7}$$

This criterion corresponds to the 'bottleneck' for the quasiequilibrium flow of systems from a configuration of reactants to one of products. If it does not occur at the top of an actual potential-energy barrier, it is a so-called 'entropy' bottleneck. Wong and Marcus (1971) have shown that this procedure is equivalent to a maximum free energy criterion.

The location of the transition state may vary with internal energy, E. Bowers and co-workers (Chesnavich *et al.* 1981, Bowers *et al.* 1983, Jarrold *et al.* 1984c) have successfully employed a Transitional State Switching (TSS) model for unimolecular and bimolecular reactions in the $C_4H_6^+$, $C_4H_8^+$ and $C_6H_6^+$ systems. For example, the reaction between an ethylene ion and an ethylene molecule, which forms an intermediate $C_4H_8^{+\cdot}$ collision complex, via chemical activation

$$C_2H_4^{+\cdot}+C_2H_4 \rightarrow [C_4H_8]^{+\cdot} \rightarrow C_3H_5^{+}+CH_3^{\cdot} \tag{8}$$

proceeds through an orbiting transition state (OTS) at low energies. However the unimolecular dissociations of $C_4H_8^{+\cdot}$, which occur at slightly higher energies, proceed via 'tight' transition states (TTS). This can be understood in the following way. Let us define the reaction flux F

$$F=\frac{W}{h} \tag{9}$$

where W is the sum of states as before and h is Planck's constant. In the case of no barrier along the reaction coordinate, at low values of internal energy $E \approx E_0$, where E_0 is the critical energy, the OTS has the minimum flux F, since the number of states is very small (Bowers *et al.* 1983). The microcanonical rate coefficient k is given by

$$k=\frac{F^{\mathrm{ORB}}}{\rho_A} \quad \text{at} \quad E \approx E_0 \tag{10}$$

where ρ_A is the density of states of the reactant. At $E > E_0$, the TTS takes over, because of the rapid increase in F^{ORB} with E. The rate coefficient k is given by

$$k=\frac{F^{\ddagger}}{\rho_A} \quad \text{at} \quad E > E_0 \tag{11}$$

where $F^{\ddagger}$ is the flux of the TTS which is located at lower r.

As the reactant moves along the reaction coordinate, a balance is struck between two factors (Bowers *et al.* 1983, Miller 1976). (*a*) The energy $E-V(r)$ decreases as r is extended; this causes a decrease in W and in the flux F; (*b*) vibrational frequencies such as bending vibrations decrease as r is extended and eventually are transformed into free rotations of the separated products; this causes an increase in W and in F. At low energies, E, the first factor is dominant; at higher Es, the two factors offset each other and a switching from an orbiting transition state to a tight one at lower r is expected.

The application of a TSS model to ionic systems has aroused a considerable degree of controversy (Dodd *et al.* 1984, 1985, Truhlar 1985, Chesnavich and Bowers 1985). Our data for bromobenzene (reaction (3)) indicate that for a fairly wide energy range above threshold the OTS is the dominant transition state (Malinovich *et al.* 1985). Chesnavich (1985) has begun to investigate VTST in ionic systems in detail. The conclusions are not yet final since the nature of the potential energy surfaces for most ionic systems is still unknown. However, if the transitional modes (i.e., the bending vibrations in which the force constants evolve toward vanishingly small values as the decomposition progresses) loosen early in the decomposition process, the OTS is the dominant transition state. If, on the other hand, the loosening occurs late in the decomposition, the OTS, although present, may always be dominated by the TTS.

7. Ion-molecule reactions; new trends in experimental techniques for rate constant and cross-section measurements

The reactions of ions with neutral molecules in the gas phase are of great importance in the chemistry of the atmosphere and interstellar space. They very seldom possess an activation barrier and as a result remain fast down to very low temperatures, such as the ones which prevail in interstellar clouds. Recently, experiments have been carried out to measure the rates of ion–molecule reactions over very wide temperature ranges and down to temperatures as low as 8 K (Böhringer and Arnold 1982, 1983, Böhringer *et al.* 1983, Smith *et al.* 1984, Rowe *et al.* 1984 a, b, 1985, van Koppen *et al.* 1984, Barlow *et al.* 1984). Ion–molecule association reactions play an important role in the synthesis of molecules in interstellar clouds. The rate coefficients for three-body association reactions, such as

$$N_2^+ + 2N_2 \rightarrow N_4^+ + N_2 \qquad (12)$$

increase steeply with decreasing temperature. However, in the interstellar medium, bimolecular radiative association may prevail due to the low densities. The measurement of the rate at 13 K for

$$CH_3^+ + H_2 \rightarrow CH_5^+ + h\nu \qquad (13)$$

has thus been of great interest (Barlow *et al.* 1984).

In general, the experimental setup called SIFT (Selected Ion Flow Tube), first developed and described in detail by Smith and Adams (1979), has been most valuable in providing temperature-dependent rate data over a wide temperature range. Basically, it is a tandem quadrupole instrument, but instead of a collision chamber, a flow tube provides the ion–neutral reaction region. The carrier gas, at a pressure of 0·1–1 torr, ensures that the reactants are thermalized. Liquid helium has been employed to achieve low temperatures in ion drift tube experiments (Böhringer and Arnold 1983). Special techniques were employed to cool the reaction systems to 13 K and 8 K—the latter employing supersonic flow (Rowe *et al.* 1984 a, b, 1985).

Selected ion flow tubes have been constructed in several laboratories around the world, yielding valuable data on ion–molecule reactions. An additional experimental setup—the flowing afterglow/Langmuir probe (FALP) instrument—is unique to the Birmingham group (Adams *et al.* 1984, Smith and Adams 1984) and has provided some striking information concerning dissociative recombination coefficients, particularly concerning H_3^+. The dissociative recombination coefficient of H_3^+ is $\alpha(H_3^+) \lesssim 2 \times 10^{-8}\,cm^3\,s^{-1}$, i.e., two orders of magnitude lower than previously assumed, necessitating major changes in existing models of the ion chemistry in dense interstellar clouds.

Tandem (double) mass spectrometers played an important role in the early days of ion beam studies of reaction cross-sections and ‘excitation functions’ which give the dependence of the reaction cross-section on the centre-of-mass kinetic energy of the reagents. The development of the so-called MS/MS tandem mass spectrometer of the in-line configuration may in fact be traced to Futrell and Miller (1966). The experiments suffered until recently from the fact that only relative cross-sections could be determined, since only a fraction of the product ions was collected and that fraction depended on the dynamics of the specific reaction under study and on the collection angle of the forward scattered product. This problem has since been circumvented (Teloy and Gerlich 1974) through the use of an ion beam guide technique (an octopole) which provides 4π collection of ionic products. This allows the determination of absolute integral cross-sections over a wide translational energy range from thermal to 500 eV in the laboratory system (Ervin and Armentrout 1985).

Ion–molecule reactions were among the earliest systems whose cross-sections have been measured as a function of the internal energy of the ion. Development of the photoionization technique has thus enabled a vibrational state-selected study of the reaction

$$H_2^+(v')+H_2(v''=0)\rightarrow H_3^+ +H \tag{14}$$

(Chupka *et al.* 1968). Photoionization mass spectrometry has recently been combined with the ion beam guide technique (Shao and Ng 1985) into a very powerful tandem photoionization mass spectrometer.

The octopole ion beam guide is formed by eight rods placed in an octagonally symmetric array around the beam path. Radio frequency (r.f.) electric potentials applied in opposite phases to alternate rods produce an inhomogeneous field which creates an effective radial potential well. The octopole traps ions in radial directions over a broad range of ion masses while not affecting the axial ion velocities. The trapping ensures that ionic products are collected regardless of scattering angle. Its development took some time from its inception in 1974, but the last year or two indicate that it will feature strongly in future studies of absolute reaction cross-sections by tandem mass spectrometry. These studies, as has already been indicated for reaction (14) by Shao and Ng (1985) and for

$$Ar^+ +H_2, D_2, HD\rightarrow ArX^+ +Y \quad \text{(where X, Y = H or D)} \tag{15}$$

by Ervin and Armentrout (1985) will allow much more informed comparisons to be made in the future between experiment and theory.

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