which has one bond each with energy E_{23}, $E_2{}^*$, and $E_3{}^{**}$, $(x - 2)$ bonds with $E_2{}^{**}$, and $(n - x - 2)/2$ each with E_{12} and E_{22} is chosen. Table I and Table I of ref 6 are used to subtract the sum of these bond energies. Then dividing by n gives

$$\text{linear ion REPA } (n,x) = \frac{\beta}{n}\left(2 \cos\left[\frac{x\pi}{2(n+1)}\right] \times \csc\left[\frac{\pi}{2(n+1)}\right] - 1.2680n + 0.5350x - 1.3944\right) \quad \text{(A10)}$$

To avoid radicals, n and x must be of the same parity; eq A10 is valid for both parities.

In the cyclic ions it is necessary to distinguish between even m (i.e., the "$4N$" systems) and odd m (the "$4N + 2$" systems); otherwise the treatment is as above and gives

$$\text{even } m \text{ cyclic ion REPA } (n,x) = (\beta/n)(4 \cos [x\pi/(2n)] \times \cot (\pi/n) - 1.2680n + 0.5350x + 0.0002) \quad \text{(A11)}$$

$$\text{odd } m \text{ cyclic ion REPA } (n,x) = (\beta/n)(4 \cos [x\pi/(2n)] \times \csc (\pi/n) - 1.2680n + 0.5350x + 0.0002) \quad \text{(A12)}$$

If eq A10–A12 are written in terms of the ratio $f = x/m$ and the limit taken as m becomes infinite with f fixed, all three cases give

$$\lim_{n\to\infty} \text{REPA} = [(4/\pi) \cos (f\pi/2) + 0.5350f - 1.2680]\beta \quad \text{(A13)}$$

This limiting REPA has a maximum of $+0.051\beta$ at $f = 0.17$ and drops to 0 at $f = 0$ and to -0.733β at $f = 1.0$.

Isotope Selective Soft Multiphoton Ionization and Fragmentation of Polyatomic Molecules

U. Boesl, H. J. Neusser, and E. W. Schlag*

Contribution from the Institut für Physikalische und Theoretische Chemie der Technischen Universität München, 8046 Garching, West Germany. *Received February 2, 1981*

Abstract: The two-dimensional character of resonance-enhanced multiphoton ionization in a mass spectrometer is utilized for extracting a trace spectrum from the natural isotopic mixture of benzene molecules. ^{13}C labeled benzene molecules are selectively laser ionized and finally fragmented with visible laser light. The isotope selectivity obtained in the ionization process is preserved in the following fragmentation process.

Focused (10^7 W/cm^2) visible laser light can be employed to efficiently ionize molecules in the ion source of a mass spectrometer[1] if absorption proceeds via a real intermediate state. If the intensity is further increased to some 10^9 W/cm^2 a very efficient fragmentation[2] of the molecular ions is observed, finally leading to atomic ions.[3] The mechanism of this ionization and fragmentation process has been investigated in our previous work[4] and it was shown that, at least for the case of benzene, molecules first climb a ladder of the neutral molecule that barely leads to ionization of the molecules and then switch to a process in which all further absorption leads to climbing a ladder of ions. Under suitable experimental conditions[5] it is possible to avoid the fragmentation process and to achieve highly efficient "soft" ionization of a series of molecules which allows a sensitive detection of a parent molecular ion within a mixture.[5,6] In the "soft" ionization process two or three photons at most are absorbed via a real intermediate state of the molecule until the ionization potential is reached. In this case molecules are ionized by climbing only the first ladder of neutrals, the intensity being too low to lead to substantial climbing of the subsequent ion ladder. As there is a resonance condition via an intermediate state this type of ionization is particle selective to a high degree.

Even in the case of large molecules it enables one to selectively ionize particular molecules within a mixture, by employing different wavelengths.[7] In this work we shall demonstrate the high particle selectivity of a stepwise two-photon ionization by focusing on the small amount of ^{13}C labeled benzene molecules contained within a natural mixture. We shall further show that a subsequent fragmentation process does not degrade the isotope selectivity obtained in the preceding ionization process via the resonant intermediate states.

Experimental Results and Discussion

The experimental set up has been described in detail in previous work.[6] As an exciting light source we used a nitrogen pumped tunable dye laser. During this experiment an intracavity etalon was placed within the laser resonator which was pressure scanned over a wavelength range of 13 cm^{-1}. Then the laser light was frequency doubled and the UV light so produced was focused into an effusive beam of benzene molecules. The ions were withdrawn with suitable ion optics, mass analyzed in a quadrupole mass filter, and finally recorded with an ion multiplier.

Two different types of scans are possible in the mass spectrometer when measuring the ion current. The first is a wavelength scan of the dye laser at a fixed mass and the second a mass scan at different fixed laser wavelengths.

As a result, in Figure 1a the intermediate state spectrum in the two-photon ionization process is shown, when the laser

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[1] U. Boesl, H. J. Neusser, and E. W. Schlag, *J. Chem. Phys.*, **72**, 4327 (1980); D. A. Lichtin, S. Datta-Ghosh, K. R. Newton, R. B. Bernstein, *Chem. Phys. Lett.*, **75**, 214 (1980), and references cited herein.

[2] L. Zandee and R. B. Bernstein, *J. Chem. Phys.*, **71**, 1359 (1979).

[3] C. D. Cooper, A. D. Williamson, J. C. Miller, and R. N. Compton, *J. Chem. Phys.*, **73**, 1527 (1980).

[4] U. Boesl, H. J. Neusser, and E. W. Schlag, *J. Chem. Phys.*, **72**, 4327 (1980).

[5] U. Boesl, H. J. Neusser, and E. W. Schlag, *Chem. Phys.*, **55**, 193 (1981).

[6] U. Boesl, H. J. Neusser, and E. W. Schlag, *Z. Naturforsch., A*, **33A**, 1546 (1978).

[7] U. Boesl, H. J. Neusser, and E. W. Schlag in "Laser-Induced Processes in Molecules", Vol. 6, K. L. Kompa and J. D. Smith, Eds., Springer, Berlin, 1979, p 219.

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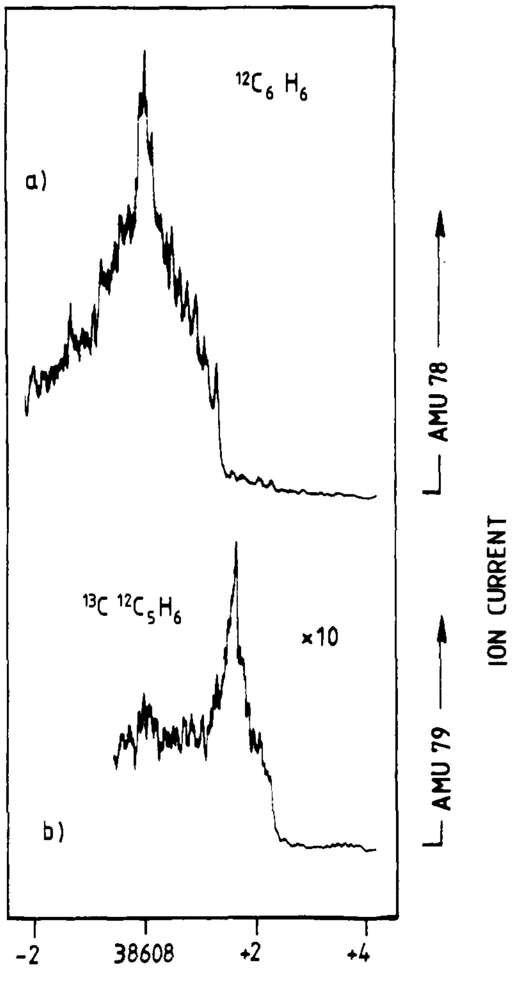

Figure 1. Intermediate state spectrum in the two-photon ionization process of (a) "light" benzene ($^{12}C_6H_6$) and (b) "heavy" benzene ($^{13}C^{12}C_5H_6$) measured in the natural isotopic mixture.

wavelength is scanned around 38 610 cm^{-1} and the mass spectrometer acts as a mass filter transparent only for ions of mass AMU 78, i.e., "light" benzene molecules. The laser bandwidth was somewhat below 0.1 cm^{-1} at a peak power of 1 kW, yielding a spectral resolution higher than 500 000 which is comparable with the conventional high-resolution absorption spectra of Callomon, Dunn, and Mills.[8] The highly structured spectrum observed at this resolution is due to the rotational structure of the one-photon 6_0^1 vibronic transition in the S_1 ($^1B_{2u}$) state of C_6H_6. Then the mass filter is tuned to AMU 79 and again the ion current is measured as a function of laser wavelength. In Figure 1b this result is given for a sensitivity increased by a factor of 10. Again a well-structured rotational contour of similar shape appears, shifted, however, by 1.6 cm^{-1} to the blue. This can be seen from the position of the outstanding sharp peak which is formed by the Fortrat parabula turning point of transitions with $\Delta J = +1$ (R branch).[8] This blue-shifted spectrum originates from ^{13}C labeled "heavy" benzene molecules of AMU 79 which are present in a concentration of 6.3% within the natural mixture due to the natural isotopic abundance of ^{13}C atoms. The concentration found from the band intensity in the measured spectrum is 7.2%, in good agreement with the expected value of 6.3%. The observed shift to higher energies is explained in terms of both an isotope effect of the vibration and an isotope effect in the zero-point energy.

In Figure 1b a small peak can be seen at 38 608 cm^{-1} which is the position of the sharp R branch for "light" benzene molecules

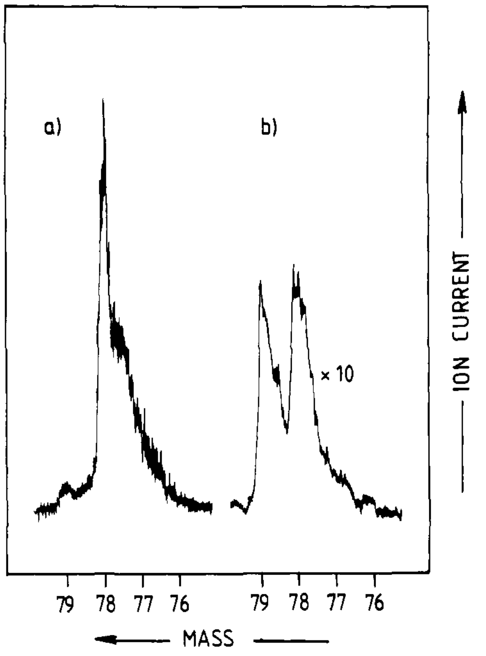

Figure 2. Mass scans of the parent ions for two slightly different ionizing laser wavelengths of 38 608 cm^{-1} (a) and 38 609.6 cm^{-1} (b) (see Figure 1). The mass spectra show different isotopic constitution because of the isotope selectivity of the intermediate state spectrum in the two-photon ionization process.

of AMU 78. This peak is an instrumental artefact and results from an incomplete mass discrimination of neighbored masses in the mass spectrometer. From the peak height we conclude a mass discrimination of 1.4:100 of neighbored masses at AMU 78. This mass discriniation is given by the characteristics of the quadrupole filter system used in our experiment. This modest mass discrimination can be increased substantially in our experiment by making use of the selectivity of the intermediate state absorption spectrum. When the ionizing laser is tuned to a special wavelength selected in the way that the absorption coefficient of both isotopic species differs as much as possible, then the instrumental mass discrimination is increased by a factor of $\alpha_{m1}:\alpha_{m2}$, the ratio of the optical absorption coefficients of the two isotopes with mass m_1 and m_2 at the selected wavelength. This improvement of the mass discrimination is due to an enrichment of one selected isotope in the ion mixture by isotope selective ionization.

This ion mixture is then mass analyzed in the conventional way by the quadrupole mass filter with its typical inherent mass resolution. The enrichment of one isotopic species within the photoions will be shown below.

In our case the absorption coefficient ratio $\alpha_{m1}:\alpha_{m2}$ is largest for the absorption peak of "heavy" benzene molecules at 38 609.6 cm^{-1} since at the same time for this wavelength at the blue side of the sharp R branch a very weak absorption by "light" molecules takes place. The effective absorption coefficient ratio is estimated to be 0.045 from a comparison of Figure 1a and Figure 1b. We have to bear in mind, however, that in Figure 1 the absorption within the laser resolution is integrated over many rovibronic transitions starting from ground-state levels with different populations n_i. Thus from the spectrum in Figure 1 we are not able to deduce the true absorption cross section of a particular transition and the intensity in Figure 1 is proportional to an averaged value $\langle \alpha n_i \rangle$ of the absorption coefficient weighed with the populations of the ground state levels. Far from saturation we may neglect this difference and the enrichment factor may be directly deduced from the intensity ratio in Figure 1 at a chosen wavelength.

In Figure 2 the isotopic constitution of the parent ions for different wavelength conditions is shown. It represents two mass scans for two slightly different fixed exciting laser wavelengths. The laser intensity has been chosen so that the ionization is completely soft and no fragmentation occurs. In Figure 2a the mass spectrum is shown when the laser wavelength (λ = 38 608

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[8] J. H. Callomon, T. M. Dunn, and I. M. Mills, *Philos. Trans. R. Soc. London, Ser. A*, **259**, 499 (1966).

Å) is tuned to the absorption peak of normal light benzene. The absorption coefficient ratio $\alpha_{m1}:\alpha_{m2}$ deduced from the wavelength positions in the rotational envelopes of both isotopic species is about 1:2. Starting from the natural abundance of 6% of $C_5{}^{13}CH_6$ we thus expect a somewhat smaller, namely 3%, concentration of the "heavy" benzene isotope within the parent ions. The measured concentration of 4% is close to this value.

In Figure 2b the result for the mass spectrum is shown when the laser wavelength is tuned by the small amount of 1.6 cm^{-1} to the blue, namely to the absorption peak of heavy benzene at 38 609.6 cm^{-1}. (Note that the sensitivity is increased by a factor of 10.) This mass spectrum is completely different from that in Figure 2a. The mass peak of light benzene has decreased drastically whereas the mass peak of heavy benzene remains constant. The concentration of the heavy molecular isotopes has increased from about 6% within the natural mixture to about 57% within the photoions. This is close to the value of 60% estimated from the absorption coefficient ratio $\alpha_{m1}:\alpha_{m2}$ at the selected wavelength. In this way by making use of the selectivity of the intermediate state spectrum the mass discrimination of the quadrupole mass spectrometer can be increased easily by a factor of 22, yielding a total mass discrimination of 6×10^{-4}. Recently it has been shown that for the case of diatomic molecules with simpler intermediate state spectra and separated rovibronic lines an even larger mass discrimination is possible.[9]

In an additional experiment it has been determined whether the isotopic selectivity obtained in the two-step ionization process is conserved during the subsequent fragmentation process.[4] For this, the remaining intense fundamental visible light is focused together with the low intensity frequency doubled light into the molecular beam so that both foci overlap. The visible light of high intensity then causes fragmentation of the ions. The fragmentation process is so efficient that mainly C^+ ions appear. The corresponding part of the mass spectrum is shown in Figure 3a,b for the two wavelengths discussed above. In Figure 3a the mass spectrum is shown for an exciting wavelength of 38 608 cm^{-1}. For this wavelength as a result of the selective two-step ionization process light benzene ions are preferentially produced. A fragmentation of these ions then yields a single mass peak at mass 12 with nearly no contribution of heavy carbon atoms with mass 13. In Figure 3b the corresponding result is given when the laser is tuned to λ = 38 609.6 cm^{-1}. For this wavelength the isotopic abundance of $C_5{}^{13}CH_6{}^+$ is substantially increased to about 57% (see Figure 2b). This enriched heavy-ion mixture is then dissociated by the intense visible light yielding the C^+ mass spectrum of Figure 3b with a relatively small $^{13}C^+$ contribution of 9%. From this result we may conclude that the fragmentation process itself does not show a strong isotope effect. It there is equal fragmentation probability for both C isotopes then we expect a probability of $^1/_6$ to obtain $^{13}C^+$ and $^5/_6$ to obtain $^{12}C^+$. In a mixture of 57% heavy and 43% light molecular isotopes $^{13}C^+$ should appear with a probability of 57% × ($^1/_6$) = 9.5% and $^{12}C^+$ with a probability of 57% × ($^5/_6$) + 43% = 90.5% of all carbon ions. Then a total of 9.5% $^{13}C^+$ are expected which is in reasonable agreement with the experimental result of 9%.

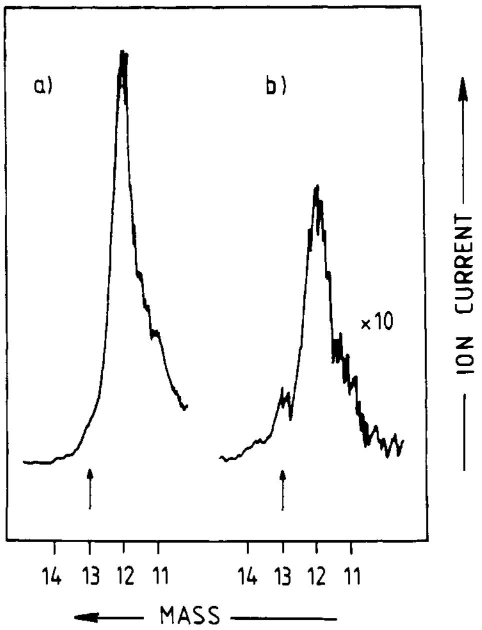

Figure 3. Mass scans of C^+ fragments produced by irradiation of the two different parent ion isotope mixtures shown in Figures 2a and 2b with intense visible laser light. The positions of $^{13}C^+$ (AMU 13) are marked by arrows.

Conclusion

In this work we demonstrated the high selectivity that can be achieved in the multiphoton ionization of polyatomic molecules.

We displayed the two-dimensional character of such data by measuring mass-selected wavelength spectra and wavelength-selected mass spectra of benzene and ^{13}C-labeled benzene in the natural mixture. By using a second beam of highly intense laser light at a second wavelength we obtained not only this isotope-selective parent ionization but also fragmentation of these selected parent ions without degrading the isotope selectivity.

Hence it appears possible not only to selectively ionize a trace component in a mixture, such as an isotope component, but to further study the mass spectral breakdown pattern of this trace component without interference from the major constituent.

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[9] H. Zacharias, H. Rottke, and K. H. Welge, *Appl. Phys.* **24**, 23 (1981).