Multiphoton ionization and chemical dynamics

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Multiphoton ionization spectroscopy is a tool for the elucidation of the structure of high-energy states of atoms and molecules. Particularly when used in combination with time-of-flight mass spectrometry and photoelectron spectroscopy, the range of applications include pure spectroscopic studies, the quantum state specific detection of reactants and products and the preparation of quantum-state-selected reactants for chemical reactivity studies. As such, the techniques have become ubiquitous in the field of chemical reaction dynamics. This paper is concerned mainly with the describing the range of these applications and techniques and a selection of typical results.

1. Introduction

Multiphoton techniques have become standard tools in the realm of physical chemistry and, in particular, chemical reaction dynamics. Although multiphoton absorption may result in either highly excited neutral molecules or ions, this review will encompass only the latter. The multiphoton ionization (MPI) techniques may be employed to create reactive ions, to probe product final states or to identify reaction products. The basis of the technique is straightforward. Irradiation of a molecule with an intense laser source leads to the absorption of two or more photons and, if the total energy absorbed by the molecule exceeds its ionization potential, an electron is ejected. The initial absorption may occur via specific electronic states of the neutral molecule (resonantly enhanced multiphoton ionization (REMPI) or in the absence of resonances (non-resonant multiphoton ionization (NRMPI)). These two pathways are shown in figure 1. In general, the ions created in the process may be detected in a non-specific manner by recording the total ion current. Alternatively, these ions may be mass selectively detected via the addition of a mass spectrometer or by means of photoelectron spectroscopy. The major advantage of the MPI technique lies in the ability to probe high-energy states of atoms and molecules, states that would under single-photon conditions require the generation of vacuum ultraviolet radiation. The MPI spectrum provides details of high-lying spectroscopic states of the neutral atom or molecule as well as a means of monitoring the 'purity' of quantum state selected ion experiments.

In REMPI, the initial excitation occurs via a real intermediate state of the neutral molecule, as shown in figure 1. This state may be accessed by a single photon or multiple photons. Ionization occurs from this excited state of the neutral, and resonances in the ion current measurements reflect the matching of the laser wavelength with the transition energies of the neutral molecule. Typically, the excited state is a Rydberg molecule and the geometry of the Rydberg state is very nearly identical with that of the final ion state. Using this technique, it is theoretically feasible to pump selected vibrational levels of the ion using the Rydberg state as a stepping stone. Of course, as a practical matter, it is essential to monitor the actual quantum
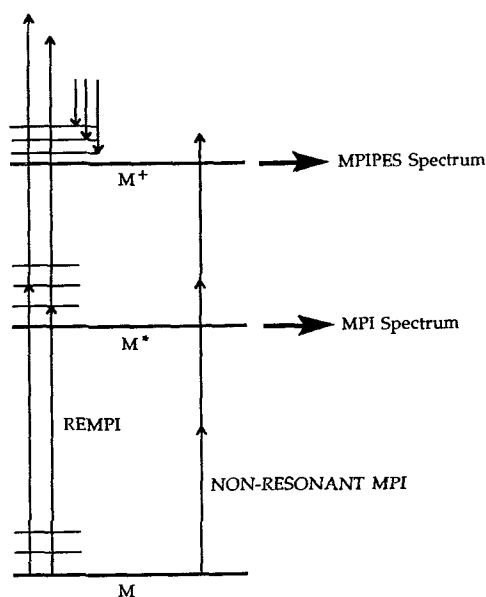
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Figure 1.   Schematic representation of multiphoton processes.

state distribution of the ion, since other factors may leading to state mixing and limit the extent of production of a particular level. In NRMPI, the wavelength of the laser is such that there is no match between the energy of the incident radiation and the transition energies of the neutral molecule. Photons are absorbed until the threshold for ionization is attained and the electron is ejected. It is possible in either case, REMPI or NRMPI, to ascertain the distribution of ionic quantum states by means of multiphoton ionization photoelectron spectroscopy (PES). However, depending upon the exact technique employed, different data are extracted. For example, if the energies of the resonant states in REMPI are known, then the kinetic energies of the electrons are diagnostic for the vibrational levels of the ionic quantum states. Conversely, knowledge of the final ionic levels allows for assignment of the intermediate resonant state. In non-resonant MPI, the kinetic energies of the ejected electrons are indicative of the distribution of final ionic states provided that the number of absorbed photons may be unambiguously determined by other means. In practice, this is not a trivial matter.

The development of MPI techniques and many of the early applications, including multiphoton ionization mass spectrometry (MPIMS) were reviewed by the pioneers in the field (Johnson 1980, Robin 1980, Antonov and Letokhov 1981, Johnson and Otis 1981, Lichtin *et al.* 1981, Schlag and Neusser 1983, Parker 1983). Later reviews (Baer 1984, 1987) covered developments up to 1987. The applications of photoelectron spectroscopy techniques have also been reviewed up to 1987 (Kimura 1985, 1987, Dehmer *et al.* 1987). There are also several excellent monographs detailing both experimental and theoretical methods (Letokhov 1983, Lin *et al.* 1984, Lambropoulos and Smith 1984).

2.   Experimental procedures

Here I describe the basic apparatus required for each type of MPI technique. These methods include simple ion current measurements, mass-selective measurements and photoelectron spectroscopy. The intention is to relate the fundamental principles

behind each type of procedure rather than to provide intricate details of the apparatus. Construction details and the detailed theoretical aspects of instrument assembly are contained in the cited references.

Regardless of the ion detection technique, all MPI methods require the availability of a tunable high-intensity laser source for single-colour measurements and two such lasers for the more detailed two-colour spectra in which one wavelength is employed to reach a resonant state and a second to ionize the molecule from that resonance. Typically, this need has been met by means of a (nanosecond) pump source such as an excimer, neodymium-doped yttrium aluminium garnet or nitrogen laser coupled with a dye laser. In addition, many ionization schemes require tunable near-utraviolet radiation so that appropriate nonlinear mixing crystals and/or Raman shifting cells are required. More recent studies have taken MPI spectroscopy into the faster time regime employing both picosecond (for example Gobeli *et al.* (1984), Tai and El-Sayed (1986), Szaflarski and El-Sayed (1988), El-Sayed and Tai (1988), Beuerman and Stuke (1989) and DeBoer and Muller (1992)) and femtosecond (for example Baumert *et al.* (1990), Dantus *et al.* (1991) and Wei *et al.* (1992)) laser pulses. The picosecond time frame generally promotes the formation of molecular ions over fragment ions, a decided advantage in yield being of importance to measurements of molecular ion decomposition. The femtosecond studies have been primarily focused on the use of MPI as a quantum-selective tool for the identification of product species in ultra-fast time frames. The faster time regime promotes the ladder mechanism of ion formation rather than the more complex ladder switching mechanism. Some recent studies have involved the use of two-photon schemes built upon the availability of vacuum untraviolet laser radiation (Ng 1991). These energetic photons are produced by nonlinear processes in rare gases and metal vapours.

2.1. *Ion current measurements*

These are the simplest MPI measurements. The apparatus consists of an evacuated cell fitted with a pair of quartz windows and a set of electrodes (Johnson 1980). The electrodes may be a set of parallel plates, usually fabricated from stainless steel or another inert metal or, alternatively, may be a cylindrical repelling electrode with a concentric collector wire, again constructed of inert materials. Experimental measurements consist of recording the total ion current as a function of the laser wavelength. Typically, a fast current amplifier or a boxcar averager is used in the detection circuit. These cells may be used over a wide range of pressure, but care must be taken to ascertain the regime in which the cell is operated, that is ionization cell, amplified counter, etc. (Korff 1955). In addition, any attempt at quantitative results requires careful monitoring of the windows so that the laser is not attenuated by deposits from photofragments. A wide range of spectroscopic and mechanistic experiments have been carried out in ionization cells, including some in which the photophysics are such that the ion detection is essentially mass selective even in the absence of a mass spectrometer. Although simple in design and operation, this device remains an important tool in MPI experiments.

2.2. *Time-of-flight mass spectrometry*

MPI spectroscopy may also be carried out in the source region of a time-of-flight (TOF) mass spectrometer. The typical TOF mass spectrometer source region consists of a repeller plate and one or more acceleration fields. This category of experiment is

carried out in a high-vacuum chamber with a pulsed nozzle source and, in most instance, a differentially pumped flight chamber. Pressures are in the range of 10^{-6} Torr and ion detection is accomplished by means of an electron multiplier and a fast digital oscilloscope (Siuzdak and BelBruno 1990). Resolution is controlled by 'focusing' effects (Wiley and McLaren 1955) and is related to the length of the flight tube and the applied potentials in the source and acceleration regions. By means of suitable delays the target in these experiments may be either the ion itself or a neutral fragment created in the initial photochemical preparation. In addition, this is a convenient apparatus for the study of the transitions of radicals and reactive ions not readily prepared in the absence of molecular beams. In these experiments, the detection system may be gated to accept only ions of a particular mass and the ion current is recorded as a function of the laser wavelength (for example Hudgens *et al.* (1987), Johnson *et al.* (1989) and Johnson and Hudgens (1991)).

Mass resolution has been dramatically improved by the development of reflectron mass spectrometers in which the ion spatial distributions are compensated by the presence of a reflecting field at the end of the flight tube (Karataev *et al.* 1971, Boesl *et al.* 1982, Kühlewind *et al.* 1983, Lubman *et al.* 1983). Reflectrons having a resolution of up to 10 000 have been reported (Walter *et al.* 1986) and these instruments find ready application in the study of the spectroscopy and dynamics of cluster ions.

Finally, the added mass spectrometer need not be a TOF device. Quadrupole instruments have been modified to accept laser ionization sources. These instruments provide single-mass detection but surrender the advantage of recording the entire mass spectrum for each laser pulse inherent in the TOF mass spectrometer.

2.3. *Photoelectron spectroscopy*

Several different types of photoelectron energy analysis systems have been reported. The simplest are TOF tubes of a design similar to those used for ion analysis (Meek *et al.* 1980, Hepburn *et al.* 1982, Appling *et al.* 1988, Hillenbrand *et al.* 1990). In these experiments, the photoelectrons are detected by an electron multiplier after passage through a relatively short (about 15 cm) drift tube. In some instances, very low potential fields are used to focus the electrons into the analyser. The photoelectron drift tube must be carefully shielded from stray magnetic fields.

Electrostatic analysers have also been employed (Compton *et al.* 1980) and at least one commercial system is available (Comstock 1993). Finally, several novel detectors have been reported for the study of zero-kinetic-energy photoelectrons. These include a compact deflection analyser (Takahashi *et al.* 1992) and a capillary system (Takahashi *et al.* 1991). These devices may be easily inserted into a TOF mass spectrometer and therefore offer the advantage of direct correlation of electron energy with a corresponding ion.

3. Results

MPI is employed in a wide range of chemical experiments. It is impossible to cover all these applications in a single review. Therefore, this report will concentrate on only three aspects of the field. These include (1) the use of MPI in mass spectrometry for the purposes of mechanistic interpretation of photochemical events, (2) unimolecular reactivity of ions produced by MPI and (3) the use of MPI as a detection technique in bimolecular reaction dynamics.

3.1. *Multiphoton ionization mass spectrometry of organic molecules*

MPIMS was first introduced approximately 15 years ago (Antonov *et al.* 1978, Boesl *et al.* 1978, Zandee *et al.* 1978, Rockwood *et al.* 1979, Lubmann *et al.* 1980). The technique has been employed to great advantage in the study of the photofragment-ation of fragile molecules and ions, especially in those instances where electron impact ionization leads to indiscriminate fragmentation of the parent ion. It appears that the extent of fragmentation may be controlled not only by the wavelength and the laser intensity but also by the temporal width of the ionizing radiation. Nanosecond lasers result in fragmentation via the ladder-switching mechanism, while faster lasers produce parent ion via the ladder mechanism.

Generally, one may classify the research in MPIMS into three categories. First, there are studies of the dynamics of the fragmentation of 'small' molecules, up to, for example, the size of substituted benzenes. Next are studies of the unimolecular dynamics of organometallic molecules of various sizes, controlled by the nature of the ligands on the central metal atom. Finally, many large biomolecules, proteins, nucleic acids, ets., are actively under study. Our interest, for purposes of this review, is limited to the first two categories.

One particular target of these studies has been small heterocyclic ions (BelBruno 1991, BelBruno and Christophy 1992, BelBruno 1993a, b). Comparison was made, using non-resonant MPIMS, between the cyclic ions and the analogous acyclic ions so that information could be inferred on the stability of the ring-closed and ring-opened forms of the heterocyclic ions. Some of the proposed reaction pathways are presented in scheme 1. High-level *ab-initio* calculations were also made of the stability of ring-opened and ring-closed forms of the ions. The results indicated that the thiirane ion was

$$CH_3CH_2\overset{+}{\underset{H}{N}}CH_2CH_3 \longrightarrow C_4H_{10}N^+ \longrightarrow C_2H_4N^+$$
$$\longrightarrow C_3H_8N^+ \longrightarrow CH_3N^+$$

$$c\text{-}C_4H_9N^+ \longrightarrow C_4H_8N^+ \longrightarrow C_2H_4N^+; C_2H_4^+ \longrightarrow CH_2N^+$$

$$CH_3\overset{+}{S}CH_3 \longrightarrow CH_3S^+; CH_3^+ \longrightarrow HCS^+ \longrightarrow CS^+$$

$$c\text{-}C_2H_4S^+ \longrightarrow HCS^+; HS^+ \longrightarrow CS^+; S^+$$

$$CH_3\overset{+}{O}CH_3 \longrightarrow CH_3OCH_2^+ \longrightarrow H_2CO^+; HCO^+$$

$$c\text{-}C_2H_4O^+ \longrightarrow C_2H_3O^+; HCO^+ \longrightarrow CO^+$$

$$CH_3CH_2OCH_2CH_3 \longrightarrow C_3H_7O^+ \longrightarrow C_2H_5O^+ \longrightarrow C_2H_5^+; O?$$
$$\longrightarrow H_3CO^+; HCO^+$$

$$c\text{-}C_4H_8O^+ \longrightarrow C_3H_7^+ \longrightarrow C_3H_3^+ \longrightarrow C_2H_x^+ \longrightarrow C^+$$

Scheme 1. Comparision of fragmentation pathways.

more stable in its ring-closed form, while the opposite was noted for the oxirane ion. The difference was attributed to the ability of the larger heteroatom to accommodate the severe bond angle in the ring-closed form. The ring-closed form of both five-membered rings were shown to be more stable than the ring-opened forms, apparently because of the less severe strain in these larger ions. Experimental results were in agreement with the theoretical predictions.

Some MPIMS experiments reflect the dynamics of the neutral parent molecule rather than those of the parent ion. This is generally true for the organometallic molecules discussed below, but also for nitroaromatic molecules (Marshall et al. 1992, 1993). In these experiments, various nitroaromatic molecules were shown, using MPI excitation, to pre-dissociate with subsequent ionization of the fragments. Interestingly, rotational MPI spectroscopy of the NO fragment was sufficient to identify the parent ion source of the NO fragment, a potentially useful signature for nitro-explosives.

A number of other 'small' molecules have been studied under conditions similar to those noted in detail above. Some of the more recent studies include alkyl cations (Kühlewind et al 1985), octafluorocyclooctatetraene (BelBruno et al. 1988), propanal (Liu et al. 1989), butylamine cations (Siuzdak and BelBruno 1990), aniline (Zimmerman and O'Malley 1990), propynal (Optiz 1991), the rotational isomers of m-chlorophenol (Cocket et al. 1991) and $C_7H_7^+$ (Lablanquie et al. 1993).

3.2. Multiphoton ionization spectroscopy and multiphoton ionization mass spectrometry of organometallic molecules

The other major application of MPIMS has been to the study of the photodissociation of neutral organometallic complexes (Chaiken 1993). MPIMS, in this case, is a state-specific detection technique for the product metal atoms formed by molecular dissociation. Alternatively, one may dispense with the mass spectrometer completely and use REMPI as a specific detector for the photoproduced metal atoms. In only a few isolated cases does ionization precede dissociation. This is a major difference with respect to the organic molecules discussed in § 3.1. The impetus in these experiments has been the desire to understand and control the vapour-phase chemistry necessary for efficient chemical vapour deposition (CVD) of thin films and the need to understand both chemistry occurring at surfaces and ablation processes. Much of the earliest research on organometallics was reviewed in a report which ranks as one the foundations for nonlinear photochemistry (Gedanken et al. 1982). A large variety of metal-containing complexes have been studied since the publication of the earliest work. This section includes a selection of the recent research presented as representative of that reported over the past 7–8 years. The actual number of organometallics studied is much larger than indicated here.

The most widely studied organometallic complexes have been the iron and chromium carbonyls. Results for these complexes have involved ion current measurements, mass spectrometry and photoelectron spectroscopy, with excitation most commonly into S_2, the ligand field transition of the iron complex (although some charge transfer excitation studies are known). The results appear to be independent of the nature of the initially excited state of the complex. In the case of iron complexes a wide range of ligands have been employed in an attempt to understand the effects of energy redistribution in the final states of the iron atoms produced under visible and near-ultraviolet radiation (for example Karny et al. 1978, Duncan et al. 1979, Enkelking 1980, Whetton et al. 1983, Harrison et al. 1985, Liou et al. 1986, Nagano et al. 1986, BelBruno et al. 1987, Niles et al. 1990, Mitchell and Hackett 1990). In

general the 'large' ligands with many vibrational degrees of freedom, such as cyclopentadiene, undergo intramolecular vibrational energy redistribution rapidly and decompose either by direct photodissociation or via a pre-dissociative state. On the other hand, the pentacarbonyl appears to represent a case of statistical reaction with sequential loss of –CO ligands subsequent to excitation. Tricarbonyl iron complexes represent a middle ground between the large ferrocene molecule and the small iron pentacarbonyl. Surprisingly, the kinetic behaviour of these complexes also represents an intermediate case. Unimolecular dissociation begins as a statistical process until all three –CO groups have been lost. At that point, the direct photodissociation of the unsaturated organoiron leads to production of atomic iron which is detected via $2 + 1$ REMPI. The overall rate constant for the process is controlled by the statistical part of the reaction channel and, hence, the size of the organic ligand. While spectroscopic measurements and mass spectrometric data indicate that some molecular ionization occurs, the only directly detected products have been the iron atoms. An example of a typical ion current measurement is shown in figure 2.

The chromium studies have primarily involved the hexacarbonyl (for example Fisanick *et al.* 1981, Tyndall *et al.* 1989 and Venkataraman *et al.* 1990) and the arene tricarbonyls (for example Hossenlopp *et al*, 1986 and Hossenlopp and Chaiken 1992). In experiments similar in character to those described for the iron complexes, the chromium carbonyls were observed to dissociate via two concurrent pathways. These were inferred to be a direct dissociation following multiphoton absorption and a sequential absorption–fragmentation initiated by one-photon absorption of the parent complex.

Molecules relevant to CVD are often alkylmetals. One class of molecules important to the CVD field is those containing selenium. Recent studies have focused on alkylselenium compounds (BelBruno *et al.* 1991b, 1993). For example, dimethyl-selenium was studied using REMPI and MPIMS employing excitation through the linear $^1A_1$ excited state. This excitation promotes photodissociation since it involves excitation of a non-bonding electron to a σ^* orbital. REMPI spectra exhibit sharp resonances due to ground-state atomic selenium superimposed on a broad structured background attributed to molecular excitations. Typical TOF spectra are shown in figure 3. The extent of fragmentation increases with increasing laser frequency so that the ratio of parent ion to unsaturated fragment to atomic selenium decreases and the
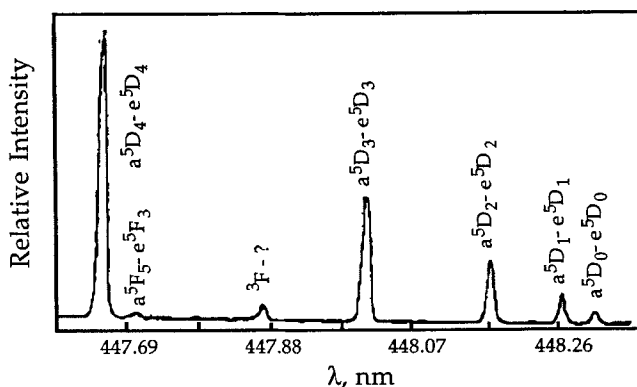

Figure 2. A portion of the REMPI spectrum of the products of the photodissociation of $Fe(CO)_3C_4H_6$.
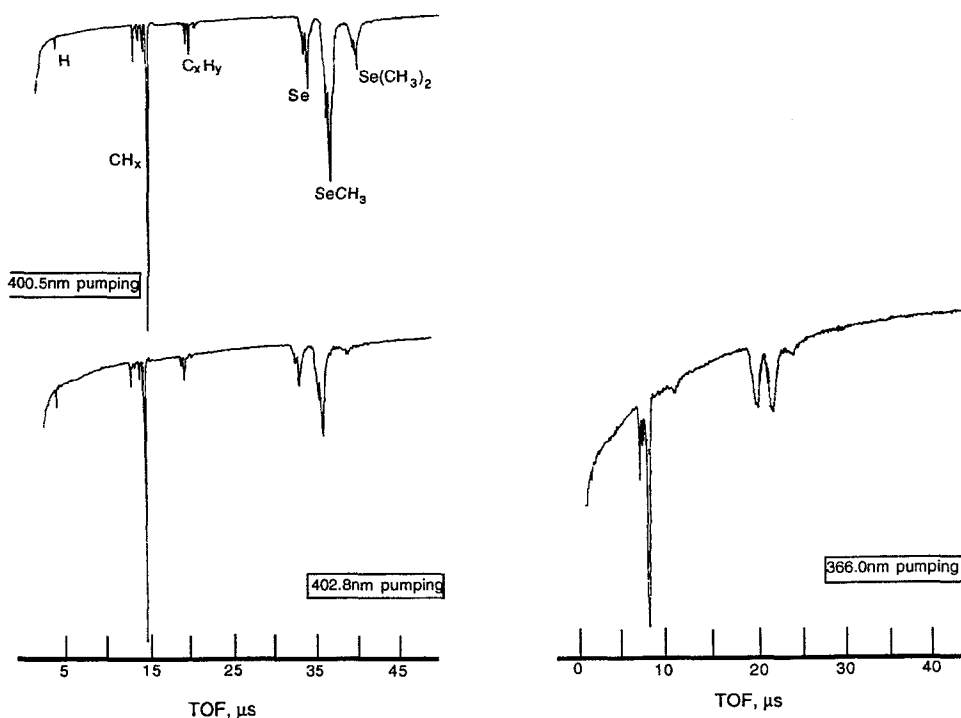
Figure 3.   TOF mass spectra for dimethylselenium (BelBruno *et al.* 1991).

parent ion becomes a pure source of selenium as the laser wavelength is moved into the ultraviolet region of the spectrum. The presence of the molecular background and the molecular fragments in the TOF spectra are indicative of two competitive dissociation schemes. In the first, atomic selenium is produced by dissociation of the neutral parent with subsequent ionization of the atoms. In the second, Se^+ is produced by photodissociation of the parent ion. The laser frequency and intensity control the competition.

A study combining REMPI and MPIMS of $Ge(C_2H_5)_4$ has recently been reported (Antman *et al.* 1993). Clearly, this molecule also has important implications for semiconductor applications. The parent molecule was observed to produce Ge^+ via both an ionic and a neutral photochemical channel. Under selected irradiation conditions, the ratio of molecular to neutral atomic products could be controlled and indications were that the parent molecule would be a useful source for CVD.

$Ga(CH_3)_3$ is another potential CVD source material. Multiphoton dissociation–MPI had been applied to the photochemistry of this molecule (Mitchell *et al.* 1985). In addition, time-resolved MPI was employed to aid in the identification of the neutral products. As was true in the case of the alkylselenium molecules, the nature of the photodissociation depends upon both the frequency and the intensity of the laser. In these REMPI and MPIMS experiments, the fragmentation mechanism in the visible wavelength range produced $Ga(^2Pj)$ via sequential loss of CH_3. However, in the near ultraviolet, 308 nm, only ionic products were observed. Finally, at 222 nm, the predominant product was $GaCH_3$, with small yields of atomic gallium.

3.3. *Unimolecular reactions of energy selected ions*

Unimolecular ion chemistry has been studied for a number of years and has involved a range of methods for the introduction of the excitation energy. These have included electron impact, charge exchange and conventional photoionization. Generally, the goal in these types of experiment is testing the statistical models of chemical reactivity that the majority of reactions have been found to follow. However, in any such experiment, the comparison with theory requires that the ion be produced in either a specific quantum level or in a narrow well defined internal energy range. The photoion–photoelectron coincidence (PIPECO) technique achieves the best energy resolution of the conventional techniques, since only those ions in coincidence with electrons of well defined energy are detected. As an alternative to these methods, REMPI has a number of inherent advantages. Using a single laser for two-photon ionization, one must select a wavelength such that the resonant intermediate state is slightly higher in energy than half-way to the ionization continuum. In this case, absorption of the second photon will lead to production of an ion with a slight excess of energy above the ionization limit. In general, the distribution of this excess energy between the vibrational states of the ion and the photoelectron will be a function of the Franck–Condon factors for excitation from the resonant intermediate state to the ion. Much greater control over the internal energy of the ion is afforded by two-colour two photon experiments in which the second laser is tuned to a particular vibrational transition. In either case, the state selection must be analysed by photoelectron spectroscopy. As an example of the state selectivity possible using this technique, figure 4 contains the photoelectron spectra produced by two-photon ionization of benzene (Neusser 1987). It is readily observed that the ion may be produced cleanly in either the v'_{16} or v'_0 vibrational state by variation of the laser wavelength in one-colour two-photon excitation.
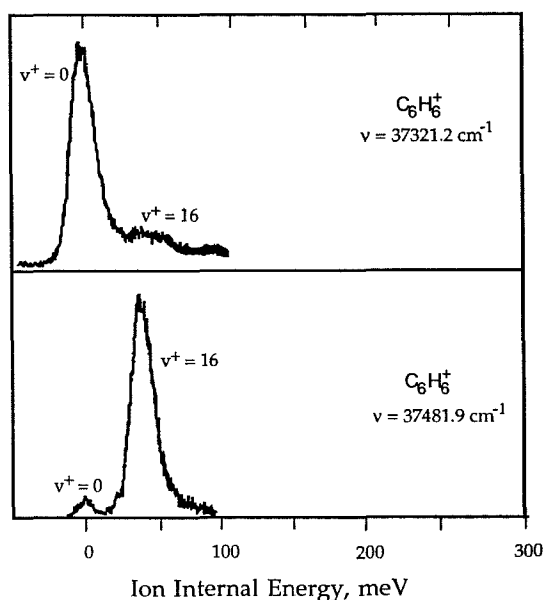

Figure 4. Photoelectron spectra from two-photon ionization of benzene (Neusser 1987).

3.4. Reflectron experiments

The selectivity shown in figure 4 was employed to study the energy dependence of the metastable unimolecular rate processes in benzene ions using a reflectron TOF mass spectrometer. Four product ions, namely $C_6H_5^+$, $C_6H_4^+$, $C_4H_4^+$ and $C_3H_3^+$, were observed. Since there are two channels present, carbon loss and hydrogen loss, the immediate question posed is whether or not these channels occur via different electronic states. The hydrogen-loss channels could not be examined by PIPECO due to the small mass change, so that this question remained unanswered for some time. The results (Kühlewind et al. 1985) show that all four channels exhibit the identical production rate, 0.57×10^6 s^{-1} at 5·19 eV and 1.5×10^6 s^{-1} at 5·37 eV. The constancy of this production rate indicated formation of both carbon-loss and hydrogen-loss product ions from the same precursor. Moreover, the individual rate constants as a function of excess energy, shown in figure 5, are in excellent agreement with the results of Rice–Ramsperger–Kassel–Marcus (RRKM) calculations.

In another study from the same laboratory (Neusser et al. 1985), the energy-selected decomposition of aniline was examined using the same technique. In this single-laser three-photon experiment using the reflectron TOF spectrometer, the internal-energy-dependent rate constant for the formation of HCN from excited aniline ions was determined. The production rate for $HCN + C_5H_6^+$ was found to be in agreement, at low excess energies, with measurements previously reported via PIPECO techniques and metastable line-shape analysis. Deviations at higher excess internal energies were attributed to the uncertainty in the internal energy due to the high levels of excitation and indicated the need for two-colour experiments.

An alternative technique based upon the reflection TOF mass spectrometer allows for pump-probe interrogation of the ion formation rate (Gobeli et al. 1985), a pulsed-excitation pulsed-extraction study of rate constants (El-Sayed and Tai 1988, Tai and El-Sayed 1986) or a determination of the rate at which initial excitation energy is redistributed prior to fragmentation (Gobeli et al. 1984), depending upon the exact
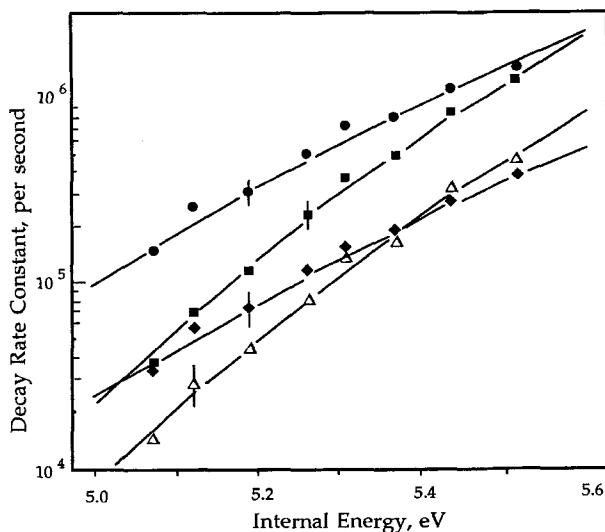

Figure 5. Energy dependent rate constants for carbon-loss and hydrogen-loss processes in benzene ions (Kühlewind et al. 1985): (———), the RRKM fit; ($\bullet$), $C_6H_6^+ \to C_6H_5^+ + H$; ($\blacklozenge$), $C_6H_6^+ \to C_6H_4^+ + H_2$; ($\blacksquare$), $C_6H_6^+ \to C_4H_4^+ + C_2H_2$; ($\triangle$), $C_6H_6^+ \to C_3H_3^+ + C_3H_3$.
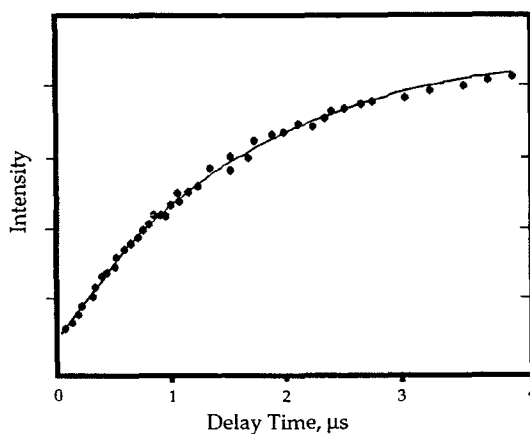
Figure 6. Rate of formation of $C_6H_4Cl^+$ from metastable 1,4-dichlorobenzene ion (Tai and El-Sayed 1986).

experimental arrangement. In the latter experiment the technique, using picosecond lasers and a linear TOF spectrometer, was employed in the first attempt to study. directly the redistribution of energy in 2,4-hexadiyne. The fourth harmonic of the yttrium aluminium garnet laser is used to populate S_1 by a one-photon absorption and the second harmonic produces ions from this vibronic state by means of a two-photon process. Changes in the mass spectrum, particularly in the peak attributed to the parent ion, on the time scale of the delay between the two colours reflects the time scale (about 25 ps) and nature of the energy redistribution process. The radiationless process was attributed to isomerization from a linear to a bent structure, occurring without an activation barrier. In addition, the mass spectrum showed evidence of variation in the intensities of the $C_4H_4^+$ fragment. Although no direct evidence could be provided, speculation was that the intensity of this fragment reflected a mechanism involving electronic excitation of the parent ion, relaxation to a vibrationally hot ground-state ion and subsequent formation of the fragment.

The rate of formation of $C_6H_4Cl^+$ from metastable 1,4-dichlorobenzene ions was studied using the pulsed-picosecond-laser pulsed-extraction-field technique (El-Sayed and Tai 1988). The metastable dichlorobenzene is ionized or excited by absorption of three ultraviolet photons, prior to dissociation. The detector in this case is a linear reflectron mass spectrometer and the rate of formation of the fragment is monitored by the peak area as a function of the delay time between the laser and the extraction field. The results are shown in figure 6 for 266 nm excitation. The rate constant for formation of $C_6H_4Cl^+$ is measured to be $4\cdot3 \times 10^5\,s^{-1}$, in agreement with reported measurements for this rate constant by other techniques.

3.5. *Linear time-of-flight experiments*

The unimolecular reactivity of *trans*-1,3-butadiene has been examined by several techniques, including MPI (Woodward *et al.* 1984). In the MPI experiments, a two-colour $2+1$ ionization–excitation scheme was employed for internal energy selection in the parent ion. Woodward *et al.* avoided the need to analyse mass spectrometric line shapes by employing a field-free dissociation region prior to the final acceleration field in a linear TOF mass spectrometer. In this way, the metastable parent ion appears as a sharp peak at a non-integral mass. A portion of the mass spectrum obtained by this
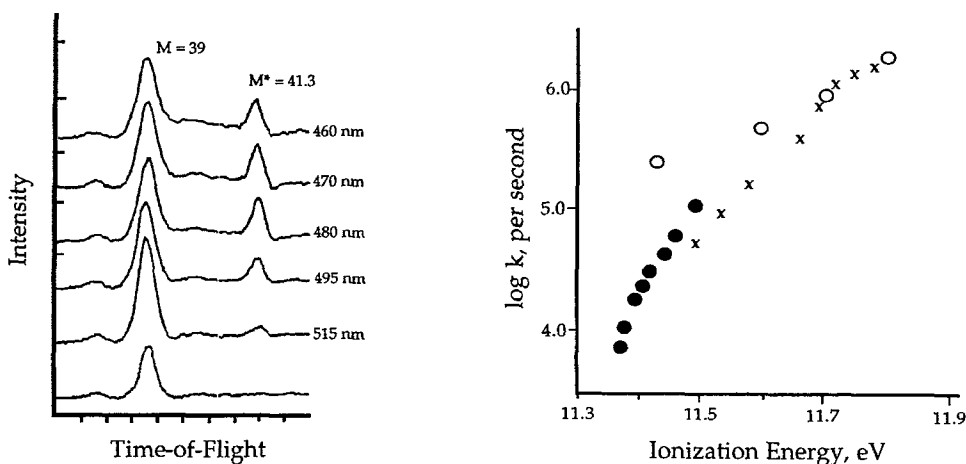
Figure 7. (a) Mass spectrum for *trans*-1,3-butadiene (Woodward *et al.* 1984). (b) Energy-
dependent rate constants for *trans*-1,3-butadiene compared with RRKM results (Wood-
ward *et al.* 1984).

procedure is shown in figure 7 (a). The rate constants for unimolecular decay of the
metastable butadiene ion are obtained by comparison with a calculated spectrum to fit
the relative yields of the various fragments in the spectrum. The results agree with
RRKM theory and are plotted in figure 7 (b) as a function of total energy input
(ionization plus internal energy). The results were found to be in agreement with those
obtained by the PIPECO technique, indicated by the circles and crosses in the figure.

Unimolecular ion kinetics may be studied using direct ionization followed by line-
shape observation in a linear TOF mass spectrometer. If fragmentation of a metastable
ion occurs during acceleration, the fragment ion peak is asymmetrically distorted, with
the peak shape controlled by the rate of dissociation and the absorbed energy. This
method was first applied to aniline (Proch *et al.* 1981) using one-colour 1 + 1 REMPI.
In these experiments, metastable aniline was observed to decay to $C_5H_6^+$ with the
release of HCN. The rate constant for this reaction was a direct function of the
ionization laser wavelength, increasing with increasing excess internal energy. The
spectral results are presented in figure 8. At 266 nm, analysis of the line shape using only
the rate constant for metastable decomposition as a fitting parameter indicated a value
of k of approximately $2 \times 10^6 \, \mathrm{s}^{-1}$. More extensive detail was provided for an analogous
experiment in the same laboratory (Durant *et al.* 1984), involving the metastable loss of
chlorine from chlorobenzene ion. The ions were created by a one-colour 1 + 1 resonant
MPI with excitation by absorption of a single additional photon. The photoelectron
spectra for chlorobenzene ion and the phenyl ion were identical, indicating a common
source for these two ions. Moreover, the phenyl ion peak in the mass spectrum was
broadened asymmetrically toward the higher masses. Photoelectron spectroscopy
experiments enabled Durant *et al.* to place upper and lower bounds on the internal
energy of the metastable chlorobenzene. By means of a Fourier transform, the internal-
energy-dependent rate constant was determined to be in the range from 5×10^5 to
$1 \times 10^6 \, \mathrm{s}^{-1}$ for total absorbed energy in the range from 13·6 to 13·9 eV. The rate
constant was independent of laser power. This range of rate constants was in agreement
with simple RRKM predictions of about $10^5 \, \mathrm{s}^{-1}$. Once again the results may be
favourably compared with those obtained by PIPECO methods.

18.00 18.20 18.40 μs

266 nm

270 nm

275 nm
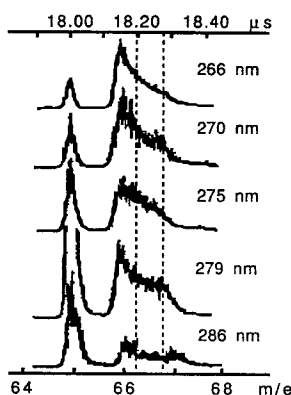
279 nm

286 nm

64   66   68 m/e

Figure 8. Energy-dependent rate constant for the metastable aniline decaying to $C_5H_6^+$ (Proch *et al.* 1981).

Rate constants (excitation via the 12_1^0 vibrational state of the neutral molecule) for metastable loss of Cl from $C_6H_5Cl^+$ (Ripoche *et al.* 1991).

E_{total} (eV)	k $(10^6 \, s^{-1})$
13·312	0·31 ($\pm 10\%$)
13·385	0·46 ($\pm 5\%$)
13·501	0·75 ($\pm 5\%$)
13·579	1·02 ($\pm 5\%$)

A similar MPI–TOF mass spectrometry technique has been employed (Lemaire *et al.* 1987) to study the unimolecular ion chemistry of phenetole. The TOF apparatus was of the conventional linear design. Ionization and/or excitation was accomplished using three colours in an attempt to minimize the error in the determination of the internal-energy-dependent rate constants. The metastable phenetole ion was observed to decay to $C_6H_6O^+ + C_2H_4$ with rate constants in the range from 2×10^6 to $5 \times 10^6 \, s^{-1}$ for internal energies of 2·6–3·2 eV. The reported errors are relatively large and the agreement with RRKM theory is poor, unless a somewhat convoluted mechanism is employed. The experiments lacked the spectral narrowing obtained using a supersonic expansion and, perhaps, were testing a molecule that was too complex to fit simple models.

The same technique using two colours was employed in the study of the formation of $C_6H_5^+$ from metastable chlorobenzene (Ripoche *et al.* 1991). These experiments further improved on the many earlier measurements on this reaction system. The experiment reduced the reported errors in the energy-dependent rate constants to as low as 5% as indicated in the table.

Two additional experiments involving ion decay are less certain in the energy content of the ion and rely on spectroscopic arguments to set the range of the internal excitation. The first involves the unimolecular chemistry of CF_3I^+ (Waits *et al.* 1992). Excitation was through a two-photon resonant Rydberg state of the neutral that has no equivalent one-phonon transition. Production of either CF_3^+ or I^+ is controlled by
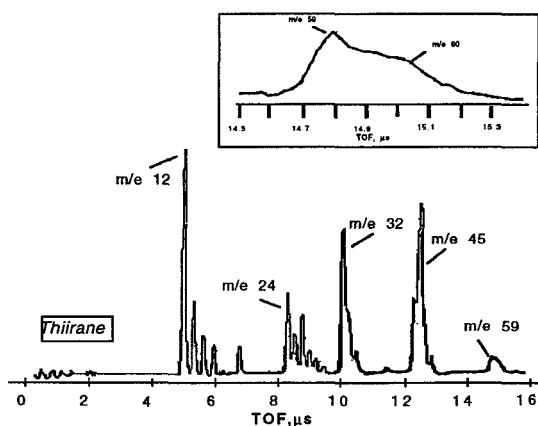
Figure 9.   TOF spectrum for ethylene sulphide. The metastable peak is shown in the inset.

excitation to either the ground ionic state of CF_3I^+ ($^2E_{3/2}$) by $2+1$ REMPI to produce CF_3^+ *or the excited $^2A_1$ state by absorption of an additional photon to produce a mixture of CF_3^+ and I^+. The observations differed from those reported for the analogous CH_3I^+ chemistry.*

Metastable unimolecular reactivity has also been observed in ethylene sulphide and ethylene oxide (BelBruno 1993c). Using the TOF line-shape technique coupled with MPI, a broad asymmetric peak is observed in the mass spectrum of ethylene sulphide, extending from mass 59 to mass 60, the parent ion. An example of such a spectrum is shown in figure 9. The peak is assigned to the metastable loss of $-H$ from the parent $C_2H_4S^+$ during acceleration of the ion in the mass spectrometer. Preliminary analysis of the line shape indicates that the rate constant for this process using approximately $100\ MW\,cm^{-2}$ at $355\ nm$ is $7\cdot4 \times 10^6\,s^{-1}$ with the internal energy in the range $4\cdot5$–$5\cdot9\ eV$. The wavelength selected represents the energy required for a $2+1$ ionization of the parent molecule. Similar preliminary results for ethylene oxide indicate the existence of a metastable pathway for formation of $C_3H_3^+$ from the parent ion with a rate constant in the range of $3 \times 10^6\,s^{-1}$.

3.6. *Bimolecular dynamics*

MPI spectroscopy has been often used as a probe to follow the course of bimolecular chemistry and to examine physical phenomena such as flames (for example Baulch *et al.* 1991 and Bernstein *et al.* 1993). While many detection applications are routine, some of the ionization schemes prove to be challenging and interesting. For example, REMPI may be used to follow the reaction between $N(^2P)$ and oxygen by monitoring the concentration of nitrogen atoms (Phillips *et al.* 1987). In a similar way, the course of the catalytic oxidation of methane may be observed by REMPI of the methyl radicals formed in the process (Gulcicek *et al.* 1990). One of the most interesting ionization schemes has been applied to the detection of molecular hydrogen, formed in one instance by elimination from cyclohexadiene (Cromwell *et al.* 1991) and, in another, to follow the concentration of H_2 (or its isotopic variants) in an accurate measurement of the rate constant for the $D+H_2$ and $H+D_2O$ reactions (Adelman *et al.* 1992, 1993). The technique and the requisite analysis are presented in an earlier paper (Rinnen *et al.* 1991). In brief, any isotopic variant of H_2 may be state specifically detected by $2+1$ REMPI using laser radiation near $215\ nm$. The lasers populate the

ground vibrational state of the E,F $^1\Sigma_g^+$ electronic state via a Q-branch transition and with sufficiently narrow-bandwidth lasers the isotopes are readily differentiated. The other schemes noted above are implemented in similar manner; however, the detection of H_2 has historically been a difficult problem until the application of MPI spectroscopy.

4. Future directions

Speculation on future developments is always a subjective exercise. One hopes to look at recent developments and project which of these experiments will have an impact over the next few years, but each researcher brings a different set of prejudices to this exercise. Below are two aspects of recent work in MPI that may predict the future directions of this science.

4.1. *Photofragment imaging*

One of the most interesting, and potentially revolutionary, developments in MPI studies is the use of two-dimensional electron–ion detectors (Chandler and Houston 1987, Chandler *et al.* 1989, 1990, Thoman *et al.* 1988). Application of this methodology to CH_3I and isotopic variants has been reported. In these experiments, MPI is used to detect methyl radicals produced from the photodissociation of neutral parent molecules. The technique employs the position of the ions as well as their arrival time to determine the velocities of state-selected fragments. The goal is the reproduction of the spatial distribution of particular fragments at a specific point in time following photodissociation. Signals appear as concentric rings representing methyl radicals produced in concert with $I(^2P_{1/2})$ and $I(^2P_{3/2})$. Both the branching ratio for these two reaction channels as well as the rotational energy distribution in the methyl radicals is reported. The technique offers the possibility of *directly* obtaining a wealth of state-specific photochemical data as well as mechanistic information and should be more generally applied in future studies of bimolecular as well as unimolecular reaction dynamics.

4.2. *Ultra-fast multiphoton ionization*

Another exciting development in MPI has been the increased availability of ultrafast lasers. Femtochemistry includes MPI among its diverse applications as both a detection technique and as a pumping mechanism to create molecular ions. A review has recently appeared (Zewail 1993) and an entire issue of the *Journal of Physical Chemistry* (97 (48)) has been devoted to ultra-fast reaction dynamics. The production of molecular ions is favoured over fragment ions as the temporal resolution of the laser increases. This is attributed to the fact that the ladder mechanism becomes dominant over the ladder-switching mechanism. Clearly, reaching the limit of femtoseconds takes us to the extreme of this 'fast' regime.

The second interesting application of ultra-fast MPI is to the probing of real-time reaction dynamics, that is directly observing reactions on the time scale of a molecular vibration. Pump and probe experiments have been reported for sodium dimers (Baumert *et al.* 1990), sodium trimers (Kühling *et al.* 1993) and IHgI (Baumert *et al.* 1993, Pedersen *et al.* 1993). In the case of Na_3, the experiments directly proved that the excited D state of the trimer was pre-dissociative and produced Na_2^* and Na as products. This resolved a controversy ignited by the incongruent nanosecond and picosecond results. The fragmentation time was reported to be in the range from 260 to 640 fs. In the mass-selected IHgI study, the various product fragments were shown to

evolve on a time scale comparable with the vibrational period and the fast technique was capable of distinguishing three different processes all producing different final states. The possibilities for MPIMS as a detection technique using ultra-fast lasers in real-time reaction dynamics are promising and exciting.

References

ADELMAN, D. E., FILSETH, S. V., and ZARE, R. N., 1993, *J. chem. Phys.*, **98**, 4636.

ADELMAN, D. E., SHAFER, N. E., KILNER, D. A. V., and ZARE, R. N., 1992, *J. chem. Phys.*, **97**, 7323.

ANTMAN, M., HILT, L., CHRISTOPHY, E., and BELBRUNO, J. J., 1993, *Chem. Phys. Lett.* (in press).

ANTONOV, V. S., KNYAZEN, I. N., LETOKHOV, V. S., MATIUK, V. M., and MORSHEV, V. G., 1978, *Optics Lett.*, **3**, 37.

ANTONOV, V. S., and LETOKHOV, V. S., 1981, *Appl. Phys.*, **24**, 89.

APPLING, J. R., WHITE, M. G., KESSLER, W. J., FERNANDEZ, R., and PLOIAKOFF, E. D., 1988, *J. chem. Phys.*, **88**, 2300.

BAER, T., 1984, *Ionic Processes in the Gas Phase. NATO Adv. Stud. Inst. Ser., Ser. C*, **118**, 205.

BAULCH, T., BUEHLER, B., THALWEISER, R., and GERBER, G., 1990, Springer Proceedings in Physics, Vol. 49 (Berlin: Springer), p. 240; 1991, *Proc. R. Soc.* A, **434**, 399.

BAUMERT, T., PEDERSON, T., and ZEWAIL, A. H., 1993, *J. phys. Chem.*, **97**, 12447.

BELBRUNO, J. J., 1991, *Trends phys. Chem.*, **2**, 185; 1993a, *Appl. Phys.* B, **56**, 263; 1993b, *Int. J. Mass Spectrom. Ion Processes* (submitted).

BELBRUNO, J. J., BARNES, E., JALKUT, M., and CHRISTOPHY, E., 1993, *Chem. Phys. Lett.* (submitted).

BELBRUNO, J. J., and CHRISTOPHY, E., 1992, *Int. J. Mass Spectrom. Ion Processes*, **115**, 111.

BELBRUNO, J. J., GREENFIELD, S. R., CARL, R. T., and HUGHES, R. P., 1988, *J. phys. Chem.*, **92**, 267.

BELBRUNO, J. J., KOBSA, P. B., CARL, R. T., and HUGHES, R. P., 1987, *J. phys. Chem.*, **91**, 6198.

BELBRUNO, J. J., SPACEK, J., and CHRISTOPHY, E., 1991, *J. Phys. Chem.*, **95**, 6928.

BERNSTEIN, J. S., FEIN, A., CHOI, J. B., COOL, T. A., SAUSA, R. C., HOWARD, S. L., LOCKE, R. J., and MIZIOLEK, A. W., 1993, *Combust. Flame*, **92**, 85.

BEUERMAN, T., and STUKE, M., 1989, *Chemtronics*, **4**, 189.

BOESL, U., NEUSSER, H. J., and SCHLAG, E. W., 1978, *Z. Naturf.* (a), **33**, 1546.

BOESL, U., NEUSSER, H. J., WEINKAUF, R., and SCHLAG, E. W., 1982, *J. phys. Chem.*, **86**, 4857.

CHAIKEN, J., 1993, *Laser Chemistry of Organometallics*, ACS Symposium Series, Vol. 530 (New York: ACS).

CHANDLER, D. W., and HOUSTON, P. L., 1987, *J. chem. Phys.*, **87**, 1445.

CHANDLER, D. W., JANSSEN, M. H. M., STOLTE, S., STRICKLAND, R. N., THOMAN, J. W., and PARKER, D. H., 1990, *J. phys. Chem.*, **94**, 4839.

CHANDLER, D. W., THOMAN, J. W., JANSSEN, M. H. M., and PARKER, D. H., 1989, *Chem. Phys. Lett.*, **156**, 151.

COCKET, M. C. R., TAKAHASHI, M., OKUYAMA, K., and KIMURA, K., 1991, *Chem. Phys. Lett.*, **187**, 250.

COMPTON, R. N., MILLER, J. C., CARTER, A. E., and KRUIT, P., 1980, *Chem. Phys. Lett.*, **71**, 87.

COMSTOCK, INC., 1993, *Model AC-902 Electrostatic Analyzer and Accessories Data Sheet.*

CROMWELL, E. F., LIU, D. J., VRAKKING, M. J. J., KUNG, A. H., and LEE, Y. T., 1991, *J. chem. Phys.*, **95**, 297.

DANTUS, M., JANSSEN, M. H. M., and ZEWAIL, A. H., 1991, *Chem. Phys. Lett.*, **181**, 281.

DEBOER, M. P., and MULLER, H. G., 1992, *Phys. Rev. Lett.*, **68**, 2747.

DEHMER, P. M., DEHMER, J. L., and PRATT, S. T., 1987, *Comments at. mol. Phys.*, **19**, 205.

DUNCAN, M. A., DIETZ, T. G., and SMALLEY, R. E., 1978, *J. phys. Chem.*, **44**, 415.

DURANT, J. L., RIDER, D. M., ANDERSON, S. L., PROCH, F. D., and ZARE, R. N., 1984, *J. chem. Phys.*, **80**, 1817.

EL-SAYED, M. A., and TAI, T. L., 1988, *J. phys. Chem.*, **92**, 5333.

ENKELKING, P. C., 1980, *Chem. Phys. Lett.*, **74**, 207.

FISANICK, G. J., GEDANKEN, A., EICHELBERGER, T. S., KUEBLER, N. A., and ROBIN, M. B., 1981, *J. chem. Phys.*, **75**, 5215.

GEDANKEN, A., ROBIN, M. R., and KUEBLER, N. A., 1982, *J. phys. Chem.*, **86**, 4096.

GOBELI, D. A., MORGAN, J. R., ST. PIERRE, R. J., and EL-SAYED, M. A., 1984, *J. phys. Chem.*, **88**, 178.

GOBELI, D. A., SIMON, J. D., SENSHARMA, D. K., and EL-SAYED, M. A., 1985, *Int. J. Mass Spectrom. Ion Processes*, **63**, 149.

GULCICEK, E. E., COLSON, S. D., and PFEFFERLE, L. D., 1990, *J. phys. Chem.*, **94**, 7069.

HARRISON, W. W., RIDER, D. M., and ZARE, R. N., 1985, *Int. J. Mass Spectrom. Ion Processes*, **65**, 59.

HEPBURN, J. W., TREVOR, D. J., POLLARD, J. E., SHIRLEY, D. A., and LEE, Y. T., 1982, *J. chem. Phys.*, **76**, 4278.

HILLENBRAND, S., ZHU, L., and JOHNSON, P. M., 1990, *J. chem. Phys.*, **92**, 870.

HOSSENLOPP, J. M., and CHAIKEN, J., 1992, *J. phys. Chem.*, **96**, 2994.

HOSSENLOPP, J. M., ROONEY, D., SAMORISKI, B., and CHAIKEN, J., 1986, *J. chem. Phys.*, **86**, 3326, 3331.

HUDGENS, J. W., DULCEY, C. S., LONG, G. R., and BOGAN, D. J., 1987, *J. chem. Phys.*, **87**, 4546.

JOHNSON, P. M., 1980, *Accts. Chem. Res.*, **13**, 20.

JOHNSON, P. M., and OTIS, C. E., 1981, *Rev. phys. Chem.*, **32**, 139.

JOHNSON, R. D., and HUDGENS, J. W., 1991, *J. chem. Phys.*, **94**, 5331.

JOHNSON, R. D., TSAI, B. P., and HUDGENS, J. W., 1989, *J. chem. Phys.*, **91**, 3340.

KARATAEV, V. I., MAMYRIN, B. A., and SHMIKK, D. V., 1971, *Soviet Phys. tech. Phys.*, **16**, 45.

KARNY, Z., NAAMAN, R., and ZARE, R. N., 1978, *Chem. Phys. Lett.*, **59**, 33.

KIMURA, K., 1985, *Adv. chem. Phys.*, **60**, 161; 1987, *Int. Rev. phys. Chem.*, **6**, 195.

KLINER, D. A. V., ADELMAN, D. E., and ZARE, R. N., 1991, *J. chem. Phys.*, **95**, 1648.

KORFF, S. A., 1955, *Electron and Nuclear Counters* (New York: van Nostrand).

KÜHLEWIND, H., KIERMEIER, A., NEUSSER, H. J., and SCHLAG, E. W., 1986, *J. chem. Phys.*, **85**, 4427.

KÜHLEWIND, H., NEUSSER, H. J., and SCHLAG, E. W., 1983, *Int. J. Mass Spectrom. Ion Processes*, **51**, 25; 1985, *J. phys. Chem.*, **89**, 5593, 5600.

KÜHLING, H., RUTZ, S., KOBE, K., SCHREIBER, E., and WÖSTE, L., 1993, *J. phys. Chem.*, **97**, 12 500.

LABLANQUIE, P., OHASHI, K., and NISHI, N., 1993, *J. chem. Phys.*, **98**, 399.

LAMBROPOULOS, P., and SMITH, S. J., 1984, *Multiphoton Processes* (Berlin: Springer).

LEMAIRE, J., DIMOCOLI, J., and BOTTER, R., 1987, *Chem. Phys.*, **115**, 129.

LETOKHOV, V. S., 1983, *Nonlinear Laser Chemistry* (Berlin: Springer).

LICHTIN, D. A., ZANDEE, L., and BERNSTEIN, R. B., 1981, *Lasers in Chemical Analysis*, edited by G. M. Heitje, J. C. Travis and F. E. Lytle (New Jersey: Humana Press), p. 125.

LIN, S. H., , FUJIMURA, Y., NEUSSER, H. J., and SCHLAG, E. W., 1984, *Multiphoton Spectroscopy of Molecules* (Orlando: Academic).

LIOU, H. T., ONO, Y., ENKELKING, P. C., and MOSELEY, J. T., 1986, *J. phys. Chem.*, **90**, 2880, 2990.

LIU, H. X., LI, Z. L., LI, S. T., QIAN, Y. L., WANG, Y., and WU, C. K., 1989, *Chem. Phys.*, **129**, 495.

LUBMAN, D. M., BELL, W. E., and KRONICK, M. N., 1983, *Anal. Chem.*, **55**, 1437.

LUBMAN, D. M., NAAMAN, R., and ZARE, R. N., 1980, *J. chem. Phys.*, **72**, 3034.

MARSHALL, A., CLARK, A., JENNINGS, R., LEDINGHAM, K. W. D., SANDER, J., and SINGHAL, R. P., 1992, *Int. J. Mass Spectrom. Ion Processes*, **116**, 143.

MARSHALL, A., CLARK, A., LEDINGHAM, K. W. D., SANDER, J., and SINGHAL, R. P., 1993, *Int. J. Mass Spectrom. Ion Processes*, **125**, R21.

MEEK, J. T., JONES, R. K., and REILLY, J. P., 1980, *J. chem. Phys.*, **73**, 3503.

MITCHELL, S. A., and HACKETT, P. A., 1990, *J. phys. Chem.*, **93**, 7813.

MITCHELL, S. A., HACKETT, P. A., RAYNER, D. M., and HUMPHRIES, M. R., 1985, *J. chem. Phys.*, **83**, 5028.

NAGANO, Y., ACHIBA, Y., and KIMURA, K., 1986, *J. phys. Chem.*, **90**, 1288.

NEUSSER, H. J., 1987, *Int. Mass Spectrom. Ion. Processes*, **79**, 141.

NEUSSER, H. J., KÜHLEWIND, H., BOESL, U., and SCHLAG, E. W., 1985, *Ber. Bunsenges. phys. Chem.*, **89**, 276.

NG, C. Y. (editor), 1991, *Vacuum Ultraviolet Photoionization and Photodissociation of Molecules and Clusters* (Singapore: World Scientific).

NILES, S., PRINSLOW, D. A., WIGHT, C. A., and ARMENTROUT, P. B., 1990, *J. chem. Phys.*, **93**, 6186.

OPTIZ, J., 1991, *Int. J. Mass Spectrom. Ion Processes*, **107**, 503.

PARKER, D. H., 1983, *Ultrasensitive Laser Spectroscopy*, edited by D. S. Klinger (New York: Academic Press), p. 233.

PEDERSEN, S., BAUMERT, T., and ZEWAIL, A. H., 1993, *J. Phys. Chem.*, **97**, 12 460.

PHILLIPS, C. M., STEINFELD, J. I., and MILLER, S. M., 1987, *J. phys. Chem.*, **91**, 5001.

PROCH, D., RIDER, D. M., and ZARE, R. N., 1981, *Chem. Phys. Lett.*, **81**, 430.

RINNEN, K. D., BUNTINE, M. A., KLINER, D. A. V., and ZARE, R. N., 1991, *J. chem. Phys.*, **95**, 214.

RIPOCHE, X., DIMICOLI, I., and BOTTER, R., 1991, *Int. J. Mass Spectrom. Ion Processes*, **107**, 165.

ROBIN, M. B., 1980, *Appl. Optics*, **19**, 3941.

ROCKWOOD, S., REILLY, J. P., HOHLA, K., and KOMPA, K. L., 1979, *Optics Commun.*, **28**, 175.

SCHLAG, E. W., and NEUSSER, H. J., 1983, *Accts. Chem. Res.*, **16**, 355.

SIUZDAK, G., and BELBRUNO, J. J., 1990, *J. phys. Chem.*, **94**, 4559.

SZAFLARSKI, D. M., and EL-SAYED, M. A., 1988, *J. phys. Chem.*, **92**, 2234.

TAI, T. L., and EL-SAYED, M. A., 1986, *Chem. Phys. Lett.*, **130**, 224.

TAKAHASHI, M., OZEKI, H., and KIMURA, K., 1991, *Chem. Phys. Lett.*, **181**, 255; 1992,THOMAN, J. W., CHANDLER, D. W., PARKER, D. H., and JANSSEN, M. H. M., 1988, *Laser Chem.*, **9**, 27.

THOMAN, J. W., CHANDLER, D. W., PARKER, D. H., and JANSSEN, M. H. M., 1988, *Laser Chem.*, **9**, 27.

TYNDALL, G. W., and JACKSON, R. L., 1989, *J. chem. Phys.*, **91**, 2881.

VENKATARAMAN, B., HOU, H., ZHANG, Z., CHEN, S., BANDUKWALLA, G., and VERNON, M., 1990, *J. chem. Phys.*, **92**, 5338.

WAITS, L. D., HOROWITZ, R. J., DANIEL, R. G., GUEST, J. A., and APPLING, J. R., 1992, *J. chem. Phys.*, **97**, 7263.

WALTER, K., BOESL, U., and SCHLAG, E. W., 1986, *Int. J. Mass Spectrom. Ion Processes*, **71**, 309.

WEI, S., PURNELL, J., BUZZA, S. A., STANLEY, R. J., and CASTLEMAN, A. W., 1992, *J. chem. Phys.*, **97**, 9480.

WHETTEN, R. L., FU, K. J., and GRANT, E. R., 1983, *J. chem. Phys.*, **79**, 4899.

WILEY, W. C., and MCLAREN, J. H., 1955, *Rev. scient. Instrum.*, **26**, 1150.

WOODWARD, A. M., CHUPKA, W. A., and COLSON, S. D., 1984, *J. phys. Chem.*, **88**, 4567.

ZANDEE, L., BERNSTEIN, R. B., and LICHTIN, D. A., 1978, *J. chem. Phys.*, **69**, 3427.

ZEWAIL, A. H., 1993, *J. phys. Chem.*, **97**, 12427.

ZIMMERMAN, J. A., and O'MALLEY, R. N., 1990, *Int. Mass Spectrom. Ion Processes*, **99**, 169.