Concerning the ionization of large polyatomic molecules with intense ultrafast lasers

Merrick J. DeWitt and Robert J. Levis
Department of Chemistry, Wayne State University, Detroit, Michigan 48202

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The relative photoionization/dissociation probabilities are presented for the molecules benzene, naphthalene, and anthracene upon interaction with 780 nm laser radiation of duration 170 fs and intensity $3.8 \times 10^{13} \text{W cm}^{-2}$. Both the ionization probability and the dissociation yield increase exponentially from benzene to anthracene as measured by time-of-flight mass spectra. A structure-based model is presented for the excitation of large polyatomic molecules by intense laser irradiation with pulse widths on the time scale of molecular vibration (100 fs) and with peak field strengths of 1–2 V Å$^{-1}$. The model accounts for molecular structure and is able to accurately predict the transition from multiphoton ionization (MPI) to tunnel ionization. It is also demonstrated that this structure-based model can quantitatively predict the experimentally measured ionization probabilities. In comparison, models employing the more conventional zero-range potential do not accurately predict either the transition or the relative ion yield measured experimentally. © 1999 American Institute of Physics. [S0021-9606(99)01623-2]

INTRODUCTION

The interaction of UV, visible, and infrared radiation with polyatomic molecules is well understood at intensities where photophysical events are dominated by one- and two-photon processes. At laser intensities sufficient to drive high order processes in polyatomic molecules, the mechanisms for radiative coupling have yet to be elucidated. For accurate, time-dependent, quantum mechanical calculations current computational power is sufficient only to investigate high order processes for the simplest molecules: $\text{H}_2$, $\text{H}_3^+$, $\text{H}_5^{2+}$, etc. 1–6 For diatomics of heavier atoms and for polyatomic molecules, the complexity of the system prohibits detailed calculations of field-molecule interactions at high laser intensities. In the absence of time-dependent quantum-mechanical calculations, models for the field-molecule coupling interactions are of value for predicting relative ionization probabilities and dissociation yields. This is essential when intense fields are used in detection schemes for chemical dynamics investigations. A structure-based model is presented in this paper for predicting both the mechanisms of intense radiation-molecule coupling and the relative ionization probabilities in the limit of tunnel ionization. We test the model by comparison to relative photoionization probabilities as measured using intense laser ionization time-of-flight mass spectrometry for benzene, naphthalene, and anthracene.

There are two limiting regimes in the coupling of intense radiation fields with polyatomic molecules. One is the multiphoton regime in which $n$ photons couple simultaneously into the molecule to allow excitation to an intermediate electronic state or directly to an ionic state. The other regime for radiation-molecule coupling involves the production of field ionization via tunneling or barrier suppression. This can occur when the electric field of the laser significantly distorts the electrostatic potential of the atom or molecule. To produce a substantial tunneling rate, extremely high laser intensities must be employed. The intensity dependence of the electric field of the laser, $E_0 (\text{V m}^{-1})$, is given by

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

where $I$ is the intensity of the laser (W m$^{-2}$), $\epsilon_0$ is the vacuum permittivity, and $c$ is the speed of light in vacuum. Intensities on the order of $10^{14} \text{W cm}^{-2}$ correspond to electric field strengths of several V Å$^{-1}$. Such fields will significantly perturb the molecular potential. Whether a neutral molecule can survive until the peak in the electric field depends upon the rise time of the laser pulse, and ultimately on the pulse duration.$^7$

A theory for predicting the interaction mechanism between atoms and intense lasers was proposed by Keldysh$^8$ in 1964. This theory involves estimating the competition between multiphoton ionization and tunnel ionization rates, and has been shown to accurately model not only the behavior of atoms, but many diatomics as well. In this approach, the Keldysh adiabaticity parameter, $\gamma$, is defined as the ratio of the laser frequency to the tunneling frequency of the perturbed system. If $\gamma$ is much less than unity, the coupling mechanism is in the tunneling limit. If $\gamma$ is much greater than unity, the coupling mechanism is in the multiphoton ionization limit. The tunneling time, $t_{2KR}$, is defined as the time required for an electron of kinetic energy equivalent to the ionization potential, IP, to traverse the length of the barrier, $l$, produced by the superposition of the externally applied electric field, $E_0$, and the zero-range potential. The tunneling frequency$^9$ is the inverse of this value as given by

$^a$Author to whom correspondence should be addressed.
$^b$Camille Dreyfus Teacher Scholar and Sloan Fellow.
where $m_e$ is the electron mass and $e$ is the electron charge. The Keldysh adiabaticity parameter, $\gamma$, is given by the ratio of the laser frequency, $\omega_0$, and the tunneling frequency:

$$\gamma = \frac{\omega_0}{\omega_t} = \frac{(2IP/e)^{1/2}}{eE_0}. \tag{3}$$

One of the issues discussed in this work concerns the validity of applying the Keldysh adiabaticity parameter, based on the zero-range potential, to polyatomic molecules having delocalized electronic orbitals.

The key experiments seeking to identify the radiation-molecule coupling mechanism have focused either on measuring ion yield as a function of laser intensity or on measuring the photoelectron kinetic energy spectra. In the case of the photoion measurements, the logarithm of the ion yield is plotted as a function of the logarithm of the laser intensity to determine the order of the process from:

$$Y = \sigma_n I^n, \tag{4}$$

where $Y$ is the ion yield, $\sigma_n$ is the $n$th order cross section in units commensurate with the units used for intensity, and $n$ is the order of the process. The order is typically equivalent to the smallest number of photons required to reach either the ion state or an intermediate, long-lived eigenstate of the system.\(^\text{10}\) In the case of tunneling, the apparent order of the process is usually much less than the number of photons required to ionize the system.\(^\text{11}\) Unfortunately, beam inhomogeneities, shot-to-shot laser fluctuations, and saturation of the ion yield make the interpretation of orders resulting from high-intensity laser experiments difficult. Photoelectron spectra have proven to be a more reliable test of the coupling mechanism. In the case of multiphoton coupling, discrete peaks are observed in the spectrum, typically in the form of above-threshold ionization (ATI).\(^\text{12-14}\) In ATI, more photons are absorbed by the atomic or molecular system than are required for ionization and the resulting photoelectron peaks are repeated at intervals of the photon energy. In the case of tunnel ionization, a featureless photoelectron spectrum extending from low kinetic energies to energies above the ponderomotive potential of the laser is typically observed.\(^\text{15}\)

Spectra consistent with a transition between these two regimes have been observed\(^\text{14}\) in the series of noble gas atoms ranging from He, with a photoelectron spectrum indicating tunneling, to Xe, with a structured photoelectron spectrum indicating ATI. A similar transition from multiphoton to field-dominated ionization has been observed for the series of molecules discussed in this paper.\(^\text{16}\) Under the same laser conditions employed in this study, benzene’s photoelectron spectrum was shown to contain contributions from both MPI/ATI and tunneling ionization events. The naphthalene spectrum also contained evidence of both mechanisms, but with much less contribution from MPI/ATI events. The anthracene spectrum showed no evidence for MPI/ATI ionization. However, the Keldysh adiabaticity parameter suggests that benzene, naphthalene, and anthracene all undergo multiphoton ionization when exposed to radiation sources of the intensities employed in these experiments. Clearly this issue demands further consideration.

In this paper, we present the ion spectra\(^\text{17,18}\) for the series of molecules benzene, naphthalene, and anthracene obtained over a range of ionizing laser intensities. We consider the effect of molecular structure in determining the mechanism of intense near-infrared excitation. We then present a theoretical framework for predicting the experimental results based on the superposition of the electric field of the laser and the molecular electrostatic potential energy surface.\(^\text{9,16,19}\)

This structure-based model defines a modified adiabaticity parameter, $\gamma(\phi)$, which is shown to more accurately predict the results of previously published photoelectron measurements.\(^\text{16}\) Finally, tunneling calculations based on the model are shown to compare favorably to the relative ion yields measured.

**EXPERIMENT**

The data obtained in this investigation were derived from the detection of intact ions and ionized dissociation products formed in the ultrafast excitation of molecules under intense field conditions. These were measured using a linear time-of-flight (TOF) mass spectrometer employing dual-slope extraction with a total imparted extraction potential of approximately 600 eV. A chevron-stacked dual-microchannel plate assembly was used for amplification of the ion signal. The time-of-arrival traces were recorded using a digital oscilloscope. Similar systems have been discussed previously.\(^\text{9,16-19}\)

The laser was a Ti:sapphire-based 10 Hz regenerative amplifier system (Fig. 1) which produced energies of 0.5 mJ per pulse. Seed pulses for the amplification system were centered at 780 nm with an autocorrelated pulse width of 150 fs.
full width at half maximum (FWHM). The pulses were produced by a Coherent Mira oscillator pumped in multiline visible mode by a Coherent Innova 310 argon-ion laser at 8 W. After pulse stretching, amplification, and pulse compression, the final autocorrelated pulse width (Fig. 2) was measured to be 170 fs, FWHM. These pulses were focused into the TOF spectrometer with a 30 cm focal length lens producing a maximum intensity of $3.8 \times 10^{13} \text{W cm}^{-2}$ corresponding to a field strength of 1.7 V Å$^{-1}$.

EXPERIMENTAL RESULTS

A comparison of the TOF spectra for benzene, naphthalene, and anthracene as measured using the highest laser intensity is shown in Fig. 3. The 780 nm wavelength laser has no first or second-order resonances with any intermediate electronic states in benzene, naphthalene, or anthracene. One interesting aspect of the spectra depicted in Fig. 3 is that the degree of fragmentation exhibited in each spectrum is significantly less than would normally be expected for nonresonant multiphoton ionization with longer pulse length lasers near threshold ionization intensities. Benzene ionization via femtosecond excitation results in virtually no fragment ion products. Similar studies using nonresonant wavelength lasers of nanosecond pulse duration show extensive fragmentation of polyatomic hydrocarbons with H$^+$ and C$^+$ being the dominant product channels. Although Fig. 3 displays an increase in the fragmentation yield for naphthalene and anthracene, there is also parent ion observed for each molecule. The detection of intact parent ion is not possible in the case of ionization of large polyatomic molecules via nonresonant nanosecond excitation.

The time-of-flight mass spectra for benzene, naphthalene, and anthracene are plotted as a function of laser intensity in Figs. 4, 5, and 6, respectively. In the case of benzene, the spectrum taken at the highest laser intensity displays little evidence for dissociation in the channels which result in ion formation. As the peak intensity of the ionizing laser is reduced even the small amount of fragmentation seen at the highest intensities is quickly suppressed, as shown in Fig. 4. Figure 5 displays the naphthalene spectra as a function of 780 nm laser intensity. At the highest laser intensity naphthalene shows moderate fragmentation with approximately 80% of the integrated ion signal detected in dissociation/ionization channels. As with benzene, the fragmentation yield is greatly diminished as the laser intensity is lowered.
The TOF spectra for anthracene taken at various laser intensities are shown in Fig. 6. At the highest laser intensity anthracene shows significant fragmentation yield, although, even at these intensities there is still detectable parent ion signal. As with benzene and naphthalene, fragment ion production decreases substantially as the laser intensity is lowered. At a laser intensity of $2.3 \times 10^{13} \text{ W cm}^{-2}$, the parent ion peak for anthracene becomes the largest peak in the mass spectrum. However, there is no intensity at which fragment ion yield becomes an insignificant part of the total ion signal, as is the case with benzene and naphthalene.

DISCUSSION

It is now well established that intense near-infrared radiation on the femtosecond time scale can be used to ionize polyatomic molecules with diminished dissociation in comparison to nanosecond experiments. This was first reported by this laboratory in 1995. The phenomenon has since been confirmed for a wide spectrum of molecules exhibiting a variety of bonding character. Figure 3 shows the time-of-flight mass spectra of benzene, naphthalene, and anthracene. As the number of atoms increases in the series, an increase in the dissociation probability is observed. This tendency toward increasing dissociation with increasing degrees of freedom has since been observed for a number of molecular species. One explanation for this observation may be an increase in nonradiative relaxation rates corresponding to the increased molecular degrees of freedom. However, the molecules discussed here are known to display nonstatistical behavior with respect to simple intersystem crossing rates (i.e., the intersystem crossing rate does not increase monotonically with degrees of freedom in the series benzene, naphthalene, and anthracene). It is therefore difficult to predict what effect the intramolecular redistribution of energy may have on the ultimate observables in this experiment. In the case of the multiphoton coupling mechanism, an increase in intramolecular energy redistribution leads to both molecular dissociation and an associated decrease in ionization probability. The observation of increasing dissociation is also consistent with the case of field ionization where dissociation may be mediated by electronic polarization induced by the electric field of the laser. In the series considered here, the molecular polarizability increases in the series: 10.5, 16.5, and 25.4 Å$^3$ for benzene, naphthalene, and anthracene, respectively. In general, as molecules become more complex (e.g., increasing alkyl chain length, additional rings, etc.), the polarizability increases monotonically. As the intensity of the laser is decreased, the intensity of the molecular ion increases with respect to the fragment ions. These trends are readily observed in Figs. 5 and 6.

The order of the ion yield as a function of laser intensity is a common predictor of ionization mechanism for nanosecond duration laser pulses. In the case of multiphoton ionization, a plot of the logarithm of the integrated ion signal versus the logarithm of the laser power typically yields a line whose slope is equivalent to the number of photons necessary to reach the ion state according to Eq. (4). In the case of resonance-enhanced multiphoton ionization (REMPI) where an intermediate state between the ground and ion states is energetically resonant with one or more photons, a log-log plot will typically yield a line whose slope is equivalent to the number of photons required to reach the intermediate state. Figure 7 depicts the log-log data for the three molecules benzene, naphthalene, and anthracene. The slopes for all of the molecules are nearly identical and range from 8.0 to 8.5. Because the slopes are approximately the same, one can define a relative ionization cross section for the molecules over the range of laser intensities investigated. The relative total signal intensity for each of these molecules at the greatest laser intensity increases exponentially in a ratio of 1:20:200 for benzene:naphthalene:anthracene. The coupling model described in this paper will be tested using these relative intensities.

While the orders were 8.0–8.5 for these molecules, only six photons are energetically required to exceed each of the ionization potentials. This suggests that an additional 2–3 photons may be involved in the ionization process. There are several possible explanations for the excess order observed. The additional photons may be due to a shift in the ionization potential to higher energy because of the ponderomotive potential of the intense laser pulse. This effect arises from the oscillating electric field interacting with the free electron state. The ponderomotive shift of the ionization potential is...
TABLE I. Apparent orders and ponderomotive effects for aromatic hydrocarbons.

<table>
<thead>
<tr>
<th></th>
<th>Benzene C\textsubscript{6}H\textsubscript{6}</th>
<th>Naphthalene C\textsubscript{10}H\textsubscript{8}</th>
<th>Anthracene C\textsubscript{14}H\textsubscript{10}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vertical ionization potential (eV)</td>
<td>9.386</td>
<td>8.575</td>
<td>8.045</td>
</tr>
<tr>
<td>Expected order (IP/h\nu)</td>
<td>6 (5.9)</td>
<td>6 (5.4)</td>
<td>6 (5.1)</td>
</tr>
<tr>
<td>IP + U\textsubscript{p} (eV)</td>
<td>11.54</td>
<td>10.73</td>
<td>10.20</td>
</tr>
<tr>
<td>Expected order (\frac{IP + U_p}{h\nu})</td>
<td>8 (7.3)</td>
<td>7 (6.7)</td>
<td>7 (6.4)</td>
</tr>
<tr>
<td>Measured order</td>
<td>8.1</td>
<td>8.5</td>
<td>8.0</td>
</tr>
</tbody>
</table>

\[ U_p = \frac{e^2 E_0^2}{4 \pi \omega^2}. \] (5)

At the maximum laser intensity, a ponderomotive shift of 2.2 eV is obtained. For the molecules considered in this study, a ponderomotive shift in the vertical IP would result in effective ionization potentials of 11.54, 10.73, and 10.20 eV for benzene, naphthalene, and anthracene, respectively. These effective IPs would be expected to produce orders of 8 (for benzene), 7 (for naphthalene), and 7 (for anthracene) as detailed in Table I. An alternative rationalization for the high order of the ionization process might be the presence of above threshold ionization during the excitation and emission processes. In this case, the molecule absorbs more photons than are energetically required to produce ionization. Exactly how this would affect the apparent orders is as yet unknown.

Keldysh adiabaticity parameters for the three molecules in this study are included in Table II. As can be seen multiphoton ionization is predicted (\(\gamma > 1\)) for all of the molecules under the laser conditions employed in this study using the zero-range model. The study of atomic ionization by Mevel et al.\(^{14}\) demonstrating the applicability of the zero-range model to atoms also suggests that the relatively low IP of these molecules (all less than the IP of xenon) and the relatively short wavelength of the exciting laser (near-infrared) should lead to ionization via the MPI mechanism. Recent photoelectron kinetic energy measurements,\(^{16}\) however, show that the ionization mechanisms for each of these three molecules are markedly different. The photoelectron spectra suggest that both multiphoton and tunnel ionization are prevalent in the case of benzene, and that the tunnel ionization mechanism is dominant in the cases of naphthalene and anthracene. These results are not consistent with the predictions of the zero-range model, suggesting that a more accurate representation of the potential energy surface may be necessary.

To establish a more suitable model for determining the adiabaticity parameter (and therefore predict the fundamental mechanisms controlling ionization) we employ the molecular electrostatic potential energy surface in the calculation of a structure-based adiabaticity parameter, which we denote as \(\gamma(\phi)\). An \textit{ab initio} calculation determines the geometry of the neutral molecule. This geometry (frozen coordinates) is used to calculate the wavefunction of the +1 ion. A one-dimensional potential is then derived from the ion wavefunction for the determination of \(\gamma(\phi)\). The potential is also modeled as a rectangular well with a width equivalent to the distance between classical turning points and a depth equivalent to the vertical ionization potential of the molecule. An external potential, equivalent to the electric field of the laser, superimposed upon this rectangular well allows calculation of the tunneling rate via the Wentzel–Kramers–Brillouin (WKB) method. A more detailed description of the selection criteria for the one-dimensional potential follows.

As an introduction to the structure-based model, we first consider the simpler case of the zero-range potential as considered by Keldysh [Fig. 8(a)]. The zero-range potential is perturbed by a strong external electric field to develop a barrier to electron motion. The length of this barrier (the distance between classical turning points within and without the potential barrier) can be expressed as

\[ l = \frac{IP}{eE_0}, \] (6)

where \(e\) is the electron charge and \(E_0\) is the field strength. This length is then used to determine an effective tunneling time, tunneling frequency, and finally, the adiabaticity parameter which is defined as the ratio of the laser frequency to the tunneling frequency via Eq. (3). For the case of the zero-range potential, the values of IP, \(E_0\), and the laser frequency completely determine the value of the adiabaticity parameter, and therefore the predicted ionization mechanism.

A more realistic model for high field interactions can be obtained by replacing the zero-range potential of the Keldysh
model with the Coulomb potential [Fig. 8(b)]. As potentials more sophisticated than the zero-range potential are considered, the issues of origin location and axis orientation arise. In the case of the Coulomb potential, the only logical choice for the origin position is at the center of the potential. Axis orientation is arbitrary in the Coulomb potential. Superimposing an external electric field upon the potential results in the development of a barrier to electron motion. This barrier is employed in exactly the same manner as the barrier produced in the Keldysh formalism to determine adiabaticity values. The results of the Keldysh and Coulomb-based adiabaticity parameter calculations are shown for the molecules benzene, naphthalene, and anthracene over a range of electric field strengths in Fig. 9, as well as the values for the structure-based model to be detailed subsequently. Rederiving the adiabaticity parameter based on the Coulomb model potential leads to results with several important distinctions from the Keldysh calculation. First, the values for the Coulomb-based adiabaticity parameter are always lower than those obtained by the zero-range definition, as has been shown previously. Second, while the Keldysh adiabaticity parameter has real values for all field strengths, the Coulomb-based adiabaticity parameter reaches a value of zero at the classical barrier suppression ionization (BSI) field strength and is undefined for all greater field strengths. Finally and most importantly, is the effect that Coulomb and structure-based potentials have on the inner barrier to electron motion. The structureless zero-range potential has an inner barrier that is located at the origin for all field strengths and for systems of any IP. The Coulomb potential has an inner barrier that moves away from the origin as the electric field is increased. For any given field strength, the inner barrier for systems with relatively low ionization potentials is also farther from the origin than the barrier for systems with higher ionization potentials. The outer barrier for systems with relatively low ionization potentials is always closer to the origin than the outer barrier for systems with higher ionization potentials. These effects on the inner and outer barrier position lead to a dramatic reduction in the barrier length (with respect to the zero-range model) for species with relatively low ionization potentials ($\leq 10$ eV). Since the tunneling frequency in the definition of the adiabaticity parameter depends upon the barrier length, the structure-based models can have a dramatic effect upon the interpretation of field ionization mechanisms. We conclude that an adiabaticity parameter derived from the Coulomb potential is therefore a more realistic descriptor of the ionization mechanism. Finally, it is worth noting that tunneling formulas determined with the zero-range potential should be in ever increasing error as the field strength of the excitation source approaches and exceeds $F_{\text{BSI}}$. This is not only due to the significant difference in barrier length as determined by the two models, but also to the substantial depression of the barrier height. This latter effect is not accounted for in the zero-range model; in the Keldysh formalism the barrier high is equal to the ionization potential at all field strengths.

While an adiabaticity parameter calculated using a Coulomb potential does address the issue of structure in the electrostatic potential energy surface, the Coulomb potential does not accurately model the delocalized potentials associated with molecules, especially polyatomic species. An advance from the completely isotropic Coulomb potential [Fig. 8(b)] to more realistic molecular potentials [Figs. 8(c), 8(d)] requires consideration of the issues of origin placement and axes orientation to determine the one-dimensional potential. Fortunately, for the current study, all of the molecules are planar and highly symmetric so that these issues are less difficult to resolve than in the full-dimensional nonsymmetric case. A diatomic molecule can be used to illustrate the application of the model employing an $ab\ initialo$ molecular potential. The choice of axes orientation for the diatomic case is unarguably determined by the bond axis, not only because this is the axis of highest symmetry, but because it is the axis which most exemplifies the molecular character of the species: bonding and multiple charge centers.23

The two model potentials for diatomic systems depicted in Figs. 8(c) and 8(d) show that a complication exists for the molecular case; the highest lying electron may or may not be free to move within the outer classical turning points of the unperturbed molecular potential. For this reason, the definition of the axis position for tunneling calculations must depend on the details of the molecular electrostatic potential. For instance, in the strongly bound diatom depicted in Fig. 8(c), the origin would be located at the symmetry center and the tunneling axis would lie along the diatomic bond. Electrons are free to move between the outer classical turning

FIG. 9. Calculated adiabaticity parameters using the zero-range, Coulombic, and molecular potential energy surfaces for benzene, naphthalene, and anthracene.
points of the unperturbed molecular system, so that an externally applied field can have maximum effect on the developed barrier. The weakly bound diatom shown in Fig. 8(d), however, depicts a case in which a similarly placed tunneling axis would not define a path of free electron motion between outer classical turning points. In this case, when an external field is applied it cannot be assumed to have the full effect on the bound electron. For systems in which the internal barrier of the unperturbed potential is substantial, the system is expected to exhibit ionization behavior more similar to that of two isolated atoms.

The determination of axis orientation and origin position can be extended to arbitrarily large molecules. Determining the most appropriate one-dimensional potential involves locating the orientation which yields the greatest distance between classical turning points in the unperturbed electrostatic potential energy surface. As long as molecular symmetry is high, as in the molecules investigated here, both the origin location and axis orientation can be chosen with confidence. A calculation of the molecular potential along the axis determines whether the orientation has only two classical turning points, as in the case of Fig. 8(c), or if the orientation has multiple turning points as in case of Fig. 8(c). After determining the most appropriate one-dimensional potential, calculations of both the adiabaticity parameters and relative tunneling rates (via the Wentzel–Kramers–Brillouin method) are performed as described previously. A complete description of the WKB method as employed here is described subsequently.

For the molecules in this study: benzene, naphthalene, and anthracene, the most appropriate one-dimensional potentials lay along axes defined by the most distant hydrogen nuclei, and are illustrated in the top row of Fig. 10. This simple rule seems to hold true in general for aromatic molecules. A determination of the appropriate one-dimensional potential for cyclohexane (both twisted-boat and chair structures) showed that this is not universally true, however. The electric field is superimposed upon the one-dimensional potential to obtain a barrier through which electrons can tunnel. The adiabaticity parameter is then calculated via Eq. (3), wherein the tunneling frequency for the zero-range barrier is simply replaced with the tunneling frequency for the molecular barrier. Calculations of the adiabaticity parameter for the structure-based model are shown in Fig. 9. All of the adiabaticity parameter values for the molecules and laser conditions in this study are well within the tunneling limit, suggesting that tunneling ionization is the dominant ionization mechanism observed. Benzene has the highest adiabaticity parameter at all intensities suggesting that, of the three molecules, benzene ionization would exhibit the most MPI character. Anthracene has the lowest adiabaticity parameter (less than 1, even at the much lower intensity of 0.75 V Å⁻¹) indicating significant tunnel effects. The predictions are consistent with the previously observed photoelectron spectra.

The relative ionization probabilities of benzene, naphthalene, and anthracene were approximated by a calculation of the WKB tunneling rates for the rectangular potentials in a quasistatic electric field as described previously. The rectangular potentials with superimposed electrostatic fields are shown in the bottom row of Fig. 10. The width of each rectangular well is defined as the distance between the classical turning points shown in the middle row ab initio potentials. The well depths are defined as the ionization potential of the molecule. The applied electric field depicted corresponds to 0.75 V Å⁻¹. For these aromatic systems, the distance between inner classical turning points increases from benzene to naphthalene to anthracene. This corresponds to an increase in the length of the rectangular well and thus increases the effect of the applied electric field on the barrier to ionization. The WKB tunneling probability is

\[
\begin{align*}
\text{probability} &= e^{-W}, \\
W &= 2 \int_{r_1}^{r_2} [2(V(r) - E)]^{1/2} dr,
\end{align*}
\]

where \(V(r)\) is the perturbed rectangular potential and \(r_1\) and \(r_2\) are the classical turning points determined by the ionization potential and the field-perturbed potential energy surface. The values of \(r_1\) and \(r_2\) also bound the shaded region on the rectangular-well potential for each molecule as shown in Fig. 10. The relative tunnel rates calculated using Eq. (7) are included in Table II along with the experimental values. The mass spectrometric measurements of ionization probabilities exhibit a ratio of 1:20:200 for benzene, naphthalene, and anthracene, respectively. These values are in reasonable agreement with the predictions of the tunneling model: 1:28:195 for benzene, naphthalene and anthracene, respectively. Since all of the molecules in this study have similar apparent orders (as determined by the log-log plots), the measured ion ratios are similar for the range of ionization intensities studied. The tunneling calculation was performed at a field strength of 1.4 V Å⁻¹ (corresponding to an intensity of \(2.6 \times 10^{15} \text{ W cm}^{-2}\)) to meet the requirements of the WKB approximation for all three molecules: \(W > 1\). The calculated ratios of ionization probabilities are considered to be good throughout the range of laser intensities studied. If the log-log dependence shows that the molecules of interest do not have similar apparent orders (as is shown in Fig. 7), then care must be taken to determine the range over which reported tunneling calculations are valid.
The relative ionization probabilities for a number of other molecules have been predicted using this model and, in general, the agreement between the experimentally measured values and the calculations is found to be good. Published results include molecular series such as: benzene, 1,3,5-hexatriene, cyclohexane, and hexane; benzene, toluene, ethylbenzene, and \( n \)-propylbenzene; \(^{17} \) (reported here) benzene, naphthalene, and anthracene (see also Refs. 16, 17); and several experiments being prepared for submission including: acetylene, ethylene, and ethane; 1,2-, 1,3-, and 1,4-benzenedi; and benzene, biphenyl, diphenylmethane, and diphenylethane.\(^{23} \) Two of the molecules in this list, \( n \)-hexane and \( n \)-propyl benzene, do not yield relative ionization probabilities which agree well with the model. However, these molecules undergo considerable dissociation under the experimental conditions, which is believed to have a tangible effect on the ultimate observable ion signal. Further experiments with shorter pulse duration lasers are underway to more fully investigate the competition between dissociation and ionization modes.

The model should be applicable to all polyatomic molecules. The rules developed thus far for the model’s application can be trivially applied to relatively simple molecules with high structural symmetries. Were this symmetry to be broken by molecular shape, or more importantly by the presence of heteroatoms, determining the optimal tunneling axis would be performed in the same manner as described, but locating the origin for purposes of determining the field suppression would become less certain. One possible solution for locating the axis origin, particularly for the case of diatomics, might be the charge centroid, or possibly the relative electronegativities of the atoms would determine the origin. For large, three-dimensional, nonsymmetric, heteratomic molecules this problem requires further consideration.

CONCLUSIONS

The photoion mass spectra for the molecules benzene, naphthalene, and anthracene as a function of laser intensity upon excitation at 780 nm and 170 fs reveal ionization orders ranging from 8.0 to 8.5. The similarity of slope allows a direct comparison of relative ionization probabilities, \( \sigma_{\text{rel}} \), which scale as 1:20:200, experimentally, for benzene, naphthalene, and anthracene, respectively. To model the ionization process we present a theory that incorporates electronic orbital structure. The structure-based model is utilized for both the tunneling calculations and to derive the modified adiabaticity parameter values. It is based on a one-dimensional potential located within the full electrostatic potential energy surface of the molecular system. The peak value of the electric field of the laser is superimposed as a static field upon the one-dimensional potential to develop a barrier to electron motion. This barrier is used directly in the modified adiabaticity calculation, and to model the rectangular well for the tunneling calculation. The modified adiabaticity parameter produces a consistently lower value than the classical Keldysh adiabaticity parameter: 3.33–1.95 for benzene; 3.10–1.30 for naphthalene; and 3.08–0.47 for anthracene, for the Keldysh and modified adiabaticity parameter values determined at a field strength of 0.75 V \( \text{A}^{-1} \). Although the zero-range Keldysh calculation predicts that all of these molecules are well within the MPI limit, the modified adiabaticity calculation more accurately predicts that all are near the MPI tunneling cross-over, and that anthracene exhibits the greatest propensity for tunnel ionization. This is consistent with the mechanism of ionization as determined by previously observed photoelectron spectra.\(^{16} \) The tunneling calculations reproduced the trends in ionization probability. The calculated relative ionization probabilities are 1:28:195 at 1.4 V \( \text{Å}^{-2} \). A tunneling mechanism may also explain the limited fragmentation observed. Including these structure-based effects in the consideration of radiative coupling to molecular systems demonstrably improves the predictive quality of well-established theories, and leads to the conclusion that a tunnel ionization model accurately describes the radiation-molecule coupling process. Tunnel ionization may occur at much lower electric field strengths for molecules with extended electronic orbitals than for atoms of similar ionization potential.


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