Nonadiabatic dynamics of polyatomic molecules and ions in strong laser fields

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Ionization and/or fragmentation of large organic molecules in strong laser fields can be quantitatively understood as a transition from adiabatic to nonadiabatic dynamics of the electronic degrees of freedom. Measurements of fragmentation patterns demonstrate regular trends as a function of the size and electronic structure of a molecule. A theoretical model is presented that agrees quantitatively with the measurements for a series of polycyclic aromatic molecules.

The combination of intense femtosecond pulses with adaptive control [1] and pulse shaping [2] has allowed breakthroughs in the control of chemical and physical processes in complex systems. Examples range from controlling the generation of high harmonics [3] to selective bond cleavage [4,5] and rearrangement [5] in polyatomic molecules. Despite the remarkable progress in controlling complex chemical systems adequate description of the physics of the excitation process is virtually absent. Here, we present a conceptual model of strong-field excitation of polyatomic molecules that is capable of quantitative predictions. We investigate the model by measuring the fragmentation patterns as a function of laser intensity for a series of related molecules of increasing size (benzene, naphthalene, anthracene, and tetracene).

Understanding physical mechanisms of energy deposition into polyatomic molecules by strong nonresonant laser fields is critical for predicting and controlling fragmentation patterns [4–6], as well as for predicting regimes for intact ionization [7] as opposed to substantial fragmentation and nuclear rearrangement in mass spectrometric experiments. Little understanding has been achieved so far, mainly due to the complexity of real systems. In particular, the role of specific molecular properties in intense field excitation is unknown, but is also essential for predicting photoexcitation pathways as a function of laser intensity, frequency, and pulse duration. The interplay of ionization and fragmentation processes is not understood (and should also depend on specific molecular and laser-pulse properties).

An appealing physical picture of a quasicontinuum (QC) formed from all of the electronic states of a molecule by efficient nonadiabatic electronic transitions was suggested in Ref. [8]. Within this QC, plasmalike classical energy absorption should take place. Here, we develop a theory of nonadiabatic energy deposition that applies the QC concept to the manifold of excited states. The theory is based on the following key elements: (i) a population transfer from the ground state to the QC via a doorway charge-transfer electronic transition, (ii) an exponential enhancement of this transition by collective polarization of all electrons, and (iii) sequential (here—two-stage) nonadiabatic excitation of the neutral molecules and resulting molecular ions. At the first stage, the nonadiabatic excitation of neutral molecules results in ionization, forming relatively cold molecular ions. At the second stage, the nonadiabatic excitation of the ion provides a sufficient amount of energy to break the molecular bonds, resulting in fragmentation. The latter outcome is determined by the details of the ionic energy-level structure.

Although the motion of nuclei ultimately discriminates the outcomes of a laser-molecule interaction, the energy is initially absorbed by electrons. In quasistatic limit, the electronic response of atoms in strong laser fields is adiabatic [9]. However, even for small systems, electron dynamics may become nonadiabatic due to correlation effects [10,11]. In diatomic molecules stretched to large internuclear distances the electron dynamics becomes highly nonadiabatic, affecting ionization, dissociation, and high harmonic generation [12–17]. For larger polyatomic molecules, nonadiabatic electron dynamics should start at lower field intensities, due to increased molecular size and multielectron correlation effects.

To quantitatively test the model, we measured the intensity dependence of ionization and fragmentation for several aromatic molecules of varying structure and π-electron delocalization. Here, we present the results for a series of molecules of similar electronic structure, but increasing size. Additional results for a larger set of molecules will be presented elsewhere [18]. Ion spectra were measured using a linear 1-m time-of-flight mass spectrometer in dual slope continuous extraction mode. A 1 mm aperture was placed between the ionization and detection regions to restrict the signal collection to the near-focal cylindrical volume of the laser beam [19]. Previously described [20] 10 Hz regeneratively amplified Ti:sapphire laser produced 1.5 mJ, 60 fs pulses centered at 800 nm. The pulses were focused to a spot of 50 μm diameter; the intensities were calibrated by comparison to the appearance thresholds for multiply charged argon. Solid

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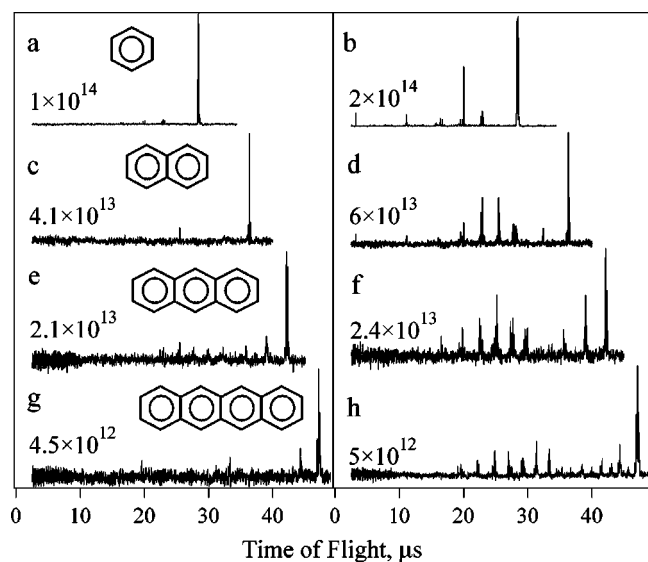*Corresponding author. Email address: rjlevis@temple.edu

FIG. 1. Time-of-flight mass spectra of (a,b) benzene, (c,d) naphthalene, (e,f) anthracene, (g,h) tetracene, obtained using 800 nm, 60 fs laser pulses. The laser intensity in $W\,cm^{-2}$ is shown in each spectrum.

samples sublimed directly in vacuum to attain a pressure of 1×10^{-6} Torr; the background pressure for the spectrometer was 1×10^{-8} Torr. Benzene was delivered through a controlled leak valve.

The mass spectra were obtained at laser intensities from 0.10 to 25.0×10^{13} $W\,cm^{-2}$. At all laser intensities, the extent of fragmentation increases with increasing molecular size. At low laser intensities, the spectra of all molecules are dominated by parent molecular ion; see the left column of Fig. 1. As the laser intensity is increased, fragments emerge at an exponentially increasing rate, starting at some onset intensity value I_{fragm}. Finally, the fragmentation saturates at higher intensities. The right column of Fig. 1 shows the ion spectra at laser intensities greater than I_{fragm} but below the saturation. To quantitatively define the value of I_{fragm}, we plot the ratio of fragment ion signal to the total ion signal vs the laser intensity; these data are shown in Fig. 2. We define I_{fragm} as the point where the five-point running average value of this ratio exceeds the background value by two standard deviations. The I_{fragm} intensities reported in Table I reveal that the onset of extensive dissociation occurs at lower laser intensities with increasing molecular size.

To quantitatively model the dissociative ionization measurements, we develop a theory based on nonadiabatic excitation from ground state of a molecule, $|g\rangle$, to excited neutral and ionic states. Since $|g\rangle$ is separated from the excited-state manifold by an energy gap much larger than both the interlevel spacing in the manifold and the photon energy, the $|g\rangle \rightarrow QC$ transition is the rate-limiting step in the excitation. This coupling needs to be established and treated separately. Though many of the excited states may be connected to $|g\rangle$, our calculations [18] show that the transition occurs mainly through the doorway state $|DS\rangle$ that is most strongly coupled to $|g\rangle$ (i.e., has the maximum $\mu \mathcal{E}_0 / \Delta$, where Δ_0 and μ are the transition energy and transition dipole moment; $\mathcal{E}_0$ is the
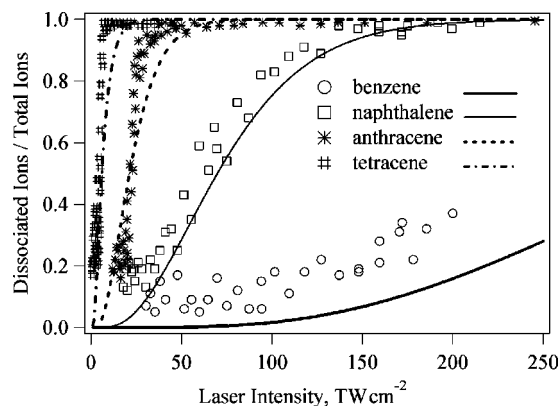

FIG. 2. Measured and calculated outcomes of nonadiabatic excitation as a function of laser intensity. The markers represent the measured ratio of fragment ion signal to the total ion signal; the curves represent the calculated ratio of dissociated ions to the total number of produced parent ions.

electric-field amplitude). For each of the molecules considered here, the $|DS\rangle$ state is the lowest-energy charge-transfer state. (The calculated values of Δ_0 and μ for the $|g\rangle \rightarrow |DS\rangle$ transition for the molecules studied are shown in Table I.)

The natural framework for treating the $|g\rangle \rightarrow |DS\rangle$ transition is provided by the Dykhne formalism [21] in which the energy of an electronic state adiabatically follows the oscillations of the laser electric field, $\mathcal{E}(t) = \mathcal{E}_0 \sin(\omega t)$. The time dependence of the adiabatic electronic states induces nonadiabatic Landau-Zener interstate transitions. This approach has been extensively used [21] to describe transitions in two-state systems and transitions to true continuum; here, we apply it to the $|g\rangle \rightarrow QC$ transition. The transition probability during one-half laser cycle is given by

$$P_{|g\rangle \rightarrow |DS\rangle} = \exp\left[-\frac{2}{\hbar} \text{Im}\left\{ \int_{t_1}^{\tau^*} \Delta E_{|g\rangle, |DS\rangle}(t) dt \right\} \right], \quad (1)$$

where $\Delta E_{|g\rangle, |DS\rangle}$ is the time-dependent transition energy from $|g\rangle$ to $|DS\rangle$. The upper limit in the integral, τ^*, is given by the saddle point condition $\Delta E_{|g\rangle, |DS\rangle}(\tau^*) = 0$. As for the particular expression of the transition energy, the simplest assumption is to use the two-state model [22] leading to $\Delta E_{|g\rangle, |DS\rangle}(t) = \sqrt{\Delta_0^2 + 4\mu^2 \mathcal{E}^2(t)}$. This results in a half laser cycle transition probability of $P_{|g\rangle \rightarrow |DS\rangle} = \exp\{-\pi \Delta_0^2 / 4\hbar \omega \mu \mathcal{E}_0\}$. In this approximation, the values of $P_{|g\rangle \rightarrow |DS\rangle}$ (shown in Table I) are too small to account for ionization, let alone the fragmentation of a molecule. This is not a surprise, since in the multi-state system of a polyatomic molecule both $|g\rangle$ and $|DS\rangle$ states may couple to many other states, significantly affecting $\Delta E_{|g\rangle, |DS\rangle}(t)$.

When a multistate system is subjected to a low-frequency strong field, the shift of an energy level is determined not only by the virtual transition to the most strongly coupled state but also by the adiabatic polarization of the entire electronic system. When a strong electric field transfers charge across a molecule, the $|DS\rangle$ state contributes only a fraction to the total polarizability of $|g\rangle$ (compare μ^2 / Δ_0 and actual

TABLE I. Measured and calculated properties of the molecules.

Molecule	$I_{fragm} \times 10^{13}$ (W cm^{-2})	$\Delta_{|g\rangle \to |DS\rangle}$ [a] (eV) Neutral (ion)	$\mu_{|g\rangle \to |DS\rangle}$ [a] (eÅ) Neutral (ion)	$P_{|g\rangle \to |DS\rangle}$ Two-state	α_g(800 nm) [a] (eÅ^2 V^{-1}) Neutral (ion)
Benzene C_6H_6	16 ± 3	7.00 (7.23)	2.01 (0.905)	3.0×10^{-2}	0.779 (0.679)
Naphthalene $C_{10}H_8$	4.1 ± 0.5	5.88 (5.90)	1.57 (1.41)	2.0×10^{-3}	1.70 (2.25)
Anthracene $C_{14}H_{10}$	2.1 ± 0.2	5.17 (5.13)	2.10 (1.91)	6.5×10^{-3}	3.02 (5.13)
Tetracene $C_{18}H_{12}$	0.45 ± 0.05	4.65 (4.59)	2.58 (2.35)	7.8×10^{-4}	4.75 (15.67)

[a]Gaussian 01 development version [23] with B3LYP DFT using 6-31+G (d) basis set.

polarizability α in Table I). Since the polarization of the electronic system substantially contributes to the $|g\rangle \to |DS\rangle$ transition, we must include this multielectron effect to describe the time-dependent energy gap ($\Delta E_{|g\rangle, |DS\rangle}(t)$) for Eq. (1) correctly. The new expression for $\Delta E_{|g\rangle, |DS\rangle}(t)$ incorporating the effect of all electrons on the Stark shift of $|g\rangle$, expressed through the polarizability, is

$$\Delta E_{|g\rangle, |DS\rangle}(t) = \sqrt{\left(\Delta_0 + \frac{\alpha_g^*}{2} \mathcal{E}^2(t) \right)^2 + 4\mu^2 \mathcal{E}^2(t)}. \quad (2)$$

Here, the effective dynamic polarizability of the ground state, α_g^*, excludes the contribution from the $|DS\rangle$ state, which is accounted for by the term $4\mu^2 \mathcal{E}^2(t)$; the shift of the $|DS\rangle$ state itself is negligibly small [18].

Once the system is in the QC, there is a fast energy absorption [8] that leads to ionization. However, the onset (and even saturation) of a $|g\rangle \to QC$ transition will not immediately (nor automatically) result in the formation of ionized fragments: energy deposition within the QC is much more probable than promotion of another electron to the QC through the $|DS\rangle$. Because the ionized electron takes away most of the energy gained by a molecule prior to ionization, the molecular ion is formed in a relatively cold state. (Here, we exclude the exotic scenario of ionization through highly excited autoionizing states.) To access the repulsive states in the ionic quasicontinuum QC$_i$, the bottleneck for the transition from the ionic ground state $|g_i\rangle$ to QC$_i$ must be overcome.

Nonadiabatic $|g_i\rangle \to QC_i$ transitions in the molecular ion provide access to the repulsive electronic states, resulting in the formation of the detected ionic fragments. The $|g_i\rangle \to QC_i$ transition in molecular ions is similar to that in neutral molecules: the ionic $|g_i\rangle$ state is most strongly coupled to the $|DS\rangle$ state in the ionic excited-state manifold, $|DS_i\rangle$, (the lowest charge-resonance state of the ion); the $|g_i\rangle \to |DS_i\rangle$ transition is enforced by the dynamic polarizability of the ion. However, the dynamic polarizability of large molecular ions is qualitatively different from that of neutral molecules because molecular ions possess a number of low-energy electronic transitions, corresponding to an electron hole migrating through the orbitals below the highest occupied molecules orbital of the ion. Such $\pi \to \pi$ and $\sigma \to \pi$ transitions typically reside in the visible or near IR range of the spectrum. These transitions have no analog in neutral molecules (they are forbidden in closed-shell systems by the Pauli exclusion principle). The additional electronic transitions contribute substantially to the dynamic polarization of large polyatomic ions. This can be seen in Table I: with the exception of benzene (the smallest molecule) the $|g_i\rangle$ polarizabilities are greater (for tetracene much greater) than polarizabilities of the neutral molecules. The significant increase in the dynamic polarizability of large polyatomic ions (in comparison with that of neutral molecules), accelerates the energy deposition at the second excitation stage even though $\mu_{|g\rangle \to |DS\rangle}$ decreases following ionization (see Table I).

Using the two-stage nonadiabatic excitation model, we calculated the fraction of ions fragmented as a function of laser intensity; see the curves in Fig. 2. Substituting Eq. (2) into Eq. (1), we calculated the excitation probability per half cycle $P_{|g\rangle \to |DS\rangle}$ as a function of laser intensity for the studied molecules. As in the case of transitions to a true continuum [21], we sum conditional probabilities over all the half cycles of the laser pulse to obtain the total probability as determined by the envelope $\mathcal{E}_0^2$. At the second stage of the excitation, the probability of the $|g_i\rangle \to QC_i$ excitation of a parent ion was computed from the remaining interaction time with the laser pulse after the ion formation.

The calculated fractions of ions fragmented as a function of laser intensity, presented in Fig. 2 by the solid curves, match well with the experimental data on the fragmented ion fractions. This agreement, achieved with no fitting parameters in the theory, strongly suggests that the three elements of our model of nonadiabatic excitation of polyatomic molecules capture the most important features of nonresonant lasers-molecule coupling leading to dissociative ionization. The remaining discrepancy at high laser intensities (near the saturation limit) noticeable for anthracene and tetracene may be caused by multiple ionization. (If at high laser intensities the sequential excitation includes more than two stages, the amount of detected ionic fragments will be greater than predicted by the two-stage model.)

The model developed here has a general significance and predictive power. It is not limited to two-stage excitations. Given a suitable laser-pulse frequency, intensity and duration, multiply charged polyatomic ions may be produced on the leading edge of the temporal profile of a laser pulse [24,25]. The model can handle multiple ionization events and the ensuing runaway sequence of nonadiabatic excitations. The model is also applicable to other laser-induced phenomena in polyatomic molecules. The charge-transfer transitions enhanced by multielectron polarization are undoubtedly important for high harmonic generation [26,27] in large mol-

ecules. Also, the theory can address the interplay of neutral fragmentation channels [28] (dark channels), intact ionization, and ionized fragmentation channels in polyatomic molecules. For example, the electronic absorption by polyatomic ions at the fundamental laser wavelength (800 nm) was recently reported to significantly enhance parent ion fragmentation [29]. These IR electronic transitions, related to the above-mentioned hole dynamics, do not involve the high-energy repulsive states and thus cannot by themselves induce the ion dissociation. However, the increase in the ion polarizability due to these resonances will boost the $|g_i\rangle \rightarrow QC_i$ transition probability [see Eq. (2)], enhancing the ion fragmentation.

In conclusion, a general theory for nonadiabatic excitation of large molecules in strong laser fields is proposed to account for the observed trends in fragmentation of related molecules. The key element of the nonadiabatic process is the bottleneck transition from the system's ground to the doorway state of the excited-state manifold; this transition is enabled and fostered by the dynamic multielectron polarization. The theory predicts the laser intensities for the onset of highly nonadiabatic coupling regime, resulting in the rapid onset of extensive fragmentation of a molecule. The formation of ionized fragments is a sequential process comprising nonadiabatic ionization of a neutral molecule and subsequent energy deposition in the resulting ion. The sequential nonadiabatic processes are expected to form a basis for strong-field control of ionization, fragmentation, and chemical reactivity of polyatomic molecules in gas and liquid phases, as well as to have ramifications in solid-state systems.

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