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Behavior of Polyatomic Molecules in Intense Infrared Laser Beams

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In the present Letter we report that a number of polyatomic molecules (M) when irradiated with short pulse lasers <90 fs at 750−790 nm and intensities up to 10^{15} W cm^{-2} produce multiply charged parent ions and do not fragment to any great degree. This surprising observation is found in both linear and ring structured molecules and is very similar to the behavior of inert atoms such as xenon under the same irradiation conditions. This is a very different behavior from irradiating with nanosecond pulses at 10^9 W cm^{-2} where low-mass fragments dominate the spectrum. For the hydrocarbon molecules presented in this work, there exists an envelope of 2^+ ionized peaks, which corresponds to the parent and a number of (M − *n*H) satellites. This feature is characteristic of these molecules in the intensity region 10^{14-15} W cm^{-2} and is interpreted as evidence for tunneling or barrier suppression. Coulomb explosion leading to multiply charged atoms, which is evident for CS_2, does not seem to be operating for the larger hydrocarbon molecules.

Introduction

It is well-known that stepwise multiphoton ionization and fragmentation of polyatomic molecules such as benzene can yield exclusively parent ions at 10^7 W cm^{-2} using nanosecond laser pulses in the UV (soft ionization). As the intensity is increased to about 10^9 W cm^{-2}, dissociation increases dramatically until low-mass fragments dominate the spectrum with the parent peak often being missing entirely.[1−3] This process is called ladder-switching fragmentation. For ladder switching to occur, fragmentation and subsequent photon absorption from the excited-state neutral or parent ion must occur within the laser pulse width. On the other hand, if the laser pulse is extremely short, then the ladder-climbing mechanism should dominate. It has been shown[4] that dissociation can largely be suppressed using intense (normally IR) laser beams up to 10^{14} W cm^{-2} with the parent ion often being the strongest peak. This has also been observed recently for aromatic molecules using intense near-infrared radiation.[5,6]

The multiple ionization of molecules in intense laser fields has become one of the most active areas of current study in atomic and molecular physics. In particular using picosecond and femtosecond lasers with intensities in the range 10^{14-16} W cm^{-2}, the electric fields generated are no longer small compared to the binding molecular fields of the valence electrons, and hence new physical effects are expected. For example, for the irradiation of small molecules in intense laser fields, doubly charged parent ions can be detected and higher charged parent ions are present as transient species.[7−12] A special feature of this intense laser field ionization is multielectron ionization followed by dissociation through Coulomb explosion of charged fragments.[13]

Although the understanding of the interaction of intense laser beams with polyatomic molecules is at a preliminary stage,[6] many laboratories are now showing considerable interest. The object of the present work is to demonstrate that a number of polyatomic molecules irradiated by intense laser beams with short laser pulses <90 fs and in the wavelength range 750−790 nm produce multiply charged parent ions and do not fragment appreciably to produce light particles. This was noticed without comment by Cornaggia[8] for C_3H_4 and has recently been demonstrated by Smith et al.[14] for benzaldehyde. In this sense the molecules behave more like atoms.

Experimental Section

In the experiments described in this Letter the details of the apparatus have been described in a number of previous papers[14−17] dealing with one of the applications of this technology, namely, femtosecond laser mass spectrometry (FLMS). Suffice it to say that a time-of-flight mass spectrometer (TOF) was used with unit mass resolution up to 100 D. Gases were introduced effusively to the vacuum chamber at pressures up to 10^{-5} Torr. A laser beam was focused with a 100 mm mirror into the sensitive volume of the TOF to irradiate the molecular samples. The specifications of the laser pulses were pulse width 50−90 fs, wavelengths 750−790 nm with intensities up to 2×10^{15} W cm^{-2}.

Results and Discussion

Figure 1a shows a typical mass spectrum of deuterated benzene (C_6H_5D) with a purity of 98%. The irradiation conditions were 2×10^{15} W cm^{-2} at 50 fs and at 790 nm. From previous work done in our laboratory on benzene[4] at high laser

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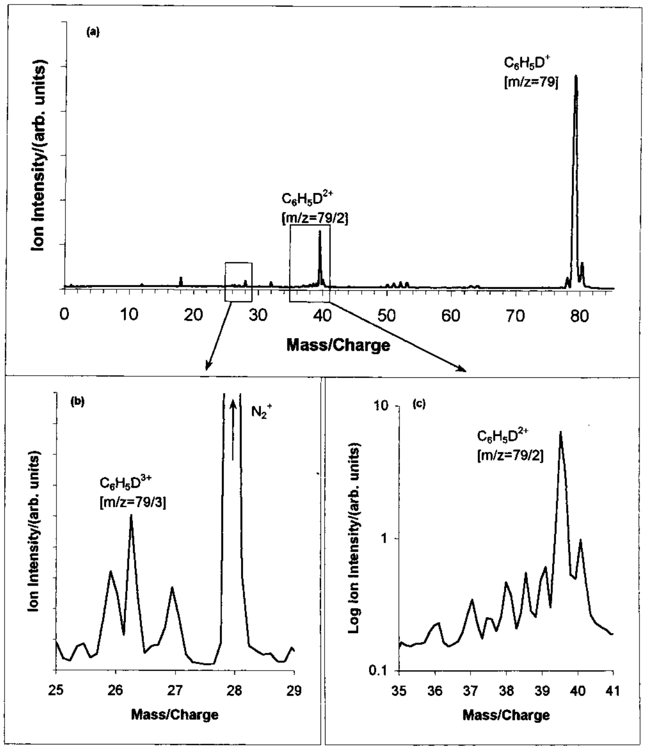

Figure 1. Mass spectrum of deuterated benzene with expanded areas around the 2^+ and 3^+ parent ion. The laser intensity is 2×10^{15} W cm^{-2} with a pulse width of 50 fs and a wavelength of 790 nm.

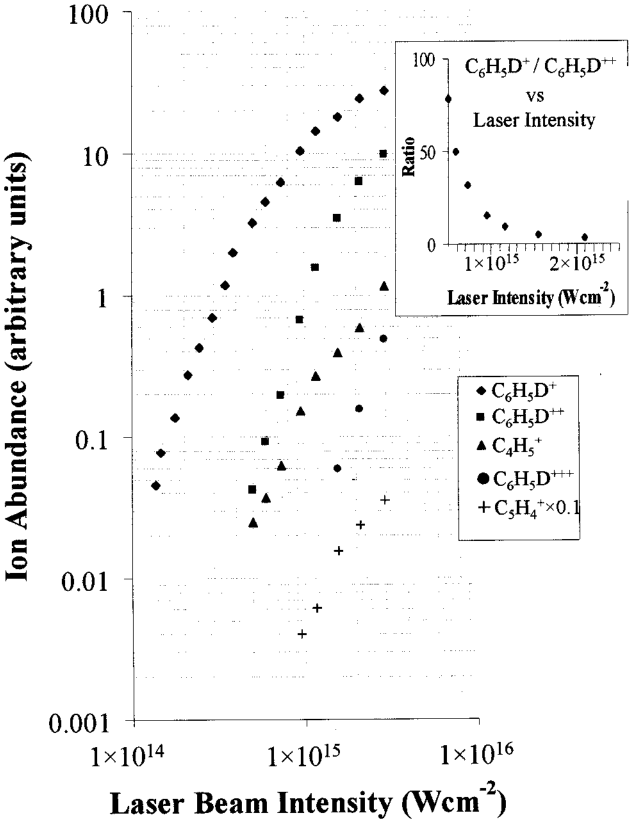

Figure 2. Ion abundances of a number of fragments and multiple charged species from deuterated benzene as a function of laser intensity under the laser conditions mentioned in Figure 1. The gradients of the 2^+ and 3^+ ion curves are steeper than the others.

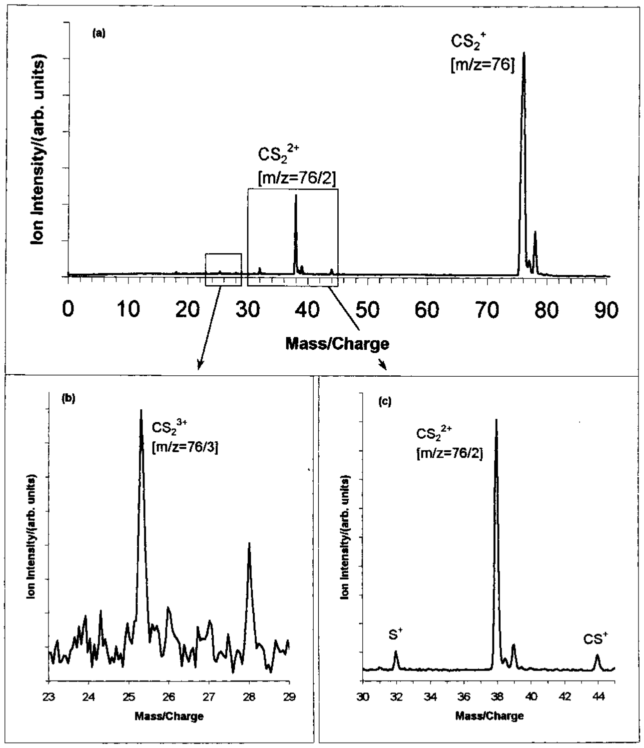

Figure 3. Mass spectrum of the linear molecule CS_2 with the areas around the 2^+ and 3^+ entities enlarged. The laser conditions are similar to those described in Figure 1.

intensities, it was noticed that a strong peak appeared at mass 39, which could be due to the symmetric fragmentation of the parent to $C_3H_3^+$ or the doubly ionized parent mass. With deuterated benzene such an ambiguity was eliminated. It can be seen that the parent ion mass (79) is by far the strongest peak in the spectrum. The two expanded areas (b, c) correspond to the 3^+ and 2^+ charged parent ion peaks. The 2^+ peak at $m/z = 39.5$ is the second strongest peak in the spectrum. This graph has been presented in logarithmic form to show clearly the small peaks between $m/z = 36-40$ on either side of the main peak. The 3^+ parent molecule produces an unambiguous peak at $m/z = 26.3$. There were impurity peaks at 18 (H_2O), 28 (N_2) and 32 (O_2), but these caused no confusion. To the knowledge of the authors, this is the first time that highly ionized parent masses have been observed for medium mass molecules following intense laser irradiation.

It is worth pointing out that the appearance potentials of the 2^+ and 3^+ deuterated benzene are respectively 26 and 44 eV[18] and that the appearance potential for C^+ in the fragmentation of benzene using a UV nanosecond laser is also about 26 eV.[1] The fact that the 2^+ parent ion peak was at least an order of magnitude larger than the carbon ion suggests that the normal fragmentation routes for nanosecond irradiation were being bypassed in the femtosecond irradiations. To return to the double-ionized spectrum in Figure 1c, the small peaks on either side of the main peak also deserve comment. First of all there are two-half mass peaks at 37.5 and 38.5. These correspond to $C_6H_3^{2+}$and $C_6H_3D^{2+}$ respectively, and the peak at mass 40 is due principally to the ion $C_5{}^{13}CH_5D^{2+}$. This also has the correct carbon isotope ratio for a molecule that contains six carbon atoms (7%). Thus the peaks at mass 38 and 39 are also likely to have a substantial doubly ionized component. The envelope of doubly ionized peaks every half-mass corresponding to the parent molecule (M) and a number of (M − nH) satellites seems to be characteristic of polyatomic hydrocarbon molecules when irradiated in the infrared at the high laser intensities 10^{14-15} W cm^{-2}, and the other hydrocarbon molecules presented in this paper all show this doubly ionized cation group. This can always be distinguished from fragments by the small half-mass

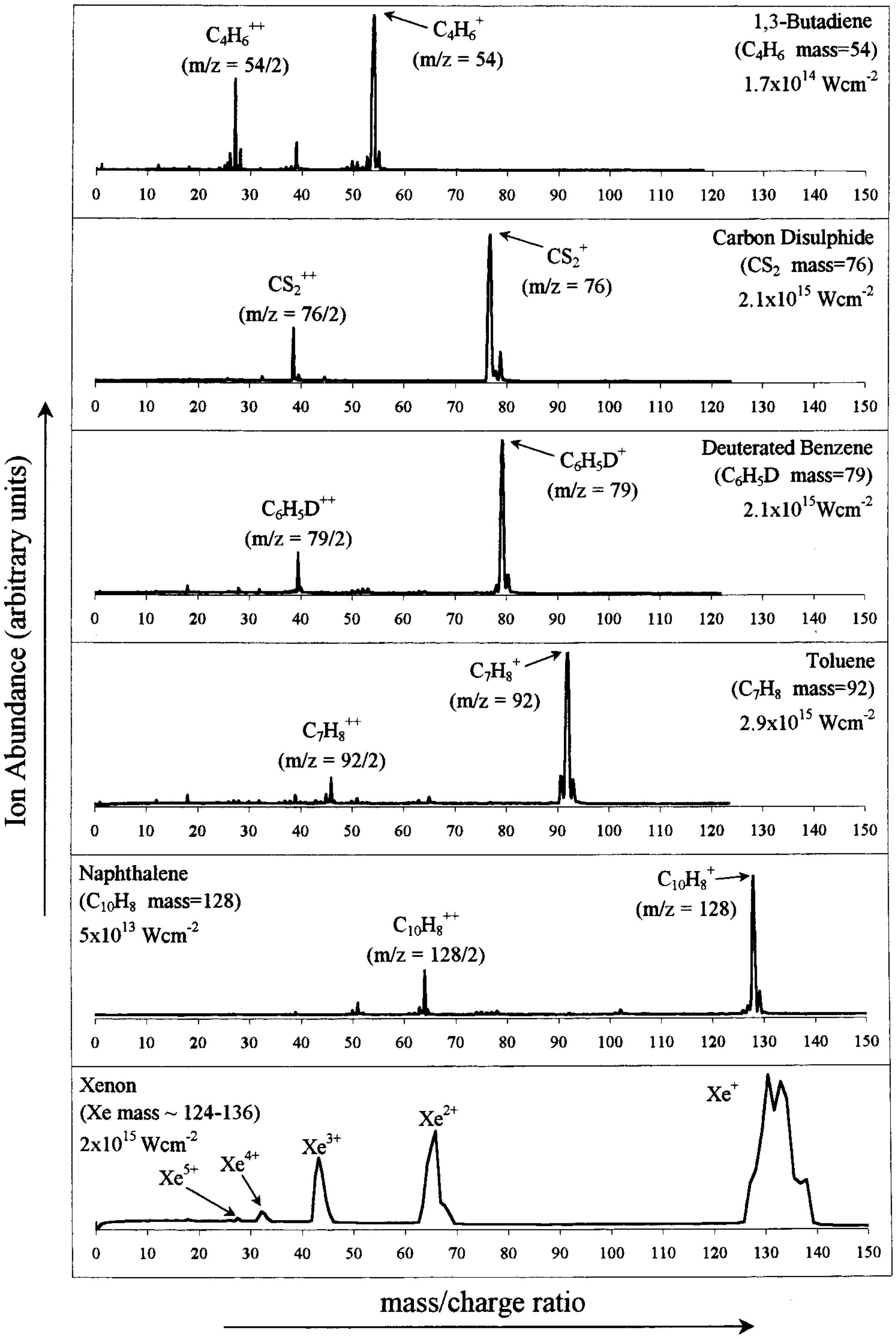

Figure 4. A number of mass spectra of polyatomic molecules under laser conditions between 5×10^{13} and 2×10^{15} W cm^{-2}. The laser wavelength is in the range 750−790 nm and the pulse width between 50 and 90 fs. This is compared with the atomic Xe spectrum taken at the same intensity. In all of the molecular spectra, the 1^+ and 2^+ charged parent peaks are the principle entities and any fragmentation is very small. This behavior is similar to that of the inert atoms.

peak at $(M - 3)^{13}C^{2+}$, which must have the correct isotopic ratio. There was little evidence of multiply charged carbon atoms, which is characteristic of Coulomb explosion for lighter molecules.[13]

The intensities of the 1^+, 2^+, and 3^+ parent peaks as well as some of the larger fragments from deuterated benzene are shown as a function of laser intensity in Figure 2 at 790 nm and 50 fs pulse width. It would appear that the C_4H_5 and C_5H_4 ion peaks follow the intensity dependence of the parent ion while the 2^+ and 3^+ parent ion peaks have a stronger laser intensity dependence. It can be seen in the inset diagram that the ratio of the 1^+ to 2^+ charged peaks is a strong function of the laser intensity. The value at 10^{15} W cm^{-2} is close to the 1^+ to 2^+ ion ratio for atomic xenon at similar laser intensities, which was carried out under identical experimental conditions to the molecular work.

Figure 3 shows the mass spectrum of the linear molecule CS_2 at a laser intensity of 10^{15} W cm^{-2} for 790 nm and 50 fs. The appearance potentials of CS_2^{2+} and CS_2^{3+} are 27.5 and 53.6 eV respectively.[19] This spectrum looks very similar to that of deuterated benzene with the 1^+ and 2^+ peaks being by far the strongest components and also an unambiguous CS_2^{3+} signature being visible. Any other fragmentation is very small. There was however evidence for Coulomb explosion in this molecule since small peaks of multiply charged C and S were present.

Finally in Figure 4 the mass spectra of a number of different molecules are shown at various intensities in the IR for pulse widths less than 90 fs. For all the molecules presented here, the 1^+ and 2^+ ion peaks are the dominant entities and that any other fragmentation is small. The spectrum for xenon is also presented. A general theme from the present work seems to be emerging. For laser intensities in the infrared at intensities in the range $5 \times 10^{13}-10^{15}$ W cm^{-2}, the fragmentation for the molecules described in this paper is small. Multiply charged ions are evident up to 3^+, and for the hydrocarbon molecules an envelope of 2^+ ions of (M $-$ nH) entities is visible. Exceptionally the 3^+ ion for toluene was not seen. The characteristic envelope of 2^+ ions for the hydrocarbon molecules had intensity thresholds $>5 \times 10^{13}$ W cm^{-2}. The low degree of fragmentation observed in the present work is in agreement with the studies of DeWitt et al. on aromatic molecules. These authors did not observe multiple charging in their spectra, and this is also in accord with the present work since their maximum laser intensity was about 4×10^{13} W cm^{-2}, marginally lower than the thresholds mentioned above.

Conclusions

Under the intense laser irradiation reported in this Letter, the polyatomic molecules that have been studied show remarkable stability and electronic dynamics similar to that in atoms. Clearly ladder-switching fragmentation of the type reported for nanosecond pulses[1−3] is not taking place to any great degree.

The simplest model of the molecular behavior in the strong IR laser fields observed in the present experiment is as follows. The molecules reach the 1^+ ion level by multiphoton processes during the rise time of the pulse. Having reached this level, they absorb more photons sequentially and reach the 2^+ and 3^+ levels either by tunneling ionization or by barrier suppression.[13] This was the sequential mechanism proposed by Lambropolous[20] for multiple ionization of atoms by intense pulsed lasers. His calculations showed that multiply charged ions are only produced for laser intensities approaching 10^{14} W cm^{-2}. For sequential ionization, a charge state can be produced only after the previous charge state begins to volume saturate.[21] This would certainly describe the data in Figure 2 where the onset of the 2^+ signal coincides with the flattening off of the parent ion intensity. It is thought that much of the intensity of the single ionization peak comes from the lower intensity wings of the laser beam.

Coulomb explosion ionization is a possible mechanism for CS_2 since the multiply charged atoms of C and S are observed although at low intensities. No similar evidence for Coulomb explosion is evident for the hydrocarbon molecules studied here. However, an envelope of 2^+ cations is observed for these molecules, and this shedding of hydrogen atoms at the 2^+ level or a mixture of charged and uncharged hydrogen atoms from the 3^+ level is a striking characteristic of this intensity regime.

Conventional Coulomb explosion is unlikely to explain the present observations. For light molecules, multiply charged ions that lead to Coulomb explosion are only transient species,[13] while in the present work the 2^+ and 3^+ parent ions have lifetimes at least of the order of the flight time in the TOF (about tens of microseconds). Any dissociation, particularly the shedding of hydrogen atoms, seems to be a rather gentle process similar to ordinary photodissociation after excitation to a predissociating electronic state. Newton has claimed that multiple ionization is favored for molecules which have sufficient numbers of nonbonding or delocalized electrons.[19]

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