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Perturbation of water by intense light-induced fields of picosecond duration and ion-induced fields of attosecond duration

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The possibility of subjecting molecules to intense electric fields of ultrashort duration using fast beams of highly charged ions is explored. The morphology of dissociative ionization of H_2O in intense fields of picosecond and attosecond duration is found to be significantly different. Such fields, produced in laser-H_2O interactions and in collisions with 50–100 MeV $Si^{3+,8+}$ ions, are of approximately the same magnitude but have different directional properties. [S1050-2947(99)04304-8]

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The behavior of matter in external fields that are as strong as the internal Coulombic fields within atoms and molecules is a subject of much contemporary interest. Such strong fields are generated by tightly focusing light from intense lasers capable of producing light pulses of picosecond and femtosecond duration. In the context of molecular systems, these time scales are of importance in the context of typical rotational and vibrational time periods (tens of picoseconds and tens of femtoseconds, respectively). Moreover, the linear polarization vector of such light also specifies the direction of the intense field that is applied. Experiments on intense field-molecule interactions are powerful probes of molecular dynamics in the nonperturbative regime. Can such dynamics be probed in intense fields that are of even shorter duration?

It is the purpose of this paper to explore this possibility by using fast beams of highly charged ions. The correspondence of ion-induced fields to those produced by intense light pulses is not straightforward, but the prospect of broadening horizons for intense-field-induced dynamics to subfemtosecond time scales was alluring enough for us to undertake studies of the similarities and differences between ion- and light-induced fields, and the effect these might have on the morphology of field-induced dissociative ionization (DI) of simple molecules. By way of illustration, we focus attention on the H_2O molecule. Exposure of H_2O to high voltages, to surfaces and interfaces, or to certain solutes, can give rise to local and far-ranging structural effects that influence the energy, entropy and molecular dynamics. Studies of field-perturbed H_2O are important in diverse environmental and technological areas, and in the chemical and biological sciences [1], and intrinsically, because strong fields are known to induce nonlinear phenomena such as self-focusing and supercontinuum production [2]. As shown below, H_2O is also an apt molecule for our experiments from the viewpoint of untangling the effects of the directional properties of the applied field from its magnitude.

We have collided H_2O with 50–100 MeV $Si^{3+,8+}$ ions in order to generate intense electric fields of *attosecond* duration while picosecond-duration fields were generated using 35-ps wide light pulses (wavelength 532 nm) from an Nd:YAG laser that were focused to $\sim 30\ \mu$m. In our experiments, H_2O was introduced into the field-irradiation zone as an effusive beam. Ions formed were analyzed by time-of-flight (TOF) spectrometry.

In exploring the correspondence of ion-induced fields to light-induced ones, it is useful to consider three ion-velocity regimes. For relativistic ion beams (energy ∼ GeV/nucleon, $\beta = v/c \sim 1$), the Weizsäcker-Williams equivalent photon picture [3] equates the effect of the fields to two, orthogonally directed photon pulses. Applications of such equivalent-light pulses to studies of atomic ionization have recently attracted attention [4]. In the limit of zero-velocity ions ($\beta = 0$), the field-H_2O interaction is simply Coulombic: a field magnitude of 0.1 a.u. results if Si^{3+} is at an impact parameter, $b = 3$ Å. Our experiments were conducted in the intermediate regime and impact energies that were low enough (~ 100 MeV, $\beta \sim 0.04$) to ensure that the electric and magnetic field components associated with the ion beam did not form an electromagnetic wave as the latter component was deficient by β. In our case, we simply define an effective intensity (I_e) experienced by the target molecule in terms of the Poynting vector: $I_e(t) = (1/\mu_o)|\vec{E}(t) \times \vec{B}(t)|$. At our laser intensities, $I_e \sim 10^{13}\ \mathrm{W\,cm^{-2}}$, the corresponding applied fields are ~ 0.05 a.u.

For our ion-impact conditions, the variation of $I_e(t)$ with time (shown in Fig. 1) is a sharply peaked function, with a half-width of ~ 30 as; the peak intensity depends on impact parameter b. For $b \sim 3$ Å, the ion-induced field is equivalent to 10^{13}–$10^{14}\ \mathrm{W\,cm^{-2}}$ (similar in magnitude to our laser-induced fields). As a function of the angle that the direction of the field vector with the center of the H_2O target, however, the variation is slow, with a half-width of 90°. This constitutes one essential difference between laser- and ion-induced fields; although in terms of magnitude the two fields may be considered equivalent, the directional properties in the two cases are very different. The ion-induced fields, instead of being linearly polarized, are more akin to elliptical polarization as far as directional properties are concerned. In the context of the equivalence of the two types of fields we recall that the magnitude of laser-induced field also exhibits a time dependence that is governed by the Gaussian temporal profile of the laser pulse.

In comparing equivalent-field ion- and laser-induced DI patterns it is necessary to quantify I_e. For this, a limiting value of b has to be deduced for each ion-collision spectrum. However, in the case of molecular targets, b remains an elu-

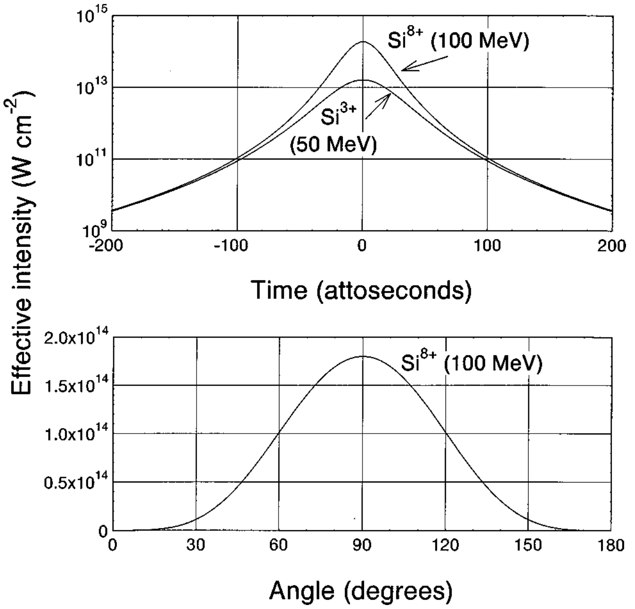

FIG. 1. Calculation of field intensities (top panel) experienced by H_2O in collision with fast Si^{3+} and Si^{8+} ions at an impact parameter of 3 Å. The time dependence of the effective intensity has a half-width of $\sim$30 as. The corresponding light-induced field intensity has a Gaussian temporal profile with a half-width of 35 ps. The bottom panel shows the ion field's directional properties expressed in terms of the angle between the field vector and the O atom in water.

sive parameter. The range of impact parameters that come into play manifests itself in the mean recoil energy (E_r) imparted to each product; the experimental manifestation is in the width of individual TOF peaks. We measured E_r of the parent H_2O^+ ion (40 meV for H_2O-Si^{8+} collisions) to deduce a *lower limit* of b using the established method [5] based on Olson's classical trajectory Monte Carlo technique [6] to deduce the impact parameter dependence of multiple ionization transition probabilities in fast-ion collisions. A value of 3 Å was obtained as the lower limit for b; a somewhat smaller value was obtained for Si^{3+} impact because treating this projectile as a point charge is less valid. The field generated at the target in H_2O-Si^{3+} collisions might, therefore, be larger than indicated in Fig. 1. Collisions that occur at lower values of b give rise to recoil energies far in excess of E_r and can be discriminated against by enhancing the angular resolution with which recoil ions are monitored at 90° with respect to the Si^{q+} beam. We confirmed the veracity of the method for deducing the lower limit of b by confirming values of total cross sections for formation of low-energy Ar^{q+} recoils ($q=1$–10) measured in the same apparatus.

Electron capture and loss processes also complicate the deduction of b values for production of recoil ions in q states ($q>1$). Measurements conducted in our apparatus confirmed that for Si^{q+}($q=3$–12), direct ionization dominates. (For example, in the case of Si^{10+}-Ar collisions, the direct ionization cross section for, say, Ar^{4+} recoil-ion formation was 8×10^{-17} cm^2; corresponding cross sections including 1-electron loss and capture were 3×10^{-18} and 7×10^{-19} cm^2, respectively [7].)

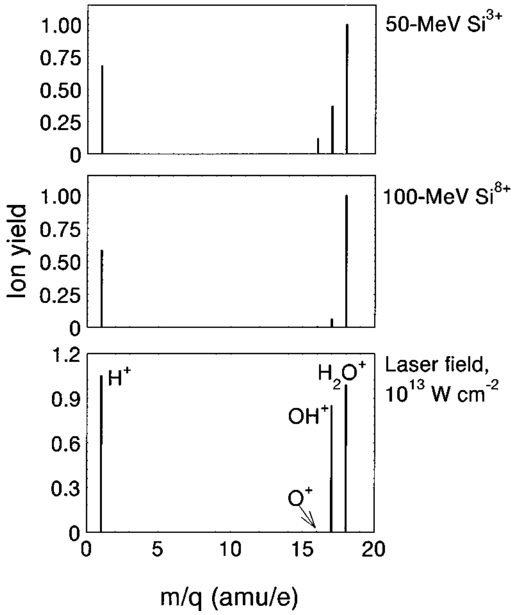

FIG. 2. Mass spectra obtained with Si^{3+} and Si^{8+} projectiles and with laser pulses of wavelength 532 nm and time duration 35 ps.

The contributions of single ionization processes to the DI patterns obtained in H_2O-$Si^{3+,8+}$ collisions and with a laser field are shown in Fig. 2. The relative intensities of H^+,OH^+, and O^+ in the two ion-impact spectra indicate a decrease in the degree of fragmentation in the case of Si^{8+} collisions. Most dramatically, the O^+ yield reduces to $<0.5\%$ of H_2O^+ from $\sim20\%$ obtained with Si^{3+} impact. With picosecond laser fields, the significant feature in the DI pattern is that the H^+ fragment is marginally more prolific than the parent H_2O^+ ion, with almost total suppression of O^+ yield. The fragment ion yields, except for O^+, are a little enhanced in the case of laser-field data but the almost-zero yield of O^+ ions is somewhat akin to the DI pattern obtained with Si^{8+}.

The fast ion-H_2O interaction is likely to involve mostly the electronic degrees of freedom: dissociation due to direct transfer of energy to nuclear degrees of freedom is unlikely. Consequently, the ion-induced DI pattern manifests ionization of H_2O into various charge states. Ionization involving inner-shell excitation is almost independent of projectile charge state [8] whereas if only valence-shell electrons are involved, the cross section falls with increasing collision energy, in conformity with the Born approximation. In our experiments we did not probe the relative importance of valence- and inner-shell processes, although the former is likely to dominate the overall dynamics. Si^{8+} ions might, therefore, be expected to produce somewhat less ionization than Si^{3+} on the basis of the collision energy being double. On the other hand, the extent to which H_2O is multiply ionized would be expected to increase with collision energy. Formation of H_2O^{q+} ions, with $q\geqslant2$, would result in an increased yield of O ions in high charge states. We probe this aspect by comparing, in Fig. 3, the yield of O^{q+} (relative to H_2O^+) obtained with the two projectiles. Two contrasting facets of this comparison are noteworthy: (i) The overall yield of O^{q+}($q>1$) relative to H_2O^+ is, somewhat counterintuitively, an order of magnitude less for higher-energy

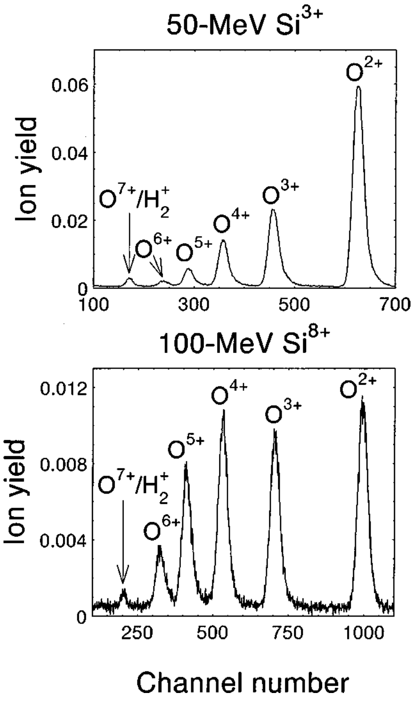

FIG. 3. Time-of-flight spectra of O^{q+} ions obtained with Si^{3+} and Si^{8+} projectiles. The channel number is proportional to the ions' flight time.

Si^{8+}-H_2O collisions. (ii) On the other hand, the distribution of q-values show that the yield of $O^{q+}(q>2)$ obtained with Si^{3+} decreases with q whereas for Si^{8+} there is a substantial enhancement of the higher charge states relative to O^{2+}. The dynamical interactions are obviously complex even when attosecond time scales imply purely electronic interactions on time scales that are shorter than rotational and vibrational periods. Both the intensity of the applied fields as well as their time duration have important implications for the dynamics. Analysis of the DI patterns in terms of zero-field structural properties of H_2O are inapplicable because of the gross distortions of potential energy surfaces that the intense fields would induce. DI patterns have recently been interpreted within the framework of molecular orbital energies [9] but application of fields that last for, say 30 attoseconds, implies an energy uncertainty of ~22 eV. This makes quantal treatments of DI processes with conventional molecular states irrelevant in the present case.

Further work is clearly necessary in order to gain insight. In contrast to the situation with $Si^{3+,8+}$ ions, at laser intensities of $\sim 10^{13}$ W cm^{-2} no evidence was found of highly charged fragment ions at yield levels of a few percent. Our data indicate that single ionization of H_2O, *followed by* H-OH bond cleavage, is the dominant channel in our laser fields, in contrast to the multiple-ionization scenario discussed in the case of fast ion impact. Is the lack of similarity of DI patterns obtained at two equivalent field magnitudes due to differences in the directional properties of the field or is it ascribable to differences in the interaction times?

We first consider the implications of differences in the directional properties of the light- and ion-induced fields in the context of the water molecule. As noted above, H_2O molecules were exposed to *linearly polarized* laser light, with the corresponding field having a well-defined, time-independent direction whereas the direction of the ion-induced field changes in the course of the interaction (Fig. 1). It is known that the interaction of initially randomly oriented molecules with linearly polarized light can result in their spatial alignment prior to DI [10] due to the interaction of the laser's electric field vector with the anisotropy of molecular polarizability (α); the resulting induced dipole moment exerts a torque on the molecules such that diatomics and linear triatomics tend to align their internuclear axes along the field direction. At laser intensities of $\sim 10^{13}$ W cm^{-2}, the field-molecule interaction energy overwhelms the field-free rotational energy [10] and the extent of alignment depends on α and the field intensity. For H_2O, however, recent angle-resolved experiments at these intensities [11] have shown that both O^+ and OH^+ fragments possess *isotropic* angular distributions. The relative magnitudes of the components of the induced dipole moment that lie parallel and perpendicular to the molecular symmetry axis influence the angular distributions and calculations show that although the parallel component of the dipole moment increases with field magnitude, and the perpendicular component decreases marginally, the perpendicular component dominates up to field magnitudes of ~0.1 a.u., much larger than the fields in our measurements (~0.05 a.u.). The interaction potential under such conditions has minima at $\pm 90°$ and, as a result, would induce H_2O to be spatially oriented in a direction that is perpendicular to the applied field [11]. When the field is applied along the symmetry axis, the perpendicular component is zero and the molecule would tend to align in the field direction. Consequently, when a field is applied to a randomly oriented ensemble of H_2O molecules, as the interaction potentials have minima in orthogonal directions, the net torque experienced by the molecules is negligible. H_2O molecules are, therefore, not aligned in any preferred direction when they interact with linearly polarized electric fields. *This leads us to postulate that the directional properties of the applied fields do not significantly determine the intense-field DI dynamics of* H_2O. Consideration of interaction times might, therefore, be pivotal in attempts to gain insight into the differences between ion- and light-induced DI patterns.

In summary, we have explored the possiblity of using fast beams of highly charged ions to irradiate molecules with intense, attosecond-long electric fields. Such fields are similar to laser-induced ones in that both have time-dependent magnitudes (Gaussian for laser-induced fields, and dependent on impact parameter and velocity for ion-induced ones). Comparison of DI patterns obtained using ion-induced and light-induced fields of approximately the same magnitude reveal intriuging similarities and differences that ought to encourage further explorations. It is clear that the dynamics of field-induced ionization and fragmentation of even a simple triatomic like water is very complex and more work is mandatory before insights can be developed. We believe that the present morphological findings provide useful guideposts for further experiments and more elaborate theoretical treatments.

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