Near-infrared femtosecond photoionization/dissociation of cyclic aromatic hydrocarbons

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Pulses of 780 nm light of duration 170 fs and power densities up to $3.8 \times 10^{13}$ W cm$^{-2}$ are used to study the photoionization/dissociation processes in the series of gas phase, cyclic aromatic hydrocarbons including benzene, naphthalene, phenanthrene, and anthracene. The near-infrared ionization process leads to the production of intact molecular ions for all of the molecules studied. Measurements of the ion intensity as a function of laser fluence revealed the order of the ultrafast ionization process to be $8.0 \pm 0.1$ for anthracene, $6.9 \pm 0.1$ for phenanthrene, $8.5 \pm 0.1$ for naphthalene, and $8.1 \pm 0.1$ for benzene. The relative femtosecond photoionization cross section decreased from 1.0 for anthracene to 0.2 for phenanthrene to 0.1 for naphthalene to $\sim 0.005$ for benzene. The relative order and cross section of the femtosecond ionization processes suggest that a field ionization mechanism is operative. © 1995 American Institute of Physics.

The use of femtosecond duration laser pulses for photoionization of molecules is currently an area of considerable interest because of interaction times shorter than the time scale for the excited state decay into electron ejection, perturbation of the molecular Hamiltonian by the intense electric field, and the potential for coherent control using the wide bandwidth of excitation frequencies ($\sim 6.5$ nm for a 50 fs pulse at 800 nm). The high peak powers readily available with amplified femtosecond laser pulses give rise to ionization pathways distinct from resonant excitation processes. Investigations$^{1-3}$ of atomic and molecular systems using intense laser pulses of nanosecond duration reveal that field$^{4-6}$ ionization mechanisms can be operative at peak powers in the range of $10^{14}$ W cm$^{-2}$. The field ionization mechanisms are a direct consequence of the electric field generated by the laser pulse as given by

$$E_0 = \left[ \frac{2I}{\epsilon_0 c} \right]^{1/2},$$

where $E_0$ is the electric field strength (V m$^{-1}$), $I$ is the intensity of the laser beam (W m$^{-2}$), $\epsilon_0$ is the permittivity of free space, and $c$ is the speed of light. A laser pulse of $10^{15}$ W cm$^{-2}$, corresponding to an electric field strength of $\sim 8.7$ V Å$^{-1}$, is sufficient to field ionize most molecules and many atoms. Even at several orders of magnitude lower laser fluences, the electric field strength is sufficient to produce a measurable rate of tunneling through the Coulombic barrier.$^3$

In the case of the multiphoton ionization of a polyatomic system using a resonant intermediate state, an ultrashort pulse permits excitation to the ionization state on a time scale which competes with excitation of nuclear motion.$^7$ Increasing the intensity of a resonant nanosecond excitation laser can result in fragmentation of cluster systems$^8$ via the absorption–dissociation–ionization mechanism.$^9$ Recent investigations of photoionization using femtosecond excitation pulses, however, reveal no increase in fragmentation with increasing pulse intensity over several orders of magnitude.$^{10,11}$ The use of ultrafast radiation can also reduce the subsequent absorption of photons by the ion state thus limiting the absorption–ionization–dissociation mechanism.$^{12}$ This results from the excitation pulse being shorter than the decay of the excited state via electron ejection, requiring hundreds to millions of femtoseconds in simple cluster systems.$^{12-15}$

Here we report the near-infrared (780 nm) photoionization of aromatic molecular systems ranging in size from 12 to 24 atoms using amplified pulses of duration 170 fs. The optical system used to generate the femtosecond laser pulse was a Ti:sapphire oscillator coupled to a solid-state regenerative amplifier modeled on a system described previously.$^{16}$ A 76 MHz pulse train of 150 fs pulses was stretched using two diffraction gratings to $\sim 150$ ps. A single pulse was then amplified in a 10 Hz, Nd:YAG-pumped, regenerative Ti:sapphire amplifier. The pulse was then recompressed in a dual grating configuration to produce a final energy of 500 $\mu$J. The pulses were centered at 780 nm with a spectral width of approximately 10 nm. The full width at half-maximum of the autocorrelated pulse was 170 fs. The nanosecond pulses used for ionization, 532 nm (3.5 ns) and 266 nm (2.5 ns), were generated from the second and fourth harmonics of a Nd:YAG laser. The nanosecond pulse at 780 nm was produced in an H$_2$ Raman frequency shifter from a 590 nm Nd:YAG-pumped dye laser pulse. The femtosecond pulses were focused into the chamber to a diameter of 100 $\mu$m to give a maximum power density of $3.8 \times 10^{13}$ W cm$^{-2}$, while the nanosecond pulses were more tightly focused to a diameter of approximately 50 $\mu$m. Time-of-flight mass spectrometry was used to detect the ionized species produced in the multiphoton ionization/dissociation schemes investigated.

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The mass spectrometer was a linear TOF design employing dual-slope ion extraction, a 20 cm field-free drift region, and a chevron-stack microchannel plate assembly coupled with a CuBe conversion dynode for signal detection. A similar instrument has been described in detail previously.17 Solid samples were introduced into the TOF chamber and allowed to sublime freely into the vacuum at 298 K. Benzene was leaked into the chamber through a baffled pulsed nozzle to produce a background at 298 K. Sample pressures are shown in Table I.

The spectroscopy of benzene, naphthalene, phenanthrene, and anthracene have been studied extensively.18–20 At the centroid of the wavelengths of the femtosecond laser used in this study, 780 ± 5 nm, the gas phase molecules have single and two photon absorption cross sections of essentially zero. At 260 nm (corresponding to the three photon process), the molecules have solution phase (hexane) single photon cross sections ranging from 3.8 × 10⁻¹⁷ cm² (Ref. 18) for phenanthrene to ~1 × 10⁻¹⁹ cm² (Ref. 18) for benzene. The 260 nm single photon absorption cross sections are collected in Table I. For reference, the adiabatic and vertical ionization potentials of the molecules have also been included in Table I.

A comparison of the photoionization of phenanthrene using laser pulses of nanosecond and femtosecond duration is shown in Fig. 1. Figure 1(a) shows a typical mass spectrum resulting from photoionization using 780 nm pulses of duration 170 fs and power density of 2 × 10¹³ W cm⁻² and Fig. 1(b) shows a mass spectrum for ionization using 532 nm pulses of duration 3.5 ns and power density 1 × 10⁹ W cm⁻². In the femtosecond experiment, while the peak power density is >10⁶ times that of the nanosecond case, limited fragmentation producing C₁₂H₉ and smaller fragments is observed well above the threshold power density required for ion detection. Note that the femtosecond excitation at 780 nm requires at least six photons for ionization. For the nanosecond ionization process we observed production of C₆H₆ clusters with n ≈ 5 at the threshold laser intensity for ion production even though it is a 2+2 excitation process. Clearly for the nanosecond case the pulse duration is long enough that multiple excitation events will occur at the minimum power density required for ion production. Parent ion was not detectable at any power density using the nanosecond duration pulse. Experiments using 266 nm laser pulses of duration 2.5 ns reveal parent molecular ion near the threshold laser power for ion production as observed previously.22 Increasing the laser power further results in substantial fragmentation at 266 nm. An experiment using a 780 nm pulse of duration 5 ns produced no detectable signal for laser power densities up to 2.2 × 10⁸ W cm⁻².

To gain some insight into the mechanism of the ionization of large molecules using femtosecond duration pulses of 780 nm light we determined the order of the ionization process for each of the cyclic aromatic hydrocarbons. To determine the order, the logarithm of the measured ion yield is plotted as a function of the logarithm of the measured femtosecond laser fluence. To sequentially and reproducibly decrease the laser fluence, 160 µm thick coverslips are placed into the beam path at an angle of 5° from normal to the direction of light travel. Calibration of the attenuation factor for the coverslips reveals that the 780 nm beam is reduced 5.0% in intensity per coverslip. For example, less than 20 coverslips were necessary to reduce the benzene signal intensity by three orders of magnitude. Pulse width measurements using both single-shot and free-running autocorrelation techniques showed no measurable temporal broadening of the pulse width when all of the intensity attenuating coverslips and the chamber window were inserted into the laser beam path. A plot of the logarithm of the ion intensity versus the logarithm of the laser intensity for the four molecules is shown in Fig. 2. This series of data sets for the four molecules was collected with no alteration of the focal length of the lens, laser beam position, pulse duration, or initial pulse energy. The ion intensity has been corrected for the background pressure of the four molecules. The linear least squares fit to each of the data sets is shown as a solid line and the slopes of these four fits are included in Table I. Measurements were made from the onset of the lowest detectable signals until saturation of the detector occurred, which corres

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**TABLE I. Physical properties and experimental parameters for the cyclic aromatic hydrocarbons studied.**

<table>
<thead>
<tr>
<th></th>
<th>Benzene</th>
<th>Naphthalene</th>
<th>Phenanthrene</th>
<th>Anthracene</th>
</tr>
</thead>
<tbody>
<tr>
<td>σ₃₀₀₅₀nm(Å²)</td>
<td>~0.001ₜ</td>
<td>0.056ₜ</td>
<td>0.3ₜ</td>
<td>0.058ₜ</td>
</tr>
<tr>
<td>Adiabatic IP (eV)</td>
<td>9.2ₜ</td>
<td>8.1ₜ</td>
<td>7.8ₜ</td>
<td>7.4ₜ</td>
</tr>
<tr>
<td>Vertical IP (eV)</td>
<td>9.3ₜ</td>
<td>8.5ₜ</td>
<td>8.4ₜ</td>
<td>8.0ₜ</td>
</tr>
<tr>
<td>Sample pressure (Torr)</td>
<td>~2 × 10⁻³</td>
<td>3.0 × 10⁻³</td>
<td>1.0 × 10⁻⁵</td>
<td>4.0 × 10⁻⁷</td>
</tr>
<tr>
<td>780 nm order</td>
<td>8.1 ± 0.1</td>
<td>8.5 ± 0.1</td>
<td>6.9 ± 0.1</td>
<td>8.0 ± 0.1</td>
</tr>
<tr>
<td>Relative fs σᵢ</td>
<td>~0.005</td>
<td>0.1</td>
<td>0.2</td>
<td>1</td>
</tr>
<tr>
<td>Order × 1.59 eV</td>
<td>12.9</td>
<td>13.5</td>
<td>11.0</td>
<td>12.7</td>
</tr>
</tbody>
</table>

ₜSee Ref. 18.  
ₜSee Ref. 19.  
See Ref. 20.  
See Ref. 21.  

Note that the pressure values are not corrected for ionization efficiency in the Bayard–Alpert pressure gauge.  

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**FIG. 1.** A comparison of the laser photoionization, time-of-flight mass spectra for 170 fs, 780 nm excitation (a) and 3.5 ns, 532 nm excitation (b) for the molecule phenanthrene. Each mass spectrum is the average of 1000 laser shots.
responded to roughly a factor of 3 in laser power density.

Note that the range of laser power densities is limited because the order of the ionization process is greater than 7.

Also included in Table I is the effective energy required to ionize the molecules (the order multiplied by the energy of a 780 nm photon, 1.59 eV). Finally we note that for phenanthrene and anthracene significant fragmentation is observed at the highest laser powers. A plot of the total ion yield including fragments produced at higher femtosecond laser intensities reveals an order which is identical to that measured for the parent ion.

A number of semiquantitative theories have been proposed to identify the mechanism of ionization. A qualitative determination of the mechanism can be obtained by the adiabaticity parameter \( \gamma \), as set forth by Keldysh:23

\[
\gamma = \frac{\epsilon_0^2 h^2}{\pi e^5 \rho^2 m_c^2 a_0^2} \left[ \frac{2}{\omega} \right]^{1/2},
\]

where \( \omega \) is the angular frequency, IP is the ionization potential (eV), \( h \) is Planck’s constant (J s), \( e \) is the electron charge (C), \( m_c \) is the electron mass (kg), and \( a_0 \) is the Bohr radius (m). If \( \gamma \approx 1 \) the process is in the field ionization regime, if \( \gamma \gg 1 \) the process is in the multiphoton ionization regime. The adiabaticity parameter for these experiments ranges from 1.3 (anthracene) to 1.5 (benzene), at the highest laser power densities and from 2.6 (anthracene) to 4.5 (benzene) at the lowest laser power densities used. These values are in the intermediate region between field ionization and resonant ionization mechanisms. To determine whether the photoionization process is in the tunneling ionization or barrier suppression ionization (BSI)24 regime, the field strength required to produce barrier suppression ionization can be calculated. In the barrier suppression model, typically applied to atoms, the highest lying electron is held in a one-dimensional Coulombic well. When an electric field is applied across the atom, the barrier for the electron escaping to the free continuum is in one direction. To calculate the field required for barrier suppression ionization, \( F_{\text{BSI}} \), the expression developed for atoms24 is used:

\[
F_{\text{BSI}} = \frac{\epsilon_0^2 h^2}{e^3 m_c a_0} \frac{[\text{IP}]^2}{Z},
\]

where \( Z \) is the charge of the resulting ion. For the conditions employed in this experiment, sufficient laser intensity (corresponding to 1.7 V Å\(^{-1}\)) is present for barrier suppression ionization of the molecules anthracene (\( F_{\text{BSI}} = 1.1 \) V Å\(^{-1}\)), phenanthrene (\( F_{\text{BSI}} = 1.2 \) V Å\(^{-1}\)), and naphthalene (\( F_{\text{BSI}} = 1.3 \) V Å\(^{-1}\)). Benzene, on the other hand, is quite close to the threshold intensity for BSI (1.5 V Å\(^{-1}\)) at the highest laser power employed in this study and presumably enters the regime for tunneling ionization with only modest attenuation of the laser intensity. In the tunneling mechanism, the order of the ionization process is lower than the field ionization order.24 One would also expect the yield or cross section for the tunneling process to be less than in the field ionization case, as is observed when comparing the yield for benzene and naphthalene.

Four additional observations shed some light on the mechanism of ionization. The relative ionization probability is a function of the size of the delocalized \( \pi \) molecular orbitals of the molecules. This is consistent with a field ionization mechanism and is conceivably consistent with a resonant ionization mechanism. Second, resonance-enhanced multiphoton ionization experiments on the nanosecond time scale typically show a power dependence correlating to the number of photons necessary to reach a resonant state. The orders observed in these measurements, 6.9 to 8.5, greatly exceed the expected order for the 3+3 process expected for resonant ionization. It should be noted that if the excitation pulse is significantly shorter than the lifetime of the intermediate state (fs laser pulse duration vs ns lifetime, for instance), the resonant order may simply not be apparent. A third observation is that the apparent orders measured for the molecules correspond to an additional 2 to 3.3 photons in excess of the energy required for adiabatic ionization. This is consistent with field ionization and would be consistent with multiphoton ionization only if a highly excited ion state had a much higher multiphoton absorption cross section than lower lying resonant ion states. Finally, a nonintegral order is apparent in the ionization of naphthalene, and may also be present in some or all of the remaining systems. This, again, is clearly inconsistent with multiphoton ionization schemes. These observations lead us to conclude that a field ionization mechanism best describes the observed phenomena.

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