The role of electron delocalization in the ionization of C₆ hydrocarbons using intense 780 nm laser pulses of femtosecond duration

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The photoionization/dissociation mass spectra are reported for the series of molecules benzene (C₆H₆), 1,3,5-hexatriene (C₆H₉), cyclohexane (C₆H₁₂), and n-hexane (C₆H₁₄) as a function of laser power intensity from 1 to 3.8×10¹³ W cm⁻² using a pulse duration of 170 fs and wavelength 780 nm. The ionization orders are localized around 8.3 for benzene, 1,3,5-hexatriene, and cyclohexane and the relative ionization probabilities are measured to be 1.79, and 0.15, respectively. No ion current was observed for n-hexane. The dissociation yield is observed to increase exponentially as a function of the number of atoms in the molecule with cyclohexane undergoing the most dissociation and benzene undergoing essentially no dissociation. These observations are interpreted in light of a field ionization model that incorporates both the ionization potential and the electronic and nuclear structure of the molecule. © 1998 American Institute of Physics.

The electronic and nuclear structure of a polyatomic molecule determine the photophysical processes occurring when a given molecule interacts with an intense laser pulse. Such structure should therefore play a role in determining whether a field or a multiphoton picture is operative in the excitation mechanism. Existing theories have been developed for the structureless atom¹⁻⁴ and in the Keldysh¹ model the multiphoton ionization mechanisms may occur in molecules having both low ionization potential and high intensity, the field ionization mechanism will be dominant. In the case of an atom with high ionization potential and a laser with low frequency and high intensity, the field ionization mechanism will be dominant. In the case of an atom with low ionization potential coupled with a high frequency and low intensity laser pulse the multiphoton ionization process is dominant. Experimental verification of this simple Keldysh picture for more complex systems has not yet been accomplished, particularly when electronic orbitals have appreciable density extending over distances of many angstroms. We have previously performed ab initio calculations for atomic, diatomic, and polyatomic systems that suggest that the predictions of the Keldysh model become increasingly inaccurate as the extent of electron delocalization increases. For instance it may be possible, in principle, that field ionization mechanisms may occur in molecules having both low ionization potential (IP) and extensive delocalization where the Keldysh model predicts that the multiphoton ionization (MPI) process should dominate. The nature of the chemical bonding constituting a given molecule should also have a pronounced effect on the ionization rate. This is because the probability of channeling excitation energy into dissociation modes (leading to dark states for ionization detection) depends in part on the strength of the bonds involved.⁶

In this investigation we compare the laser-induced photoionization/dissociation spectra for a series of C₆ hydrocarbons having significantly different bonding structures to elucidate the coupling of the radiation field to various polyatomic molecules. Photoexcitation is performed using a 780 nm laser having a pulse duration of 170 fs. The laser is a regeneratively amplified Ti:sapphire system that has been described previously.⁷ After amplification, the laser pulse energy was 0.5 mJ resulting in an intensity of 3.8×10¹³ W cm⁻² when focused to a 100 µm beam diameter. The laser was focused into a vacuum chamber containing a static pressure of a given C₆H₉ molecule. The molecular weights of the resulting ions were measured using a linear time-of-flight system that has been described in detail previously.⁷ The series of molecules investigated included benzene (C₆H₆), 1,3,5-hexatriene (C₆H₉), cyclohexane (C₆H₁₂), and n-hexane (C₆H₁₄). The molecules in this series have similar ionization potentials as recorded in Table I. The electronic structures for these molecules are significantly different, however. Benzene and 1,3,5-hexatriene have highly conjugated bonding with the largest electronic orbitals extending over 6.3 and 8.4 Å, respectively. Cyclohexane and n-hexane have no conjugated orbitals because the molecules consist exclusively of sigma bonds.

The photoionization/dissociation mass spectra for the molecules benzene, 1,3,5-hexatriene, and cyclohexane are shown in Fig. 1 at full laser intensity, 3.8×10¹³ W cm⁻². The molecule n-hexane had no observable ion intensity under these excitation conditions. Essentially no dissociation is observed in the benzene spectra even at the highest laser intensities, as has been reported previously.¹ The overall dissociation yield is observed to increase as the degree of

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sigma-type bonding is increased. The 1,3,5-hexatriene spectra has a lower dissociation yield as compared to cyclohexane, but the amount of hydrogen ion produced in 1,3,5-hexatriene is orders of magnitude higher than in cyclohexane. Finally in the 1,3,5-hexatriene mass spectra, as the fragments become lighter, the resolution actually decreases with a discernible splitting in the C$_2$H$_x$ features.

The relative ionization probability is one experimental observable that can be used for determining the mechanism of coupling between the radiation field and the molecule. To determine the relative ionization probabilities of the molecules in question we first plot the log$_{10}$ of the total ion yield as a function of the log$_{10}$ of laser intensity as shown in Fig. 2. The slope of benzene and 1,3,5-hexatriene lines are approximately 7.9 ± 0.1, and the slope of the cyclohexane line is 8.5 ± 0.1 over the range of laser intensities employed in this study. The relative 780 nm, femtosecond photoionization cross sections are calculated from the total ion intensity at the most intense laser conditions and are normalized to benzene. The relative cross sections, $\sigma_{780,fs}$, for benzene, 1,3,5-hexatriene and cyclohexane scale as 1, 79, and 0.15 at maximum laser intensity as reported in Table I. Note that the relative cross sections will vary slightly with laser intensity over the range investigated (because of the differing slopes).

A simple tunneling model can be applied to these systems to predict the relative ionization probabilities. To apply the model, the potential energy surface of each molecule was first approximated by a rectangular well with a depth equivalent to the ionization potential. The width of the well was chosen to be equivalent to a length determined from an $ab$ initio calculation at the Hartree–Fock level of theory using a 6-311g++G basis set. To determine the maximum width of the rectangular well two points on the potential energy surface were found using the following two criteria. The energy of the points were required to be equal to the electron binding energy chosen as IP and the potential determined as a function of position along a line between these two points was required to remain less than IP for all ordinates between the two chosen points. If both of these criteria were satisfied then the valence electron was considered to be free to move between these points. Thus the effective width of the rectangular well was chosen to be equal to the distance between the points. In the case of benzene this line contains the para-hydrogen pairs. The $ab$ initio calculation shows that for a line containing the para-hydrogens the distance as defined above is 11.86 bohr. For the case of 1,3,5-hexatriene, the calculation is performed for the molecule’s $E$ form (the sample contained a mixture of both $E$ and $Z$ forms). The distance between a pair of hydrogen atoms located on opposite terminal carbons in the $E$ form is the greatest distance which can be assumed by two nuclei of this molecule. As with benzene, the line containing these nuclei meets the condition to qualify as the dimension of the rectangular well width. The dimension for 1,3,5-hexatriene is thus 15.85 bohr. The boat form of cyclohexane was chosen for calculation of its potential energy surface. The greatest length in cyclohexane satisfying the criteria was determined to be a line containing the equatorial hydrogens of carbons 1 and 3, giving a barrier width of 10.36 bohr. The greatest length in $n$-hexane turns out to be the distance between the terminal hydrogens, or 17.53 bohr.

To determine a tunneling rate the electric field of the laser is superimposed on the rectangular potential as shown in Fig. 3. A tunneling rate is then calculated using Wentzel–Kramers–Brillouin (WKB) theory. The tunneling rate scales as:

$$w \propto \left( \frac{E}{IP} \right)^{-\frac{3}{2}}$$

FIG. 1. A comparison of the time-of-flight mass spectra for the molecules benzene, 1,3,5-hexatriene, and cyclohexane after excitation using 3.8 \times 10^{13} \text{ W cm}^{-2}, 780 nm radiation of duration 170 fs.

FIG. 2. A plot of the logarithm of the integrated ion intensity in the mass spectrum as a function of the logarithm of the 780 nm laser intensity for benzene, 1,3,5-hexatriene, and cyclohexane.

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>C$_6$H$_6$</th>
<th>C$<em>{6}$H$</em>{10}$</th>
<th>C$<em>6$H$</em>{12}$</th>
<th>C$<em>6$H$</em>{14}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionization potential</td>
<td>9.38</td>
<td>8.3</td>
<td>9.86</td>
<td>10.13</td>
</tr>
<tr>
<td>780 nm order</td>
<td>8.1</td>
<td>8.3</td>
<td>8.5</td>
<td>N/A</td>
</tr>
<tr>
<td>Relative $\sigma_{780,fs}$</td>
<td>1</td>
<td>79</td>
<td>0.15</td>
<td>0</td>
</tr>
</tbody>
</table>
potential barrier, and
where $IP$ is the ionization potential,
2
electric field of $1.2 \text{ V Å}^{-1}$ is superimposed on the rectangular well and the
ionization rate is calculated using WKB theory for benzene, 1,3,5-
hexatriene, and cyclohexane.

\begin{equation}
\begin{align*}
w &= \exp\left[-2 \int_{r_1}^{r_2} \left\{2\left[IP - V(r)\right]\right\}^{1/2} dr\right],
\end{align*}
\end{equation}

where IP is the ionization potential, $V(r)$ is the perturbed
potential barrier, and $r_1$ and $r_2$ are the classical turning
points determined by the ionization potential and the field-
perturbed potential energy surface. This model successfully
predicts the observed relative ionization probabilities for
these molecules as shown in Fig. 3 for an electric field
strength of $1.2 \text{ V Å}^{-1}$. While the precise ratio of ionization
probabilities is not constant with varying electric field
strength over the laser powers accessible in this experiment,
the order and relative intensities do not change significantly.
Thus the relative ionization probabilities are consistent with a
field ionization model for the molecules where ions are
formed. In the case of $n$-hexane the model predicts a relative ion intensity approximately seven times that of benzene. The lack of ion production in the case of $n$-hexane is presumably due to a photodissociation rate that exceeds the ionization rate. We have demonstrated previously that for a series of alkyl-substituted benzene molecules increasing the alkyl chain length results in substantial channeling of energy into dissociation modes that are dark to ion detection.\(^6\) In fact, the extension of one carbon unit from ethylbenzene to $n$-propylbenzene was sufficient to decrease the ionization probability one order of magnitude. Thus it is not surprising that $n$-hexane has virtually no ion current at this laser pulse du-
ration. Experiments using shorter duration laser pulses are
under way to address this point. It should be noted that the relative ionization probability for benzene and 1,3,5-
hexatriene scales well with the $\sigma_{260 \pm 5 \text{ nm}}$ cross section as measured by UV-VIS absorption spectroscopy.\(^{10,11}\) This might imply that photoionization proceeds via a $3+3$ MPI process for the 780 nm pump beam if the three photon cross sections were proportional to the single photon $\sigma_{260}$ cross sections. However, as indicated above the overall order was eighth and not third as would be expected in the simple MPI model. If the MPI model was correct, we would also expect the overall dissociation yield to be lower for the molecule with the largest MPI absorption cross section, because lower laser powers can be employed to produce ion signal. The lower laser intensity decreases the probability of the ion state absorbing additional photons that enable subsequent disso-
ciation. Benzene, however, has both a lower cross section than 1,3,5-hexatriene using 780 nm excitation and a lower fragmentation probability at all laser powers. This suggests that the MPI mechanism may not be operative for these con-
jugated molecules.

The relative ionization/dissociation probability is an-
other experimental observable that contains information re-
garding the radiation molecule coupling mechanism. As
stated previously, the mass spectra for the series of mol-
ecules reveals that as the degree of sigma-type bonding in-
creases the dissociation probability also increases; see Fig. 1.
An exponential increase in the dissociation rate is observed
with increasing number of atoms in a molecule. The mecha-
nism for increasing dissociation yield with molecular size has
not yet been determined. One possibility is that the sigma-bonded cyclohexane has a lower bond dissociation en-
ergy and with a given quantity of excitation energy will al-
ways fragment more than 1,3,5-hexatriene or benzene. An-
other possibility is that the channeling of energy into disso-
ciation modes may be due to the higher rate of energy transfer from the electronic coordinates to nuclear coordi-
nates as the density of states increases. The density of states is much greater in cyclohexane in comparison with benzene. Yet another possibility is that weaker force constants for vi-
bration in cyclohexane in comparison to benzene may lead to
enhanced dissociation. In this model, the electric field of the
laser polarizes the valence electrons to the ends of electronic
orbitals that are aligned with the laser’s $E$ field. Dissociation
can then be induced by nuclear rearrangement during and
after the laser pulse in response to such electron polarization.
The transfer of energy from electron polarization to nuclear
degrees of freedom should occur more rapidly in the alkane
system having lower force constants to nuclear motion. The
photoionization-dissociation spectra are consistent with such
a hypothesis. It is worth noting that for the linear $C_6$ hydro-
carbon $n$-hexane, a molecule that should undergo the most
substantial energy transfer from electronic to nuclear modes, we
were unable to observe an ion signal.

The kinetic energy distributions of the photodissociation
products are reflected in the time-of-arrival distribution (i.e.,
the full width at half-maximum) of each ion product. More
direct evidence for a field-induced dissociation mechanism
may be found in the shape of the individual ion peaks in the
mass spectra for cyclohexane and 1,3,5-hexatriene. The reso-

FIG. 3. A one-dimensional model for field ionization depicting a given
molecular potential as a rectangular well with a height of IP and where the
length is approximated by the longest electronic orbital in the molecule. An
electric field of $1.2 \text{ V Å}^{-1}$ is superimposed on the rectangular well and the
ionization rate is calculated using WKB theory for benzene, 1,3,5-
hexatriene, and cyclohexane.
mechanisms are different. Note that in the cyclohexane spectra, the resolution (of \( \sim 200 \Delta t / \Delta t \)) remains constant across the spectrum. The resolution of the 1,3,5-hexatriene spectra decrease from \( t / \Delta t = 198 \) for \( C_6H_6 \) to 67 for \( CH^+ \) to 42 for \( H^+ \). Also, the \( C_1H^+ \) peaks display observable splitting. The decreasing resolution suggests that the smallest fragments undergo some impulsive excitation during dissociation. Similar trends in resolution are not observed in systems undergoing a multiphoton ionization mechanism. Note that this impulsive excitation is not due to Coulombic explosion both because the rate of multiple electron ionization is expected to be vanishingly small at the laser intensities employed in this study and because there is trace evidence for multiple charging only in the 1,3,5-hexatriene spectra. Further evidence for a field-induced ionization/dissociation mechanism is found in the splitting of the \( CH^+ \) ion peaks. The energy difference of the forward and backward scattered peaks is on the order of 10 eV. The splitting of the \( C_1 \) fragments is consistent with a field ionization mechanism where the electric field of the laser is aligned along the axis of the time-of-flight tube. In this case the maximum energy of polarization is expected to be on the order of the electric field strength times the length of the delocalized electronic orbital or 1.7 V/Å × 8.4 Å = 14.28 eV. Assuming the C–C bond strength is 5 eV, this leaves roughly 10 eV for translational energy in the forward and reverse directions, assuming all of the energy stored in electron polarization is converted to nuclear motion aligned along the polarization axis. In this model, the ions are dissociated with kinetic energy along the polarization axis and the dissociation occurs before the molecule has time to rotate. The 1,3,5-hexatriene spectra also has a predominant \( H^+ \) ion feature that is almost equal in intensity to the parent ion peak. Such a dissociation mechanism is not normally seen in nanosecond photodissociation/ionization experiments where either the \( H^+ \) or the intact ion will dominate by many orders of magnitude. The field-induced dissociation may produce such spectra either by \( H^+ \) tunneling from the ends of the molecule or by a polarization-induced dissociation mechanism as outlined above. Such dissociation phenomena are not likely to be caused by subsequent absorption of photons by dissociation products because the laser pulse duration is less than dissociation time scales for these larger polyatomic molecules.

A significant question concerns whether the MPI model is also consistent with the observed photoionization trends. The most convincing evidence for the presence of the MPI model is the scaling of the relative ionization probability with the \( \sigma_{260} \) nm single photon absorption cross section for benzene and 1,3,5-hexatriene. However, one should note that the same properties that determine the extent of the polarization contribution to the electronic absorption cross section also control the magnitude of the field ionization coupling, namely the spatial extent of the electronic molecular orbitals and the ionization potential. Thus a similar scaling is expected in either model. It may also be argued that the MPI model can produce translationally energetic \( H^+ \) ions at high intensity. The mechanism for this is the Coulomb explosion but, as noted, we observed no evidence of the multiple electron ejection (i.e., doubly and triply charged ions) necessary for Coulomb explosion.

We conclude that the coupling between the intense 780 nm radiation pulse and either of the two molecules with electron delocalization, benzene and 1,3,5-hexatriene, occurs through a field mechanism rather than a multiphoton process. This conclusion is reached from the success of the field mechanism in predicting relative ionization probabilities, the ionization-dissociation yields, and the \( H^+ \) and \( C_1H^+ \) ion kinetic energy distributions.

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