Multiply Charged Intact Ions of Polyatomic Cyclic Molecules Generated by a Strong Laser Field

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The interaction of strong laser fields ($\sim 10^{16}$ W/cm^2) with cyclic polyatomic molecules have been studied at $\lambda = 790$ and 395 nm. The induced ionization/fragmentation processes were analyzed by means of a time-of-flight mass spectrometer. The production of multiply charged intact ions is found to be related to molecular structure. Doubly charged intact ions were observed for aromatic molecules (aniline, furan, and pyridine) with significant abundance at both wavelengths used. No evidence for doubly charged species appeared in the mass spectra of the cycloketones. The single ionization mechanism is believed to be different at the wavelengths used. There is evidence that multiply charged ion production is taking place through sequential ionization processes, although the rescattering model cannot be excluded.

Introduction

The interaction of strong laser fields with atoms and molecules leads to the production of multiply charged species. The observation of highly charged atomic ions produced by intense laser beams has been reported a few years ago[1−3] and was later extended to molecular ions.[4−5]

Multiply charged molecular ions may offer significant advantages in quantitative analysis and structure determination, notably isomer distinction and peptide analysis. Therefore, considerable effort has been focused on their production even in the prelaser era. The first report on doubly charged molecular ion production was published almost 70 years ago,[6] and since then many different techniques have been developed in order to increase the efficiency of their production. For electron impact (EI) ionization the relative abundance was found to be between 0.001% and 10% of the base peak, while by MALDI and electrospray techniques the abundance of doubly protonated species can be increased up to 10−50% of the base peak, but the latter techniques demand sample preparation.[7] Furthermore, spectroscopic methods with synchrotron radiation source have been used to gain some knowledge about the structure of these multiply charged species, and the first observation of the vibrational structure of polyatomic dication ($C_6H_6{}^{2+}$) was presented a few years ago.[8]

Recently, multiply charged intact ions induced by a femtosecond laser have been observed for some polyatomic molecules.[9−11] It is interesting to note that in some cases (like that of 1,3-butadiene) the abundance of the double ionized parent peak was more than 50% of the base peak in the spectrum, under laser irradiation at 790 nm and $I = 1.7 \times 10^{14}$ W/cm^2. This observation, in conjunction with the potential of femtosecond laser-induced mass spectrometry discussed earlier,[12] may have an important bearing on analytical applications.

The mechanism for the production of these species it not clear yet. Two main mechanisms have been proposed for the production of multiply charged atomic ions. For the sake of simplicity, we restrict the discussion to the case of doubly charged ions. According to the first mechanism, called stepwise ionization, initially only one electron is detached from the atom while the second electron is subsequently ejected from the singly charged ion. The second mechanism is a nonsequential one and is referred to as the simultaneous detachment of two electrons. Cornagia and Hering[13] have reported nonsequential ionization for a number of small molecules.

In the present work, the interaction of some cyclic polyatomic molecules with strong laser beams ($10^{15}-10^{16}$ W/cm^2) is studied. De Witt and Levis[14−16] and Castellejo et al.[17] have studied the relation between the molecular structure and the ionization/dissociation yield of polyatomic molecules under strong laser fields. They have concluded that ionization yield of the parent molecule is related to the molecular structure and decreases as a function of the number of atoms in the molecule, due to an exponential increase in the molecular dissociation.

The main aim of the present work is to explore the role of molecular structure, if any, in multiply charged intact ion generation under strong laser irradiation and the influence of the frequency and the intensity of the laser beam. We have focused on cyclic molecules because, at first sight, it is expected that intact multiply charged ions could be more pronounced for these species, since their fragmentation requires the rupture of at least two molecular bonds. The molecules have been chosen in such a way as to also investigate the influence, if any, of aromaticity for some homo- and heterocyclic compounds. It is important also to check the significance of the nature of the higher occupied molecular orbitals (MO). The π-type MO are delocalized and spread over the entire molecular ring. On the other hand, the n-type MO are localized on a particular site of the molecular skeleton and the electrons occupying these MO participate weakly in the construction of the molecular ring. These remarks may lead to the assumption that molecules with

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an n-MO as the highest occupied MO (HOMO) could be very efficient in multiply charged intact ion production. Therefore, the femtosecond laser-induced mass spectra of some nonaromatic cyclic molecules with an n-type HOMO are compared to those of some homo- and heterocyclic aromatic molecules with a HOMO of n- or π-type MO.

Experimental Details

The experimental set up used is described in detail elsewhere.[11] Briefly, the system consisted of a mode-locked titanium−sapphire oscillator pumped by an argon ion laser (both from Spectra Physics). The system produced a train of pulses of 50 ± 5 fs duration and 9 nJ energy. Chirped pulse amplification (CPA) techniques were used to increase the pulse energy. Wavelengths of 790 nm and frequency doubled (by a 0.2 mm thick type I BBO crystal) 395 nm were generated with pulse energy up to a maximum of 500 μJ (790 nm) and 120 μJ (395 nm). Both wavelengths being vertically polarized. Controlled attenuation of the beam energy was achieved by a variable neutral density filter, with the corresponding energies being measured in front of the vacuum chamber by a Molectron joulemeter and having been corrected for losses from the optical components used. Laser intensities were estimated to be accurate to 10−15%.

The time-of-flight (TOF) mass spectrometer is of conventional linear arrangement with ion optics based on a Wiley−McLaren design and an einzel lens placed immediately after the extraction optics to increase the ion transmission through the system. The samples were admitted effusively from the inlet system to the vacuum chamber via a needle valve after passing through a hole ($2R = 1$ mm) in the repeller electrode of the TOF.

The laser beam was focused using a concave mirror of focal length 3 cm at about 4 mm from the repeller. Optimum spatial ionizing conditions were achieved using a *xyz* vernier-controlled mechanism coupled to the focusing mirror. The mass resolution was typically 200 at 100 D.

A Thorn EMI electron multiplier coupled to a Lecroy 9304 digital oscilloscope recorded the mass spectra, typically averaging over hundreds of laser shots for each spectrum.

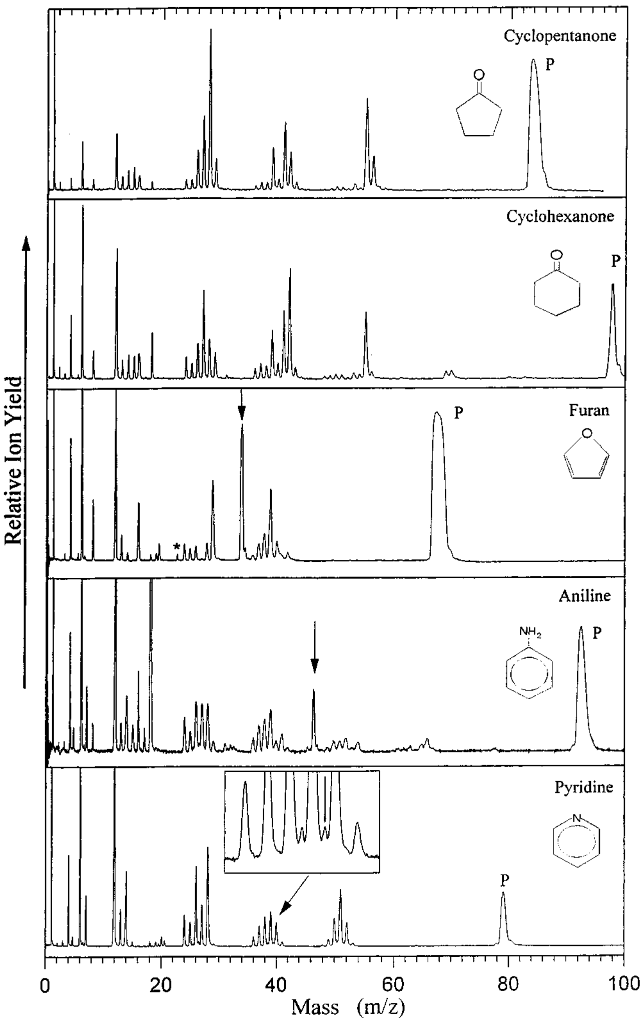

Figure 1. TOF mass spectra of cycloketone, cyclohexanone, furan, aniline, and pyridine at 790 nm. The spectrum of cyclopentanone has been recorded at $I = 3 \times 10^{14}$ W/cm^2, while for the other molecules at $I = 4 \times 10^{15}$ W/cm^2. The parent ion is denoted by a P, the doubly charged parent ion by an arrow, and the triply charged parent ion in the spectrum of furan by a star. In the spectrum of pyridine, the area close to the doubly charged intact ion is shown in an inset.

Results and Discussion

In a recent publication, the generation of stable multiply charged polyatomic ions using strong laser fields has been demonstrated.[9−11] The discrimination of the doubly charged parent ions is much easier for molecules with odd molecular weight. Nevertheless, in some cases, such as that of furan (C_4H_4O, MW = 68), studied in the present work, the assignment of the peak at $m/z = 34$ (Figure 1) as doubly charged parent molecular ion (P^{2+}) is unambiguous, since this peak cannot be attributed to any other $C_xH_yO_z$ combination. In Figure 1, the mass spectra of cyclopentanone, cyclohexanone, furan, pyridine, and aniline are presented. These spectra have been recorded at 790 nm. Cyclopentanone (CP) and furan have a five-membered ring, while cyclohexanone (CH), pyridine, and aniline a six-membered one. Except CP and CH, the other three molecules are aromatic, and only aniline is a homocyclic aromatic molecule. CP, CH, and pyridine have a n-MO as the HOMO, while aniline has a π-type MO.

The spectra in Figure 1 have some common features.

(a) The parent ion peak was clearly observed for all molecules. It is worth noting that for CP and CH the parent ion peak is extremely weak in the mass spectrum induced by nanosecond laser pulses at $\lambda \approx 360$ nm.[18] This observation is consistent with earlier reports on the potential of femtosecond laser mass spectrometry for production of intact molecules.[12,19,20]

(b) Many highly charged atomic fragments have appeared in the mass spectra of all molecules studied at these laser intensities. The origin of these ions and the fragmentation processes will be discussed in a forthcoming paper[21]

(c) A strong hydrogen ion peak is present in all mass spectra. Such a dissociation process (−H loss) has been reported earlier for hydrocarbons under strong laser irradiation.[12,22] In the present work, it is found that the H^+ peak increases rapidly with laser intensity and it is the base peak in the spectrum at the higher powers used. It has been suggested that H^+ is produced via field ionization either by H^+ tunneling from the ends of the molecule or by a polarization-induced mechanism.[15] The present data seems to support this suggestion. The H^+ production is not likely to be caused by subsequent photon absorption by transient molecular fragments, because the laser pulse duration is less than dissociation time scales for these molecular species. On the other hand, the strong intensity dependence of the H^+

peak is compatible with H^+ tunneling, because at higher laser field strengths barrier suppression is expected to be more efficient.

(d) The parent ion peak is broad, especially at high laser intensities. This broadening is attributed to molecular ionization from the vicinity of the laser focus area due to the high laser intensity used ($\sim 10^{16}$ W/cm^2). Ion signals were recorded even at about 2.5 mm away from the TOF axis, as found by moving the laser focus area. In the typical operating conditions (coincidence of the TOF axis with the focus), the laser intensity is sufficient to lead molecules to ionization via MPI at a distance of 2.5 mm away from the axis, especially when high laser intensities were employed. Ions generated at these distances have to travel a longer time to reach the detector and therefore contribute to an asymmetrical broadening of the parent ion peak. Such an asymmetrical broadening was observed only for the parent ion peak. For many of the other peaks, a decrease in the mass resolution was observed too, but this may reflect the different kinetic energy distribution of the photodissociation products and suggests that the ionization/dissociation mechanism is not the same for all species.[15]

As far as the multiply charged ion production is concerned, intact double and triple ions have been observed only for aromatic molecules in the present work, i.e., molecules which have π-MO. It also seems that, for aromatic molecules, the multiply charged intact ion generation is efficient regardless of the nature of the HOMO (π-MO for benzene,[10] toluene,[10] and aniline and n-MO for pyridine, triazine, etc.). In the spectra of CP and CH (Figure 1), there is no evidence for a stable doubly charged parent ion production. Also, there are no ion peaks that could be attributed to doubly charged hydrocarbon fragments. Therefore, it is concluded that multiply charged intact ion production is favored for aromatic molecules or, in other words, for species with relatively high molecular stability.

The abundance of the doubly and triply charged intact ions induced by strong laser fields is found to be large and is a function of the laser intensity. For the case of furan, at 790 nm and $I \approx 2 \times 10^{15}$ W/cm^2, the ratio of the area of the parent ion to that of the doubly charged is found to be $P^{2+}/P^+ \approx 0.3$. Doubly charged parent ion for furan has been also recorded by 70 eV EI with a $P^{2+}/P^+ = 1.6 \times 10^{-2}$.[23,24] Obviously, under strong laser irradiation a significant increase in the P^{2+} abundance has been achieved. Such a comparison cannot be made for the other molecules because there are no multiply charged ion peaks, at least with significant intensity, in their 70 eV EI mass spectra. Multiply charged intact ions have been observed with high abundance also at $\lambda = 395$ nm (Figure 2).

In Figure 3, the ratio P^{2+}/P^+ as a function of laser intensity at $\lambda = 790$ and 395 nm is presented for a furan, pyridine, and aniline. For furan, the ratio P^{3+}/P^+ is also presented. It is worth noting that triply ionized hydrocarbons have rarely been observed. For furan and pyridine, the ratio P^{2+}/P^+ increases as a function of intensity and at higher laser intensities becomes more or less constant (plateau) for 790 nm. The latter is not observed for 395 nm. The ratio P^{2+}/P^+ for aniline has an inverse wavelength dependence compared to that observed for furan. Moreover, it is found for pyridine that the abundance ratio P^{2+}/P^+ is higher at 395 nm than that at 790 nm. These differences suggest that the mechanism for multiple ion production is not the same for all species and could be related to molecular structure.

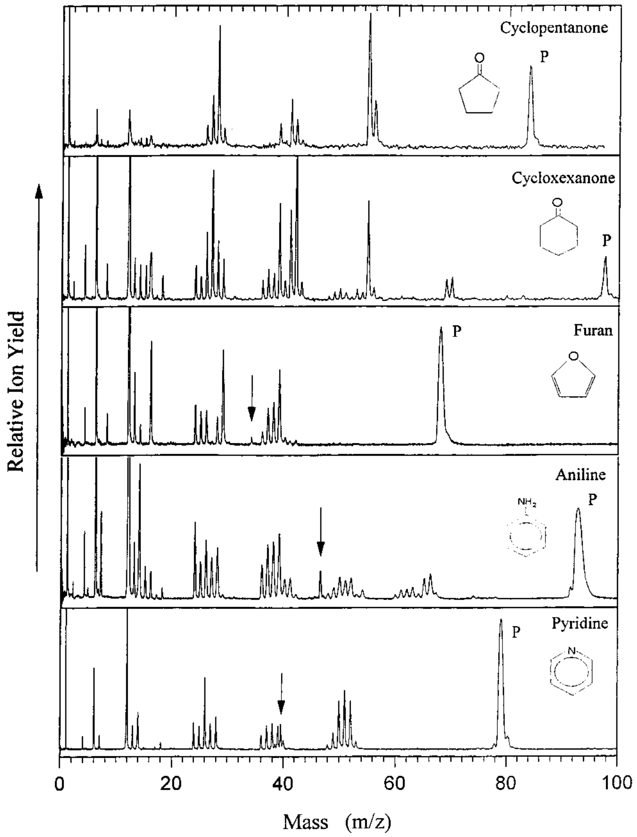

Figure 2. TOF mass spectra of cycloketone, cyclohexanone, furan, aniline, and pyridine at 395 nm. The spectrum of cyclopentanone has been recorded at $I = 3 \times 10^{13}$ W/cm^2, while for the other molecules at $I = 4 \times 10^{15}$ W/cm^2. The parent ion is denoted by a P, and the doubly charged parent ion by an arrow.

Molecular ionization could be attributed to multiphoton ionization processes (MPI) and/or to a field ionization mechanism. Of course, in any case, MPI is expected to contribute to ion production on the laser pulse wings. At the laser pulse peak intensity, even for the lower intensities employed, the Keldysh parameter γ defined by[25]

$$\gamma = (\mathrm{IP}/(1.87 \times 10^{-13})I\lambda^2)^{1/2}$$

(where IP stands for ionization potential in electronvolts, I for laser intensity in W/cm^2, and λ in micrometers) is found to be smaller than 1 for both wavelengths used (for furan, γ is estimated to be 0.44 at $\lambda = 790$ nm and 0.55 at 395 nm). These γ values are indicative of tunneling ionization, and the single ionization at 790 nm is attributed to a field ionization mechanism.

This conclusion cannot be a priori extended to 395 nm because at this wavelength it is likely that ionization through MPI depletes the ground state (ionization saturation) before the molecule experiences intensities for which $\gamma < 1$. It has been observed that the mass resolution for the fragment ion peaks is reduced at 790 nm compared to spectra recorded at 395 nm, even for laser intensities where the P^{2+} was hardly seen. The comparison is made for spectra recorded under the same laser power and with similar total ion signal yield (in order to exclude contribution from space charge effects) achieved by regulating the gas pressure. DeWitt and Levis have also reported a mass resolution reduction for spectra recorded at 780 nm, and they have interpreted it as evidence for field ionization, since, for molecules undergoing MPI, similar trends in resolution are not observed.[15] Therefore, for the present work, it is believed that the single ionization mechanism is not necessarily the same for both wavelengths and that at 395 nm there exist, at least, a strong contribution from MPI processes.

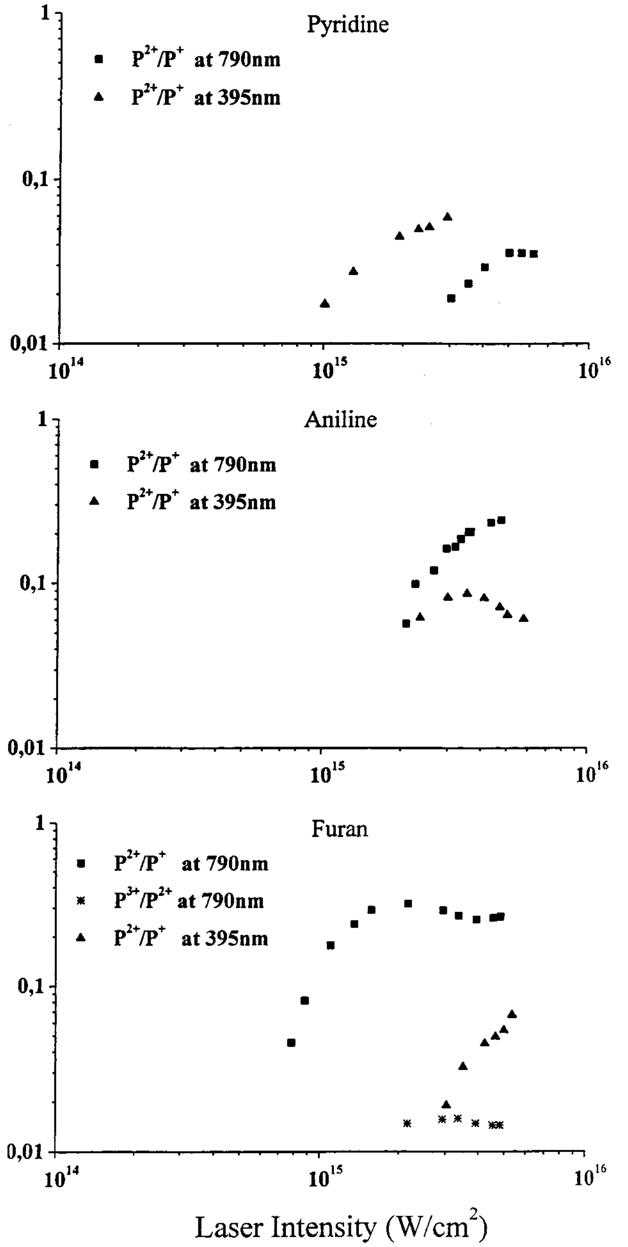

Figure 3. Abundance ratios of doubly charged parent (P^{2+}) ion to single ionized parent (P^{+}) for furan, aniline, and pyridine at 790 and 395 nm are presented. For furan, the ratio of the triply (P^{3+}) to doubly charged intact ion at 790 nm is also shown.

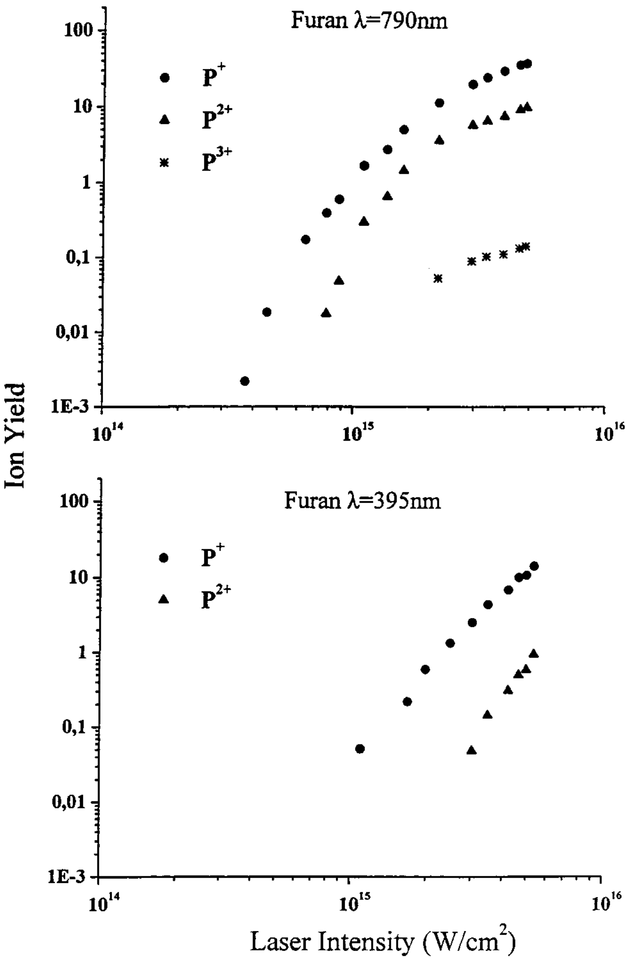

Figure 4. Intensity dependence of the total ion yield, the parent ion (P^{+}), the doubly charged (P^{2+}), and the triply charged (P^{3+}) parent ions of furan is presented at 790 and 395 nm.

TABLE 1: Intensity Threshold for Doubly ($I_{th}P^{2+}$) and Triply ($I_{th}P^{3+}$) Charged Ion Production of Furan, Aniline, and Pyridine Are Presented at 790 and 395 nm[a]

	λ = 790 nm		λ = 395 nm	
	$I_{thr}P^{2+}$ (W/cm^2)	$I_{thr}P^{3+}$ (W/cm^2)	$I_{thr}P^{2+}$ (W/cm^2)	IP^{2+} (eV)
furan	8×10^{14}	3×10^{15}	3×10^{15}	25
aniline	2×10^{15}		2×10^{15}	21.7
pyridine	3×10^{15}		1×10^{15}	26.4

[a] The double ionization energy (IP^{2+}) for these molecules, estimated in accordance with ref 29, is also shown.

It is possible that the recorded double and triple intact ion have been produced through a simultaneous detachment or a stepwise process. As mentioned before, double ionization of some small molecules has been attributed to simultaneous ejection of two electrons (direct, nonsequential ionization).[13] Recently, in the case of atomic Li, it has been proposed that single photon absorption can even lead to direct triple ionization of the atom.[26] For multiple, nonsequential ionization, two different mechanisms have been proposed. Corkum[27] proposed a rescattering model in which the first electron, ejected via tunneling, oscillates in the strong laser field and it revisits the vicinity of the ionic core and knocks off the second electron. Fittinghoff et al.[28] proposed an alternative explanation known as the shake off model. According to this mechanism, the first electron is removed quickly enough that the second electron does not adiabatically adjust to the loss of screening, and thus there will be some amplitude of the second electron wave function in excited ionic states or in the continuum. Unfortunately, the explanation for two-electron ejection in an intense laser field remains largely unresolved even for atoms, despite the careful efforts of many groups.

In Figure 4, the dependence of the total ion signal, the parent ion, the doubly, and the triply charged parent ion on the laser intensity at λ = 790 and 395 nm is presented for the case of furan. No doubly charged intact ions could be recorded for laser intensities where the yield of the single charged parent ion was not close to saturation. This observation is valid for both wavelengths and could be considered as evidence, although not a proof, for a stepwise (sequential) ionization process, involved in the production of the P^{2+} ion. The same observation is valid for the P^{3+} production (P^{3+} observed for laser intensities above the saturation of P^{2+}).

In addition, from the same figure, the intensity thresholds for P^{2+} production ($I_{thr}{}^{2+}$) at λ = 790 nm and 395 nm can also be estimated. A value of $I_{thr}{}^{2+} = 8 \times 10^{14}$ W/cm^2 is found for

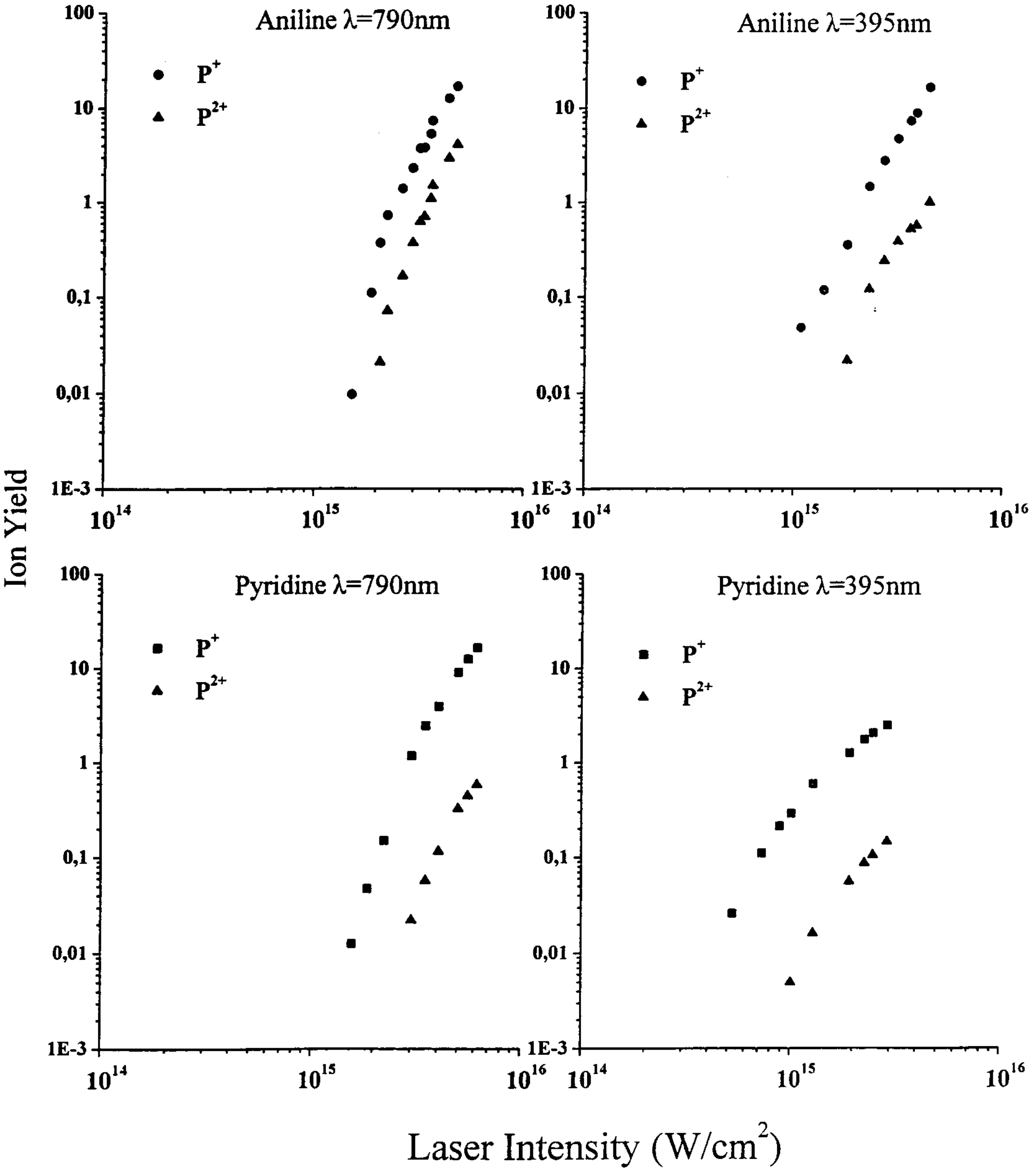

Figure 5. Intensity dependence of the parent ion (P^+) and the doubly charged parent (P^{2+}) of aniline and pyridine is presented at 790 and 395 nm.

$\lambda = 790$ nm, while at 395 nm it is determined to be 3×10^{15} W/cm^2. In Table 1, the intensity thresholds for P^{2+} and P^{3+} are presented.

If the rescattering mechanism was involved in the multiply charged ion production, then the maximum kinetic energy of the returning electron is expected to be 3.17Up [where Up is the pondermotive potential, Up = $(9.33 \times 10^{-14})I\lambda^2$, ($I$ in W/cm^2 and λ in μm)], and this energy should be enough to eject the second electron, i.e., higher than the ionization potential for P^{2+} generation. Tsai and Eland[29] have found a good correlation between single and double ionization energies for aromatic molecules: double ionization energy is 2.8 ± 0.1 times that of single ionization. These values are presented in Table 1. The maximum kinetic energy of the returning electron at the determined intensity thresholds for furan should be 148 eV at 790 nm and 138 eV at 395 nm, while the IP^{2+} is estimated to be only 25 eV. It is clear that from this point of view, the rescattering mechanism could be also involved in the doubly charged ion production, although the maximum kinetic energy of the electron corresponds to much higher energies than those needed for P^{2+} generation. The above conclusion is valid also for aniline and pyridine. It is believed that the polarization dependence of the ion yield will provide further information on the details of the ionization mechanism.

In Figure 5, the intensity dependence of the parent ion and the doubly charged intact molecule are presented for aniline and pyridine at 790 and 395 nm.

Finally, for the triply charged intact furan ion, it should be noted that the observed threshold intensity is relatively close to that estimated by the barrier suppression ionization model (BSI).[30] The intensity threshold for BSI is given by

$$I_{\mathrm{BSI}} = \frac{E_{\mathrm{i}}^4}{16Z^2}$$

and corresponds to the minimum laser intensity required for a bound electron to escape without tunneling. In practical units I_{BSI} (W/cm^2) = $4 \times 10^9[E_{\mathrm{i}}^4$ (eV)/$Z^2]$, where E_{i} is the ionization potential and Z the ionic charge state. Despite the weakness of not including the influence of the laser pulse duration, this model predicts reasonably well the yield of higher charged ions for the heavier noble gases, created by sequential processes.[31] For furan, the E_i for the triply charged ion can be estimated by an empirical rule which relates, for closed-shell molecules, the single and triple ionization energies by the relationship $IP^{3+} = (5.0 \pm 0.2) \times IP^{+}$.[32] The calculated IP^{3+} is 44.4 ± 0.2 eV. Thus, a value of $I_{BSI} = 1.7 \times 10^{15}$ W/cm^2 is estimated, which is close to that experimentally determined ($I = 2.9 \times 10^{15}$W/cm^2).

Conclusions

The multiply charged intact ion production from cyclic polyatomic molecules has been studied by means of strong laser pulses at 790 and 395 nm. It is found that molecular aromaticity favors the multiply charged intact ion generation regardless of the nature of the HOMO. Doubly charged intact ions were observed for homo- and heterocyclic molecules with five- and six-membered rings at both wavelengths in high abundance. No evidence for multiply charged intact ions exists in the mass spectra of cycloketones studied in this work.

The ionization mechanism seems to be different at the wavelengths used. Tunneling ionization is believed to be the dominant mechanism at 790 nm, while MPI is expected to have a strong contribution in the ion yield at 395 nm.

There is evidence that multiply charged ion production is taking place through a sequential process, although the rescattering model cannot be excluded.

An unambiguous triply charged intact molecule is recorded for furan at 790 nm. The intensity threshold for P^{3+} was found to be relatively close to that predicted by the barrier suppression model, assuming a sequential ionization process. The latter, in conjunction with the power dependence of the P^{3+} yield supports the idea that this species is produced through a sequential ionization process.

Obviously, the multiple ionization process for these polyatomic molecules needs further investigation. Nevertheless, it seems that irradiation with femtosecond lasers can provide a source of multiply charged intact ions for a series of molecules with significant abundance, which could have significant impact in analytical work, especially if similar results are obtained for larger systems such as biomolecules.

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