Elementary Electron and Ion Dynamics in Ionized Liquid Water

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Abstract: Polarization-resolved femtosecond coherence spectroscopy is used to observe the dealignment of the injected electron, hole orbital motion, solvent reorganization, and ballistic proton transport in ionized liquid water. The lifetime of the H_2O^+ cation is also determined.
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1. Introduction

The ionization of liquid water is a universal phenomenon that accompanies the interaction of high-energy radiation with matter in aqueous environments [1]. The ensuing cascade of chemical reactions that involves ions, electrons, and radicals forms the basis of radiation chemistry and biology. The direct products of water ionization are the H_2O^+ radical cation and the injected electron, both of which are highly reactive species. H_2O^+ undergoes an ion-molecule reaction with a neighboring H_2O molecule to yield the hydronium cation and a hydroxyl radical. The timescale of this process is predicted to be ~100 fs, although experimental attempts at the determination of its lifetime have thus far been inconclusive [2]. In comparison, the spectroscopy and dynamics of the hydrated electron have been studied extensively [3]. However, the possible formation of an intermediary p state electron by the ionization of liquid water has yet to be verified [4].

Here, femtosecond coherence spectroscopy is combined with polarization anisotropy measurements to investigate the early-time electron and ion dynamics triggered by the multiphoton ionization (MPI) of liquid water [5]. The peak intensity of the 800-nm ionization pump pulse (2×10^{13} W/cm^2) yields a Keldysh parameter of $\gamma \approx 2$. Accordingly the MPI process can be characterized as being in the strong-field regime. The 800-nm probe pulse interrogates the $s \rightarrow p$ transitions of both the hydrated s electron and its presolvated precursor. The manner in which the intermolecular vibrational coherences of liquid water modulate the electron $s \rightarrow p$ absorption is analogous to the way in which a vibrational wave packet that is launched on a molecular potential energy surface modifies the energy and amplitude of its associated electronic transitions. By relying on the observation of coherences and polarization anisotropies that are associated with the various intermediates, our approach complements earlier methods based on optical pump−probe transient absorption (TA) spectroscopy.

2. Experiment

The femtosecond coherence spectroscopy setup employs the 800-nm, 30-fs output from an amplified Ti:sapphire laser system as both pump and probe pulses. Such a degenerate pump-probe scheme minimizes degradation of time resolution caused by sample-induced group velocity mismatch between pump and probe pulses. Polarization anisotropy measurements are performed by rotating the half-wave plate placed in the path of the pump beam. The sample target consists of a 40-μm-thick, wire-guided flowing jet of distilled water, with a sufficiently high flow rate to guarantee that each individual laser pulse encounters a fresh sample. The typical pulse energy and focal spot diameter of the pump beam are 70 μJ and 180 μm ($1/e^2$), respectively. The probe beam has a reduced focal spot size (3×) and pulse energy (100×) compared to the pump beam. Fluence dependence measurements reveal a 9-photon ionization pump process and a linear absorption probe. The total energy deposition of 14.0 eV by the pump pulse is significantly above the vertical ionization potential of liquid water (11.16 eV). At this input energy, the large electron ejection length of 35 Å [6] allows access to the collective dynamics of ~10^4 water molecules.

3. Results and Discussion

Ionization of liquid water results in the observation of a pronounced differential absorption polarization anisotropy at early times, which vanishes for time delays that exceed ~350 fs (Fig. 1a). Analysis of the time-dependent polarization anisotropy within a framework that considers only the s ground and p_z excited states of the injected electron yields, in the case of H_2O (D_2O), values of 0.94 ± 0.05 (0.92 ± 0.04) for the initial fractional p_z population and 79 ± 5 fs (101 ± 6 fs) for the p_z lifetime. The creation of an aligned electron distribution in this work is facilitated by the use of a strong-field-ionizing pump pulse. While the initial fractional populations of the p_z electron generated in H_2O and D_2O are identical, the retrieved p state lifetimes are clearly dependent on H/D isotopic
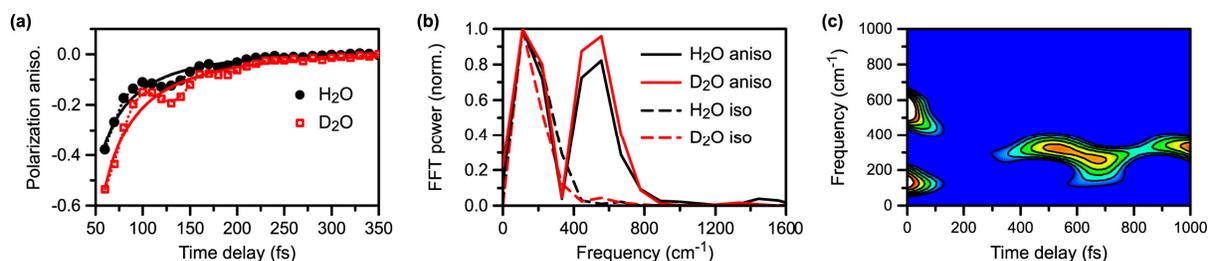
Fig. 1(a) The polarization anisotropy shows that the *p* electron is produced by the MPI of liquid water. The symbols correspond to the experimental data, dashed lines serve as guides, and solid lines are fits to the theoretical model. (b) The FFT power spectra of the residual polarization anisotropies reveal frequency components at 150 and 500 cm^{-1} (solid lines), both of which are independent of H/D substitution. For comparison, the FFT power spectra of the isotropic signals are also shown (dashed lines). (c) The time-frequency spectrogram for the anisotropic signal shows the disappearance of the 150 and 500 cm^{-1} frequency components at early times and the concomitant rise of the frequency component at 310 cm^{-1}.

substitution. The factor of ~1.3× longer lifetime in D_2O than H_2O is reminiscent of previous results obtained on the internal conversion dynamics of the photoexcited hydrated electron [7], which suggests the participation of solvent librational motion in the relaxation of the injected *p* electron.

Oscillatory features in the polarization anisotropy decay indicate a periodic reorientation of the probe transition dipole moment that is concomitant with the electronic relaxation of the *p* state electron. The FFT power spectra reveal oscillation frequencies of 150 and 500 cm^{-1}, neither of which exhibits a perceptible shift with H/D substitution (Fig.1b). For both frequency components, time-domain analysis yields exponential damping times of 70 ±12 fs and 64 ± 7 fs for H_2O and D_2O, respectively. The 150-cm^{-1} component that arises in both isotropic and anisotropic signals is assigned to a Raman-active intermolecular hindered translation along the hydrogen bond coordinate. The appearance of this mode is a manifestation of solvent reorganization that accompanies the ionization of water. The isotopic behavior of the 500-cm^{-1} component rules out solvent librational motion as its origin. Instead, this frequency is attributed to valence hole orbital motion in ionized liquid water that involves closely-spaced ion states with orthogonal hole densities.

At long time delays (>300 fs), a new oscillation feature characterized by a frequency of 310 cm^{-1} appears and persists beyond 1 ps (Fig. 1c). This component is assigned with the aid of ab initio calculations to the hindered translation between a hydronium (H_3O^+) species and its neighboring water molecules. The observation of this intermolecular mode, which is associated with excess proton transport [8], signifies long-lived ballistic proton transport in ionized liquid water. Because H_3O^+ is initially produced by the transfer of a proton from the H_2O^+ cation to a neighboring water molecule, the onset of ballistic proton transport is expected to correlate with the population decay of the H_2O^+ species. Fitting the growth of the 310-cm^{-1} component to pseudo-first-order kinetics yields a lifetime of 196 ± 5 fs for the H_2O^+ radical cation.

4. References

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