Supplemental Material for

"Nonlinear Electronic Excitation in Water under Proton Irradiation: A First Principles Study"

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SI1. Electronic excitation dependence on water structure

The optical absorption spectrum was calculated to assess the dependence of the electronic excitation on the water structure. All spectra are generated by perturbing the system with a 0.005 a.u. electric field "delta kick" in the x-direction, then propagating the electronic states in the MLWF gauge for 6 fs [1, 2]. Figure S1 shows the optical absorption spectrum comparison using the 162-water classical molecular dynamics (CMD) structure and that from four 162-water first-principles molecular dynamics (FPMD) structures. Only very minor differences are observed, and the high-energy parts of the spectra are identical. Additionally, an absorption spectrum for a 256-water CMD structure was used to validate the convergence with respect to the simulation cell size, as in shown Figure S2. 256-molecules has been reported to give an accurate representation of the electronic density of states (EDOS) for Gamma-point only calculations [3].



FIG. S1. Optical absorption spectra from the CMD structure and from the spectral average of 4 FPMD snapshots of identical size (162 water molecules).



FIG. S2. Optical absorption spectra for the 162-water CMD molecule structure and for a 256-water molecule CMD structure. The 256-water structure is scaled by the ratio of water molecules (162/256).

SI2. Effect of using complex absorbing potential to remove electrons localized on proton.

We examined the possible necessity of employing a complex absorbing potential (CAP) to remove the electron density residing on the projectile proton before the proton is removed at the end of the simulation cell. The charge accumulated within one Bohr of the proton was calculated using Voronoi analysis [4]. A localized, spherical CAP was applied to remove the charge residing on the proton [5, 6]. The CAP was centered on the proton and the size was set at one Bohr [7], unless a neighboring water molecule was within one Bohr of the proton at the end of the simulation cell, in which case the size of the CAP was adjusted so that its boundary resided halfway between the water molecule and the proton. The CAP was applied until the electron charge accumulated on the projectile proton was removed. The proton was then removed from the system, and the system was evolved for an additional 250 a.u. time. Fig. S3 shows the "dielectric function" spectra calculated, with and without a CAP, for the 1.90 a.u. velocity. Usage of the CAP was determined to be unnecessary since the difference is negligibly small.



FIG. S3. Dielectric function spectra generated from simulation of electronic stopping with the projectile proton velocity of 1.90 a.u., with and without the CAP.

SI3. Ionization character of excitation.

To determine the degree of ionization in the electronic stopping excitation, the TD-MLWFs were projected onto a set of unoccupied eigenstates that covers all states up to the vacuum level [8]. Excitations of electrons into electronic states above this range were considered ionizations. For the peak (1.90 a.u.) velocity and the 4.43 a.u. velocity, the excitation is largely ionization in character, with less than 25% of the excited electrons captured below vacuum level. For the 0.63 a.u. velocity the excitations are noticeably less ionizing, with more than 40% of the excited electrons captured below vacuum level.



FIG S4. Percentage of excited electrons captured when projecting the TD-MLWFs onto the set of eigenstates in the energy manifold from conduction band minimum (CBM) to 10.75 eV above the CBM.

SI4. The rate of hole decay and formation

The rates at which the hole population changes are quantified. A running mean, with a window of 0.24 fs (10 a.u.), was used to determine the change in number of holes in time. For the 1.90 a.u. velocity, the region closest to the path ($R < 5.25 a_0$) shows a sharp decrease in excitation rate, while the region 5.25-9.55 a_0 from the path shows an equivalent increase, both plateauing around 75 a.u (Fig S5). Regions far from the path ($R > 12 a_0$) show a constant increase in hole population for the duration of the 250 a.u., following proton removal. Velocities of 0.63 and 4.43 a.u. show similar excitation rates compared with the 1.90 a.u. case (see Fig S6).



FIG S5 (Top panel). Rate of the hole population change in each spatial region for the 1.90 a.u. velocity. A window of 0.24 fs (10 a.u.) was used to calculate the running mean. (Bottom panel) Enhanced view of the hole population change rate in regions greater than 9.55 a_0 from the projectile path. Dashed line at 0 is shown for reference.

FIG S6. (a, b). Rate of the hole population change in each spatial region for the 0.63 a.u. velocity. (c, d). Rate of the hole population change in each spatial region for the 4.43 a.u. velocity. A window of 0.24 fs (10 a.u.) was used to calculate the running mean. Dashed line at 0 is shown for reference.

SI5. Diffusion model

In order to fit the data to the cylindrical diffusion model, we employed a Savitzky-Golay (S-G) filter to smooth the data [9]. To estimate the flux at the center of the cylinder (center of projectile path), the total hole population change following projectile proton removal was fit to a linear function, giving a rate of $2.1e^{-3}$ holes/a.u. (time). The flux at the edge of the cylinder (edge of farthest region) was again estimated using a linear fit to the change in hole population in said region (R > 15 a₀), giving a value of $-1e^{-5}$ holes/a.u. (time). A least-squares fit was used for each case. We also tested how sensitive the diffusion model is to larger and smaller D values. Figure S7 shows that the observations are rather insensitive to the particular coefficient value.

Figures S8 and S9 shows the hole distributions for the 0.63 a.u. (S8) and 4.43 a.u (S9) velocities, overlaid with the least-squares fitted diffusion models for each velocity. The 0.63 a.u. and 4.43 a.u. give slightly larger diffusion constants of $1.1 \times 10^{-2} holes/(a.u.(time)^2 * a_0)$ and $1.3 \times 10^{-2} holes/(a.u.(time)^2 * a_0)$, respectively. Both exhibit the same key differences observed in the 1.90 a.u. case as discussed in the main text.

FIG S7. 2-D projections of the diffusion model (solid lines) and S-G filtered data (dashed lines) for the 1.90 a.u. velocity at specific times following proton removal. (a) Shows the diffusion model with $4 \times 10^{-3} \frac{holes}{(a.u.(time)^2 * a_0)}$ as the diffusion coefficient and (b) shows the model with $1 \times 10^{-2} \frac{holes}{(a.u.(time)^2 * a_0)}$ as the diffusion coefficient.

FIG S8. Temporally and spatially dependent hole distributions for the 0.63 a.u. proton velocity, overlaid with diffusion model (shown as a dark mesh) in $R < 10 a_0$ (top panel) and $R > 10 a_0$ (bottom panel).

FIG S9. Temporally and spatially dependent hole distributions for the 4.43 a.u. proton velocity, overlaid with diffusion model (shown as a dark mesh) in $R < 10 a_0$ (top panel) an $R > 10 a_0$ (bottom panel).

SI6. Hole formation and decay in terms of MLWF types

On each water molecule, there exists two distinct pairs of TD-MLWFs; one for lone-pair electrons and one for OH bond electrons (see FIG 4(a)). In the primary excitation by the projectile proton, lone-pair electron orbitals and OH bond electron orbitals contribute near equally to the excitation, as seen in figure S10. For the 1.90 and 0.63 a.u. velocities, the hole decay following proton removal is primarily lone pairs, with 76% and 78% of decay coming from the lone pairs, respectively. The 4.43 a.u. velocity shows a slightly smaller contribution, with 62% of the hole decay coming from lone pairs. In the secondary excitation, both lone-pair electron orbitals and

OH bond electron orbitals are responsible for the hole population growths, with the 4.43 a.u. velocity showing a slightly larger contribution from the lone pairs compared to the other velocities.

FIG S10. Hole generation per water for the water molecules within 5.25 a₀ of the projectile path, for the (left) 1.90 a.u. velocity, (middle) 0.63 a.u. velocity and (right) 4.43 a.u. velocity.

FIG S11. Changes in hole per water for the **0.63 a.u**. velocity, decomposed into contributions from lone-pair holes and O-H bond holes for (left) $R < 5.25 a_0$. (middle) 5.25-15 a_0 . (right) $R > 15 a_0$. Black represents total hole changes per water, while blue and red represent lone pair holes and bond centered holes respectively. **78%** of the hole decay seen in the left figure can be attributed to the lone-pair electron orbitals.

FIG S12. Changes in hole per water for the **4.43 a.u**. velocity, decomposed into contributions from lone-pair holes and O-H bond holes for (left) $R < 5.25 a_0$. (middle) 5.25-15 a_0 . (right) $R > 15 a_0$. Black represents total hole changes per water, while blue and red represent lone pair holes and bond centered holes respectively. **62%** of the hole decay seen in the left figure can be attributed to the lone-pair electron orbitals.

SI7. Hole energetics

In general, for all velocities, the farther the region from the proton path, the greater the number of holes formed close to the VBM (E = 0 eV), as seen in figure S13. For regions close to the path, the energetics of the holes formed remains constant in time once the projectile proton is removed. For regions farther from the path, the energetics of the holes converge in time towards the population seen at t = 250 a.u.

FIG S13. Normalized hole populations at t=250 a.u. for the 1.90 a.u. velocity (left), 0.63 a.u. velocity (middle) and 4.43 a.u. velocity (right). DOS is shown for reference.

SI8. Dependence on XC Functional

The optical absorption spectrum was calculated using the SCAN meta-GGA functional[10] to assess the dependence of the electronic excitation on the exchange correlation functional. SCAN is known to accurately describe the electronic properties of water[11]. Figure S14 shows the optical absorption spectrum comparing the PBE and SCAN XC functionals using the 162-water classical molecular dynamics (CMD) structure. Only minor differences are observed between the two spectra, with SCAN showing a slight shift (less than 0.5 eV) to higher energies. Additionally, although PBE is known to give artificial charge delocalization in some cases, previous work on liquid water has shown hybrid functionals such as PBE0 give nearly identical results to PBE when comparing projectile charge state[12].

FIG. S14. Optical absorption spectra comparing PBE and SCAN for the 162-water CMD molecule structure. A cutoff energy of 100 Rydberg was used for the SCAN functional.

SI8. Unit Conversions

1 a.u.(time) = 0.0241 fs

0.63 a.u.(velocity) = 9.92 KeV 1.90 a.u.(velocity) = 90.19 KeV 4.43 a.u.(velocity) = 490.66 KeV

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