Photoionization/dissociation of alkyl substituted benzene molecules using intense near-infrared radiation

Merrick J. DeWitt, David W. Peters, Robert J. Levis *

Department of Chemistry Wayne State University, Detroit, MI 48202 USA

Received 8 August 1996

Abstract

The photoionization products for benzene, toluene, ethylbenzene and n-propylbenzene are measured using time-of-flight methods upon interaction with 780 nm radiation pulses of duration 170 fs and intensity $10^{13-15.6}$ W cm$^{-2}$. The relative ionization yields scale as 1, 1.2, 1.4, and 0.35 for benzene, toluene, ethylbenzene and n-propylbenzene at maximum laser intensity. Limited dissociation was observed for benzene and toluene at all laser power densities. A significant (> 5%) dissociation/ionization yield was observed for ethylbenzene and n-propylbenzene at the lowest laser power densities. The dissociation increased as 11th order and 9th order processes for ethylbenzene and n-propylbenzene, respectively to a maximum of 70% dissociation/ionization for n-propylbenzene at $3.8 \times 10^{13}$ W cm$^{-2}$. At $3.8 \times 10^{13}$ W cm$^{-2}$ the dissociation yield increases quadratically with alkyl chain length for the series. The observed ionization/dissociation trends are consistent with a model which incorporates both field ionization and energy redistribution concepts.

1. Introduction

The electric fields present during the photoionization and dissociation of molecules using intense (> $10^{13}$ W cm$^{-2}$) laser pulses approach the fields binding valence electrons to nuclei. A detailed theoretical understanding of the interaction of such intense radiation with large molecules is difficult if not impossible due to the fact that lowest order perturbation theory is inapplicable at the field strengths present. Investigations of atomic systems [1,2] indicate that field as well as multiphoton processes become important at laser power densities above $10^{12}$ W cm$^{-2}$. Effects such as Stark shifting [3] and above threshold ionization (ATI) [4] are observed even in the multiphoton regime due to the high electric fields present. Considerably less work has been performed concerning photoionization of diatomic molecules using intense near to mid-IR [5-11] radiation. The understanding of the intense laser-induced processes in polyatomic molecules is in a nascent stage. This laboratory has previously reported the ionization of cyclic aromatic hydrocarbons using near-infrared photoionization [12-14] and found that a tunnel ionization model was consistent with the observations. In this report we focus on the internal energy redistribution during photoionization using near infrared radiation. The photoionization yields and dissociation patterns for a series of alkyl-substituted benzene molecules are reported as a function of laser intensity at 780 nm.

In the infrared photoionization of polyatomic molecules there are two interesting questions which

* Corresponding author.
1 Camille Dreyfus Teacher–Scholar and Alfred P. Sloan Fellow.
arise. These can be broken into two broad categories: i, how is energy deposited into the molecule; and ii, how is this energy redistributed during/after the energy deposition? At the relatively low field conditions present in most laser ionization schemes the non-resonant excitation of molecules is dominated by linear and lower-order nonlinear processes. Under high field conditions the effects of higher-order nonlinear processes become increasingly important, and must be considered in a more complete understanding of energy deposition. Intrinsic properties of the molecule fundamentally effect the higher-order processes that dominate the interaction with intense fields. Molecular properties such as ionization potential and polarizability may also be at the heart of understanding the way in which energy is redistributed within the molecule upon excitation. The density of states should also affect the redistribution of energy within the molecule and should be important in the dissociation of polyatomic molecules.

Current investigations of the interaction of molecules with intense radiation pulses focus primarily on the processes of dissociation, ionization, multiple ionization leading to Coulombic explosion and alignment in the field of the laser. Investigations of ionization and dissociation using 10 μm radiation have focused on measurement of the ion yield as a function of laser power density. At this wavelength molecules including: \( \text{H}_2 \) [5], \( \text{N}_2 \) [5], \( \text{O}_2 \) [5], CO [5], HCl [7], NO [5], CO\(_2\) [5] and I\(_2\) [6] ionize in a manner consistent with tunneling. The bulk of the investigations at wavelengths less than 1 μm have focused on multiple ionization with corresponding Coulomb explosion. A number of molecular systems have been investigated at shorter wavelength, including: \( \text{H}_2 \) [15], \( \text{D}_2 \) [15], \( \text{O}_2 \) [16,17], Cl\(_2\) [18], I\(_2\) [19], CO [17,20], N\(_2\) [17,20–23], CO\(_2\) [24], C\(_2\)H\(_2\) [22,25], C\(_2\)H\(_4\) [22], C\(_3\)H\(_4\) [26] and C\(_3\)H\(_8\) [26]. These studies indicate a common excitation mechanism using laser intensities greater than 10\(^{15}\) W cm\(^{-2}\). In this mechanism the molecules begin to align with the high electric field, then lengthen under the perturbation [26]. At some elongated bond distance correlating to the electric field strength, the molecules ionize rapidly [27]. This sequence of events leads to Coulombic explosion aligned along the laser E field with kinetic energies substantially lower than that expected for prompt ionization/dissociation at the equilibrium bond distance [28]. In addition to the phenomena described above, Zavriyev, et al., have observed the processes of bond softening, above threshold dissociation and above threshold ionization when H\(_2\) and D\(_2\) were exposed to intense laser fields of nanosecond duration [15].

With increasing molecular complexity (> H\(_2\)) exact quantum theoretical investigations of the interaction of molecules with the intense electric fields associated with ultrafast lasers becomes less tractable [29,30]. For more complex systems classical and semiclassical methods have been employed to investigate the molecule–radiation interaction [27,30]. Reasonable agreement is obtained between the Coulomb explosion data and simple tunneling models for 10 μm excitation. The tunneling model has also been applied to the ionization of diatomic and small polyatomic molecules. Ilkovic and coworkers [5] demonstrated that the tunneling model developed by Ammosov, Delone and Krainov [28] fit the data for relative ionization yield as a function of laser intensity for CO\(_2\) laser excitation of H\(_2\), N\(_2\), CO, CO\(_2\) and NO. This implies that under such conditions the excitation potential exclusively determines the ionization physics. However, as molecules become larger and laser frequencies become shorter it is not clear that simple tunneling models [31] will suffice. For instance, Dietrich, et al. [6] have noted that both the polarizability and Stark shifts are larger in molecules than in atoms because the electronic motion is allowed to traverse distances on the order of molecular orbitals. Thus at wavelengths shorter than 10 μm, where tunneling would not play the dominant role for atomic systems, molecular properties may still allow a classical model to adequately describe the ionization process.

This contribution focuses on understanding the interaction of intense, near-infrared pulses with benzene and various alkane derivatives of benzene. The benzene derivatives offer an interesting test for theoretical models. We have chosen a series of molecules where the trends in size, ionization potential and polarizability change smoothly as the number of atoms increases. This paper focuses on the role of such molecular properties in ionization using high intensity short pulse lasers. The remainder of the paper is organized as follows: In Section 2 the femtosecond laser and time-of-flight apparatus are
described. In Section 3 the relative photoionization cross sections are measured for the molecules benzene, toluene, ethylbenzene and n-propylbenzene. The degree of dissociation of the ionized species is also measured as a function of the ionization laser power using time-of-flight mass spectrometry. In Section 4 the relative ionization cross section, \( \sigma_{\text{rel},780} \), for the molecules are interpreted in terms of ionization potential and polarizability and energy transfer arguments. This model is supported by the analysis of the photodissociation rate for the molecular ions as a function of laser pulse energy.

2. Experimental

2.1. Femtosecond laser

The regeneratively amplified femtosecond laser system used in this study was based upon the design of Squier, et al. [32]. To produce the seed pulse for the system a Coherent Mira Ti:Sapphire laser was employed. This laser was pumped with a Coherent Innova 310 Argon-Ion laser in multiline visible mode at a power of 8 W. The oscillator repetition rate was approximately 76 MHz with an average power output of 800 mW (at 150 fs) indicating a per pulse energy of 10 nJ. The temporal pulse width of the oscillator was determined by a free-running autocorrelator based on the design of Yasa and Amer [33].

Pulse amplification was accomplished in an unstable resonator cavity with a Ti:Sapphire gain medium. The cavity was pumped by 532 nm nanosecond pulses produced via second harmonic generation of a Nd:YAG pulsed laser operating at 10 Hz. Typical pump energies were \( \equiv 40 \text{ mJ} \) per pulse. Losses in the isolation optics and pulse stretcher resulted in typical energies for the injected seed pulse of 2–3 nJ. Typical gain coefficients in the cavity reached \( 10^6 \), resulting in regenerated pulse intensities of 1–2 mJ. Further losses occurred during pulse compression.

This laser delivered pulse energies of 500 \( \mu \text{J} \) and autocorrelated temporal pulse widths (FWHM) of 170 femtoseconds. When focused to 50 \( \mu \text{m} \) diameter in the time-of-flight chamber a maximum intensity of \( 3.8 \times 10^{13} \text{ W cm}^{-2} \) was attained. This pulse intensity corresponds to an electric field strength of 1.69 V Å\(^{-1}\). Shot-to-shot stability was within 5%. The amplified pulse width was determined by a single-shot autocorrelator based on the design of Salin et al. [34].

2.2. Time-of-flight mass spectrometer

A schematic of the mass spectrometer used in this investigation is shown in Fig. 1. This system employed a dual-slope extraction region to enhance mass resolution. Positive ions were extracted through an 800 V potential into a 12 cm field-free region. The detector consisted of a chevron-stacked dual microchannel plate assembly, and signals were averaged and stored on a LeCroy 7200 A digital oscilloscope. Data were downloaded to a PC for long term data storage and analysis. A similar system was described in greater detail in an earlier publication [35]. The desired molecule was introduced to the ionization region via a pulsed nozzle which was not directly coupled to the ionization region of the spectrometer so that static, thermalized, room-temperature gas was the state of all of the analytes in the experiment. Gas pressures were maintained between \( 6 \times 10^{-6} \) torr and \( 1 \times 10^{-5} \) torr for all experiments.

3. Results

The principal experimental observable in this investigation is the time-of-flight mass spectrum resulting from interaction of the intense near-infrared radiation with a given analyte molecule. A comparison of the time-of-flight mass spectra for positive ions produced during 780 nm photoionization of benzene, toluene, ethylbenzene and n-propylbenzene using the

![Fig. 1. Schematic representation of the time-of-flight mass spectrometer used in the study. The length of the field-free region is approximately 12 cm.](image-url)
highest laser intensity, $3.8 \times 10^{13}$ W cm$^{-2}$, is shown in Fig. 2. For the case of benzene, 2a, the major component in the spectrum is the intact radical cation. The same is true for toluene, as shown in Fig. 2b. The resulting mass spectra for ethylbenzene, 2c, and n-propylbenzene, 2d, display significantly more dissociation/ionization as detailed subsequently.

To elucidate the mechanisms of ionization and dissociation, mass spectra were recorded as a function of laser intensity. For the molecules benzene and toluene, essentially no change in the dissociation pattern was observed. For the case of benzene at $3.8 \times 10^{13}$ W cm$^{-2}$ trace dissociation was observed at: $m/e = 40$, corresponding to C$_2$H$_4^+$; $m/e = 51$, 52 and 53, corresponding to C$_4$H$_8^+$ ($x = 3$–5); and $m/e = 64$, C$_5$H$_6^+$. At lower laser intensities no fragmentation was observed. There was no evidence for multiple charging in the spectra. For the case of toluene limited dissociation was also observed and the results were quite similar to those of benzene, with the addition of a C$_2$H$_4^+$ peak at $m/e = 26$ and C$_3$H$_5^+$ and C$_5$H$_7^+$ peaks at $m/e = 63$ and $m/e = 65$, respectively. In addition, there was also a shift of the C$_4$H$_8^+$ peaks observed for benzene to a single C$_4$H$_7^+$ peak at $m/e = 50$ for toluene. As with benzene, fragmentation was eliminated at lower laser intensities.

Ethylbenzene and n-propylbenzene mass spectra are plotted as a function of laser intensity in Figs. 3 and 4, respectively. There are two marked differences in comparison to benzene and toluene. The first difference was that even at the threshold ionization power for detecting ion signal, there was still a noticeable dissociation yield. The lowest power ethylbenzene spectra contained a fragment peak at $m/e = 91$, corresponding to C$_2$H$_7^+$ (removal of CH$_3$). This peak made only a minor contribution to the total ion yield. The second difference was that excitation using the highest laser powers led to numerous additional dissociation channels. For instance, ethylbenzene displayed ion masses ranging from H$^+$ and C$_1$H$_7^+$ to C$_6$H$_{10}^+$ and all carbon numbers in between at the highest laser powers. However, at the highest laser powers employed the integrated ion
signal for ethylbenzene fragments did not exceed the parent ion signal. In the case of n-propylbenzene, the integrated fragment ion signal was greater than that for the parent ion signal at the highest laser powers.

4. Discussion

Observation of parent molecular ions produced by near-infrared photoionization of large polyatomic molecules is intriguing. This phenomenon was first described by this group in earlier papers [12–14], and is interesting because infrared lasers have primarily been used to induce multiphoton dissociation in polyatomic systems. The unexpected observation of intact molecular ions indicates the poor understanding of the photophysical processes occurring in large molecules subjected to extremely intense laser fields. The understanding of the photoionization/dissociation of molecules subjected to these intense field, short duration conditions is the subject of this investigation.

4.1. Ionization mechanisms using intense near-infrared pulses

Under the conditions of relatively low field strengths, photoionization of atoms and molecules is predominantly driven by multiphoton absorption processes. In multiphoton ionization experiments measurement of ion yield with respect to laser power will indicate one of two possible excitation mechanisms for ion production: non-resonant or resonance-enhanced multiphoton ionization [36]. In the most general case of non-resonant photoionization a plot of the logarithm of the ion yield versus the logarithm of laser power will give a line whose slope is equal to the smallest integer number of photons whose total energy is sufficient to remove an electron from the atom or molecule. Because of the relatively low cross section for absorption of a non-resonant photon, typically on the order of \(10^{-24n}\) cm\(^2\), where \(n\) is the number of photons absorbed, this technique is ordinarily operative only for molecules requiring few photons (2–3) to exceed the

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Benzene</th>
<th>Toluene</th>
<th>Ethylbenzene</th>
<th>n-Propylbenzene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionization potential (eV)</td>
<td>9.24</td>
<td>8.82</td>
<td>8.77</td>
<td>8.72</td>
</tr>
<tr>
<td>Apparent ionization order, total ion yield (\times h\nu)</td>
<td>8.1 [12.9]</td>
<td>8.8 [14.0]</td>
<td>8.2 [13.0]</td>
<td>7.2 [11.4]</td>
</tr>
<tr>
<td>Apparent ionization order, parent ion (\times h\nu)</td>
<td>8.1 [12.9]</td>
<td>8.6 [13.7]</td>
<td>7.3 [11.6]</td>
<td>5.8 [9.2]</td>
</tr>
<tr>
<td>Apparent ionization order, all fragments (\times h\nu)</td>
<td>N/A</td>
<td>9.5 (^a) [15.0]</td>
<td>11.1 [17.6]</td>
<td>8.7 [13.8]</td>
</tr>
<tr>
<td>Relative ionization cross-section, total ion yield (^b)</td>
<td>1</td>
<td>1.4</td>
<td>2.4</td>
<td>0.35</td>
</tr>
<tr>
<td>Relative ionization cross-section, parent ion yield (^b)</td>
<td>1</td>
<td>1.3</td>
<td>1.4</td>
<td>0.11</td>
</tr>
<tr>
<td>Relative ionization cross-section, fragment ion yield (^b)</td>
<td>N/A</td>
<td>0.07</td>
<td>0.94</td>
<td>0.24</td>
</tr>
<tr>
<td>Average electric dipole polarizability (Å(^3))</td>
<td>10.5</td>
<td>12.3</td>
<td>14.2</td>
<td>17.8</td>
</tr>
</tbody>
</table>

\(^a\) Based on limited fragmentation data

\(^b\) All cross-sections are reported for the highest laser fluence: \(3.8 \times 10^{13}\) W cm\(^2\)
ionization potential, i.e., with visible or UV energy sources. In the case where a long-lived intermediate state of the molecule can be accessed by one or more photons (i.e., a symmetry-allowed resonant transition), the slope will be equal to the number of photons required to reach that intermediate state [36]. This apparent order of ionization in the resonance-enhanced scheme indicates the rate limiting step in the overall chemical reaction being measured: the population of the intermediate excited state. At higher field strengths the contributions of non-linear terms increase, and with them the importance of both off-resonance interactions and field-induced resonances. The off-resonance interactions include multiphoton effects and dressed-state interactions. It has been shown that at the field strengths present in these experiments Stark shifting can produce energy level shifts on the order of an electron volt or more [37]. Stark shifting on this scale can easily bring even widely spaced energy levels to within the quantum energy of the field. The relative contributions of each of these effects is difficult to gauge, but it is safe to say that all make significant contributions to the overall excitation event which leads to ionization/dissociation at high laser intensity.

The four molecules in this study: benzene; toluene; ethylbenzene; and n-propylbenzene, all have an energetic requirement of six photons (1.59 eV per photon) to reach or exceed their respective ionization potentials as listed in Table 1. The logarithm of the total integrated ion yield for all ions is plotted as a function of the logarithm of laser intensity as shown in Fig. 5. In the case of benzene, the apparent ionization order is 8.1. This value is more than two photons above the energetic requirement for ionization. Toluene and ethylbenzene have apparent ionization orders of 8.8 and 8.2, respectively, again showing an excess of more than two photons in the apparent ionization energetics. For n-propylbenzene we see similar behavior with an apparent order of ionization of 7.2 (the apparent orders of ionization are also collected in Table 1). This is in excess of the six photon order expected for non-resonant ionization, but this time by approximately one photon, suggesting that the excitation/ionization process of n-propylbenzene is somewhat dissimilar to the other molecules in the study. All of the apparent orders observed are consistent with multiphoton ionization of the molecule without population of an intermediate state.

For each of the molecules represented in Fig. 5 the apparent order indicates that one or more photons are absorbed in excess of the energetic requirement for ion production. Absorption of additional photons is not consistent with a simple MPI mechanism because one would expect that the lowest order process leading to ionization, e.g., 6th order for all molecules, would have the highest probability. One explanation for the excess photon order might be contributions of ATI to the apparent orders [4]. In studies of the high-field ionization of atoms, measurements of photoelectron energies in these experiments indicated the absorption by the atoms of quanta in excess of the energetic requirement for ionization before electron loss. The number of photons absorbed in excess of the energetic requirement for ionization, S, was shown to be an increasing function of the laser power. The ATI mechanism might be employed to explain the aberrantly high orders, but several arguments against this interpretation may be made. First, the linearity of the data suggests that the average number of photons involved in the ionization process is the same at all laser powers employed. If ATI were making significant contributions to the overall effect one would expect a moderate increase in slope with laser power. Second, the dis-

![Graph showing the logarithm of the integrated total ion yield as a function of the logarithm of ionizing laser power using 780 nm light, 170 fs duration for (a) benzene, (b) toluene, (c) ethylbenzene and (d) n-propylbenzene.](image-url)
sociation data, at least for benzene and toluene, suggest that there are not a significant number of excess photons being absorbed by the molecule. For benzene's apparent order of 8.1 (indicating that \( S = 2.1 \)) to be explained by ATI effects, one would expect weighted contributions of \( S = 1, 2, 3, 4 \), and possibly higher order ATI channels, with \( S = 2 \) being the most probable, leading to the observed average. Since dissociation is essentially absent from the mass spectra, absorption of three or more photons of excess energy (4.77 eV or more above IP) into the molecule is almost certainly ruled out, assuming that all of the excess energy is not imparted to the photoelectron. Finally, if ATI were an important contributor to the ionization process, one might expect the ATI contributions to increase successively in the series as molecular complexity increased. This argument is based on the expectation that state densities at a given energy increase in the series, and therefore cross-sections for photon absorption in the high energy regime of the molecular manifold (near and above the IP) should increase accordingly, in turn increasing the probability for ATI events. In fact, there is no obvious trend in apparent ionization order.

Since detailed calculations of multiphoton absorption by large polyatomic molecules in high electric fields at high order perturbation theory are not tractable at this time, it is advantageous to explore the correlation between the intrinsic properties of the systems in question and the experimental observations. The most obvious intrinsic property of any system which affects its ability to ionize is the ionization potential (IP) itself. As the IP of an atom decreases, the total number of quanta, \( n \), required for the highest lying electron to reach the continuum is also decreased. The total cross-section for non-resonant ionization is the product of \( n \) successive one photon absorption cross-sections, wherein the highest lying electron is concertedly promoted via subsequent one photon absorptions from the ground state to the continuum. Since the cross-section for absorption of any single non-resonant photon is essentially the same for all of the intermediate absorptions, the total absorption cross-section is then found to be well approximated by the one photon absorption cross-section raised to the power \( n \). Absorption cross-sections are always less than unity (in atomic units), so that it can be unequivocally stated that for any given \( m \text{th} \) order cross-section the \((m + 1)\text{th} \) order cross-section is lower (more specifically, \( \sigma_{m+1} = \sigma \cdot \sigma_m \)). The ionization probability is given by:

\[ P_I = \sigma_{total} I^n \]

where \( \sigma_{total} \) is the total \((n\text{-th order}) \) ionization cross-section and \( I \) is the laser intensity. From this it is easily shown that, for fixed laser intensity and photon energy, the relative ionization probability (via non-resonant photon absorption) monotonically decreases with increasing ionization potential. More specifically:

\[ P_I = (\sigma I)^{IP/\hbar \omega} \]

where \( \sigma \) is the cross-section for single photon absorption and \( IP/\hbar \omega \) is an expression for \( n \). This relationship is valid in the regime of low laser intensity (\( \sigma I \ll 1 \)), and is valid even for non-integer values of \( IP/\hbar \omega \) because of the intensity gradient within the focused laser pulse. When the product of the laser intensity and the single photon absorption cross-section approaches or exceeds 1 the total ionization probability is greater than 1, resulting in an unphysical condition. This condition represents one example of a breakdown of lowest order perturbation theory. Simple perturbation theory treats the externally applied field as a small perturbation to the molecular Hamiltonian. In high field conditions, the perturbation is on the same order of magnitude as the molecular fields, and the unperturbed molecular Hamiltonian no longer provides a good approximation to the system. Even within the limit of low laser intensity the inverse proportionality between IP and ionization probability implied in Eq. 3 is greatly complicated for molecules by the existence of non-electronic (vibrational and rotational) modes for the deposition of energy. In fact, in large polyatomic molecules the number of ways in which photon energy can be redistributed into vibrational and rotational degrees of freedom is so massive that many have been led to conclude that the ionization of large molecules cannot be accomplished using nanosecond excitation [40].

To determine whether the ionization probabilities correlate with any molecular properties we first examine the relationship between relative ionization probability and the molecular ionization potential.
The relative ionization probability at a given laser power can be obtained directly from Fig. 5. At the highest laser intensities studied, the relative number of ions produced at any given laser intensity increased through the series benzene, toluene, ethylbenzene. The relative ionization yield for n-propylbenzene is marked by a significant decrease with respect to that of the other molecules. Fig. 6 displays a plot of the relative ionization probability of the molecules with respect to IP. While the ionization probability increases with decreasing IP for the series benzene, toluene and ethylbenzene, the failure of n-propylbenzene to follow this trend demonstrates that IP is not the dominant predictor for ionization probability. In fact, since n-propylbenzene has the lowest IP we expect this molecule to have the highest ionization probability based on the trend established by the other three molecules. However, n-propylbenzene has the lowest ionization probability, suggesting that other properties contribute to the observed relative ionization probability.

Molecular polarizability is another important factor in light/matter interaction. The molecular polarizability describes how a molecule reacts to the presence of an external electric field and is the second order term in the series expansion describing light/matter interaction. The average electric dipole polarizabilities of the molecules investigated are shown in Table 1. The relative total ion yield with respect to molecular polarizability is shown in Fig. 7. The total ion yield increases monotonically with polarizability for benzene, toluene, and ethylbenzene, but again, n-propylbenzene is not in agreement with the trend. This suggests that, while polarizability may be an important factor in predicting molecular photoionization probability under intense field conditions, that another important factor contributes to the observed n-propylbenzene ionization probability. Note that systems with limited dissociation channels have a reasonable correlation between ionization potential/polarizability and ionization probability [38,39].

4.2. Dissociation mechanisms using intense near-infrared pulses

During and immediately following the photoexcitation event, the energy that has been deposited into the molecule by the field can develop along several competing pathways leading to: electron ejection, nuclear (vibrational) excitation, and/or dissociation. The degree of dissociation observed in this study ranges from essentially none for benzene to approximately 70% for n-propylbenzene under the most intense laser conditions. We approach the dissociation process from the point of view of energy redistribution within the molecule. As shown in Fig. 8, a molecule, M, which has been electronically excited
to a state \( M^+ \) above the ionization potential (preionization state) may proceed along two pathways: ion formation to \( M^+ \), or dissociation to \( m^+ + m \). Since all channels other than the ion channel are dark to our detection method, all inferences must be drawn from ion observation. Species entering the dark channel, \( m^+ + m \), may re-enter the ion channel, \( m^+ \), via \( m^+ \rightarrow m^+ \), but once a moiety has entered the ion channel it must remain there intact or fragment to produce another species in the ion channel. Multiple ion formation from a single excited molecule is expected to be rare because of energetic considerations, so that while several fragments may be produced from a single excited molecule it is assumed no more than one of these carries a positive charge.

The ionization/dissociation yields observed in this study can be grouped into two classes. The first class, including benzene and toluene, exhibits essentially only molecular ionization. For the simplest molecule in the series, benzene, the TOF spectra exhibit little or no dissociation. This observation suggests that electron evaporation sufficiently cools the molecule so that subsequent dissociation is quenched. Another possibility for the lack of dissociation could be that the ion extraction time is short compared to the dissociation time, although experimental measurements suggest that this is not the case. Toluene also exhibits limited fragmentation.

The second group of molecules exhibits molecular ionization as well as substantial ionization/dissociation. The dissociation yield is much more pronounced for ethylbenzene and \( n \)-propylbenzene even at the lowest laser powers. The mechanism for such enhanced dissociation/ionization may involve increased energy deposition and/or redistribution rates in the longer alkane derivatives as discussed subsequently. Note that the mass resolution of the fragment peaks seen in Fig. 3 and Fig. 4 is similar to that for the parent peak. This indicates that there is an absence of Coulombic explosion during the dissociation process. This also indicates that both fragment and parent ions are produced very rapidly with respect to the ion extraction event, so that evolution to final products in the scheme depicted in Fig. 8 is complete prior to ion extraction.

The photophysics of laser-induced ionization/dissociation of molecules has been discussed previously for the case of nanosecond excitation [41–43]. Essentially, there is a competition between two dominant processes: absorption and ionization followed by dissociation; and absorption and dissociation followed by ionization. To be specific about the photophysical pathways we identify four rate constants in the scheme shown in Fig. 8: \( k_i \), the rate of molecular ion production; \( k_d \), the rate of dissociation of the parent molecules; \( k_{id} \), the rate of dissociation of the parent molecular ion; and \( k_{di} \), the rate of ion production from an excited neutral fragment. We assume that \( k_i \) is roughly constant or increasing for the four molecules in the series benzene, toluene, ethylbenzene and \( n \)-propylbenzene at a given laser intensity. This approximation is appropriate in the tunneling [31] model since \( k_i \) is determined by the laser frequency, electric field strength and the ionization potential. Increasing amounts of dissociation must then be attributed either to increasing values of \( k_d \) and \( k_{di} \) in the series, or to increasing amounts of excess energy in the parent ion, which would increase the ionization-dissociation channel. For toluene and ethylbenzene, either the ionization-dissociation or the dissociation-ionization channel (and possibly both) are operative. Ethylbenzene has both a higher total ion yield and a higher dissociation yield than does toluene. For \( n \)-propylbenzene the dissociation yield again increases with respect to the total ion yield, but the total ion yield itself drops significantly.
below that observed for the other molecules. The decrease in the \( n \)-propylbenzene ionization probability strongly suggests a marked increase in dark channel flux (pure dissociation) which is only accessible via the dissociation channel.

Earlier studies of the ionization/dissociation of molecules by impulsive excitation, including single-photon absorption in the far UV and collisions with electrons and noble gases, have shown that the evolution to ions and fragments is fairly independent of the excitation event [44]. In all cases, the ratios of the rates for ion and neutral fragment formation were constant for a given molecule excited to a given energy above the ionization threshold, regardless of excitation mechanism. One conclusion of such studies was that direct ionization (instantaneous removal of an electron upon excitation) was rare, and that the ionization and dissociation proceeded through a state such as \( M^* \) shown in Fig. 8. The ionization efficiency was therefore directly related to \( k_i \) and \( k_d \) by:

\[
\eta = P_{ss} \left[ \frac{k_i}{k_i + k_d} \right]
\]

where \( \eta \) is the ionization efficiency and \( P_{ss} \) is the probability that a system was excited to \( M^* \), the preionization state of the neutral molecule. In general, rates of dissociation were found to be on the order of the rates for ionization, significantly lowering the ionization efficiency and making molecular ionization less efficient, particularly for large molecules with high dissociation rates. It was also shown that ionization efficiency (but not necessarily total ion yield) for a given molecule tended to decrease with excitation energy, possibly indicating that dissociation rates increase with excitation energy faster than the corresponding ionization rates.

Our data shows reduced fragmentation yield for the femtosecond ionization experiment in comparison with non-resonant nanosecond experiments. It is not immediately obvious why this should be the case. The two significant differences between the femtosecond and nanosecond experiments are the pulse duration and the electric field strength of the pulses. Typical photoexcitation schemes involving the simultaneous absorption of several photons to a preionizing state would be expected to produce results similar to those for other types of impulsive excitation on the ultrafast scale (e.g., an electron with 30 eV relative translational energy and an interaction range of \( \sim 10 \) Å produces a collision time scale on the order of 1 fs). Such excitation has already been shown to produce molecular dissociation rates on the order of ionization rates. The only explanation for the marked decrease in fragmentation observed in this study, then, seems to be in an effective increase in ionization rate with respect to the dissociation rate. What effect the high field strengths might have upon the ultimate dissociation rates, if at all, is unclear, though the net result is expected to be destabilizing rather than stabilizing [27]. The high field strengths could well serve to increase the rate of crossing from a preionizing state to the ion state. A direct field ionization mechanism [31] (i.e., tunneling or barrier suppression ionization) may also account for the increased ionization rates. Any ionization events which are mediated by the presence of the laser field must have rates commensurate with the excitation pulse width (i.e., \( \sim 1/\tau \) pulse) in order for appreciable ionization to occur. In this case, ionization timescales would be determined by the laser pulse width rather than the molecule itself, thus establishing a lower limit for \( k_i \) in this series of molecules. Multiphoton IR pumping experiments have shown that IVR rates for vibrational energy transfer can be as high as \( 10^{12} \) s\(^{-1}\) [45]. At excited state energies sufficient to produce ionization, the rate of vibrational energy transfer will be even higher, requiring ionization rates greater than \( 10^{12} \) s\(^{-1}\) for significant molecular ionization to be observed. This suggests that observation of intact molecular ions for complex polyatomic molecules may require femtosecond duration pulses.

The dominant dissociation-ionization peak for \( n \)-propylbenzene corresponds to \( C_7H_7^+ \) (see Fig. 2), just as in the ethylbenzene spectra. The \( C_8H_8^+ \) (\( x = 9,10 \)) peak is almost undetectable, even though the surrounding \( C_7H_7^+ \) and parent \( C_9H_{12}^+ \) peaks are the most prominent ion signals in the spectra. These phenomena are almost certainly indications of the relative stability of the aromatic bonds in the ring as compared to the aliphatic bonds in the alkyl chain.

Another interesting question regarding the mechanism of dissociation of \( n \)-propylbenzene concerns the large fraction of molecules that dissociate during the
ionization event. As the number of atoms, \( N \), increases from 12 (benzene) to 21 (n-propylbenzene), the number of internal modes increases as well as the density of states. This higher density of states should lead to higher rates of internal energy redistribution, in accord with standard radiationless relaxation theories [46]. In addition, there are more modes to store energy as \( N \) increases. Thus, assuming equivalent excitation energies, we would actually expect less dissociation/ionization in the case of n-propylbenzene, not more. However, we observe more dissociation in n-propylbenzene. We are left to conclude that the rate of energy deposition increases throughout the series from benzene to n-propylbenzene in agreement with the initial trend shown in Fig. 6 and Fig. 7. The drop in ionization probability for n-propylbenzene is then attributed to an increase in \( k_d \) which can lead to dark channels for mass spectroscopic detection. A plot of the ratio of total fragment ion yield to parent ion yield with respect to \( N \) is shown in Fig. 9. The fragment/parent ion ratio is equivalent to or less than the \( k_d/k_i \) ratio under conditions in which the ionization-dissociation channel is closed. From benzene through n-propylbenzene the fragment yield to total ion yield ratios are: 0; 0.05; 0.39; and 0.69. Simple TOF data cannot determine whether the dissociation-ionization or ionization-dissociation channel gives rise to the observed fragment ions. The measurements suggest however, that \( k_d \) is relatively large for n-propylbenzene and increases as the length of the chain increases.

The plot of the logarithm of fragment ion yield as a function of the logarithm of laser intensity (Fig. 10) shows linear response for ethylbenzene and n-propylbenzene. Toluene dissociation is essentially reduced to the noise level within a few percent of the maximum laser intensity, and little can be said for this trend. The apparent order for the ionization/dissociation process for ethylbenzene (11.1) and n-propylbenzene (8.7) is higher than the parent or total ion orders, and this is to be expected if dissociation is to decrease with laser intensity. This trend would also be expected for resonant nanosecond lasers in the multiphoton ionization regime, but the expectations for the non-resonant case are not at all obvious. The simplest interpretation of this result by MPI arguments would be that ionization and subsequent dissociation (or vice-versa) requires more energy than either simple dissociation (whose products are not observed in the TOF device) or parent ionization.
5. Conclusion

The process of ionization under the conditions of regeneratively-amplified, ultrafast laser sources have previously focused on atomic and simple molecular systems. The tunneling model previously developed by Ammosov, Delone, and Krainov [28] has been shown to accurately predict ionization yield for small systems [5]. The observed results for complex polyatomic molecules are, however, quite different than predictions of the simple ADK model. This is because of the many degrees of freedom for energy deposition, redistribution, and disposal available in polyatomic systems, specifically vibrational and dissociation modes. These pathways for energy redistribution, are available on the subpicosecond timescale for complex molecules. Such modes are not available in atomic systems and are only poorly coupled to electronic degrees of freedom in simple diatomic systems.

A complete understanding of the behavior of complex molecules subjected to these intense fields is not possible at this time. We can, however, in light of the observations made in this study, begin to describe some predictors for the eventual outcome of such events. In these highly non-linear conditions, where both energy deposition and energy redistribution can be accomplished by several mechanisms, simple scalar properties like IP offer little predictive value. Properties which describe the way in which matter itself is effected by light, i.e., molecular polarizability and susceptibility, may be of additional value for predicting ionization probabilities. In addition, we observe that for more complex systems the ionization yield will be determined by the competition between ionization and dissociation pathways.

One of the most potentially useful outcomes of this experiment is the universality of ultrafast ionization. The data obtained with the 170 femtosecond pulse employed in this experiment suggest that, with a sufficiently brief excitation pulse, the non-destructive ionization of a number of complex molecular species may be tractable with a single (and possibly arbitrary) wavelength. However, for polyatomic molecules dissociation channels can open and become the dominant product channels even when employing pulses of duration 170 fs. The exact temporal width below which non-destructive ionization is assured has not been determined. Further studies are needed to more clearly understand this phenomenon.

Acknowledgements

The support of the National Science Foundation, the Sloan Foundation and the Dreyfus Foundation is gratefully acknowledged.

References