Two-Photon Ionization of Polyatomic Molecules in a Mass Spectrometer

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Two-photon ionization of benzene molecules in a mass spectrometer is performed with a tunable frequency-doubled dye laser. The nonlinear ionization is resonantly enhanced by real intermediate rovibronic levels in the S_1 state of the molecule. Our results show that stepwise multi-photon ionization is a very selective and versatile ionization source for a mass spectrometer.

Photoionization has been a highly selective method for the preparation of polyatomic molecular ions [1]. VUV light, usually of low intensity, must be employed; the produced ion flux has, however, often been insufficient for many interesting applications. Classical methods have employed discharge lamps or, more recently, synchrotron radiation [2]. The former is limited to a few wavelengths at which sufficient flux is available, whereas the latter requires an immense experimental effort to produce the radiation.

Lasers would here be an ideal alternative, but so far no tunable VUV lasers for this purpose have been available [3]. Frequency multiplication in metal vapors can only be employed to produce coherent light over a limited range of energy and is not very efficient [3]. Multi-photon absorption [4] would be a real alternative for large molecules particularly since VUV optics can be avoided. Multi-photon ionization has been performed in alkali metal beams [5] with low ionization potential, but for polyatomic molecules only in the dense bulk gas phase [6].

We here present results obtained in a low density molecular gas, that is in a molecular beam, carried out directly in the source of a mass spectrometer [7]. For the case of a prototype organic molecule we shall show that efficient two-photon ionization is possible with a low power frequency-doubled dye laser, in the dilute gas of a molecular beam. This

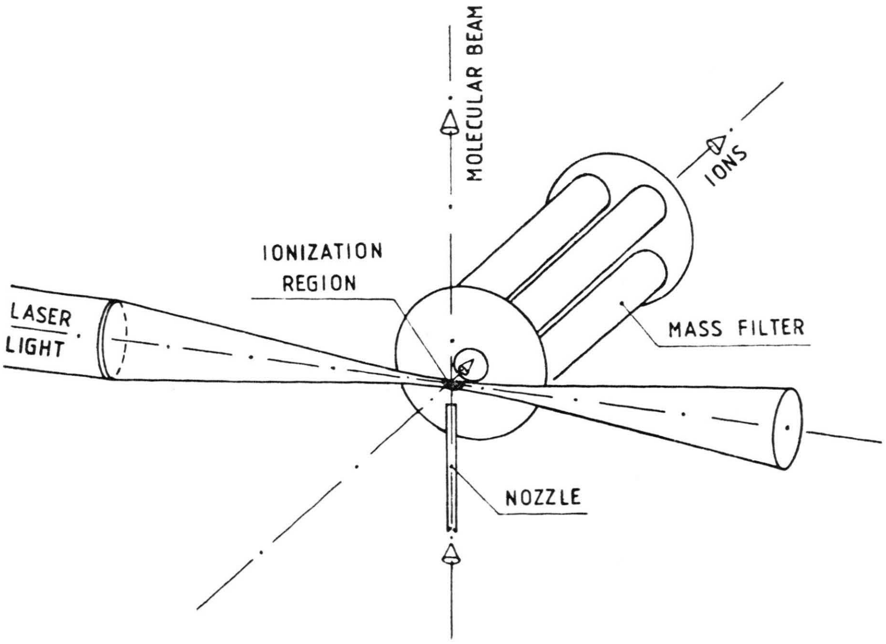

Fig. 1. Experimental scheme for two-photon ionization of benzene molecules in a mass spectrometer.

simplifies experimentation in the laboratory as it does not require the more complicated VUV technique.

A scheme of our experimental set up is shown in Figure 1. A molecular beam of benzene molecules is produced with an effusive nozzle (0.2 mm ⌀) with a flow rate of $3 \cdot 10^{-2}$ torr cm^3/sec. The molecular density n_0 in the ionization region in front of the nozzle is therefore some 10^{13} cm^{-3}. The light is focussed on the axis of the molecular beam in front of the nozzle resulting in an illuminated volume V of about $2 \cdot 10^{-5}$ cm^3 which contains about $2 \cdot 10^8$ benzene molecules. We use a pulsed tunable dye laser (Molectron DL 300) the light of which is frequency-doubled in a lithium-formate crystal yielding an average UV power of 300 W at 2500 Å. The molecular ions are withdrawn through an ion lens system into the quadrupole mass filter (UTI 100 C), mass analyzed and finally detected with a 16 stage particle multiplier with an amplification of $2 \cdot 10^5$ at AMU 28. Since the ions are produced during the laser pulse within some nsec a gated detection technique is used. The ion signal is preamplified and then directly observed on an oscilloscope or passed into a box car integrator. From there the integrated signal is sent to a strip chart recorder so that the ion current can be recorded continuously when scanning the laser or the mass spectrometer.

Benzene molecules are ionized via two-photon ionization when the laser wavelength is tuned to a real intermediate state in the S_1-system as shown in the inset of Figure 2. From the intermediate state the absorption of a second photon can then lead to an ionization of the molecule. Since the absorption spectrum of a molecule as large as benzene is hardly structured above the ionization potential of 9.247 eV (74587 cm^{-1}) [8] there is no further resonance restriction on the second step. Spontaneous decay of the intermediate states does not play a role in the ionization process and for laser pulses as short as some nsec since at low excess energies in S_1 the lifetime are sufficiently long [9, 10]. Collisional deactivation of the intermediate level can be neglected at the particle densities in the beam (10^{13} cm^{-3}).

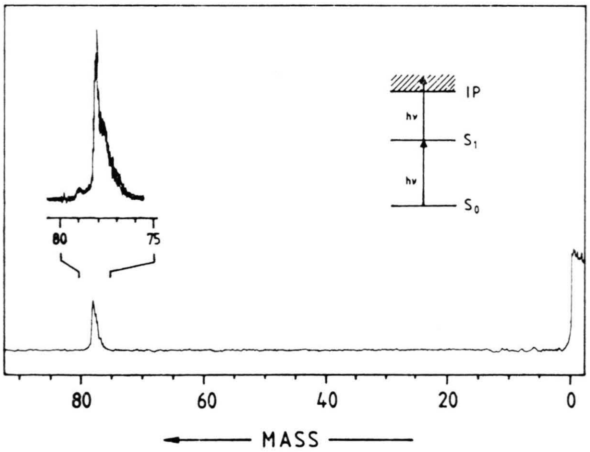

Fig. 2. Mass spectrum of natural benzene molecules ionized via two-step photoionization with a tunable dye laser.

Since the pure electronic one-photon absorption to the S_1-state of benzene is forbidden one has to tune the laser wavelength to one of the vibrationally induced transitions in the well known absorption spectrum of benzene [11]. The vibronic transitions are very broad up to nearly 100 cm^{-1} due to a rich rotational structure. Some 100 rovibronic transitions are excited within the laser bandwidth of about 1 cm^{-1} and the total process can be described by an average phenomenological value of the absorption cross section for this part of the band.

The laser wavelength was tuned to the strongest absorption band 6_0^1 which has its maximum at 38612 cm^{-1} being the sharp R-branch in the vibronic band. After the absorption of a second photon the total excitation energy is 77224 cm^{-1} being 2637 cm^{-1} above the ionization potential.

In Fig. 2 a scan of the mass spectrometer starting from mass 1 up to mass 90 is shown when irradiating the molecular beam at a wavelength of 38612 cm^{-1} (4.786 eV). This result shows a single peak at mass 78 and proves that solely benzene ions are produced without any dissociation of the molecule. This is in line with previous results of conventional photoionization which show that dissociation begins at excitation energies above 13.8 eV [12]. In Fig. 2 a portion of the mass spectrum around mass 78 under higher resolution is shown. It is interesting to note that in addition to benzene of mass 78 there appears another small peak at mass 79. The reason for this is a small amount (6%) of "heavy" benzene always contained within the natural isotopic mixture of benzene mostly due to the natural isotopic composition of carbon. It is just as possible to set the mass spectrometer at one of the two isotopic masses and scan the laser wavelength.

Such isotope specific spectra have been obtained previously in our laboratory [13].

From the peak height in the mass spectrum we are able to estimate the number of molecular ions produced by two-photon ionization within the focus volume. We have about $3 \cdot 10^3$ ions produced at UV light powers as low as 300 W.

On the other hand we can estimate the ion number from the rate equation for two-step ionization. In the limits of low intensities and small population of the intermediate levels one obtains for the ion number:

$$N_i = [\exp(-I_0 \alpha_1 \tau) - 1 + I_0 \alpha_1 \tau] \, n_0 V \alpha_0 / \alpha_1 ; \quad (1)$$

$\tau = 2$ nsec is the duration of the frequency-doubled laser pulse, I_0 is the average light intensity within the focus region, α_0 and α_1 are the absorption cross sections for the first and the second step of the two-photon ionization, respectively (see Fig. 2). $\alpha_0 = 10^{-18}$ cm^2 was taken from conventional absorption spectra, whereas $\alpha_1 \sim 10^{-17}$ cm^2 is a rough estimate obtained from the absorption cross section measured at the total excitation energy of 77224 cm^{-1} [14]. This can be done since the absorption probability into the ionization continuum should be largely independent of the symmetry of the lower state. We then obtain as the number of ions produced per laser pulse $N_i = 2 \cdot 10^4$. This is in reasonable agreement with the experimental results in view of the large uncertainties within the experimental and molecular parameters in Equation (1).

It is also interesting to estimate the ion densities which are obtained within the small focus volume. For the measured total ion number of $N_i = 3 \cdot 10^3$ we have even at the very low power level of 300 W an ion density of 10^8 cm^{-3}, which is comparable with the ion densities obtained in conventional ion beams. An important advantage of two-photon ionization is that all molecular ions are produced within a very small focal volume so that excellent focusing of the ions should be possible. Furthermore, the ions are produced within some nsec at this same position, this being of special interest for time-resolved ion spectroscopy.

Besides the spectroscopic aspects, a tunable two-photon ionization is of special interest for analytical mass spectrometry. Since the ionization spectrum has the distinct structure of the intermediate state spectrum one here obtains an additional information which is highly species specific [13]. By this means small traces of particles as well as isomers can be mass detected within a mixture of molecules.

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