Rapid Proton Transfer Mediated by a Strong Laser Field

Alexei N. Markevitch,[1] Dmitri A. Romanov,[2] Stanley M. Smith,[3] and Robert J. Levis[1,*]
[1]*Department of Chemistry, Center for Advanced Photonics Research, Temple University, Philadelphia, Pennsylvania 19122, USA*
[2]*Department of Physics, Center for Advanced Photonics Research, Temple University, Philadelphia, Pennsylvania 19122, USA*
[3]*Department of Chemistry, Wayne State University, Detroit, Michigan 48202, USA*
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Kinetic energy distributions of H^+ ejected from a polyatomic molecule, anthraquinone, subjected to 60 fs, 800 nm laser pulses of intensity between 0.2 and $4.0 \times 10^{14}\ \mathrm{W \cdot cm^{-2}}$, reveal field-driven restructuring of the molecule prior to Coulomb explosion. Calculations demonstrate fast intramolecular proton migration into a field-dressed metastable potential energy minimum. The proton migration occurs in the direction perpendicular to the polarization of the laser field. Rapid field-mediated isomerization is an important new phenomenon in coupling of polyatomic molecules with intense lasers.

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In weak-field laser-molecule interactions the laser pulse initially deposits energy in the electron subsystem and subsequent evolution of the nuclear wave packet occurs on field-free potential energy surfaces. This paradigm limits the ability to directly manipulate nuclear motion by the laser. On the contrary, a strong laser field (electric field comparable to that binding electrons within a molecule) causes significant redistribution of the electron density, which can effect nuclear motion *during* the laser pulse. The evolution of nuclear wave packets on field-dressed potential energy surfaces has been demonstrated in diatomic molecules [1,2]. Here, we present a new strong-field phenomenon, proton transfer within a polyatomic molecule into a field-dressed metastable potential energy minimum. The ability of strong laser fields to manipulate nuclear potentials, through coupling of light-dressed electronic potentials is crucial for the emerging field of strong-field control of reactivity of polyatomic molecules [3,4].

For the case of diatomic molecules responding to strong electric fields, nuclear motion is limited to alignment of the principal axis and change of the internuclear distance. For polyatomic molecules, having larger moments of inertia and correspondingly larger alignment time scales, nuclear rearrangements become a viable option for lowering the system's energy in an applied field [5–7]. In such rearrangements proton transfer plays a special role because of its fast time scale. At the same time, proton transfer is an extremely important reaction in numerous chemical and biological/biophysical systems, [8,9] and harnessing it by the means of laser control promises far-reaching practical implications. Proton transfer in hydrogen cyanide subjected to a strong IR laser field has been theoretically predicted, [10] and recently, strong-field proton migration in acetonitrile has been reported, [6] although the mechanism in the latter case is unknown.

We have recently studied the electron-nuclear dynamics of strong-field proton motion for the molecule anthracene, $C_{14}H_{10}$ [11]. Analysis of kinetic energy distributions of the H^+ ejected from anthracene revealed a new phenomenon, charge-localization assisted Coulomb explosion. Such nonadiabatic charge localization can serve as a viable tool for strong-field manipulation of nuclear motion in polyatomic molecules and ions.

Here we study how proton ejection dynamics depends on the molecular structure. We measure the H^+ kinetic energy distributions for the molecule 9,10-anthraquinone (AQN), $C_{14}H_8O_2$, which has symmetry similar to anthracene (Fig. 1). The H^+ energy distributions suggest that field-driven restructuring occurs prior to Coulomb explosion (i.e., that nuclear motion occurs during the laser pulse). A numerical model predicts fast proton intramolecular migration toward a field-dressed potential energy minimum near an oxygen atom. Counterintuitively, the proton moves in the direction orthogonal to the polarization of the laser field.

Ion spectra were measured using a linear 1 m time-of-flight mass spectrometer [12]. A regeneratively amplified Ti:sapphire laser produced 1.5 mJ, 60 fs pulses centered at

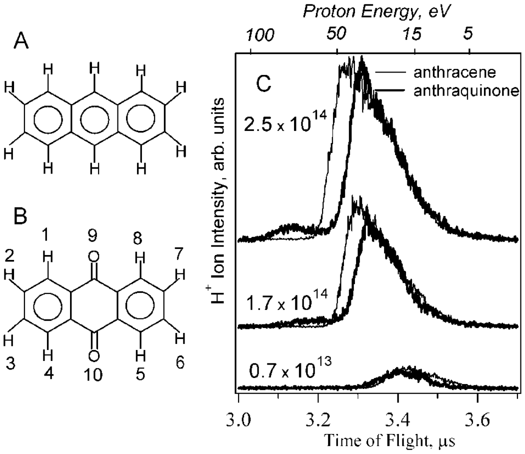

FIG. 1. Structures of anthracene (a) and 9,10-anthraquinone (b) with labeled proton positions. (c) Time-of-flight distributions of H^+ ejected from anthracene (thin line) and anthraquinone (thick line) at three different laser intensities ($\mathrm{W \cdot cm^{-2}}$).

800 nm was used to excite and ionize the sample molecules. The solid sample sublimed directly into vacuum to attain a pressure of ~1×10^{-6} Torr; the background pressure for the spectrometer was ~1×10^{-8} Torr. The procedure to determine the H^+ kinetic energies [11] included two complementary experiments. In the first, ions drifted ~5 mm in field-free conditions (prior to acceleration by a +500 Volt potential), separating according to their initial velocities. In the second, the ions were exposed to a retarding field before extraction into the time-of-flight system. Thus, the time-of-flight distributions are calibrated in terms of kinetic energy.

The H^+ kinetic energy distributions for the two molecules are similar at lower laser intensities but differ significantly at higher intensities [Fig. 1(c)]. Most notable is the appearance of the high-energy mode in the spectra of AQN. From $I = 2.0 \times 10^{13}$ up to $\sim 8.0 \times 10^{13}$ $W \cdot cm^{-2}$ the distributions of both molecules are characterized by a single mode shifting to higher energies as I increases. At $I \sim 9.0 \times 10^{13}$ $W \cdot cm^{-2}$ a high-energy mode with a cutoff value extending to approximately 83 ± 3 eV forms in the spectra of AQN.

To gain an insight into the structure-sensitive mechanism of H^+ ejection we plot the cutoff (maximum) values of the proton energy for both molecules as a function of I, in Fig. 2. The energy cutoff is significantly higher for AQN than for anthracene at $I > 1.5 \times 10^{15}$ $W \cdot cm^{-2}$. We propose that this difference is due to the presence of oxygen in AQN. The kinetic energy that a proton acquires in Coulomb explosion depends not only on the total charge on the counter ion, but also on the time-dependent redistribution of charge within the molecule [11]. The maximum kinetic energy of H^+ is estimated as $E_{H^+}(\mathrm{eV}) = 14.4q/R(\text{Å})$. Here q is the charge repelling the proton (in units of fundamental charge), and R is the initial separation of charges. The observed high cutoff energy for AQN reveals that the departing proton is initially very close to an unexpectedly large positive charge ($q \sim +6$).

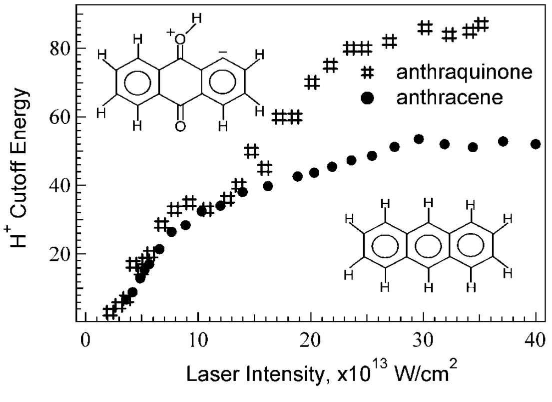

FIG. 2. Dependence of H^+ maximum kinetic energy on the laser intensity for anthracene and anthraquinone. At lower intensities the maximum H^+ energies are similar; for $I > 1.5 \times 10^{14}$ $W \cdot cm^{-2}$, the anthraquinone curve diverges, saturating at ~83 eV.

The structure of AQN reveals which protons might be located next to a large positive charge. There are two types of chemically equivalent protons in AQN, the "outer" (2,3,6,7) and the "inner" (1,4,5,8) protons, see Fig. 1. Because the AQN structure is anisotropic, the laser-molecule interaction depends on the molecule's relative orientation with the laser field. The AQN is randomly oriented in the gas phase and cannot be appreciably aligned during the ~60 fs laser pulse at the intensities used here. For molecules whose long axis is aligned with the field, the outer protons obtain the largest kinetic energy. For molecules whose O-O axis is aligned with the field (referred to as "the O-O direction"), the inner protons should acquire the highest acceleration.

The higher anthraquinone ejected proton energies (in comparison with anthracene) cannot be explained by the difference in the degree of ionization between these two molecules. Using nonadiabatic multielectron excitation theory, [13–15] the degree of ionization can be calculated as a function of laser intensity. Calculations were performed for anthracene [16] and AQN for both neutrals and +1 ions in the relevant orientations with respect to the laser field direction [Gaussian DV [17] B3LYP density-functional method with a 6-311G(d) basis set]. The rate of nonadiabatic excitation and ensuing ionization of AQN is even smaller than that previously calculated for anthracene [11]. Therefore the kinetic energies of H^+ resulting from Coulomb explosion of AQN are expected to be lower as well.

The higher H^+ kinetic energy may be explained by restructuring of AQN prior to Coulomb explosion. AQN can form an enol zwitterion where one of the inner protons migrates to oxygen creating an O-H bond, see Fig. 2. In this isomer, the length of the molecule in the O-O direction is increased. Moreover, oxygen (6 valence electrons) is capable of transiently forming higher charge states in comparison with carbon (4 valence electrons). Thus, the strong-field polarization of the zwitterion can provide the necessary degree of charge separation and ensuing nonadiabatic charge localization [11] to eject the observed high-energy protons.

Geometry optimization using Gaussian DV [17] shows a shallow energy minimum (<0.1 eV) for a proton near the oxygen. The enol isomer is 6.8 eV higher in energy than the ground-state keto structure, and thus no H^+ transfer can occur due to thermal motion on the ground-state electronic potential energy surface. Although strong-field excitation can deposit over 7 eV in the vibrational degrees of freedom, there is not enough time during the ~60 fs pulse for the proton transfer to occur as a result of statistical energy redistribution.

We also found that the isomerization cannot be ascribed to the known weak-field mechanisms involving electronically excited potential energy surfaces. Such keto-enol rearrangements on electronically excited potential energy surfaces are typical when the proton is a part of a six-membered arrangement of nuclei [18], where the migration distance is small and comparable with typical amplitudes of vibrational motion. In this case, the proton rearrangement occurs through preparation of a wave packet on electronically excited surfaces. However, in the case of AQN (where the proton is a part of a five-membered ring), quantum-mechanical modeling using Gaussian DV [17] revealed no bound excited electronic state for the enol isomer. Thus, additional dynamic strong-field effects must cause proton migration to oxygen.

To this end, we consider the forces acting on the proton when the oscillating field is applied in the O-O direction. The direct ponderomotive action of the oscillating field is negligible because a free H^+ in an electric field of amplitude $E = 3$ V/ Å and frequency $\omega = 2.4 \times 10^{15}$ s^{-1} acquires a ponderomotive energy of $E^2/4m_p\omega^2 \sim 0.1$ eV $\ll \Delta E$. The electrostatic action of the electronic charge redistribution is much more effective. In the adiabatic regime, the induced dipole moment follows the electric field as $\mu = \alpha E$ (α is the appropriate component of the polarizability tensor). Using Gaussian DV [17] we have calculated local charge distributions and found that when electrons concentrate on one of the terminal O atoms creating an additional negative charge Q. The corresponding positive charge on the opposite side of AQN is more evenly distributed over the oxygen and the adjacent carbons. The negative charge is estimated as $Q \sim \mu/l_0 = \alpha E/l_0 \sim 3e$, where l_0 is the distance between the negatively polarized oxygen and the row of positively polarized carbons. Thus, during one half cycle of the laser field oscillations, the proton (1, 4, 5, or 8) is on the positive side of the molecule, and the C-H bond is softened by the repulsive action of the positive charge on the C atom. During the next half cycle, when the electrons move to the oxygen atom, the main effect is the attraction exerted by the negative charge on the H^+, as given by the Coulomb force of $F = Qe/r^2$, resulting in ~17 eV of additional potential energy difference between the isomeric proton positions. Thus, the alternating actions of the bond softening and the attraction extract the proton out of its equilibrium position and propel it to the enol-isomer minimum.

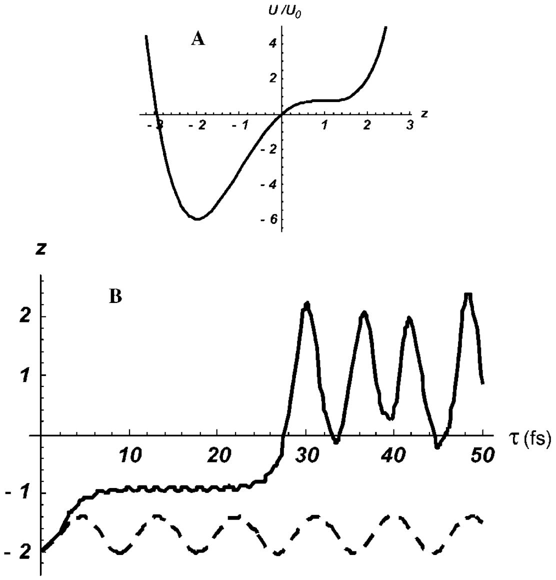

FIG. 3. (a) One-dimensional potential curve showing the equilibrium and the metastable minima; $z = x/x_0$ is the dimensionless reaction coordinate. (b) The H^+ trajectory along the z coordinate at (i) the field intensity below the transition threshold (dashed line), and (ii) above the threshold (solid line).

To illustrate this, we consider proton motion in the two-minima setting under the action of the combination of strong oscillating forces in a simple model using structural and electronic parameters of AQN. We reduce the potential surface to a one-dimensional potential [see Fig. 3(a)] whose reaction coordinate corresponds to the proton location on a straight line connecting the positions of the equilibrium minimum, x_1, and the isomeric minimum, x_2. The model potential curve, $U(x) = U_0[1/4(x/x_0)^4 - 3/2(x/x_0)^2 + 2(1 - \gamma)(x/x_0)]$, reproduces the deep minimum of the equilibrium position and a weak isomeric minimum. Here, U_0, x_0, and γ are parameters selected to model energy splitting between the ground state and isomer structure ($\Delta E = 6.8$ eV), the interminimum spatial distance ($\Delta x \approx 2.5$ Å), and the frequency of the H^+ oscillations near the equilibrium minimum ($\omega_0 = 0.63$ fs^{-1}). The parameter γ is small to ensure that the isomeric minimum is shallow. Within this model, the dimensionless equation of motion of the proton driven by the oscillating force with frequency ω is given by,

$$(9 - 8\gamma)\frac{d^2z}{d\tau^2} = -z^3 + 3z + 2(1 - \gamma) + 2\frac{\Delta x}{\Delta E}\left(\frac{9}{8} - \frac{8}{9}\gamma - \sqrt{\frac{3}{2}\gamma}\right)f(z, \beta\tau), \qquad (1)$$

where $z = x/x_0$, $\tau = \omega_0 t$, $\beta = \omega/\omega_0$. The effective oscillating force $f(z, \beta\tau)$ consists of two terms that represent the previously discussed H-O Coulomb drag and H-C bond softening induced by the polarization in the laser field.

We solve Eq. (1) numerically and trace the evolution of proton trajectories with increasing electric field strength, see Fig. 3(b). In a small field, H^+ undergoes slight oscillations near the equilibrium position. With growing field amplitude, these oscillations become more complex and their period grows, but the proton remains confined near the equilibrium minimum. However, when the field exceeds a threshold of about 2.5 V/Å, the trajectory undergoes transition to large-amplitude oscillations centered at the enol-isomer minimum. After the field reaches this threshold value, the proton migration to the field-dressed minimum takes ~25 fs. Thus, the restructuring of the molecule can occur before Coulomb explosion expels the H^+.

The actual threshold laser intensity for the proton migration is lower than that predicted here because the H^+ migration toward the oxygen increases the length of the molecule in the O-O direction. This migration increases the polarizability ($\Delta\alpha = \alpha[(l_0 + \Delta l)^3/l_0 - 1] = 0.93\alpha$) and considerably adds to the energy shift in the field. In the case of symmetric transfer of a pair of opposite protons (1 and 5, or 4 and 8), the effects of molecule elongation are even greater.

Thus, the H^+ kinetic energy distributions of AQN can be understood as follows. The lower energy parts of the distributions (from 0 to ~50 eV) result from Coulomb explosion of the regular structure, analogous to that discussed previously for anthracene [11]. The high-energy mode specific for AQN (extending up to ~83 eV at the highest laser intensity) is the result of H^+ expulsion following the intramolecular transfer into the field-dressed metastable minimum.

These results demonstrate that modification of nuclear potentials of a polyatomic molecule by a strong oscillating electric field can force nuclear rearrangement into metastable positions that are quasibound in the presence of the field. This is inherently different from weak-field rearrangements, where one-photon electronic transition is followed by internal conversion on electronically excited potential energy surfaces [18]. The strong-field proton transfer in a polyatomic molecule is more analogous to bond softening in ${H_2}^+$ (where the nuclear wave packet is localized at an increased equilibrium distance during an intense laser pulse), [1] or a related process of sequential coupling of light-dressed potentials during intense-field dissociation of ${O_2}^+$ [2]. Direct manipulation of intramolecular nuclei motion in polyatomic molecules can be achieved by using strong laser fields and can be instrumental in the control of molecular fragmentation and rearrangement by intense shaped laser pulses.

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*To whom correspondence should be addressed.

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