Observing the Transition from a Multiphoton-Dominated to a Field-Mediated Ionization Process for Polyatomic Molecules in Intense Laser Fields

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(Received 17 March 1998)

The photoelectron spectra for benzene, naphthalene, and anthracene ionized using a 780 nm, 170 fs laser pulse of intensity 3.8×10^{13} W cm^{-2} reveal a decrease in the discrete features associated with above threshold ionization with increasing molecular size. A corresponding exponential increase in the intensity of a broad featureless distribution indicates that field ionization dominates the coupling mechanism for the larger molecules. A coupling model based on a zero-range potential predicts that only multiphoton ionization should occur. This model, incorporating both the ionization potential and electronic delocalization of the molecule, correctly predicts the observed transition. [S0031-9007(98)07853-3]

The interaction of intense lasers with atomic and molecular systems is of continuing interest because the highly nonlinear coupling has led to new phenomena such as x-ray generation from high harmonics [1], above threshold ionization (ATI) [2], above threshold dissociation [3], multiple ionization [4], and molecular ionization using near-infrared laser pulses [5,6]. In 1964, Keldysh suggested that at high intensity the electric field of a laser may permit field ionization to compete with the multiphoton ionization (MPI) process [7]. Keldysh's theoretical treatment of intense laser-atom interactions has since been confirmed in numerous theoretical [8–10] and experimental investigations [11]. In these treatments a zero-range potential has been employed to approximate the atom-radiation interaction. To determine whether field or MPI processes dominate, the tunnel frequency is compared to the laser frequency to yield an adiabaticity parameter γ via

$$\gamma = \frac{\omega_0}{\omega_t} = \frac{\omega_0\sqrt{2\mathrm{IP}m_e}}{eE_0}, \qquad (1)$$

where ω_0 is the laser frequency and ω_t is the tunnel frequency [7], IP is the ionization potential, m_e is the electron mass, e is the electron charge, and E_0 is the amplitude of the electric field. If $\gamma \gg 1$ the MPI process dominates; if $\gamma \ll 1$ field ionization occurs. In these treatments the only atomic (or molecular) parameter that enters the adiabaticity calculation is the ionization potential. In fact, ω_t is dependent upon the wave function of the entire system [12] and may be represented by $\omega_t(\psi)$. For the atomic case $\omega_t(\psi)$ is well approximated by ω_t.

The application of zero-range models to both diatomic [13] and polyatomic systems [12,14] remains ambiguous. The question hinges on the ability of a zero-range potential to adequately describe electronic orbitals that can extend over many angstroms due to molecular bonding. This laboratory has suggested that the Keldysh-like models will not directly transfer to systems with extensive electron delocalization [12] and has proposed that the extent of electron delocalization must be accounted for to

more accurately model the radiation-molecule interaction. This results in a modified adiabaticity parameter that may be represented by $\gamma(\psi)$. Support for the modification to γ has come from measurements of photoionization cross sections for intense, near-infrared laser ionization of polyatomic molecules [5,6,14]. These measurements revealed an exponentially increasing ionization probability with decreasing IP that suggests a field-mediated coupling mechanism. The proposed tunnel ionization occurs, however, in an excitation regime where a multiphoton mechanism is expected from the zero-range Keldysh adiabaticity parameter.

Here we report the use of cyclic aromatic molecules to determine the effect of electron delocalization on the coupling mechanism of an intense radiation field with a polyatomic molecule. We demonstrate that the coupling mechanism can be switched from an MPI to a field-dominated ionization mechanism by altering molecular structure while maintaining a relatively constant zero-range Keldysh adiabaticity parameter. The photoelectron kinetic energy spectra are reported for benzene, naphthalene, and anthracene after interaction with 170 fs, 780 nm radiation at 3.8×10^{13} W cm^{-2}. Photoelectron kinetic energy distributions have been employed in the past to compare the ionization mechanisms for a series of noble gas atoms [11]. For MPI, a series of discrete peaks is observed that have been attributed to above threshold ionization [2], and for field ionization a broad distribution is observed extending beyond the ponderomotive energy of the laser pulse [11,15]. At a laser power density corresponding to 1.7 V Å^{-1}, all three molecules have similar Keldysh adiabaticity parameters ranging from $\gamma = 1.47$ to 1.36, all in the MPI regime. However, the electronic orbital size for the longest molecular dimension varies by approximately a factor of 2 in this series, substantially reducing the modified adiabaticity parameter, $\gamma(\psi)$. For example, at 0.75 V Å^{-1} the adiabaticity parameter for anthracene drops by a factor of 6 from $\gamma = 3.08$ to $\gamma(\psi) = 0.47$. Above 0.78 V Å^{-1} the value of the modified

adiabaticity parameter is zero [12] for anthracene, indicating that barrier suppression ionization will occur for all greater field strengths.

The photoelectron spectra resulting from intense near-infrared excitation were collected using a linear drift tube with μ-metal shielding and a drift length of 29.5 cm. The tube was floated to -3 keV and the electrons were collected and amplified using a dual microchannel plate assembly. The base pressure of the chamber was 3×10^{-7} Torr and the molecules were admitted into the chamber effusively (benzene) or were allowed to sublime directly into vacuum (naphthalene and anthracene). For these measurements the pressures of benzene, naphthalene, and anthracene were 2×10^{-5}, 2×10^{-5}, and 4×10^{-7} Torr, respectively. These pressures were chosen to maintain similar peak photoelectron intensities and to minimize space charge effects. The laser system has been described previously [6], and consisted of a Ti:sapphire oscillator (135 fs, 76 MHz) coupled to a 10 Hz regenerative amplifier. After amplification, the pulse duration and energy at 780 nm were 170 fs and 0.5 mJ, and the photoelectron spectra reported here were acquired by focusing the laser beam to a diameter of 100 μm. The polarization axis of the laser was aligned with the axis of the photoelectron spectrometer tube.

The photoelectron spectrum for benzene at a laser intensity of 3.8×10^{13} W cm^{-2} is shown in Fig. 1(a). There are a series of multiphoton features from 0.3–0.6 eV attributable to ionization from the e_{1g} molecular orbital, and these features remain apparent to the lowest laser intensities employed. Above threshold ionization features are observed from 2.5 to 15 eV and are separated by the photon energy, 1.59 eV. At the highest laser intensity up to eight ATI peaks are observed. A broad electron distribution ranging from 0 to 15 eV is also observable, which we attributed to a field ionization mechanism. Deconvolution reveals that multiphoton and field ionization

represent 43% and 57% of the total electron current, respectively. Measurements of the angular distribution of emitted electrons were obtained by rotating the polarization of the laser beam. A strongly anisotropic distribution peaked along the polarization axis of the laser is attributed to MPI/ATI emission and a moderately anisotropic distribution, also peaked along the polarization axis, is measured for the broad feature. In the latter case, the more isotropic distribution may be due to the fact that, above the threshold for tunnel ionization, electrons have an increasing probability to tunnel through the potential away from the axis of laser polarization. This may be particularly true when the field strength is above the value for barrier suppression ionization [12], as is the case for these molecules.

The photoelectron spectrum for naphthalene measured at 3.8×10^{13} W cm^{-2} is shown in Fig. 1(b). Above threshold ionization features are again observed but are superimposed on a much larger tunnel emission feature. The integrated current at maximum laser intensity corresponding to ATI is approximately 14% of the total current and 86% is attributed to a field ionization mechanism. Again the angular distribution attributed to field ionization is substantially more isotropic than that for the ATI features.

The photoelectron spectrum for anthracene at a laser intensity of 3.8×10^{13} W cm^{-2} is shown in Fig. 1(c). From threshold to maximum laser intensity, there are no discernible features other than the broad distribution. The broad feature simply increases in intensity and shifts to slightly higher kinetic energy (by approximately 0.25 eV) as the laser intensity is increased to maximum power. At no intensity are any discrete peaks attributable to MPI or ATI observed. The photoelectron distribution extends to approximately 20 eV in the case of anthracene. A typical photoelectron spectrum for the background is plotted to scale in Fig. 1(b). Previous mass spectrometric measurements demonstrate that the photocurrent is due
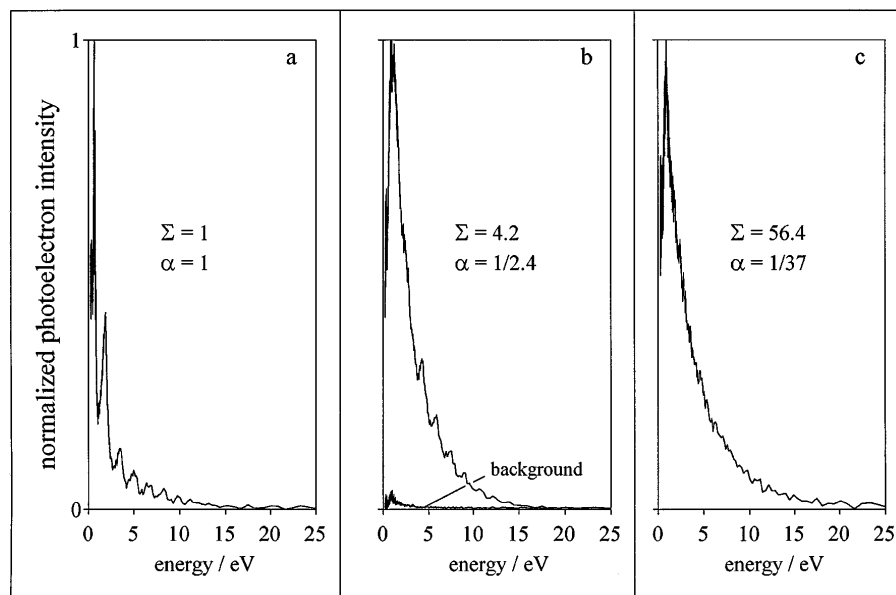

FIG. 1. The photoelectron spectra measured using 3.8×10^{13} W cm^{-2}, 780 nm, 170 fs duration laser pulses for the molecules: (a) benzene (C_6H_6); (b) naphthalene ($C_{10}H_8$); (c) anthracene ($C_{14}H_{10}$). The integrated, pressure-corrected photoelectron currents normalized to benzene are listed as Σ and the pressure-corrected scaling factors for the plots are listed as α. A typical background spectrum is plotted to scale in (b).

to ionization of the molecules in question with virtually no observable signal due to background species (that are easily detected by the ionization gauge). The features in the photoelectron spectra for these molecules remain essentially constant with respect to sample pressure from the minimum detectable pressure up to 10^{-4} Torr.

To model the excitation and ionization process, we employ both *ab initio* calculations [16] and simple one-dimensional quantum models in quasistatic calculations. These calculations can then be compared to the zero-range Keldysh adiabaticity parameters and to the experimental measurements to provide insight into the radiation-molecule coupling mechanism. We employ the one-dimensional electrostatic potential energy surface corresponding to the maximum length between classical turning points as defined by *ab initio* calculations [14]. The molecular structure, *ab initio* potential, and rectangular-well potential in the presence of an external field are shown for benzene in Fig. 2(a). The equivalent representations for naphthalene and anthracene are shown in Figs. 2(b) and 2(c). The one-dimensional rectangular wells are used for calculating $\gamma(\psi)$. The box width of each well corresponds to the longest appropriate electronic dimension [14], and the box height is given by the ionization potential. The rectangular wells have a 1 V Å^{-1} field superimposed to model the quasistatic laser field. The maximum length of the electronic dimension increases from benzene to naphthalene to anthracene, which results in decreasing barrier to tunnel ionization. Thus, the probability for tunneling is predicted to increase in the series benzene, naphthalene, and anthracene. This prediction is consistent with the photoelectron spectra displayed in Fig. 1, in which anthracene displays the most tunneling character. Note that a spectrum displaying a featureless distribution extending above the laser's ponderomotive potential is a hallmark of the field ionization regime [11,15]. There may be alternative mechanisms for the loss of ATI structure in the series such as internal conversion or some field-mediated effects.

The length of the barrier formed by the superposition of the amplitude of the radiation's electric field on the *ab initio* electrostatic potential energy surface allows a calculation of a modified adiabaticity parameter, $\gamma(\psi)$ [12]. A calculation of the modified adiabaticity parameters for an electric field strength of 0.75 eV yields values of 1.95, 1.30, and 0.47 for benzene, naphthalene, and anthracene, respectively. From these values we anticipate the radiation-molecule coupling to range from an MPI-dominated regime for benzene to a field ionization-dominated regime for anthracene, as observed. The zero-range Keldysh adiabaticity parameters γ calculated for benzene, naphthalene, and anthracene are 3.33, 3.18, and 3.08, respectively, at 0.75 V Å^{-1}, indicating a multiphoton coupling mechanism. The adiabaticity parameters for naphthalene and anthracene are markedly reduced when a more realistic potential is employed in agreement with findings for simpler systems [12].

The relative ionization probability can also be predicted using the quasistatic model and WKB theory [17] as has been described previously [12,14]. Briefly, the tunnel rate for a molecule interacting with an intense laser in the field ionization regime w scales as

$$w = \exp\left\{-2 \int_{r_1}^{r_2} 2[\text{IP} - V(r)]^{1/2} \, dr\right\}, \qquad (2)$$

where $V(r)$ 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. The values of r_1 and r_2 bound the shaded region on the rectangular-well potential for each molecule as shown in Fig. 2. The calculated tunnel rates are included in Table I along with the experimental measurements. The photoelectron current emitted along the laser polarization axis was determined by integrating the total electron yields and is shown as Σ in Figs. 1(a)–1(c). The measured yields agree with the predictions from the tunnel model. Mass spectroscopic measurements [5] of ionization probabilities yielded a ratio of 1 : 20 : 200 for
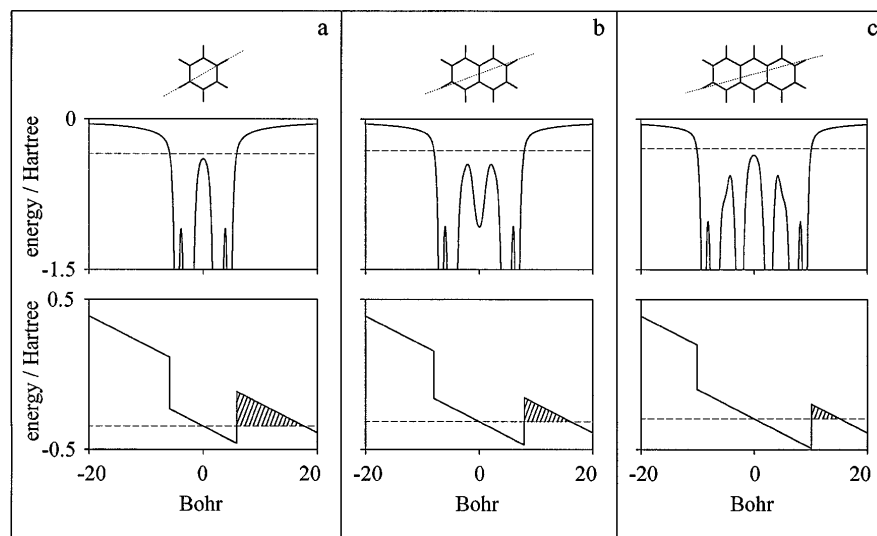

FIG. 2.   The *ab initio* electrostatic potential energy surfaces are shown for the molecules: (a) benzene (C_6H_6); (b) naphthalene ($C_{10}H_8$); (c) anthracene ($C_{14}H_{10}$). The axes of the one-dimensional slices are shown as dotted lines on the molecular structures at the top of each column. The dashed lines denote the ionization potential. The model rectangular-well potentials employed in the adiabaticity calculations are shown at the bottom of each column. Each model potential has a 1 V Å^{-1} electric field superimposed and the barrier for tunnel ionization is hatched.

TABLE I. Properties and measured values for cyclic aromatic hydrocarbons.

	Benzene	Naphthalene	Anthracene
Molecules	C_6H_6	$C_{10}H_8$	$C_{14}H_{10}$
Ionization potential [eV], [18]	9.386	8.575	8.045
% tunneling current	57	86	100
γ [0.75 V Å^{-1}]	3.33	3.18	3.08
$\gamma(\psi)$ [0.75 V Å^{-1}]	1.95	1.30	0.47
Calculated tunnel ionization probability, Eq. (2) [1.4 V Å^{-1}]	1	28	195
Integrated axial photoelectron current	1	4.2	56.4

benzene : naphthalene : anthracene using similar sample pressure and laser conditions. The ion measurements are in better agreement with the model WKB calculations. The minor discrepancy between photoelectron and ion measurements may be due to the spatial distribution of the photoelectrons. As noted previously, measurements of the angular distributions reveal a more isotropic distribution for the tunnel current as compared with a peaked distribution for the MPI/ATI current which is known to be aligned with the electric field of the laser [19]. Thus, the measured Σ must be reported as integrated photoelectron current along the laser polarization axis rather than a relative ionization cross section. There is a substantial difference between the spatial distribution of photoelectrons in benzene, where both tunnel and MPI mechanisms are present, and those of naphthalene and anthracene. Thus, the two molecules having nearly all emission due to tunnel ionization may be systematically lowered in terms of relative ionization probability when measured in our photoelectron spectrometer.

We conclude that a transition from multiphoton to field ionization can be observed in polyatomic molecules by increasing the electronic delocalization via molecular structure. Thus, benzene, naphthalene, and anthracene are observed to couple to the intense radiation field to an increasing degree through a field-mediated mechanism. This is interesting in light of the fact that the Keldysh adiabaticity parameters are similar for the three molecules and remain in the MPI limit for the intensities considered here. While benzene ionizes through both field and multiphoton mechanisms, naphthalene and anthracene have mainly field ionization character. We conclude that electronic orbital shape and size must be accounted for to more accurately predict the radiation-molecule coupling mechanism in polyatomic molecules. The structure-modified adiabaticity parameter $\gamma(\psi)$ was shown to be consistent with the experimental observations.

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