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a series of complexes, can be accounted for in terms of a stabilization of the electron-deficient transition state by electron-donating groups.

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(51) The units are $s^{-1} \times 10^5$ at 109 °C.

Multiphoton Mass Spectrometry

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With the development of intense, pulsed lasers the absorption of several photons by a single particle became experimentally feasible, and multiphoton absorption has become an interesting method for the study of both atoms and molecules. It has the intriguing possibility of employing visible or near-ultraviolet light, which is readily obtainable, to produce high-energy states otherwise only accessible to vacuum ultraviolet light, which is difficult to produce. In the gas phase the lowest order of multiphoton absorption, two-photon absorption, was first studied with atoms and later with small molecules like nitric oxide[1] and also with polyatomic molecules like benzene.[2]

Since the selection rules of a two-photon process are different from those of a one-photon absorption, this opens up interesting new possibilities for the analysis of molecular spectra and structure, the first novel assignment in the gas phase being that for benzene.[3]

The observation of a two-photon transition can either proceed by detecting the fluorescence from the two-photon excited state or by exciting the molecule from the two-photon state to the ionization continuum with additional photons.[4,5] Such experiments can be carried out in the bulk gas phase or in a molecular beam. Multiphoton absorption to produce ions either via a one-photon or a two-photon state suggests the coupling of this method of ionization to a mass spectrometer. Early work on alkali-metal dimers, which are easily ionized at low energies, pointed to such possibilities.[6]

It was not until 1978 that a detailed mass spectrum was produced from a multiphoton source. Antonov et al. in a study of benzaldehyde and benzophenone used a combination of a fixed-frequency nitrogen and a fixed-frequency hydrogen laser[7] to produce ions at a fixed wavelength. Similarly, Rockwood et al. ionized benzene with a fixed-frequency KrF laser[8] and obtained an intense mass spectrum. In the same year, however, the full power of multiphoton methods in a mass spectrometer, along with some unexpected features, became clear when variable wavelengths were employed. Schlag et al.[9] as well as Bernstein et al.[10] revealed in different ways some of the main features of multiphoton mass spectrometry. Schlag et al.[11] demonstrated that the isotopic species mono-^{13}C-benzene can be preferentially ionized in a natural isotopic mixture by shifting the wavelength by 1.6 cm^{-1} from the absorption band of light benzene. This demonstrated that trace components in a mixture can be ionized without ionizing the major components if the intermediate-state spectrum shows sharp features at a resolution of 1 cm^{-1}. In general, the optical enhancement in a mass spectrometer can be obtained if the absorption coefficient of the various components differs at any chosen wavelength, which is also given for most molecules with broad absorption spectra. In further work they showed that the laser intensity can be adjusted so that only a (very strong) parent ion peak appears. This exclusive parent ionization is difficult to produce in conventional mass spectrometry, and soft ionization appears to be possible for all molecules that can be ionized in a two-photon ionization process with a real intermediate state that is resonant with the energy of one photon. For state-

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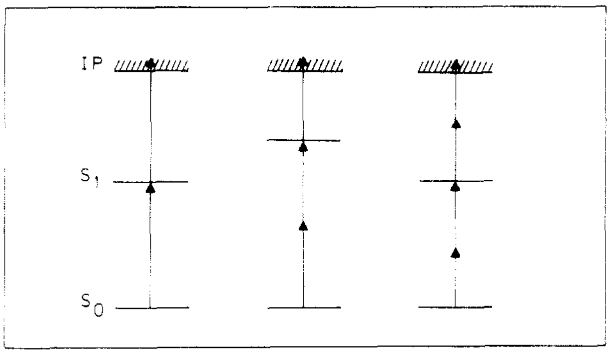

Figure 1. Three possible paths for multiphoton ionization. Several photons are required to reach ionization and here always with a real intermediate absorbing level of the molecule.

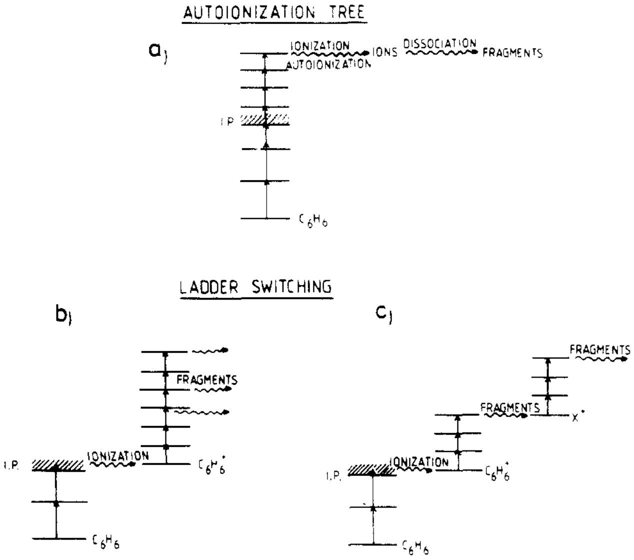

Figure 2. (a) Multiphoton ionization subsequent to multiphoton absorption into the final energetic state of the neutral molecule. (b) Multiphoton ionization occurring by autoionizing the first level to cross the ionization potential, thereafter absorption in the ion. (c) Same as b, except that absorption in the ion can lead to fragmentation to produce secondary ions, which in turn can absorb photons from the laser pulse.

of-the-art laser techniques this gives an upper limit for the ionization potential of about 10.5 eV. This, however, is not a severe limitation for analytic applications since most organic molecules have an ionization potential smaller than this.

Bernstein et al.[12] obtained a multiphoton mass spectrum for I_2 and soon followed this with some interesting observations on benzene.[10] Here they showed that, upon increasing the intensity of the laser, up to nine photons were absorbed in the multiphoton transition, thus producing increasing fragmentation of the benzene ions at higher intensities. The intensity studies add a useful third dimension to this new mass spectroscopy, which is already two-dimensional in mass and wavelength. For a resonant two-photon ionization process the light intensity allows a direct quantitative control of the ionization and fragmentation, ranging from soft ionization to produce pure parent ion mass spectra to hard fragmentation to produce small fragments that could be extended at high intensities. In this way low-energy dissociation channels are active at low intensity and, with increasing intensity, high-energy fragmentation channels become more and more active. From more recent work this is expected to be a general pattern.[13-15] In contrast only small changes in fragmentation patterns are observed in conventional mass spectra by changing the electron energies in the ionization source. Recently multiphoton mass spectrometry has found many other applications.[16]

Mechanism

To be efficient, the first several absorption steps of multiphoton ionization must involve a transition into a real intermediate level of the S_1 system (Figure 1). A second (or further) photon(s) then transports the molecule into the ionization continuum. In such a process the spectral properties of S_1 as well as the ionized state are important.

S_1 contributes the normal absorption spectrum, whereas ionization contributes the structure of the ionization continuum. From photoionization spectroscopy it is well known that there are two contributions to the cross section: (1) direct ionization to a vibronic level of the molecular ion and (2) autoionization out of Rydberg states. This second contribution results from Rydberg states within the ionization continuum, i.e., converging to higher ionic states, which are unstable to ionization.

For multiphoton ionization we expect similar behavior as long as the absorption step that crosses the ionization potential is also the final step of the total multiphoton absorption process. Intermediate-state absorption will, of course, change the expected final intensities. When an additional photon is added after having crossed the ionization potential, the absorption can proceed either via the neutral molecule or the parent ion (see below and Figure 2).

Climbing the energy ladder in a neutral molecule is only one possible route for excitation (Figure 2a). The other is shown in Figure 2b, namely, that ions are formed at the earliest possible stage, i.e., by the first photon to cross the ionization threshold. The absorption then switches from neutrals to ions immediately and indeed keeps on switching to fragments, etc. (Figure 2c). This will be referred to as the ladder switching model, proposed by Schlag et al.[17] Climbing to higher states via neutral intermediate states will be referred to as the autoionization tree model (Figure 2a). A model intermediate between these two involves energy deposition within the parent ions (Figure 2b).[14]

Some theoretical considerations are of interest here. For benzene, which has an absorption coefficient of about 10^{-17} cm^2, pumped with a N_2 laser pumped dye laser of intensity 10^8 W/cm^2, photon absorption within the absorption ladder occurs on a time scale of 100 ps. All other processes must be considered in relation to this time scale. Lifetimes in S_1 are usually longer than this.[15] In these cases optical pumping will outrun decay,

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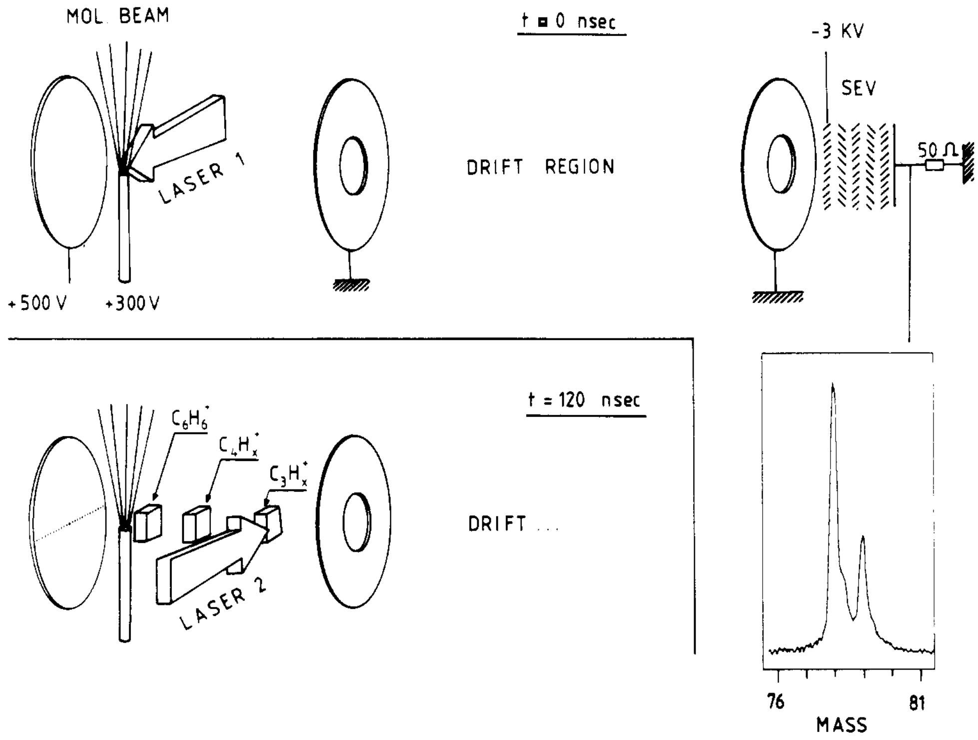

Figure 3. (a) Molecules are injected by a hypodermic needle into a region established by an electric field. Here they are ionized by laser 1. After acceleration they pass through a hole into a drift region of constant potential. Flight times are longer for larger masses, hence leading to a mass spectrum as the result of different arrival times. (b) Same as a except laser 2 intercepts the ions on their way to the hole into the drift region. Already at this point of interception the large ions fall behind so that laser 2 irradiates mass selected ions. The mass of these ions can be selected depending on the delay between laser 1 and 2.

hence preserving the electronically excited molecule until ionization. Above the ionization threshold, ionization occurs typically on a time scale of 0.1–1 ps. This now will outrun the optical pumping process. Hence optical pumping of the neutral molecule will now be interrupted, and we will cross to a new ladder of molecular ions.

This ladder switching will be typical for most molecular systems. However, exceptions may be expected in the case of high power (>1 MW) lasers and picosecond laser pulses although other mechanisms may well obscure the kinetics in such exotic systems. Another exception would be small molecules with predissociating states having lifetimes in the 10-ps range, since they would not produce intact parent molecular ions. In this case ladder switching to neutral fragments occurs even below ionization, in the neutral molecules. In this type of fragmentation the fragments will in general lose electronic energy although if the photon energy is resonant with a real state of the neutral fragment or with enough power, these neutral fragments again will lead to ionization. For most systems involving molecules beyond triatomics, for which a RRKM mechanism, i.e., statistical redistribution of energy among all degrees of freedom, can be presumed, one would expect ladder switching to be delayed until after ionization if absorption proceeds solely via the S_1 state.

When the molecular ions in turn acquire two to three photons of energy, they will dissociate into fragment ions. These fragment ions again will absorb two to three photons, leading to dissociation. This process of ladder switching continues until atomic fragment ions, C^+, etc., are finally produced (ignoring for the moment multiple ionization). These processes are sufficiently rapid that pumping and ionization, as well as several ladder switches, all can take place well within the duration of a normal laser pulse of 5–10 ns. Detailed kinetic calculations confirm this conjecture.[15]

For picosecond laser pulses this ladder switch could be interrupted at an earlier stage[19] due to the short duration of the laser pulse.

Schlag et al. carried out a series of experiments in which they first proposed and experimentally demonstrated this ladder switching mechanism for the case of benzene. In a two-color experiment[17] they showed that photon absorption switches from the neutral benzene to the molecular ion as soon as the ionization potential is crossed. Shortly thereafter a similar conclusion was reached by Meek et al.[20] from photoelectron studies. No photoelectrons of energy larger than 0.8 eV were observed for MPI of benzene with a KrF excimer laser and hence it is clear that ionization already occurs at the lowest energy level possible.

Later experiments were carried out that separated the second color not only in time but in space.[21] In these experiments the molecular ions are set into motion by the application of a strong electric field, i.e., the ions are drawn out by an extracting field before being hit by the second laser. In such a system the ions will be drawn out to varying degrees according to their mass. By moving the focus of the second color by a few microns it is possible to mass select the fragments pro-

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duced by the first color (Figure 3). In such a way the second "bleaches" the various mass peaks produced by the first color. In this manner it is shown that the fragment ions that are intermediate species of the ladder switching process are indeed able to absorb visible or UV photons to produce the known fragments of smaller mass. Recently, it has been shown by El-Sayed et al.[22] that the remaining neutral fragments do not play an important role within the ion fragmentation process. The above experiments[21] point to a consistent model, supported by model calculations[15] based on a statistical model of successive ladder switching while fragmenting (Figure 2c). Although these calculations were carried out for benzene as a prototype, they should be generally valid for typical experimental conditions and molecular systems.

Once one has understood the mechanism of fragmentation, it is easy to select conditions that diminish it and give primarily soft ionization. At low light intensities the absorption process described above is interrupted as soon as the parent ions have been produced. Generally there is a smaller probability for the parent ion to absorb photons than for the neutral in a two-step absorption with tunable lasers since the wavelength of the photon has been precisely tuned to resonance of the absorption step in the neutral parent molecule. Also, this is the reason that it is possible to have soft ionization without loss in efficiency, namely, saturation of the two absorption steps within the neutral molecule occurs before nonresonant absorption within the parent ion takes place.

Mass Spectrometer

At first it appears somewhat arbitrary which type of mass spectrometer is employed in conjunction with multiphoton ionization. This is not quite the case if the following aspects of this experiment are considered. First, the process produces ions in a very tight focus of ca. 100-μm diameter. Second, since ions are produced as soon as the ionization potential is reached, the energy of these ions is very well-defined and controllable by intensity and wavelength. Finally, almost all ions are produced within a short time, typically the 5–10-ns duration of the laser pulse. These features of space and time definition are ideal for the measurements of masses by the time-of-flight (TOF) technique. Here the ions simply proceed into a drift tube, and one can directly measure the delay between the initial laser pulse and the arrival of the ion signal.

Such TOF instruments are time honored in mass spectrometry but have usually suffered from both poor space resolution (large ion cloud) and poor time resolution due to the definition of the extraction voltage pulse. The latter is not a problem in these experiments since the time definition can now be relegated back to the laser pulse. A simple 30-cm TOF drift tube with multiphoton ionization as shown in Figure 3 enables neighboring masses to be resolved, i.e., providing single mass resolution for molecular weights up to 260. One advantage of the TOF technique in this application is that its transmission of ions is nearly unity since there are no ion-selecting parts in the instrument. A second advantage is that all the ions that originate from a single laser pulse are recorded in the mass spectrum. (In a conventional scanning instrument only one mass at a time is admitted into the detector, the remaining signal being discarded.) These two conditions no doubt are responsible for the observed high sensitivity of the multiphoton mass spectrometric technique when used in conjunction with a TOF instrument. Figure 4 shows a complete TOF spectrum, demonstrating an excellent signal-to-noise ratio with only a single laser pulse. The laser-ionized molecules were emitted from an inlet hypodermic needle and represented a concentration of ca. 10^{13} molecules/cm^3. (The lower limit of detectability is about 10^8 molecules/cm^3.) By use of laser pulsing frequency of 10/s, a complete mass spectrum can thus be sampled every 0.1 s. By moving the focus, a very narrow region in space can be sampled, as might be useful, for example, in flame boundaries.[23] Similarly, time evolution of reaction products after a starting explosion could be sampled every 10 ns by using delayed laser pulses. Since a complete mass spectrum is generated within 100 μs, this constitutes an immense amount of information that must be stored prior to the next laser shot. At the present there are still electronic difficulties in handling data at such a large rate. This problem is largely a matter of inadequate storage capacity and transfer rates of present high-speed transient recorders. The higher the resolution of such an instrument, the more storage capacity has to be provided by the transient recorder in order to be able to record a complete scan.

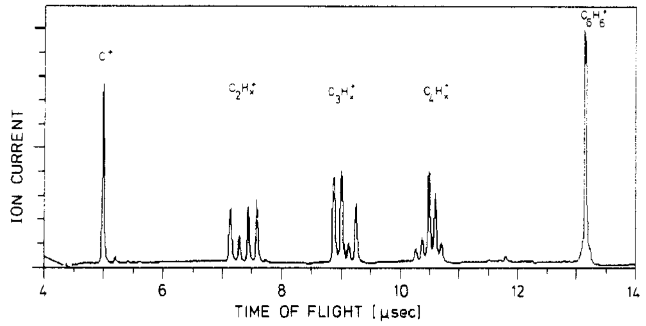

Figure 4. Complete multiphoton mass spectrum of C_6H_6 obtained from a single UV laser pulse, 6 ns wide, with a power of only 20 kW. The abscissa shows the flight time in the time-of-flight mass spectrometer. Note the good signal-to-noise ratio.

High-Resolution Mass Spectrometry

Multiphoton ionization might constitute an interesting method for high-resolution mass spectrometry because of the small kinetic energy of the ion produced. It would be most desirable to retain the high flux condition of a TOF instrument if one could overcome some of the fundamental limitations to the classical TOF technique. In particular one has a spread of energies in the ionization region due to the extension of the focus volume as well as to the natural spread of initial thermal velocities. In MPI both effects are strongly reduced, first by the excellent point focus (laser focus) of the ions, and secondly by the nature of the photoionization process. The latter assures that due to ladder switching only a small range of energies is available for each fragment ion. Some techniques have been employed to further reduce source effects,[24] but one can readily

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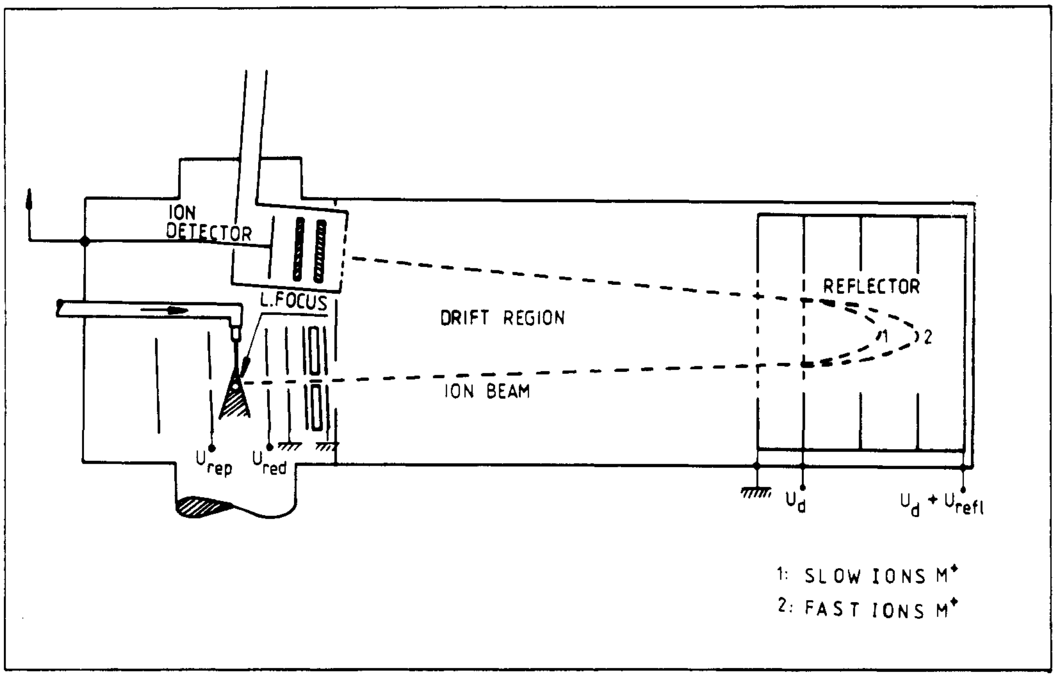

Figure 5. Schematic illustration of the reflecting time-of-flight mass spectrometer. Paths 1 and 2 reflect ions of equal mass with increasing kinetic energy content. The faster ions having the longer flight paths in the reflector arrive at the detector at the same time as the slower ions.

show that such efforts are difficult to extend far beyond a single mass resolution of about 500 for a simple linear TOF tube.

An entirely new technique of TOF mass analysis is important here which only has had limited application to date although it had been suggested earlier.[25] This technique involves folding the ions back on themselves at the end of the time-of-flight tube (see Figure 5). This folded configuration can be thought of as an electrostatic mirror that bounces all the ions back into the detector. If now the mirror is adjusted to have a soft penetration field, ions of the same mass will penetrate at various depths, depending on their spread of kinetic energy, before being reflected. For ions of equal mass this softly reflecting mirror now provides a longer flight path for fast ions, thus compensating their higher velocity. This compensation technique can be so adjusted that any velocity inhomogeneity in the forward direction is compensated over a wide range by the time the ions reach the detector. For applications in multiphoton ionization this leads to an immediate and dramatic improvement in resolution (Figure 6), demonstrating that the sharp initial conditions of the technique can be further exploited. First attempts by Boesl et al.[26] were able to reduce the time spread of the ion packet down to 8 ns for benzene molecular ions. This corresponds to a mass resolution $M/\Delta M \sim 3900$ for masses below 100 and is probably much better for molecules with even larger masses. It is conceivable that this mass resolution can be improved to the $M/\Delta M \sim 10\,000$ range. At his point one has covered the major range of applications of high-resolution mass spectrometry, applications that up to now can only be dealt with in double-focusing magnetic sector instruments.[27,28]

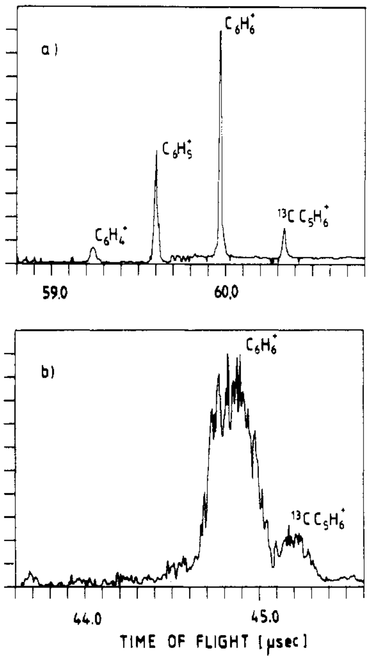

Figure 6. Illustration of the reflecting mass spectrometer (a) in comparison to the conventional linear flight tube mass spectrometer (b). In this case both spectra were obtained in the same flight tube, assuring the same path length, without energy correction. In b the reflecting mirror in Figure 5 was so adjusted that paths 1 and 2 assure simultaneous arrival at the detector for all kinetic energies. This is so for all mass peaks, larger masses arriving later in time.

It should be mentioned that here all ions produced by multiphoton ionization are mass analyzed, even under these high-resolution conditions; hence this resolution is achieved without substantial loss in throughput at higher resolution. This is a notorious problem for double-focusing instruments, where any increase in

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resolution is accompanied by a proportional decrease in signal due to the unsuitability of most of the ions for further mass analysis.

Metastables

One of the classic areas of kinetics in mass spectrometry has been the measurement of metastables. A typical flight time in a mass spectrometer is a few microseconds. The condition for correct mass detection is that the ions are produced in the ionization chamber, in some 10 ns (10^{-8} s). Some slower fragment ion production might occur in the adjoining acceleration region, or indeed in the flight tube. These ions are termed metastables. In a TOF instrument, breakdown in the acceleration region will broaden the mass peaks toward longer time of flights as the place in which the mass produced and hence its kinetic energy is not clearly defined. Breakdown in the field-free drift region will have no effect, since the arrival time will not be affected by the fragmentation processes.

The reflecting TOF mass spectrometer has an important feature that is of interest to the study of metastables. Indeed it makes this instrument the method of choice for such studies since the reflecting mirror constitutes a probing field for the ions. This tests the ion mass present at the end of the first part of the drift region independent of the ion velocity. By tuning the electrostatic mirror, in fact, the energy contents of the ion can be determined. In this way it is possible to identify the precursor ion as well as the point of origin of the fragment ion, thus yielding the rate constant of its production. For the case of small energy changes, i.e., small changes in mass due to the fragmentation, the energy shift may even be compensated by the reflecting field. This is the case if the parent ion loses a hydrogen atom in the drift tube. Boesl et al.[26] first demonstrated this feature of the reflecting TOF for the case of $C_6H_5^+$ ions. Here new sharp metastable peaks (see Figure 6) are seen and not hidden under the precursor ion peak or smeared as in a conventional TOF. Such smearing of a mass peak due to a metastable decay has been recently observed in the multiphoton mass spectrum of aniline measured in a conventional time-of-flight mass spectrometer.[29]

Another special advantage of multiphoton ionization for the study of metastables is the narrow energy range of the parent ion mentioned previously. If the parent ions are subsequently excited by the absorption of another photon, they have well-defined internal energy. In this way it is possible to study metastables originating from precursor ions at this defined energy.[30] By varying the wavelength of the photons, the energy of the precursor ions may then be precisely controlled and the dynamics of the metastable decay can be studied as a function of the internal energy.

This is a substantial improvement over conventional mass spectrometry with electron impact or even with photoionization where ions are produced in a broad energy range and the internal energy of the ions is not defined.

Concluding Remarks

The output of even a moderately strong visible dye laser is capable of ionizing molecules by multiphoton absorption with high efficiency if the laser light is converted to the UV by a nonlinear crystal and then softly focused into the molecular gas. This is the main advantage that makes multiphoton ionization an interesting new tool in mass spectrometry.

In multiphoton ionization the excitation energy is sharp at several discrete energies, being due to many monochromatic photons absorbed, depending on the light power attenuation of the laser and the softness of focus. This "picket fence" distribution of energies makes it quite easy to decide which one of just a few discrete possibilities are operative for a given system. The parent ions are all produced with very little excess energy as a consequence of the ladder-switching mechanism.[17] Further absorption occurs by absorbing but two or three photons in these ions before further fragmentation outruns further absorption by the ion, this fragmentation proceeding already before the cessation of the 5-ns laser pulse. This means that thresholds for bond-breaking processes could be accurately determined since there is little ambiguity as to the energies involved. As the laser intensity is increased, successively stronger bonds are ruptured, thus allowing successive decomposition steps in a large polyatomic molecule, a method of possible application in studies of structure.

It remains to be seen how much these future applications will be realized, or if indeed other features and applications will become important. In any case one can say that this is a new method with much unexplored potential that will make for fruitful and multifarious investigations in the coming years.

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