Multiply Charged Ions from Aromatic Molecules Following Irradiation in Intense Laser Fields

K. W. D. Ledingham,*,† D. J. Smith,† R. P. Singhal,† T. McCanny,† P. Graham,† H. S. Kilic,†,‡ W. X. Peng,†,§ A. J. Langley,‖ P. F. Taday,‖ and C. Kosmidis⊥

Department of Physics and Astronomy, University of Glasgow, Glasgow, G12 8QQ. Scotland, U.K.,
Central Laser Facility, Rutherford Appleton Laboratory, Didcot, Oxon, OX11 0QX. England, U.K., and
Department of Physics, University of Ioannina, Ioannina, Greece GR-45110

Received: November 9, 1998

It is well-known that aromatic molecules, when irradiated by UV laser beams in the nanosecond pulse width regime, yield exclusive parent ions at laser intensities of 10^7 W cm^{-2} (soft ionization). As the laser intensities increase up to 10^9 W cm^{-2}, however, extensive fragmentation takes place such that small mass fragments dominate the spectra at the expense of parent signature ions. The reason for this is that the dissociative lifetimes are shorter than the laser pulse width and ladder-switching fragmentation takes place. With the development of high power femtosecond lasers, these dissociative lifetimes can often be bypassed. Presently, at laser intensities up to the order of 10^{15} W cm^{-2} with pulse widths as short as 50 fs at near-infrared (IR) wavelengths (790 nm), soft ionization again takes place. This has been seen using a technique known as femtosecond laser mass spectrometry (FLMS). Under such conditions, stable multiply charged parent and adjacent satellite ions are observed and the fragmentation is minimal. In this paper, these effects are described for the medium-mass aromatic molecules benzene, monodeuterated benzene, toluene, and naphthalene. Other studies have shown that for diatomic and triatomic ions, the absorption of many photons produces transient highly ionized parent species which subsequently fragment on a time scale of femtoseconds, leading to multicharged atomic species. This so-called "Coulomb explosion" model has proved effective in describing the fragmentation of small molecules but seems a less attractive model to explain the results which are presented here, at the above-mentioned beam intensities. In contrast, the polyatomic molecules studied presently using IR FLMS display atomic-like characteristics.

Introduction

The multielectron 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^{13-16} 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. A number of comprehensive review articles have been written describing the behavior of atoms and molecules in very intense laser fields[1−6] and the new physics which has been elicited from these studies.

From the late 1960s, the early pioneering work on intense laser irradiation of atoms and molecules was dominated by the Saclay group led by Manus and Mainfray.[7−10] They have carried out a program of work using a Nd:YAG laser with a pulse width of 30−50 ps using laser intensities up to 10^{15} W cm^{-2}. They reported over the years that their data could be described by the equation governing an *n* photon pertubative ionization rate, R_n, given by

$$R_n = \sigma_n I^n$$

where I is the laser intensity and σ_n is the generalized *n*-multiphoton ionization (MPI) cross section.

However, as early as 1965 Keldysh[11] recognized that an alternative mechanism to MPI could occur at sufficiently intense laser fields. Under such conditions of intense field strength and long wavelength, the normal coulomb potential of the atom or molecule can become so distorted that electrons can either leak through the coulomb barrier (tunneling) or, if the laser intensity is high enough, the ground state of the atom or molecule is no longer bound and electrons are free to escape (over the barrier ionization, OTBI). OTBI can be described purely in classical terms as a superposition of the coulomb potential felt by the electrons and a quasistatic laser field.

The electric field of a focused picosecond or femtosecond laser is usually very intense and can cause the severe modifications mentioned above, and hence there is a possibility of the valence electrons tunneling through the barrier formed by the molecular potential and the instantaneous electric field of the laser. For tunneling ionization (TI) to take place in the ac field of a laser, the barrier must remain more or less static for long enough to allow the electron to cross the barrier. In fact, tunneling can occur if the mean tunneling time (t) of the electron with the corresponding frequency (ν) is less than half the period (t_0) of the laser wavelength.[12] A semiquantitative criterion for tunneling can thus be defined and is known as the

---

* Author for correspondence. E-mail: k.ledingham@physics.gla.ac.uk.
† University of Glasgow.
‡ Permanent address: Department of Physics, University of Selcuk, 42079, Konya, Turkey.
§ Permanent address: Department of Physics, Jilin University, Changchun 130023, P. R. China.
‖ Rutherford Appleton Laboratory.
⊥ University of Ioannina.

10.1021/jp984359+ CCC: $18.00

Keldysh adiabatic parameter,[11,12]

$$\gamma = \frac{2t}{t_0} = \frac{2\nu_0}{\nu} = \frac{l}{l_0} = \nu_0 \frac{(2E_i m)^{1/2}}{e\Sigma}$$

where ν_0 is the laser frequency, l_0 the mean distance that an electron travels during one-half period of the laser wavelength, and l the tunnel length. E_i is the zero-field ionization potential, e the electronic charge, and Σ the laser electric field strength. This can be written as

$$\gamma = \left[\frac{E_i}{(1.87 \times 10^{-19})I\lambda^2}\right]^{1/2}$$

with E_i in units of eV, laser intensity, I, in W cm^{-2}, and wavelength, λ, in nm.

TI therefore occurs under the condition $\gamma \ll 1$. It is evident from the above that high laser wavelengths (low frequencies) are suited to TI. Recently, this criterion has been somewhat relaxed and a more pragmatic definition for tunneling is thought to be $\gamma < 0.5$.[13] For $\gamma \gg 1$, TI will not occur and MPI is the main mechanism. In the intermediate range, i.e., $\gamma \sim 1$, a contribution to the ionization rate can be expected from both MPI and TI.

Although the criteria for multiphoton ionization and tunneling are apparently quite well defined, it has been pointed out[13] that some authors observe multiphoton results in the tunneling regime[8] and tunnel ionization in the multiphoton regime.[14] The Glasgow group has shown that the resulting dynamics of NO_2[15,16] and benzaldehyde[17] under subjection to high-intensity laser beams can be well described by multiphoton processes. This is despite γ values approaching the TI threshold. OTBI can occur instead of MPI and TI if the laser intensity is sufficiently high. The critical laser intensity I_{th} (W cm^{-2}) for OTBI has been shown to be[18,19]

$$I_{th} = (4 \times 10^9)\frac{E_i^{\,4}}{Z^2}$$

where E_i is the ionization potential in eV and Z is the ionic charge. As an example, consider xenon with $E_i = 12.1$ eV and $Z = 1$. The I_{th} *is* 8.6×10^{13} W cm^{-2}. This OTBI threshold may be significantly greater than the saturating intensity of xenon in which all the atoms or molecules within the laser focal volume are ionized. Protopapas et al.,[1] using the data of L'Hullier et al.,[20] have pointed out that the saturation intensity of xenon with a 35 ps pulse width at 1.064 μm is 2.5×10^{13} W cm^{-2}, which is considerably less than the OTBI threshold, and hence all the target entities would be ionized by multiphoton processes before the onset of tunneling or OTBI. Thus, the effect of the pulse shape is important.

In another very important paper Lambropoulos[21] has argued that substantial ionization occurs during the rising edge of the laser pulse down to the picosecond and perhaps even femtosecond range. It was therefore stated that no neutral atoms or molecules could be exposed intact to a peak power much above 10^{14} W cm^{-2} due to the pulse evolution. The singly and doubly charged entities will be reached within about 100 fs at lower intensities by multiphoton ionization processes. Both refs 1 and 21 argue that only very short pulses produce tunnel ionization especially if the wavelength is less than 1 μm. Such pulses are required to have a sharp rise in their leading edge, as well as being intense. Interferometric shaping[22] can be used to mold the leading edge of laser pulses.

Mevel et al.[23] show that the evolution from multiphoton to tunnel ionization may best be observed by looking at the energy spectra of the photoelectrons rather than total ion yield measurements. They observed that, at 617 nm and 100 fs pulses for several noble gases, above threshold ionization (a MPI characteristic) was still evident up to about 6×10^{14} W cm^{-2}. True tunneling only became evident for helium at 1.5×10^{15} W cm^{-2}. On the other hand however laser ionization of noble gases by coulomb barrier suppression has been shown by Augst et al.[18] using a picosecond Nd glass laser at 1.053 μm for laser intensities up to 10^{16} W cm^{-2}.

There exists clearly some controversy between multiphoton versus tunneling ionization in the intense laser regime, which requires careful analysis of existing and future data, particularly with respect to the length, rise time, and shape of the laser pulses.

It is important to realize that a further increase in laser intensity beyond saturation can lead to more ionization, albeit at a reduced rate. This is primarily due to an effective expansion in the interaction focal volume of the laser spot as the wings of the pulse significantly contribute to the ionization rate.[21,24,25]

Although much of the existing experimental data and theoretical analysis deals specifically with atoms, in recent years following the pioneering work lead by Codling and Frasinski[26] there has been increasing emphasis on studying the interaction of intense laser radiation with molecules, particularly those of a diatomic and triatomic nature. The theoretical treatment has been extended from atoms. This may be particularly applicable when the molecules themselves are behaving with atomic-like characteristics. Several papers[27−30] have reported that simple molecules (diatomic and triatomic) can be quasistatically tunnel ionized as if they were atoms of the same ionization potential. The Glasgow group has also discussed molecules behaving with atomic attributes.[31]

However, due to the additional degrees of freedom associated with molecules compared to atoms, the molecular case can be more complex.[5] From the widespread studies of small molecules, a general theme seems to be emerging[1−6,32−60] that, at laser intensities in the range of $\sim 10^{13}-10^{16}$ W cm^{-2}, multiphoton ionization will pre-empt field ionization (tunneling) during the leading edge of the ultrafast laser pulse. The resulting ions become aligned with the high laser electric field with field multielectron ionization occurring. The bonds lengthen somewhat from their equilibrium position with the production of transient highly ionized parent species, prior to coulomb explosions at critical internuclear distances, leading to stable multiionized atoms. This is thought to occur on a femtosecond time scale. In general, this results in kinetic energies for the fragments which are considerably less than would have been expected if the explosion had taken place at equilibrium dimensions. To date, the mechanism of electron removal is not well understood. On the other hand,[15,16] it has been shown that the dissociation/ionization of NO_2 at a number of different wavelengths and with laser intensities up to 2×10^{14} W cm^{-2} can be described adequately by multiphoton cross sections in a simple rate equation model. As the molecules become more complex, that is, from diatomic and triatomic to polyatomic species, the theoretical interpretation of what happens to them in intense laser fields becomes more difficult, but nonetheless this is becoming a very important field of current research. This is not only for theoretical reasons[12,60−63] but also because femtosecond laser mass spectrometry has considerable potential as a sensitive analytic technique[17,64−78] and in addition there is potential for molecules under the action of intense laser fields to be efficient generators of high harmonics. The present study centers on medium mass aromatic molecules.

It is well-known that aromatic molecules, when irradiated by UV laser beams in the nanosecond regime, yield exclusively parent ions at laser intensities of 10^7 W cm^{-2} (soft ionization). As the laser intensities increase up to 10^9 W cm^{-2}, however, extensive fragmentation takes place such that small mass fragments dominate the spectra with the parent mass often missing entirely. The reason is that this beam intensity accesses levels where the dissociative rate is faster than the absorption rate from that level and hence ladder-switching fragmentation takes place.[79−81]

Recently, the Glasgow group has concentrated on the intense laser radiation of medium-mass molecules and, contrary to the nanosecond regime, has found them to be very robust, especially when IR wavelengths are used.[17,31,78] Ledingham et al.[31] has generally discussed the behavior of polyatomic molecules in intense laser fields. In a previous paper,[78] Smith et al. showed that the irradiation of benzene, toluene, and naphthalene with laser pulses of intensities up to about 4×10^{14} W cm^{-2} at 750 nm and 2×10^{14} W cm^{-2} at 375 nm, with pulse widths as short as 50 fs, produced very strong singly ionized parent peaks with minimal associated fragmentation. For equal laser intensities, the fragmentation in the UV compared to the IR was always greater, although the parent peak was still the strongest peak in the spectra, an emerging characteristic of FLMS. This soft ionization is in agreement with similar studies by DeWitt et al.[75,77] using laser intensities up to $\sim 3.8 \times 10^{13}$ W cm^{-2}. Smith et al.[78] also reported that for the spectra at 750 nm a doubly ionized parent peak was becoming the second most intense entity at the highest beam intensities but was either not visible or minimally present at 375 nm where increased fragmentation was evident. Around the doubly ionized parent ions, satellite peaks were observed with substantial doubly ionized components. Also, a triple ionized parent was observed for naphthalene in the intensity range mentioned. However, DeWitt et al.[75,77] did not report any multiple ionization, most likely due to the slightly decreased laser intensities used.

The molecules studied here are benzene (C_6H_6), its monodeuterated counterpart (C_6H_5D), toluene (C_7H_8), and naphthalene ($C_{10}H_8$). In the present experiments for benzene, monodeuterated benzene, and toluene, it was decided to increase the laser intensity over previous studies[79] by an order of magnitude to $\sim 3 \times 10^{15}$ W cm^{-2} and concentrate at a near-IR wavelength which was 790 nm. This used an extensively refurbished laser system as reported in the Experimental Section. Such changes represented a progressive step when studying multicharged phenomena and the associated mechanisms. However, the data presented for naphthalene[78] is taken from the prerefurbished system[66] at a lower laser intensity. This is because the effects being described in this paper occurred at lower intensities for this molecule compared to benzene and toluene, that is, increased fragmentation, in agreement with Levis and DeWitt,[76,77] and the appearance of multiply charged species.

It was also decided to operate the laser with vertical polarization since in the previous work[78] very little difference was noticed between vertical and horizontal polarizations.

The general reason for choosing the aromatics is that a great deal of theoretical and experimental work has been carried out on the laser-induced fragmentation of these molecules in the nanosecond regime, and hence any deviations from these well-known patterns can be attributed to bypassing existing nanosecond fragmentation pathways or accessing new pathways by the femtosecond radiation.

Experimental Section

The laser system, subject to a recent refurbishment, has often been used in the past by the Glasgow group.[66,67] Recently, it has been extensively refurbished and will now be briefly described. A Spectra Physics 50 fs Ar ion laser pumped Ti:sapphire oscillator produces a 790 nm, 9 nJ pulse. A chirped amplification system is used to amplify this energy to the millijoule level. The pulses from the oscillator are stretched to about 200 ps in an all-reflective stretcher comprised of a 1500 lines per mm grating and concave mirror (radius of curvature 730 mm). The stretched pulses are then amplified in a multipass confocal amplifier. This consists of four spherical mirrors with radii of curvature 2000 mm and a 7 mm long Ti:sapphire rod with a FOM = 150, and $\alpha_{514} = 4.8$ pumped with 67 mJ from a Spectra Physics GCR 270−10 Nd:YAG laser. After five passes, the preamplified pulse train is extracted from the amplifier and passed through a pulse picker to reduce the repetition rate from 82 MHz to 10 Hz. The selected pulse is reinjected into the amplifier to boost its energy to 2 mJ. The pulse is then compressed to 50 fs using a pair of 1500 lines per mm gratings in a parallel arrangement. The output of the laser system is monitored using a single shot autocorrelator. The system will be discussed in detail in another paper.[82]

The mass spectra were recorded with a linear TOF spectrometer of drift length 1.2 m based on a Wiley McLaren design with a typical mass resolution of about 300 at 100 Da. The samples were introduced effusively from an inlet system to a vacuum chamber through a needle valve. The ions were detected by a Thorn EMI electron multiplier connected to a Lecroy 9304 digital oscilloscope. The TOF system was operated to maximize the mass resolution of the system rather than the collection efficiency of the ions. A mirror of 10 cm focal length was inserted behind the ion extraction region. The laser beam, essentially Gaussian, entered the TOF with a beam width of about 1 cm (D) and was focused using the 10 cm focal length mirror (f) to a spot size of about 5 μm radius ($r = 2f\lambda/\pi D$) between the pusher and the first extract electrode where the sample emerged.

This experimental technique has been given the name femtosecond laser mass spectrometry (FLMS).

Results and Discussion

The mass spectra of relative ion yield versus mass-to-charge ratio (m/z) for toluene, naphthalene, benzene, and monodeuterated benzene are shown in Figures 1−4, respectively. The spectra are expanded at local regions of interest. With the exception of naphthalene, which was studied at a different date, a consistent normalization of the spectra allows quantitative comparisons of ion intensity. Preliminary features were reported by Smith et al.[78] for benzene, toluene, and naphthalene, and these were a dominant parent ion with minimal fragmentation, a secondary dominant doubly charged parent molecule with envelopes of adjacent satellite peaks, and a triply charged parent molecule for naphthalene. The present paper describes these features in detail and extends the study to increased laser intensities.

Toluene (C_7H_8). A clear doubly ionized toluene parent is visible in Figure 1, evident above the minimal fragmentation. In the expanded inset of the figure, surrounding multiply charged satellite peaks can be seen, some of which fall at half m/z values and therefore are unambiguous in their doubly ionized nature. In addition, such peaks are in a region of the spectrum between the C_3H_n and C_4H_n fragment groups where there is no ambiguity between doubly charged entities with other singly charged

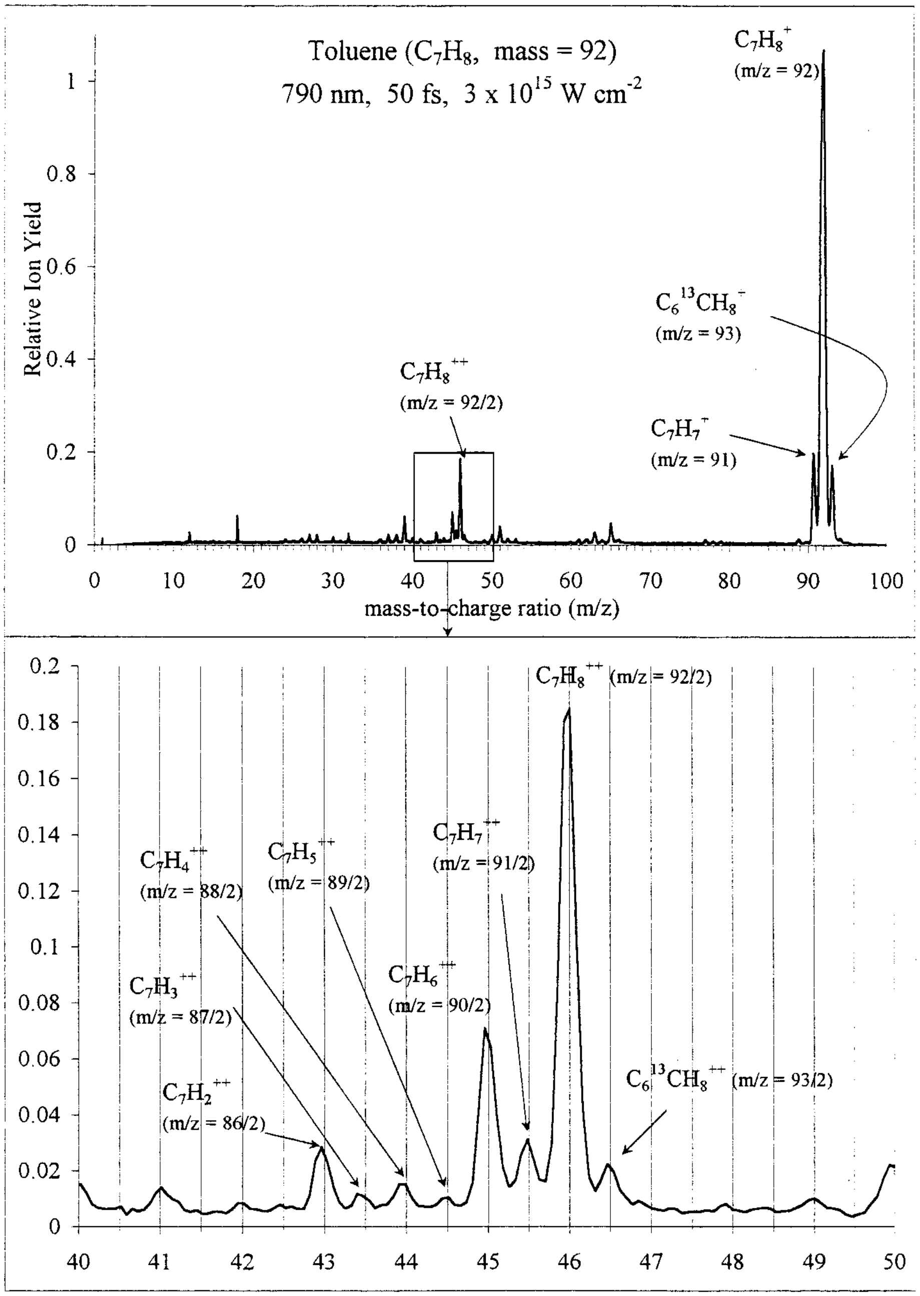

Figure 1. Toluene (C_7H_8) mass spectrum showing normalized ion yield versus mass-to-charge ratio (*m*/*z*). A dominant parent ion is evident with a secondary dominant doubly charged parent. $C_7H_8^{2+}$ is at an unambiguous *m*/*z* ratio where single fragment ions do not exist. Minimal dissociation is observed. The spectrum is expanded around the double parent ion revealing an envelope of adjacent doubly ionized satellite peaks. No triply charged ion is present.

fragments. In this respect, toluene is a particularly suitable molecule to study double ionization. From $m/z = 43$ to $m/z = 46.5$ there are eight peaks, at every half mass unit, which have been identified as $C_7H_2^{2+}$ to $C_6{}^{13}CH_8^{2+}$.

To further confirm the unambiguous presence of $C_7H_8^{2+}$, one can use an isotopic approach. For carbon, a significant naturally occurring isotopic mixture exists of $^{13}C/^{12}C$. The amounts[83] are 98.9% ^{12}C and 1.1% ^{13}C. So for a molecule containing *x* carbon atoms a ^{13}C isotope naturally exists with an approximate abundance of $(x \times 1.1)\%$. Therefore, multiply charged parent ions can be quantified by the consistency, or otherwise, of the $^{13}C^+/^{12}C^+$ to $^{13}C^{2+}/^{12}C^{2+}$ ratios. For toluene, the isotopic ratio of $C_6{}^{13}CH_8^+/C_7H_8^+$ (the peaks at $m/z = 93$ and $m/z = 92$) is ~8%, which is in close agreement with the measured peak areas. This is expected for a molecule containing seven carbon atoms. The ratio of the peaks at $m/z = 46.5$ and $m/z = 46$ is also ~8%. Finally, it is important to note that triply ionized toluene is not visible in the laser intensity range up to 3×10^{15} W cm^{-2}. Even at this high-intensity range, a pathway to produce a stable $C_7H_8^{3+}$ ion was not found.

Naphthalene ($C_{10}H_8$). A strong $C_{10}H_8^{2+}$ peak is evident in Figure 2 which can be distinguished from the fragment $C_5H_4^+$. This is because the isotopic $^{13}C/^{12}C$ isotopic ratio is approximately consistent (~11%) in going from $C_9{}^{13}CH_8^+/C_{10}H_8^+$ to $C_9{}^{13}CH_8^{++}/C_{10}H_8^{++}$ [i.e., $(m/z = 129)/(m/z = 128)$ to $(m/z = 64.5)/(m/z = 64)$]. In fact, a slightly smaller value is found for the ratio which may be attributed to a small presence of $C_4H_5^+$ at $m/z = 64$. An envelope of doubly charged components is also evident around the $C_{10}H_8^{2+}$ ion. There is also a strong peak at $m/z = 51$ which is evident because of the reduced surrounding fragmentation. This has been attributed to the doubly ionized C_8H_6 fragment. Supportive of this is the presence

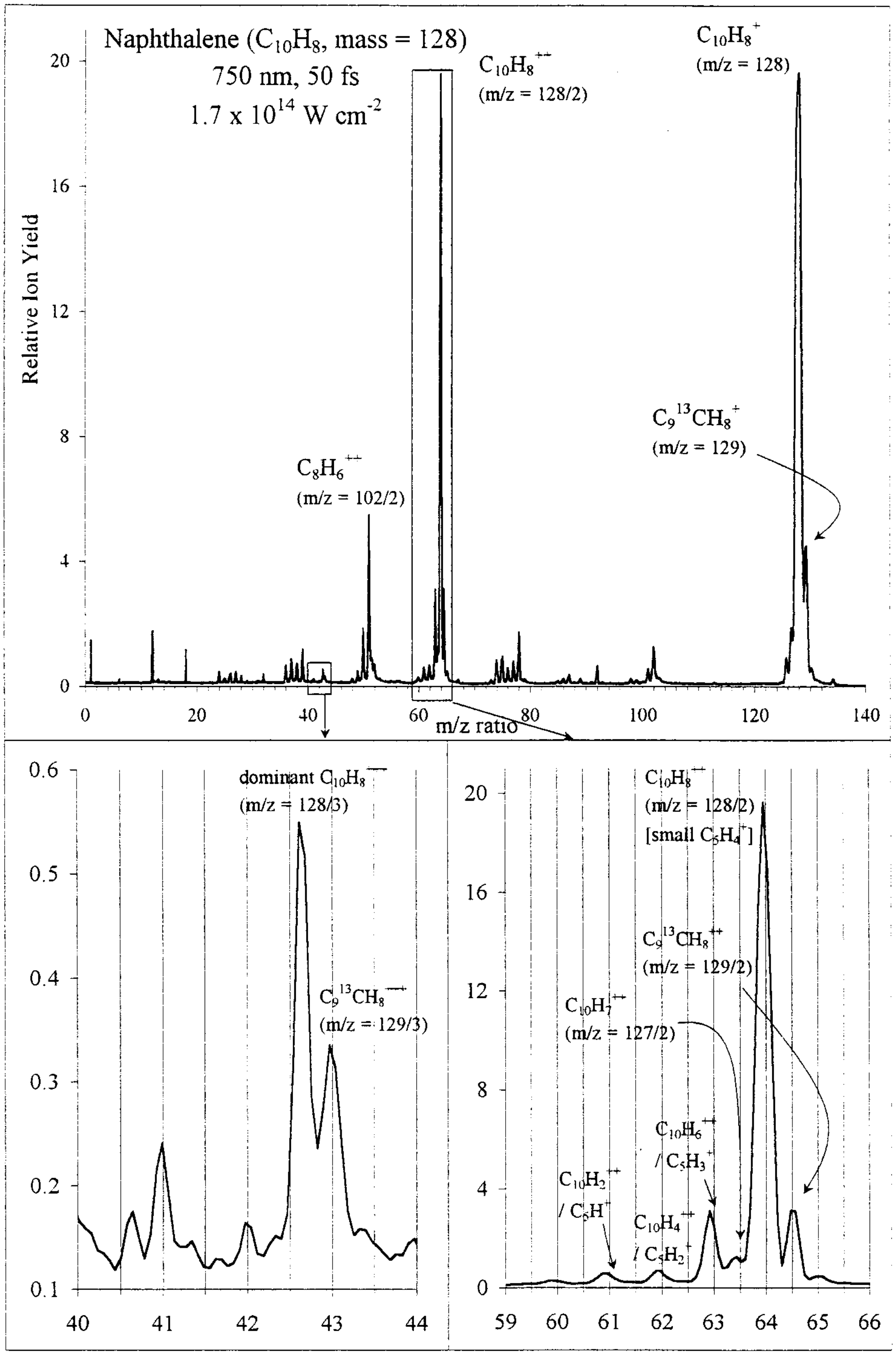

Figure 2. Naphthalene ($C_{10}H_8$) mass spectrum showing normalized ion yield versus mass-to-charge ratio (m/z). Concordant features to Figure 1 can be seen such as minimal fragmentation and a strong presence of singly and doubly charged molecular ions. The spectrum is expanded around regions of interest, that is, the doubly and triply charged parent molecule. For the $C_{10}H_8^{2+}$ inset on the right-hand side of the figure, evidence of doubly charged satellites is again seen.

of a half mass peak at 51.5 which is unambiguously $C_7{}^{13}CH_6{}^{2+}$. A triply charged parent ion, $C_{10}H_8{}^{3+}$ ($m/z = 128/3$), and accompanying $C_9{}^{13}CH_8{}^{3+}$ ($m/z = 129/3$) ion have also been observed for this molecule and can be seen in the left-hand inset of Figure 2. Again, the isotopic ratio is approximately consistent.

Additionally, for this same data, Smith et al.[78] has already shown that UV studies at similar laser intensities to the IR yields substantially increased fragmentation and very minimal multiple ionization.

Benzene (C_6H_6) and Monodeuterated Benzene (C_6H_5D). *Double Ionization.* Clear evidence exists in favor of doubly ionized benzene (Figure 3) and monodeuterated benzene (Figure 4) molecules. Surrounding doubly ionized satellite peaks are also present and expanded in the right-hand insets of Figures 3 and 4. For benzene, the strong peak at $m/z = 39$ could be the dication $C_6H_6{}^{2+}$ or could result from the symmetric dissociation of the parent ion to $C_3H_3{}^+$. However, when monodeuterated benzene is irradiated under similar conditions there is a similarly intense peak at m/z 39.5 (unambiguous $C_6H_5D^{2+}$). This proves that the doubly ionized benzene parent is far more intense than the symmetric dissociation. Such arguments are the principle reason that deuterated benzene was studied.

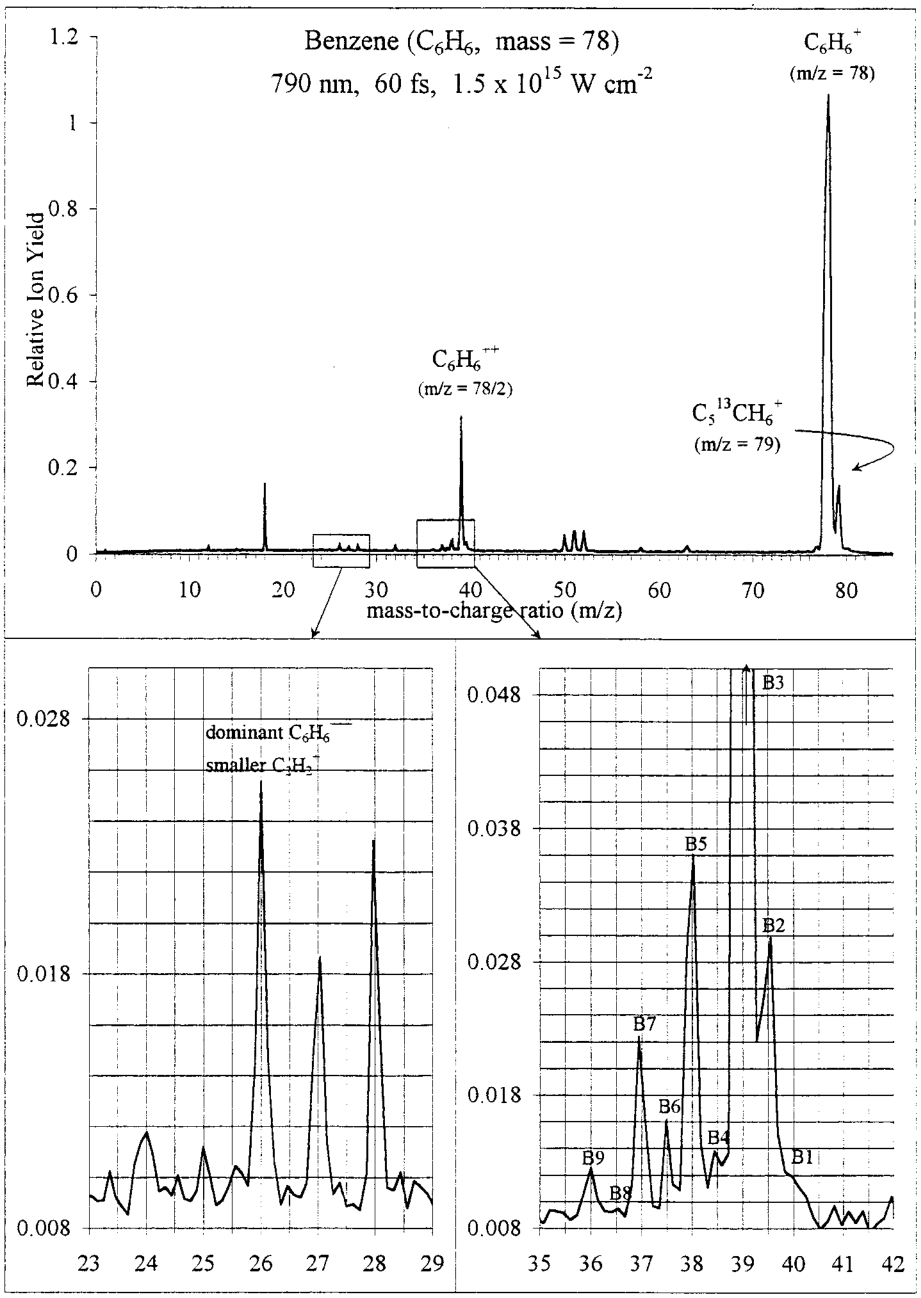

Figure 3. Benzene (C_6H_6) mass spectrum showing normalized ion yield versus mass-to-charge ratio (*m*/*z*). Similar characteristics to Figures 1 and 2 are evident. Double and triple parent ions are present which are seen in detail in the expanded insets of the figure with satellite peaks existing around $C_6H_6^{2+}$. These labeled peaks in the right-hand side inset are identified in Table 1.

By a careful comparison of the two spectra of benzene (B) and monodeuterated benzene (DB) in which the peaks at 39 and 39.5, respectively, have been normalized, the identities and intensities of the other masses are ascertained. This can be seen in Table 1. The methods used to label and estimate the intensities of the various peaks and coincident peaks (peaks having the same *m*/*z* ratio within the resolution limits of the spectra) are presented in the Appendix.

The isotopic ratio approach can be used to confirm some of the findings shown in Table 1. Consider benzene first. The $^{13}C/^{12}C$ ratios for the singly ionized parent ($m/z = 79$ to $m/z = 78$) and doubly ionized parent ions ($m/z = 39.5$ to $m/z = 39$) are consistent at a value of approximately 7% which implies that the peak at $m/z = 39$ is dominantly $C_6H_6^{2+}$, in agreement with the relevant data in Table 1. The peak at $m/z = 39.5$ is of course 100% $C_5{}^{13}CH_6^{2+}$.

Secondly consider monodeuterated benzene. At first glance, the isotopic ratios of $C_5{}^{13}CH_5D^+/C_6H_5D^+$ ($m/z = 80$ to $m/z = 79$) and $C_5{}^{13}CH_5D^{2+}/C_6H_5D^{2+}$ ($m/z = 40$ to $m/z = 39.5$) may not seem in concert at values of approximately 7% and 12%, respectively. One expects a value of 7% for a molecule containing six carbon atoms. The additional percentage in the doubly ionized case is due to more than one peak at the same *m*/*z* ratio. The ^{13}C presence is still expected to be 7%. The peak at $m/z = 39.5$ is unambiguously $C_6H_5D^{2+}$. Therefore, the peak at $m/z = 40$ must have 5% (12 − 7) abundant coincident species with the 7% abundant $C_5{}^{13}CH_5D^{2+}$. Possible species are $C_3H_2D^+$ and $C_3H_4^+$ responsible for around 40% (5/12 × 100) of the ion peak at $m/z = 40$. This is in agreement with the intensities stated in Table 1 and explained in the Appendix.

Triple Ionization. Triply ionized parent ions can be observed for benzene and monodeuterated benzene. $C_6H_6^{3+}$ and $C_6H_5D^{3+}$

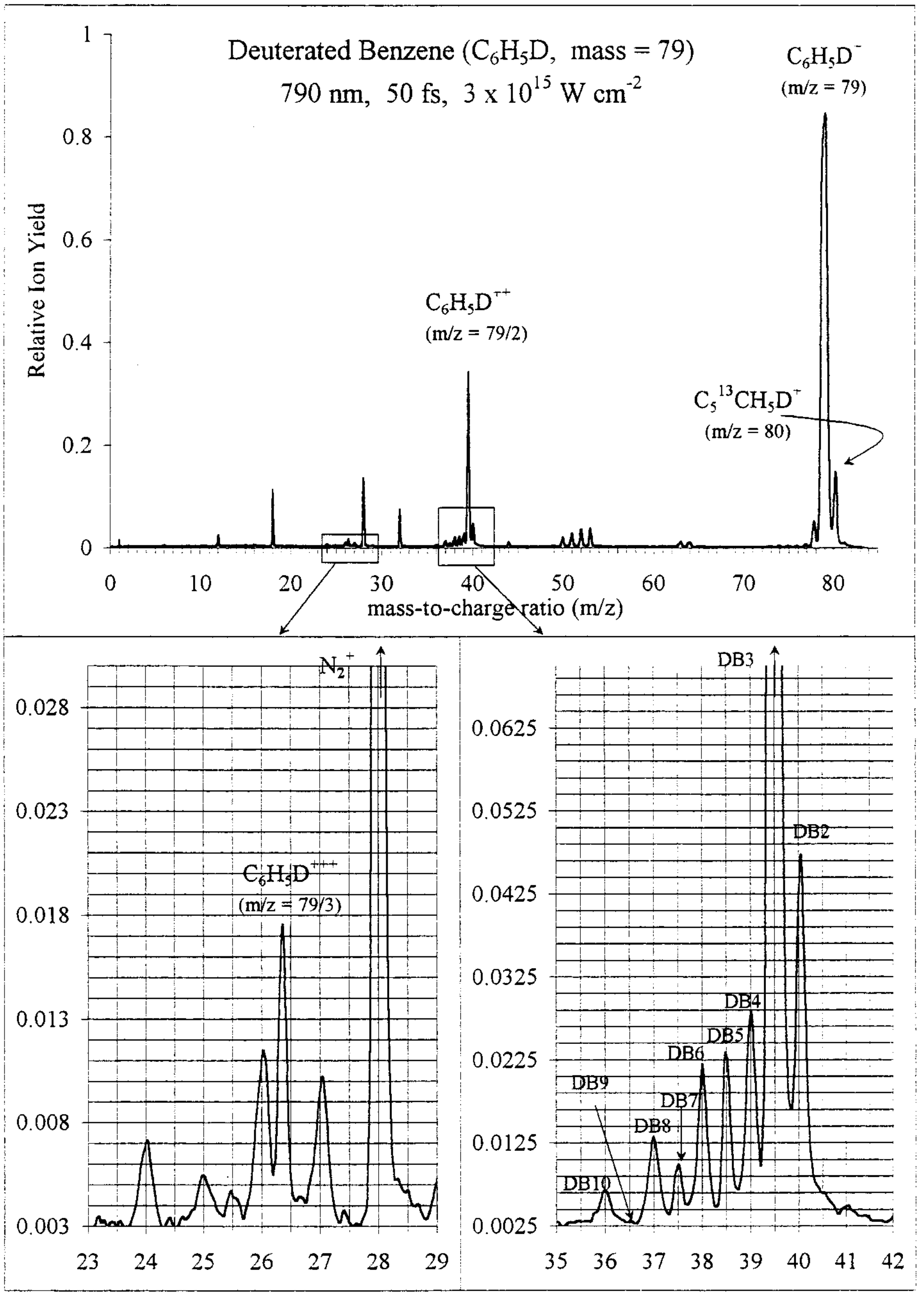

Figure 4. Monodeuterated benzene (C_6H_5D) mass spectrum showing normalized ion yield versus mass-to-charge ratio (m/z). Having similar features to Figure 3, this spectrum is used to aid identification of the peaks in Figure 3; see Appendix for details. Unambiguous doubly and triply charged parent ions are present at $m/z = 79/2$ and $m/z = 79/3$ which are shown in detail in the insets. The labeled peaks are identified in Table 1.

can be seen in the left-hand side insets of Figures 3 and 4, respectively, at the given laser intensities. The visible nitrogen contaminant at $m/z = 28$ which sometimes, along with water, proved very difficult to eliminate, should be ignored. These peaks did not materially affect the results.

For monodeuterated benzene, the triple ion is unambiguous at $m/z = 26.3$ (79/3). Using this fact and looking at the ionic yields for benzene at $m/z = 26$ (peak intensity ≈ 0.0256) and deuterated benzene at $m/z = 26.3$ (peak intensity ≈ 0.017) one can conclude that the benzene peak is predominantly $C_6H_6^{3+}$ ($\sim$65% abundant) with a lesser contribution from $C_2H_2^+$. One can also observe the single ion at $m/z = 26$ for deuterated benzene and expect a similar single component for benzene.

Laser Intensity Dependences of the Mass Spectral Peaks. Figure 5 illustrates for benzene and monodeuterated benzene a laser intensity dependence on some of the main mass peaks in the spectra including singly, doubly, and triply charged ions. The graphs are consistently normalized for quantitative comparisons. The ion curves are multiplied by various numbers in order to separate them out for ease of viewing, although their general intensity order in the mass spectra as seen in the plots is correct. Such multiplication was done prior to drawing the figure. To get the actual normalized yield, simply divide by the appropriate number.

It appears that multiply charged ion peaks have a greater gradient and therefore a stronger laser intensity dependence than single peaks. Similar effects have been observed for double charged parent ions in benzaldehyde.[17] The single charged ions seem to follow the slope of the parent ion. The different dependences may be taken as tentative evidence for multiple ion production. In terms of sequential ionization, one would expect a doubly charged state to appear as the single charged

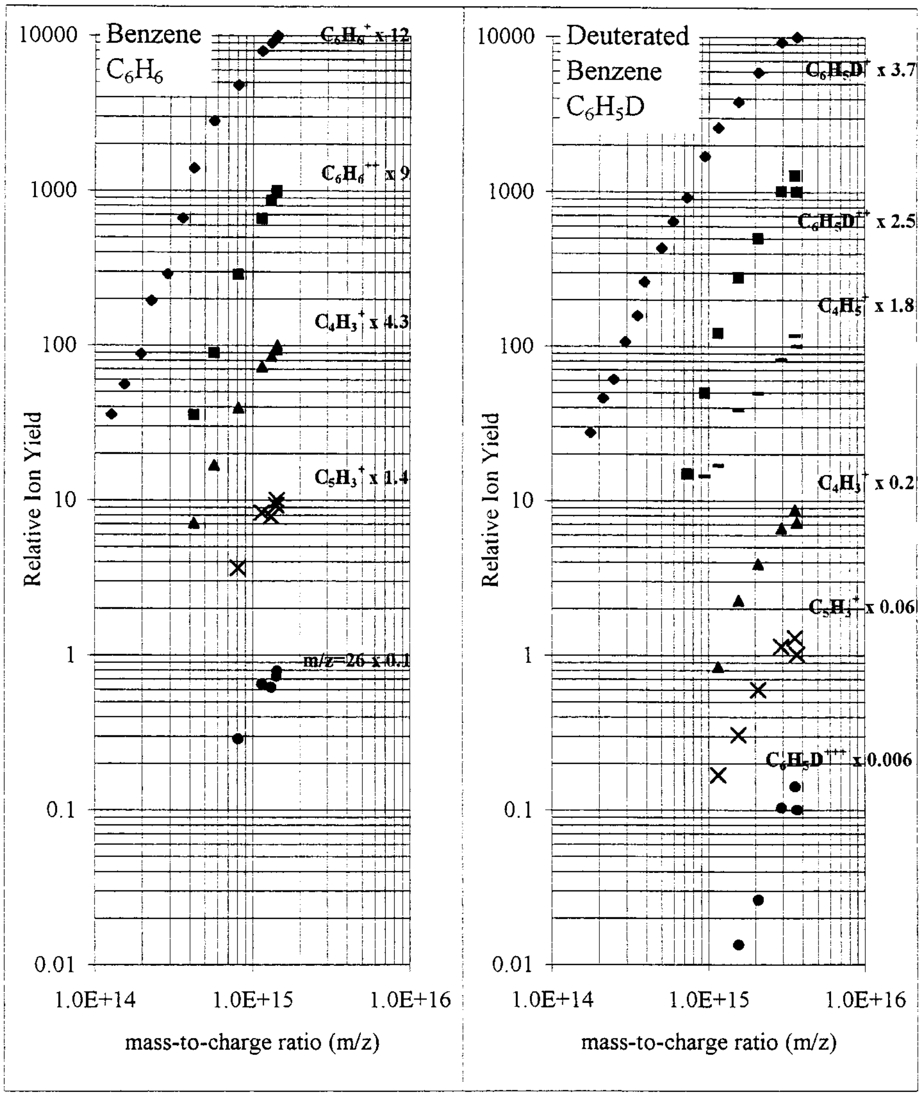

Figure 5. Dependence of ion yield versus laser intensity for benzene and deuterated benzene for some of the main mass peaks in the spectra, including singly, doubly, and triply charged parent ions, as well as some of the stronger singly charged fragment peaks. The graphs are consistently normalized such that quantitative comparisons can be made between them. For ease of viewing, the ions are separated out by multiplication factors indicated in the plots. Multiply charged peaks have a greater intensity dependence than the single parent ion. The singly charged fragments, on the other hand, seem to follow the slope of the single parent ion. Such differences may be expected for single and multiply charged peaks. The figure also shows the appearance of singly ahead of doubly ahead of triply charged parent ions as the laser intensity increases.

TABLE 1: Semiquantitative ion peak identification of the doubly ionized regions of Figures 3 and 4 for benzene (B) and monodeuterated benzene (DB), respectively. Reference should be made to the Appendix for details of the analysis

m/z ratio	peak	benzene (C_6H_6)	peak	deuterated benzene (C_6H_5D)
40.0	B1	small $C_3H_4^+$	DB2	60% $C_5{}^{13}CH_5D^{2+}$, 40% ($C_3H_2D^+$, $C_3H_4^+$), [$C_3H_2D^+ > C_3H_4^+$]
39.5	B2	100% $C_5{}^{13}CH_6^{2+}$	DB3	100% $C_6H_5D^{2+}$
39.0	B3	90% $C_6H_6^{2+}$, 10% $C_3H_3^+$	DB4	50% $C_6H_4D^{2+}$, 50% ($C_3H_3^+$,C_3HD^+, $C_6H_6^{2+}$), [$C_3H_3^+ >$ $C_3HD^+ > C_6H_6^{2+}$]
38.5	B4	100% $C_6H_5^{2+}$ but small	DB5	60% $C_6H_5^{2+}$, 40% $C_6H_3D^{2+}$
38.0	B5	65% $C_6H_4^{2+}$, 35% $C_3H_2^+$	DB6	70% $C_6H_2D^{2+}$, 30% ($C_6H_4^{2+}$, $C_3H_2^+$, C_3D^+), [$C_6H_4^{2+}/C_3H_2^+$ 65% to 35% with small C_3D^+]
37.5	B6	100% $C_6H_3^{2+}$	DB7	small $C_6H_3^{2+} > C_6HD^{2+}$
37.0	B7	$C_3H^+ \geq C_6H_2^{2+}$	DB8	$C_3H \geq C_6H_2^{2+}$ and C_6D^{2+} negligible
36.5	B8	negligible	DB9	negligible
36.0	B9	100% C_3^+	DB10	100% C_3^+

state tends toward saturation,[84] and likewise a triple charged state to appear when the double begins to volume saturate. Certainly, the figure at least illustrates the initial appearance of the singly charged parent ahead of the double parent, which is in turn ahead of the triple parent ion. Similar effects have also been observed for toluene and naphthalene.

Figure 6, with monodeuterated benzene shown as an example, confirms the above-mentioned dependence of the ratio of singly to doubly and triply charged parent peaks. The plot illustrates a strong dependence in the lower intensity range after which a leveling out occurs as saturation effects become apparent.

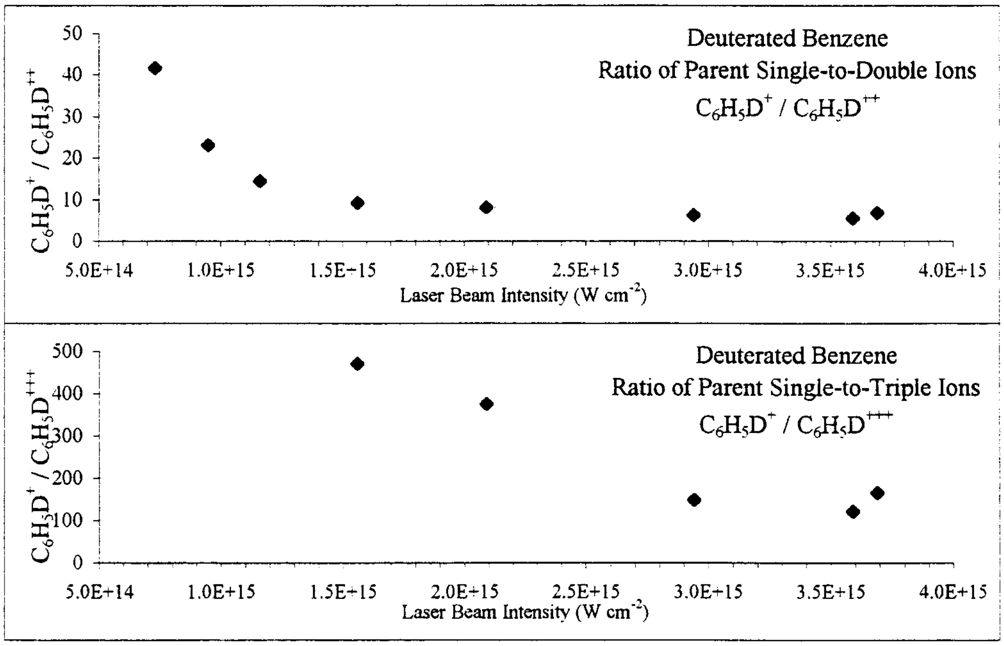

Figure 6. Monodeuterated benzene ratios of single-to-double parent ions (upper plot) and single-to-triple parent ions (lower plot), as a function of laser intensity. The figure clearly illustrates the different dependences of single and multiple ions on the laser intensity as evident in Figure 5. This is particularly evident in the lower intensity regions. As the laser intensity increases, the ratios level as saturation effects become apparent.

Ionization Mechanisms and Pathways for Single and Multiple Ion Production. As indicated in the Introduction, the nanosecond UV resonant irradiation of benzene and other aromatics has produced extensive fragmentation with laser intensities of 10^9 W cm^{-2} and above. The experimental results have indicated that dissociation of these molecules takes place in the ionic state manifold. Although neutral fragments can be produced below and above the ionization threshold, these were not ionized by the laser intensities used.[85] After absorption of about four UV photons the C_4, C_3, and C_2 fragment ion groups were formed. These ions absorbed further photons in a ladder-switching regime until finally C^+ was formed. At the highest laser intensities, the smaller fragments were produced in large quantities and the parent ion was not visible or very small. The fragmentation rates increased with the excitation energy and were maximally found to be about[80] 10^{11} s^{-1}. Additionally, the excitation did not proceed up the auto-ionization ladder of the neutral molecule, and no multiply charged ions were detected.

In the present experiments, however, with laser intensities up to the order of 10^{15} W cm^{-2}, all of the above ionic fragmentation routes can largely be bypassed, neutral molecules and fragments can be ionized, and autoionizing molecular states with typical lifetimes of 100 fs can be populated.[85] Since the parent peak is still the strongest peak at the laser intensities used in the present experiments, the ladder-switching fragmentation pathways reported for the nanosecond regime are no longer taking place to any degree.

Further evidence exists in support of this. The appearance potentials for doubly ionized benzene, toluene, and naphthalene are 26, 24.5, and 22.8 eV, respectively,[86] and the appearance potential for C^+ in the fragmentation of benzene using a UV laser is similar at about 26 eV.[87] The fact that the yield of doubly ionized parents is significantly greater than that of the carbon ions in Figures 1−4 suggests that nanosecond ladder-switching routes are being bypassed by the intense femtosecond irradiation. A dominant ladder-climbing mechanism is at work, with any small dissociation appearing via the parent continuum.

From the work presented here, the doubly ionized cation group from the parent ion (M^+) is a very strong fingerprint for femtosecond intense irradiation of hydrocarbon molecules. Invariably, this characteristic can be recognized by the small half mass peak at $M^{13}C^{2+}$ and surrounding envelope of ions, some of which fall at half *m*/*z* values. This has also been observed in other aromatic and linear organic molecules by the Glasgow group including benzaldehyde,[17] 1,3-butadiene, and carbon disulfide[88] and from the work of Cornaggia et al.[43,60] on acetylene.

In this work, Cornaggia et al. also suggested that the single ionization of molecules under intense laser irradiation occurs at the beginning of the laser pulse and then multiple ionization appears for higher instantaneous laser intensities along the pulse profile. These ideas are also supported by Lambropoulos[21] with respect to the multiple ionization of atoms. It would certainly appear that sequential multiple ionization is the likely pathway from the laser intensity dependences of the aromatic molecules studied in the present paper.

The first ionization level of the aromatic molecule is likely to be reached early on in the pulse profile. A small amount of fragmentation takes place from the parent species as it successively climbs through the first, second, and third ionization levels as the pulse evolves. When these multiply charged parent ion states are reached, they may then produce the further multiply charged entities by shedding neutral hydrogen atoms. Considering benzene (Figure 3), for example, this may occur in the following way:

$$\begin{aligned} C_6H_6{}^{2+} &\rightarrow C_6H_5{}^{2+} + H \\ &\rightarrow C_6H_4{}^{2+} + 2H \\ &\rightarrow C_6H_3{}^{2+} + 3H \\ &\rightarrow C_6H_2{}^{2+} + 4H \end{aligned}$$

It was felt that H elimination was the most likely process in this dissociation pathway and that, e.g., H_2 elimination was much more unlikely and required two hydrogen atoms coming together.

A similar process could occur from the triply charged parent state. Or the following dissociation may occur from the triple parent ion to produce protons:

$$\begin{aligned} C_6H_6{}^{3+} &\rightarrow C_6H_5{}^{2+} + H^+ \\ &\rightarrow C_6H_4{}^{2+} + H^+ + H \\ &\rightarrow C_6H_3{}^{2+} + H^+ + 2H \\ &\rightarrow C_6H_2{}^{2+} + H^+ + 3H \end{aligned}$$

This seems to be less likely since there is no large hydrogen ion peak in the mass spectrum.

In a similar manner, multiply charged ions may be produced from toluene (Figure 1), where as many as eight hydrogen atoms may have been boiled off down to $C_7{}^{2+}$, and naphthalene (Figure 2), where up to six hydrogen atoms appear to be shed.

In the Introduction, the question of multiphoton ionization versus tunneling was discussed. In the experiments described in this paper, the Keldysh parameter is as small as 0.1 for the wavelength of 790 nm at the highest laser intensities used ($\sim 3 \times 10^{15}$ W cm^{-2}). This is well into the tunneling regime, and one can expect a significant contribution to the ionization rate from this mechanism using short laser pulses.

Coulomb explosion was also discussed which described the presence of multiply charged atoms during intense irradiation of small molecules. At the present laser intensities for the molecules benzene, deuterated benzene, toluene, and naphthalene, although C^{2+} is seen, it is a very small feature and the description of events by Coulomb explosions seems unlikely. In the present case, multiply charged (2^+ and 3^+) parent ions are seen which could have lifetimes as long as the flight times in a TOF (~tens of microseconds), and 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. Up to the maximum laser intensities studied here, the process appears to be very similar to bond softening as described by Bucksbaum et al.[89] for the dissociation of H_2 in intense laser fields.

As indicated by Smith et al.[78] in a previous paper, studies in the UV wavelength region reveal a small or nonexistent presence of multiply charged peaks, compared to significant production in the IR. At present, there is no suitable explanation for this although the Keldysh values for the studies thus far in the UV are closer to 1 than in the IR. This must be coupled with the observation that the dissociation is generally more intense when UV photons are used. There are two potential explanations. First, it is possible that much higher multiply charged parent states are reached with the 375 nm photons which dissocociate predominantly to the $C_nH_m{}^+$ fragments characteristic of UV irradiation in the nanosecond regime. It is also possible that somehow they never reach multiply charged states due to some sort of population trapping in the single ionic manifold of states similar to the population trapping mechanism described by Talebpour et al.[90,91]

Conclusions

It has been shown that the irradiation of benzene, toluene, and naphthalene at laser intensities up to 3×10^{15} W cm^{-2}, pulse widths of 50 fs, and wavelengths between 750 and 790 nm leads to intense parent ion (M^+) production, minimal fragmentation, and doubly (M^{2+}) and triply (M^{3+}) ionized parent peaks. In such a sense, the polyatomic molecular spectra are similar to atomic signatures. An envelope of doubly ionized satellite peaks $(M - nH)^+$ has been observed in the vicinity of the parent double ion. Nanosecond pathways with characteristic extensive fragmentation, small parent ions, and no multiply charged states have been largely bypassed using the femtosecond irradiation.

The multiply ionized species seem to be reached by sequential ladder-climbing, and Coulomb explosion events, characteristic of multiply ionized small molecules, are not an appropriate description of the fragmentation process here since multiply charged atoms are only weak features and stable multiply ionized parent ions are strong features. It is believed, however, that these multiply charged species are a manifestation of tunneling where the Keldysh parameter can be as low as 0.1, presently. It is also believed that multiphoton ionization will pre-empt tunneling along the laser pulse profile. Whether, therefore, tunneling is allowed to significantly contribute to the ionic yield is largely dependent on the pulse characteristics. With respect to multiphoton ionization, any resonant enhancement of the ionization is likely to be very small since the bandwidth of femtosecond laser pulses is very broad (~10 s nm). Moreover, in a previous paper,[78] Smith et al. showed that for a number of aromatics at laser intensities around 10^{14} W cm^{-2}, the molecular ion yield was similar for benzene, toluene, and naphthalene, supporting the idea that any resonant enhancement was small.

Levis and DeWitt[76,77] have argued that although the tunneling theory proposed by Ammosov, Delone, and Kranov[92] (ADK theory) can account for the physics of ionization for diatomic and small polyatomic molecules, it is less suitable when applied to more complex molecules such as the aromatics. These molecules do not have the simple Coulombic potentials required by ADK theory, and other factors such as degrees of freedom for energy deposition, redistribution, and disposal may become important. Such pathways, specifically vibrational and dissociative, are available on a subpicosecond time scale. In reality, and particularly for molecules, the electrostatic potential energy surfaces are complex. Failing to take this into account may lead to Keldysh values being overestimated, which implies that tunneling may occur at lower intensities than first calculated.[12]

It should be emphasized that the effects described in this paper are best seen with a high-resolution mass spectrometer and perhaps even better with a reflectron. The TOF techniques used extensively for covariant mapping of the explosive dissociation of small molecules which gives more significance to efficiency of ion collection may be less pertinent here.

Generally, more definitive experimental and theoretical treatments are required. Of particular importance is a detailed knowledge of the laser pulse characteristics. Interferometric pulse shaping can be useful in such respects.[22]

Acknowledgment. K.W.D.L., D.J.S., R.P.S., T.M., P.G., H.S.K., W.X.P., and C.K. express thanks to the Rutherford Appleton Lab (RAL) for excellent facilities and assistance. D.J.S., P.G., H.S.K., and W.X.P. also acknowledge the EPSRC, the Turkish Government, and the University of Glasgow, respectively, for financial support.

Appendix

This section describes in detail the methods and calculations in labeling the peaks of Figures 3 (benzene) and 4 (monodeuterated benzene) as shown in Table 1. When dealing with the doubly ionized parent and satellite ions in the figures, note that an ionic peak from an undeuterated molecule has been taken as having an equivalent peak in the corresponding deuterated molecule by replacing a hydrogen with a heavier deuterium atom. This works out as an increase in *m*/*z* ratio of 0.5 for the doubly ionized peaks. The labeling system portrays equivalent peaks with equal numbers. For example, the doubly ionized benzene molecule ($C_6H_6^{2+}$ labeled as B3) located at an *m*/*z* ratio of 39 in Figure 3 has a concordant deuterated peak ($C_6H_5D^{2+}$ labeled as DB3) at $m/z = 39.5$ in Figure 4. Another point to note is it that the singly and doubly charged parent ions for the two molecules are normalized. This is a key fact in the analysis because it allows direct quantitative comparisons of ionic intensities. Additionally, the system employed to label the peaks is a model based on an assumption of so-called concordant peaks having similar probabilities of production in both molecules.

The numbers in bold correspond to particular mass-to-charge ratios for benzene (B) and monodeuterated benzene (DB). The peaks are portrayed matching the general order of analysis.

Glossary

39.5 DB	Unambiguously $C_6H_5D^{2+}$.
39.0 B	This peak could either be $C_6H_6^{2+}$ or $C_3H_3^+$. However, the intensity of 39.0 B matches or is just greater than the intensity of unambiguous 39.5 DB (∼10% greater). Therefore, it follows that 39.0 B is predominantly the doubly ionized component. This is consistent with the fact that the peak at 39.0 B is considerably greater than any other nearby peak. A 90% to 10% mixture has been estimated for $C_6H_6^{2+}$ and $C_3H_3^+$, respectively.
40.0 B	Very small presence of $C_3H_4^+$.
39.5 B	Unambiguously $C_5{}^{13}CH_6^{2+}$.
40.0 DB	This peak could have contributions from the double ionized ^{13}C DB molecule ($C_5{}^{13}CH_5D^{2+}$) or the single ions $C_3H_2D^+$ and $C_3H_4^+$. The doubly ionized unambiguous undeuterated equivalent peak at 39.5 B has an approximate intensity of 0.0282. Therefore, it is expected that the double component of the concordant deuterated peak will also be 0.0282. But the height of this 40.0 DB peak is ∼0.0475. Therefore, the singly ionized component of the peak is given by $0.0475-0.0282 = 0.0193$, i.e., $C_3H_2D^+$ and $C_3H_4^+$ contribute this intensity. This is 60% double and 40% single components. $C_3H_2D^+$ is likely to be greater than $C_3H_4^+$ due to a more likely "symmetric" fragmentation of $C_6H_5D^+$ to $C_3H_3^+$ and $C_3H_2D^+$. Also, $C_3H_4^+$ is small in benzene (40.0 B).
38.5 B	Unambiguously $C_6H_5^{2+}$.
39.0 DB	The intensity of 39.0 DB is 0.0285, and the intensity of the equivalent undeuterated peak at 38.5 B ($C_6H_5^{2+}$) is 0.014. Therefore, the concordant double component, $C_6H_4D^{2+}$, of 39.0 DB is around 0.014. A simple subtraction gives the intensity of the other coincident 39.0 DB components to be 0.0145. These could be $C_3H_3^+$, C_3HD^+, or $C_6H_6^{2+}$. Due to symmetry, $C_3H_3^+$ is more likely than C_3HD^+ and will have the same intensity as $C_3H_2D^+$ located at DB 40.0. Note that C_6H_6 is present as a 2% quantity in C_6H_5D. This gives the approximate abundances in Table 1. Due to the somewhat complex nature of this conclusion, and in light of uncertainties, a quantitative analysis is not possible.
38.5 DB	Either $C_6H_3D^{2+}$ or $C_6H_5^{2+}$, predominantly the former since $C_6H_5^{2+}$ is small in benzene. Observing the size of $C_6H_5^{2+}$ in benzene (38.5 B) as ∼0.014, one can conclude that it may have the same intensity in 38.5 DB. The size of the 38.5 DB peak is ∼0.0235. This leads to the percentages in the table.
38.0 B	38.0 B intensity = 0.036. This can either be $C_6H_4^{2+}$ or $C_3H_2^+$. Deuterated equivalent ($C_6H_3D^{2+}$) at 38.5 DB = 0.0235 intensity which is 65% $C_6H_3D^{2+}$. Therefore, the undeuterated equivalent in 38.0 B ($C_6H_4 2+$) is 65% present.
37.5 B	Unambiguously $C_6H_3^{2+}$.
38.0 DB	Intensity of undeuterated equivalent ($C_6H_3^{2+}$, 37.5 B) = 0.016. Intensity of 38.0 DB = 0.0225. Therefore, 38.0 DB $C_6H_2D^{2+}$ intensity = 0.016 to leave $C_3H_2^+$, C_3D^+, and $C_6H_4^{2+}$ contributing 0.0065 to the peak intensity. It is likely that $C_3H_2^+$ is greater than C_3D^+ with ratio of $C_6H_4^{2+}$ to $C_3H_2^+$ being similar to that found in benzene at 38.0 B. This gives the component intensities shown in Table 1.
37.5 DB	C_6HD^{2+} or $C_6H_3^{2+}$. Small amounts of each, but the latter more likely due to symmetry considerations.
37.0 B	Can either be C_3H^+ or $C_6H_2^{2+}$. Deuterated equivalent C_6HD^{2+} (37.5 DB) small, therefore C_3H^+ is perhaps more likely.
36.5 B	No peak.
37.0 DB	This can either be C_3H^+, $C_6H_2^{2+}$, or C_6D^{2+}. But there is no double concordant peak for benzene (36.5 B). Therefore, the deuterated equivalent C_6D^{2+} (37.0 DB) can be taken as zero. Similar to 37.0 B, C_3H^+ perhaps just greater than $C_6H_2^{2+}$.
36.5 DB	No peak.
36.0 B	C_3^+ or C_6^{2+}. C^{3+} likely to be the only peak present.
36.0 DB	C_3^+ or C_6^{2+}. Due to zero presence of a double peak at neighboring 36.5 DB, then peak taken as total C_3^+. This uses the argument that the presence of unambiguous doubly ionized components at half-mass peaks are suggestive of double activity in the neighboring peaks.

References and Notes

(1) Protopapas, M.; Keitel, C. H.; Knight P. L. *Rep. Prog. Phys.* **1997**, *60*, 389.

(2) Kyrala, G. A. *Comments At. Mol. Phys.* **1993**, *28*, 325.

(3) Giusti-Suzor, A.; Mies, F. H.; DiMauro, L. F.; Charron, E.; Yang, B. *J. Phys. B: At. Mol. Opt. Phys.* **1995**, *28*, 309.

(4) Freeman, R. R.; Bucksbaum, P. H. *J. Phys. B: At. Mol. Opt. Phys.* **1991**, *24*, 325.

(5) Codling, K.; Frasinski, L. J. *Struct. Bonding* **1997**, *86*, 2.

(6) Codling, K.; Frasinski, L. J. *Contemp. Phys.* **1994**, *35*, 243.

(7) Mainfray, G.; Manus, C. *Rep. Prog. Phys.* **1991**, *54*, 1333.

(8) Lompre, L. A.; Mainfray, G.; Manus, C.; Repoux, S.; Thebault, J. *Phys. Rev. Lett.* **1976**, *36*, 949.

(9) L'Huillier, A.; Mainfray, G.; Johnson, P. M. *Chem. Phys. Lett.* **1984**, *103*, 447.

(10) L'Huillier, A.; Lompre, L. A.; Mainfray, G.; Manus, C. *J. Phys. B: At. Mol. Opt. Phys.* **1983**, *16*, 1363.

(11) Keldysh, L. V. *Sov. Phys. JETP* **1965**, *20*, 1307.

(12) DeWitt, M. J.; Levis, R. J. *J. Chem. Phys.* **1998**, *108*, 7739.

(13) Ilkov, F. A.; Decker, J. E.; Chin, S. L. *J. Phys. B: At. Mol.Opt. Phys.* **1992**, *25*, 4005.

(14) Gibson, G.; Luk, T. S.; Rhodes, C. K. *Phys. Rev. A* **1990**, *41*, 5049.

(15) Ledingham, K. W. D.; Kosmidis, C.; Georgiou, S.; Couris, S.; Singhal, R. P. *Chem. Phys. Lett.* **1995**, *247*, 555.

(16) Singhal, R. P.; Kilic, H. S.; Ledingham, K. W. D.; Kosmidis, C.; McCanny, T.; Langley, A. J.; Shaikh, W. *Chem. Phys. Lett.* **1996**, *253*, 81.

(17) Smith, D. J.; Ledingham, K. W. D.; Kilic, H. S.; Singhal, R. P.; McCanny, T.; Peng, W. X.; Langley, A. J.; Taday, P. F.; Kosmidis, C. *J. Phys, Chem. A* **1998**, *102*, 2059.

(18) Augst, S.; Meyerhofer, D. D.; Strickland, D.; Chin, S. L. *J. Opt. Soc. Am. B* **1991**, *8*, 858.

(19) Augst, S.; Strickland, D.; Meyerhofer, D. D.; Chin, S. L.; Eberly, J. H. *Phys. Rev. Lett.* **1989**, *63*, 2212.

(20) L'Huillier, A.; Balcou, P.; Candel, S.; Schafer, K. J.; Kulander, K. C. *Phys. Rev. A* **1992**, *46*, 2778.

(21) Lambropolous, P. *Phys. Rev. Lett.* **1985**, *20*, 2141.

(22) Giles, A. J.; Posthumus, J. H.; Thompson, M. R.; Frasinski, L. J.; Codling, K.; Langley, A. J.; Shaikh, W.; Taday, P. F. *J. Opt. Comm.* **1995**, *118*, 537.

(23) Mevel, E.; Breger, P.; Trainham, R.; Petite, G.; Agostini, P.; Migus, A.; Chambaret, J.-P.; Antonetti, A. *Phys. Rev. Lett.* **1993**, *70*, 406.

(24) Trappe, C.; Schutze, M.; Raff, M.; Hannot, R.; Kurz, H. *Fresenius' J. Anal. Chem.* **1993**, *346*, 368.

(25) Sogard, M. R. *J. Opt. Soc. Am. B, Opt. Phys.* **1988**, *5*, 1890.

(26) Frasinski, L. J.; Codling, K.; Hatherley, P.; Barr, J.; Ross, I. N.; Toner, W. T. *Phys. Rev. Lett.* **1989**, *58*, 2424.

(27) Walsh, T. D. G.; Ilkov, F. A.; Decker, J. E.; Chin, S. L. *J. Phys. B: At. Mol. Opt. Phys.* **1994**, *27*, 3767.

(28) Walsh, T. D. G.; Decker, J. E.; Chin, S. L. *J. Phys. B: At. Mol. Opt. Phys.* **1993**, *26*, L85.

(29) Chin, S. L.; Decker. J. E.; Walsh, T. D. G.; Liang, Y.; Xu, G. *Laser Phys.* **1993**, *3*, 298.

(30) Chin, S. L.; Liang, Y.; Decker, J. E.; Ilkov, F. A.; Ammosov, M. V. *J. Phys. B: At. Mol. Opt. Phys.* **1992**, *25*, L249.

(31) Ledingham, K. W. D.; Singhal, R. P.; Smith, D. J.; McCanny, T.; Graham, P.; Kilic, H. S.; Peng, W. X.; Wang, S. L.; Langley, A. J.; Taday, P. F. *J. Phys. Chem. A* **1998**, *102*, 3002.

(32) Liang, Y.; Augst, S.; Chin, S. L.; Beaudoin, Y.; Chaker, M. *J. Phys. B: At. Mol. Opt. Phys.* **1994**, *27*, 5119.

(33) Codling, K.; Frasinski, L. J. *J. Phys. B: At. Mol. Opt. Phys.* **1993**, *26*, 783.

(34) Hatherley, P. A.; Stankiewicz, M.; Codling, K.; Frasinski, L. J.; Cross, G. M. *J. Phys. B: At. Mol. Opt. Phys.* **1994**, *27*, 2993.

(35) Posthumus, J. H.; Plumridge, J.; Thomas, M. K.; Codling, K.; Frasinski, L. J.; Langley, A. J.; Taday, P. F. *J. Phys. B: At. Mol. Opt. Phys.* **1998**, *31*, L553.

(36) Posthumus, J. H.; Giles, A. J.; Thompson, M. R.; Shaikh, W.; Langley, A. J.; Frasinski, L. J.; Codling, K. *J. Phys. B: At. Mol. Opt. Phys.* **1996**, *29*, L525.

(37) Posthumus, J. H.; Codling, K.; Thompson, M. R. *Laser Phys.* **1997**, *7*, 813.

(38) Dietrich, P.; Corkum, P. B. *J. Chem. Phys.* **1992**, *97*, 3187.

(39) Brabec, T.; Ivanov, M. Yu.; Corkum, P. B. *Phys. Rev. A* **1996**, *54*, R2551.

(40) Dietrich, P.; Ivanov, M. Yu.; Ilkov, F. A.; Corkum, P. B. *Phys. Rev. Lett.* **1996,** 77, 4150.

(41) Cornaggia, C.; Hering, Ph. *J. Phys. B: At. Mol. Opt. Phys.* **1998**, *31*, L503.

(42) Cornaggia, C.; Salin, F.; LeBlanc, C. *J. Phys. B: At. Mol. Opt. Phys.* **1996**, *29*, L749.

(43) Cornaggia, C.; Schmidt, M.; Normand, D. *Phys. Rev. A* **1995**, *51*, 1431.

(44) Cornaggia, C.; Schmidt, M.; Normand, D. *J. Phys. B: At. Mol. Opt. Phys.* **1994**, *27*, L123.

(45) Cornaggia, C.; Lavancier, J.; Normand, D.; Morellec, J.; Agostini, P. *Phys. Rev. A.* **1991**, *44*, 4499.

(46) Cornaggia, C.; Lavancier, J.; Normand, D.; Morellec, J.; Liu, H. X. *Phys. Rev. A* **1990**, *42*, 5464.

(47) Hering, Ph.; Cornaggia, C. *Phys. Rev. A* **1998**, *57*, 4572.

(48) Talebpour, A.; Larochelle, S.; Chin, S. L. *J. Phys. B: At. Mol. Opt. Phys.* **1998**, *31*, L49.

(49) Talebpour, A.; Larochelle, S.; Chin, S. L. *J. Phys. B: At. Mol. Opt. Phys.* **1997,** *30*, 1927.

(50) Talebpour, A.; Chien, C.-Y.; Liang, Y.; Larochelle, S.; Chin, S. L. *J. Phys. B: At. Mol. Opt. Phys.* **1997**, *30*, 1721.

(51) Talebpour, A.; Larochelle, S.; Chin, S. L. *J. Phys. B: At. Mol. Opt. Phys.* **1997**, *30*, L245.

(52) Safvan, C. P.; Bhardwaj, V. R.; Ravindra Kumar, G.; Mathur, D.; Rajgara, F. A. *J. Phys. B: At. Mol. Opt. Phys.* **1996**, *29*, 3135.

(53) Constant, E.; Staplefeldt, H.; Corkum, P. B. *Phys. Rev. Lett.* **1996**, *76*, 4140.

(54) Ravindra Kumar, G.; Safvan, C. P.; Rajgara, F. A.; Mathur, D. *J. Phys. B: At. Mol. Opt. Phys.* **1994**, *27*, 2981.

(55) Vijayalakshmi, K.; Safvan, C. P.; Ravindra Kumar, G.; Mathur, D. *Chem. Phys. Lett.* **1997**, *270*, 37.

(56) Frasinski, L. J.; Codling, K.; Hatherly, P. *Phys. Rev. Lett.* **1987**, *58*, 2424.

(57) Schmidt, M.; Dobosz, S.; D'Oliveira, P.; Meynadier, P.; Perdrix, M.; Bougeard, M.; Lezius, M.; Normand, D. *J. Phys. B: At. Mol. Opt. Phys.* **1997**, *30*, L749.

(58) Yu, H.; Zuo, T.; Bandrauk, A. D. *J. Phys. B: At. Mol. Opt. Phys.* **1998**, *31*, 1533.

(59) Normand, D.; Dobosz, S.; Lezius, M.; D'Oliveira, P.; Schmidt, M. *Inst. Phys. Conf. Ser.* **1996**, *154*, 287.

(60) Cornaggia, C. *Phys. Rev. A* **1995**, *52*, R4328.

(61) Sanderson, J. H.; Thomas, R. V.; Bryan, W. A.; Newell, W. R.; Taday, P. F.; Langley, A. J. *J. Phys. B: At. Mol. Opt. Phys.* **1997**, *30*, 4499.

(62) Vijayalakshmi, K.; Bhardwaj, V. R.; Mathur, D. *J. Phys. B: At. Mol. Opt. Phys.* **1997**, *30*, 4065.

(63) DeWitt, M. J.; Levis, R. J. *J. Chem. Phys.* **1998**, *108*, 7045.

(64) Ledingham, K. W. D.; Singhal, R. P. *Int J. Mass Spectrom. Ion Processes* **1997**, *163*, 149.

(65) Ledingham, K. W. D.; Kilic, H. S.; Kosmidis, C.; Deas, R. M.; Marshall, A.; McCanny, T.; Singhal, R. P.; Langley, A. J.; Shaikh, W. *Rapid. Commun. Mass Spectrom.* **1995**, *9*, 1522.

(66) Kilic, H. S.; Ledingham, K. W. D.; Kosmidis, C.; McCanny, T.; Singhal, R. P.; Wang, S. L.; Smith, D. J.; Langley, A. J. *J. Phys. Chem. A* **1997**, *101*, 817.

(67) Kosmidis, C.; Ledingham, K. W. D.; Kilic, H. S.; McCanny, T.; Singhal, R. P.; Langley, A. J.; Shaikh, W. *J. Phys. Chem. A* **1997**, *101*, 2264.

(68) He, C.; Basler, J. N.; Becker, C. H. *Nature* **1997**, *385*, 797.

(69) He, C.; Becker, C. H. *Phys. Rev. A* **1997**, *55*, 1300.

(70) He, C.; Basler, J.; Paul, A.; Becker, C. H. *J. Vac. Sci. Technol. A* **1996**, *14*, 1433.

(71) Schutze, M.; Trappe, C.; Tabellion, M.; Lupke, G.; Kurz, H. *Surf. Interface Anal.* **1996**, *24*, 399.

(72) Willey, K. F.; Brummel, C. L.; Winograd, N. *Chem. Phys. Lett.* **1997**, *267*, 359.

(73) Weickhardt, C.; Grun, C.; Heinicke, R.; Meffert, A.; Grotemeyer, J. *Rapid Commun. Mass Spectrom.* **1997**, *11*, 745.

(74) Purnell, J.; Snyder, E. M.; Wei, S.; Castleman, A. W., Jr. *Chem. Phys. Lett.* **1994**, *229*, 333.

(75) DeWitt, M. J.; Levis, R. J. *J. Chem. Phys.* **1995**, *102*, 8670.

(76) Levis, R. J.; Dewitt, M. J. In *Resonance Ionization Spectroscopy*; Winograd, N., Parks, J. E., Eds.; AIP Conference Series 388; AIP: Woodbury, NY, 1996; p 45.

(77) DeWitt, M. J.; Peters, D. W.; Levis, R. J. *Chem. Phys.* **1997**, *218*, 211.

(78) Smith, D. J.; Ledingham, K. W. D.; Singhal, R. P.; Kilic, H. S.; McCanny, T.; Langley, A. J.; Taday, P. F.; Kosmidis, C. *Rapid. Commun. Mass Spectrom.* **1998**, *12*, 813.

(79) Boesl, U. *J. Phys. Chem.* **1991**, *95*, 2949.

(80) Dietz, W.; Neusser, H. J.; Boesl, U.; Schlag, E. W.; Lin, S. H. *Chem. Phys.* **1982**, *66*, 105.

(81) Yang, J. J.; Gobeli, D. A.; Pandolfi, R. S.; El-Sayed, M. A. *J. Phys. Chem.* **1985**, *87*, 2255.

(82) Taday, P. F.; Mohammed, I.; Langley, A. J.; Ross, I. N.; Codling, K.; Ledingham, K. W. D.; Newell, W. R.; Preston, S.; Riley, D.; Williams, I.; Rutherford Laboratory Report No. RAL-TR 1998-080, 179, 1999.

(83) De Hoffman, E. *Mass Spectrometry Principles and Applications;* Wiley and Sons: New York, 1996.

(84) Fittinghoff, D. N.; Bolton, P. R.; Chang, B.; Kulander, K. C. *Phys. Rev. Lett.* **1992**, *69*, 2642.

(85) Boesl, U.; Neusser, H. H.; Schlag, E. W. *J. Chem. Phys.* **1980**, *72*, 4327.

(86) Dorman, F. H.; Morrison, J. D. *J. Chem. Phys.* **1961**, *35*, 575.

(87) Zandee, L.; Bernstein, R. B. *J. Chem. Phys.* **1979**, *71*, 1359.

(88) Graham, P.; Ledingham, K. W. D.; Singhal, R. P.; Smith, D. J.; Wang, S.; McCanny, T.; Kilic, H. S.; Langley, A. J.; Taday, P. F.; Kosmidis, C. *Proceedings of the 9th Symposium on RIS*; AIP Conference Proceedings 454; Vickerman, J. C., Lyon, I., Lockyer, N. P., Parks, J. E., Eds.; New York, 1998, p 341.

(89) Bucksbaum, P. H.; Zavriyev, A.; Muller, H. G.; Schumacher, D. W. *Phys. Rev. Lett.* **1990**, *64*, 1183.

(90) Talebpour, A.; Liang, Y.; Chin, S. L. *J. Phys. B: At. Mol. Opt. Phys.* **1996**, *29*, 5725.

(91) Talebpour, A.; Chien, C.-Y.; Chin, S. L. *J. Phys. B: At. Mol. Opt. Phys.* **1996**, *29*, 3435.

(92) Ammosov, M. V.; Delone, N. B.; Krainov, V. P. *Sov. Phys. JETP* **1986**, *64*, 1191.