Intermolecular Coulombic Decay in Water Dimers: A Computational Study

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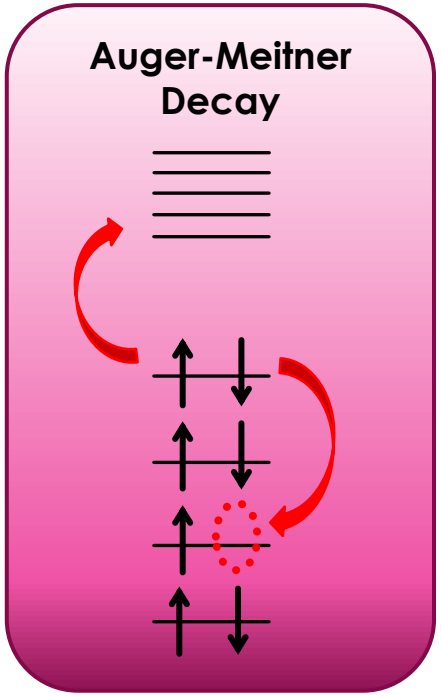
Background & Motivation

- Following inner-shell ionization within molecular systems, electrons can undergo competing ultrafast relaxation pathways:



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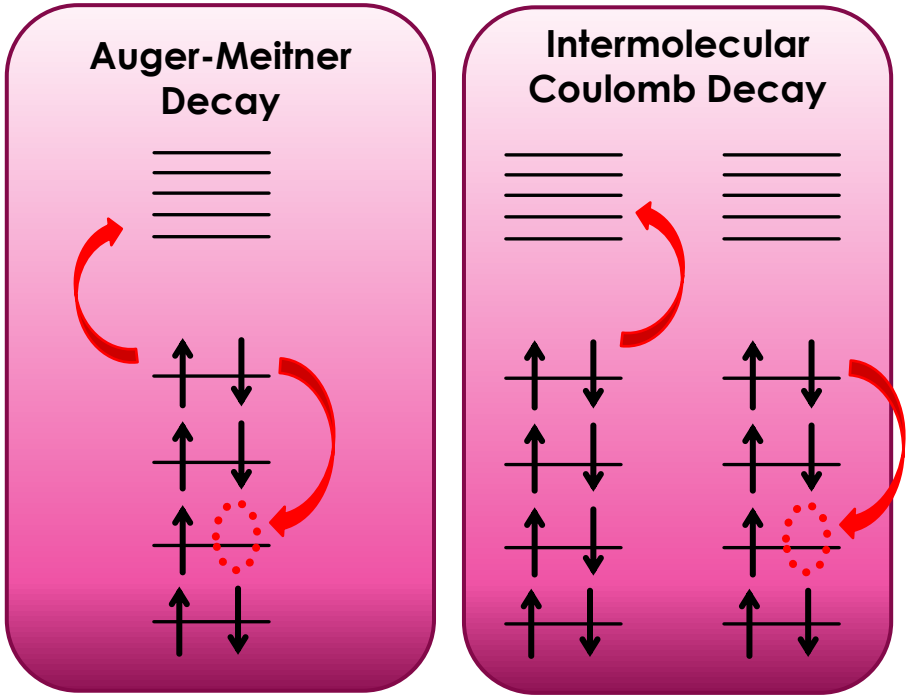

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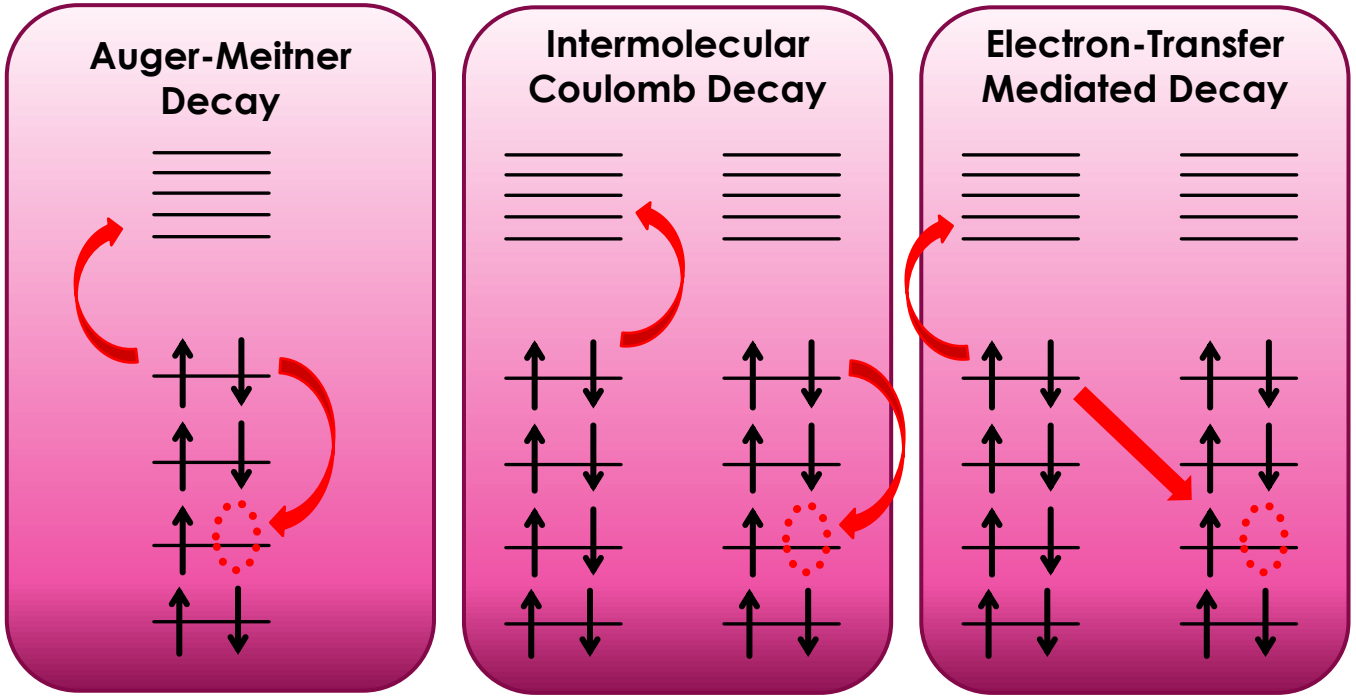

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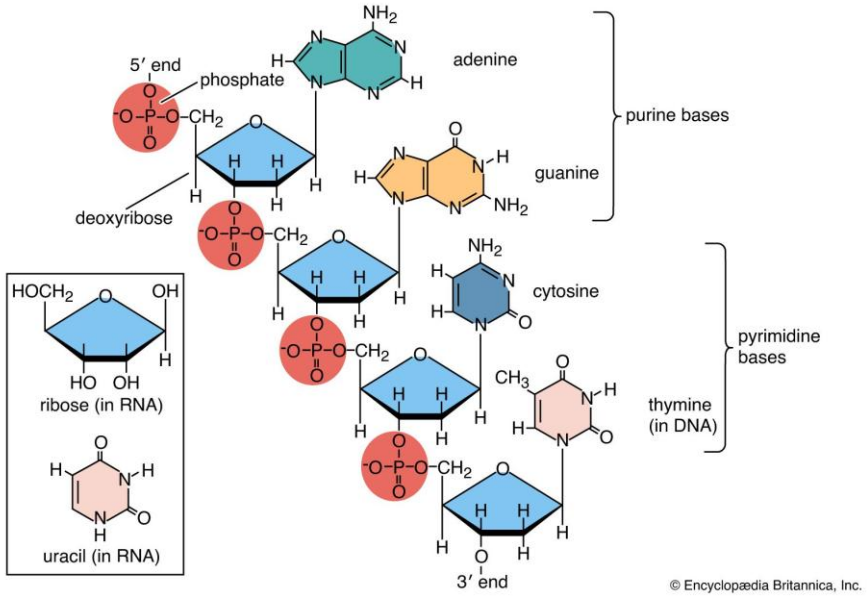
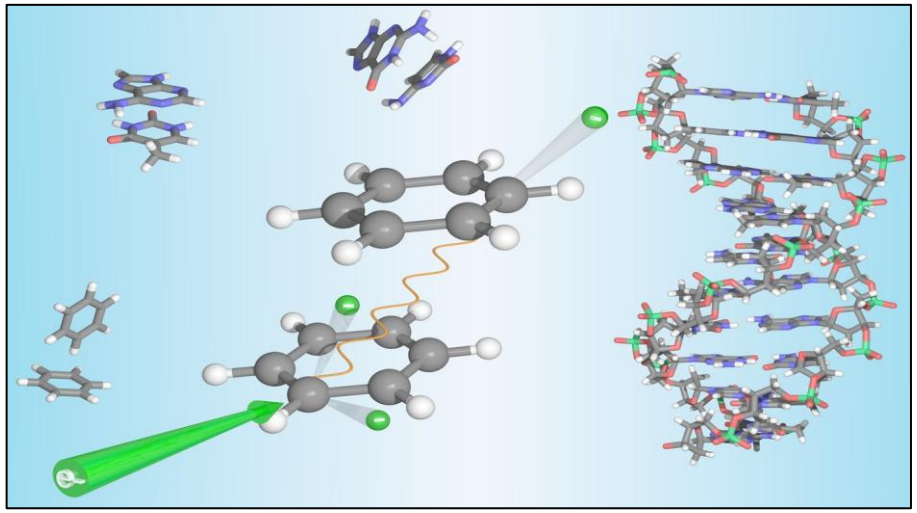
Background & Motivation

- These relaxation pathways generate secondary ionized low-energy electrons (LEEs), which can perform highly reactive downstream chemistry
- Understanding these ultrafast mechanisms could lead to new technologies for cancer prevention and targeted destruction of biomolecules





Ren, X., Zhou, J., Wang, E. *et al.* Ultrafast energy transfer between π-stacked aromatic rings upon inner-valence ionization. *Nat. Chem.* **14**, 232–238 (2022).

Methods: RT-TDDFT + CAP

- Real-Time Time Dependent Density Functional Theory (RT-TDDFT) solves for the time evolution of the 1 electron reduced density matrix

$$P_{ij} = \left\langle \psi \middle| \hat{a}_j^\dagger \hat{a}_i \middle| \psi \right\rangle \qquad i\frac{\partial \mathbf{P}}{\partial t} = [\mathbf{F}, \mathbf{P}]$$

$\mathbf{P}$ – 1 electron density matrix
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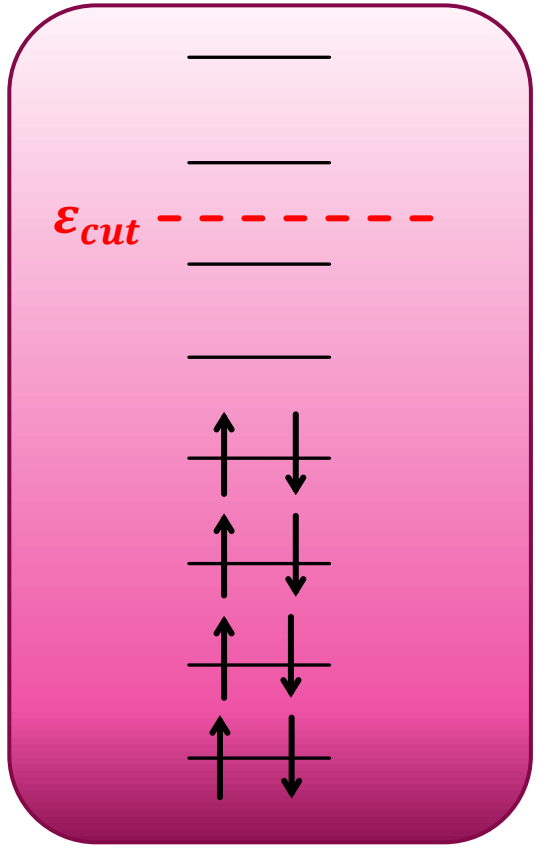
- Ionization of an electron to the free particle continuum is approximately treated using a complex absorbing potential (CAP)

$$\mathbf{F}' = \mathbf{F} + i\boldsymbol{\Gamma}$$

$$i\frac{\partial \mathbf{P}}{\partial t} = \left[\mathbf{F}'\mathbf{P} - \mathbf{P}\mathbf{F}'^{\dagger}\right]$$

$$\boldsymbol{\Gamma} = \begin{bmatrix} \gamma_1 & 0 & \dots & 0 \\ 0 & \gamma_2 & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & \gamma_i \end{bmatrix}$$

$$\gamma_i = \begin{cases} 0 & \text{if} \quad \varepsilon_i - \varepsilon_{cut} < 0 \\ \gamma_0 \left[\exp\left[\xi\left(\varepsilon_i - \varepsilon_{cut}\right)\right] - 1\right] & \text{if} \quad \varepsilon_i - \varepsilon_{cut} > 0 \end{cases}$$



Methods: RT-TDDFT + Ehrenfest

- Ehrenfest dynamics assumes nuclear motion follows the expectation value of the electronic energy

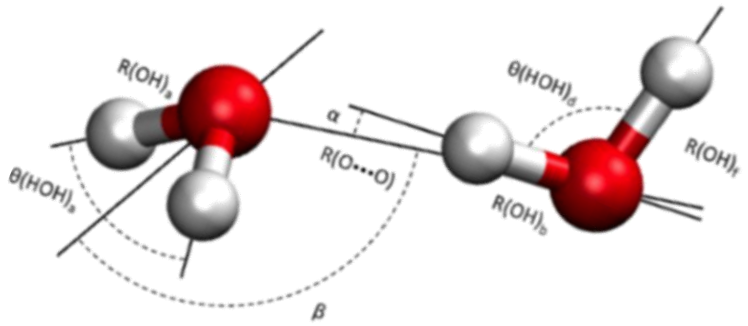
$$\mathrm{E}(\mathbf{R}) = \langle \psi | \, \hat{\mathrm{H}}(\mathbf{R}) \, | \psi \rangle$$

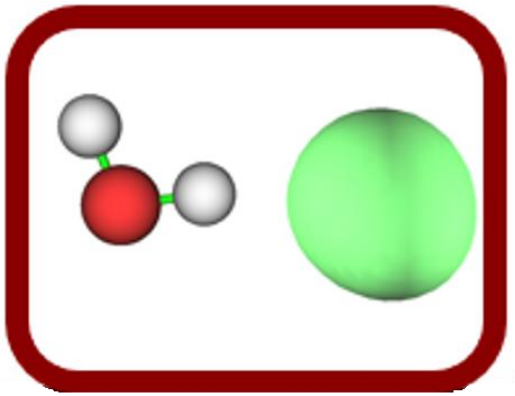
- The mean-field nuclear gradients are:

$$\mathrm{F_A} = -\frac{\partial}{\partial \mathrm{R_A}} \mathrm{E}(\mathbf{R})$$

Collaboration: Water Dimer Project

- Our experimental collaborators are looking at the fragmentation products of water dimers following ionization of the 2a1 inner-valence orbital on the oxygen atom
- Following excitation, water is expected to undergo ICD followed by coulomb explosion of the dimer
- Experimental data includes kinetic energy releases of the ionized electrons as well as the nuclear fragments following coulomb explosion





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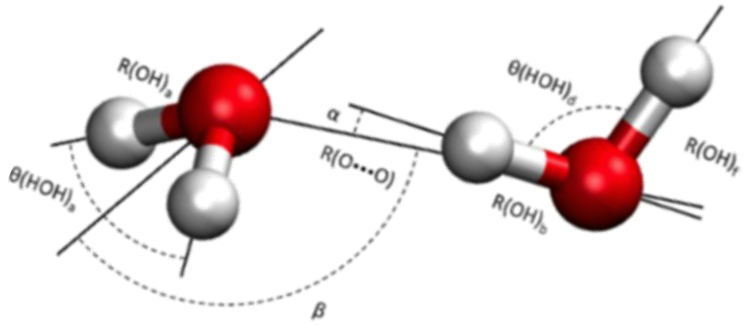
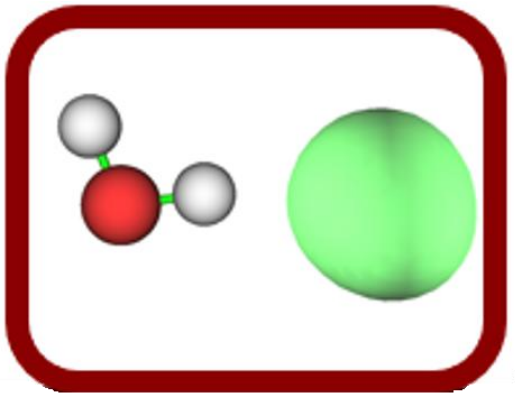
Collaboration: Water Dimer Project

Our goal is to predict the non-radiative pathways and downstream fragmentation products along with kinetic energy release through our RT-TDDFT + CAP + Ehrenfest methodology





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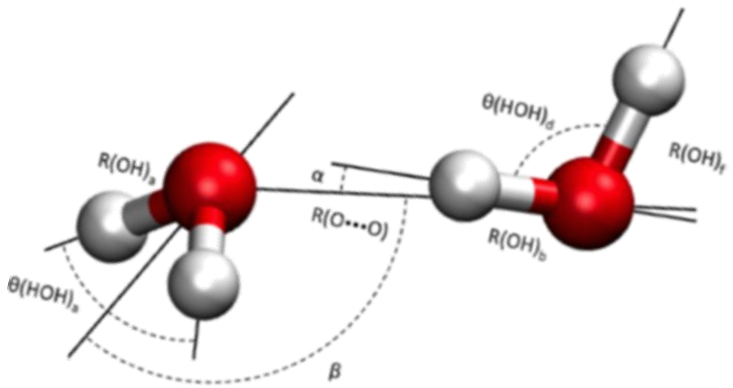
Methods: Computational Workflow

- Motivated by our experimental collaborators looking at ICD within water dimers, the full calculation can be separated into three distinct parts:
  1. NVT thermostated ab-initio molecular dynamics at 30 K



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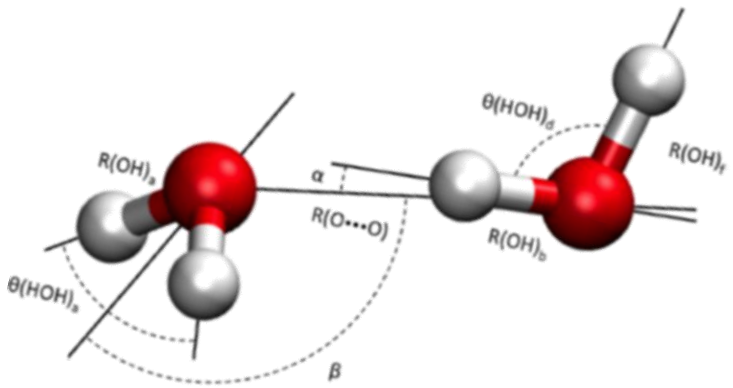

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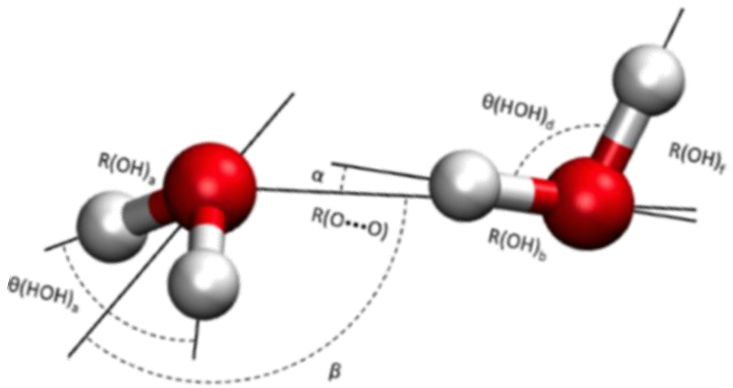
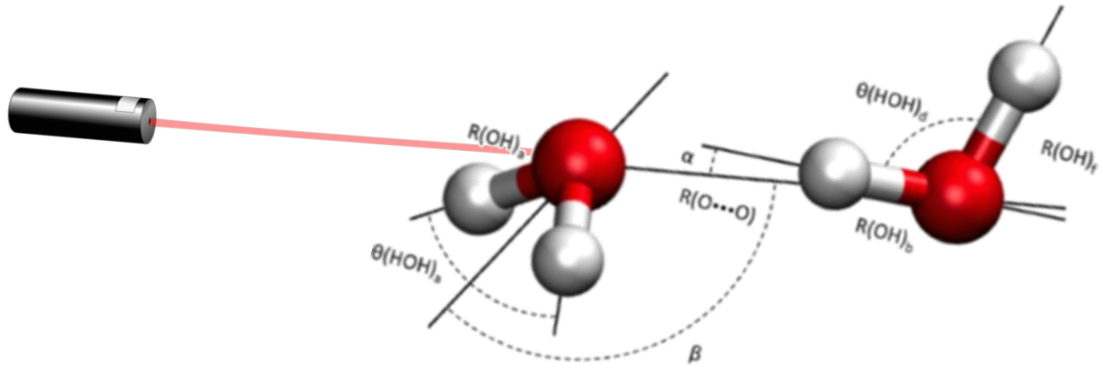


Results: Proton Acceptor Ionization



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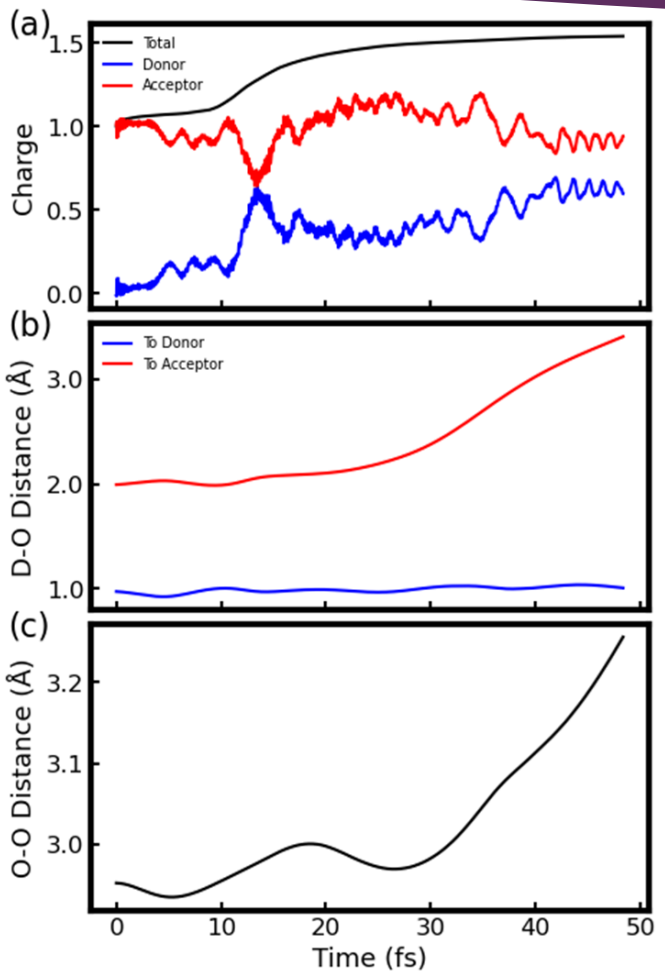

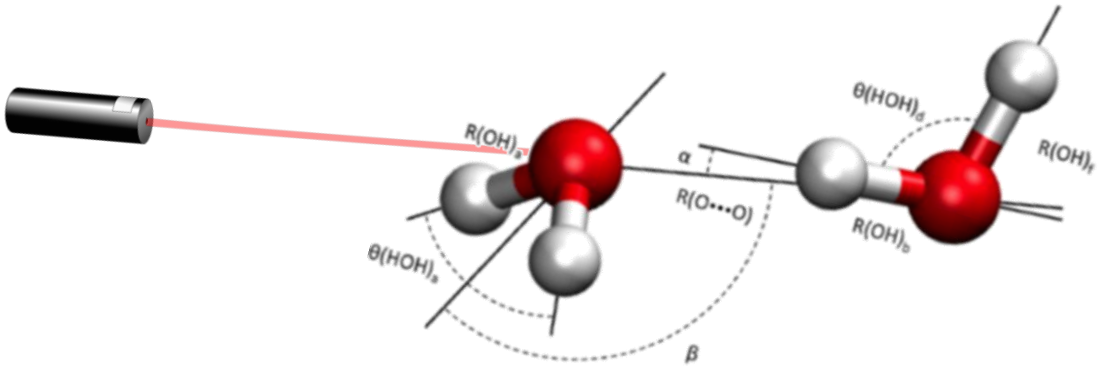

Donor

Acceptor

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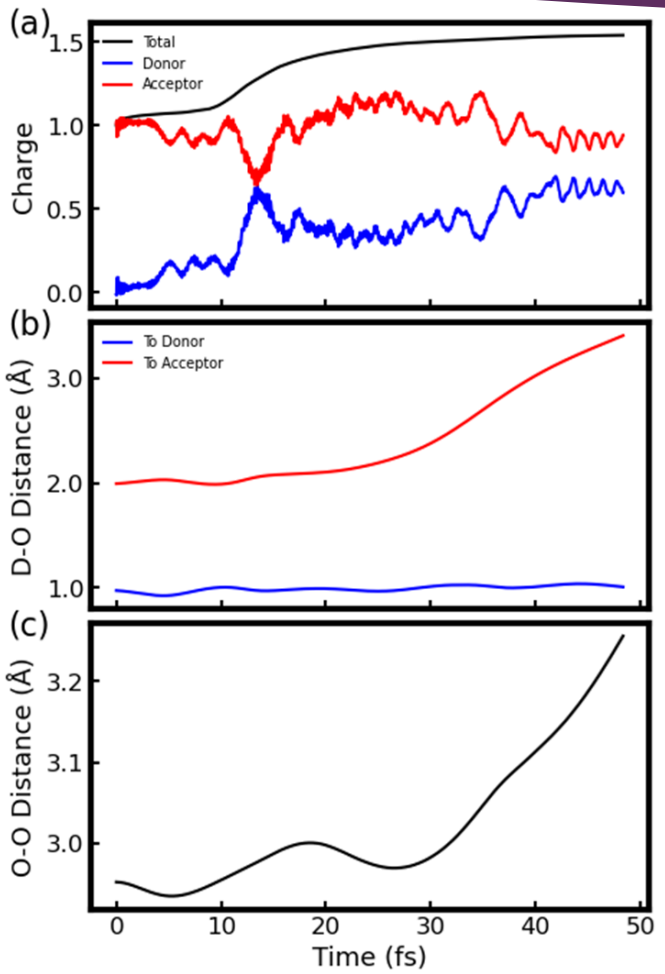

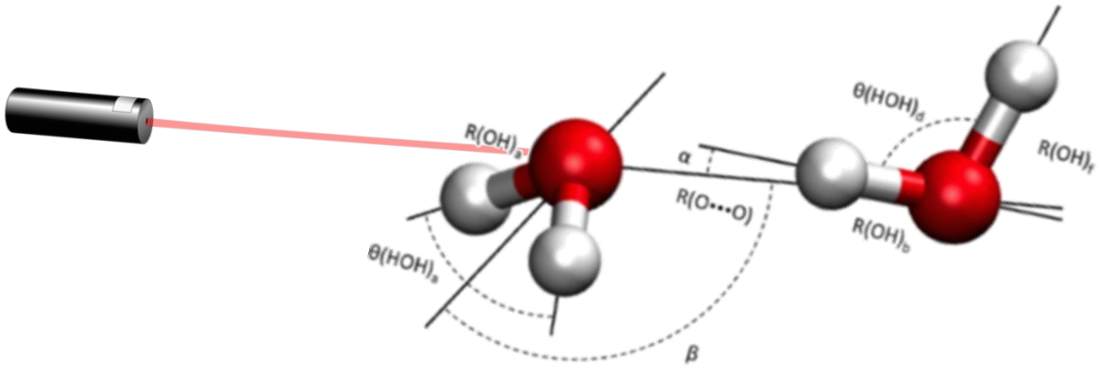

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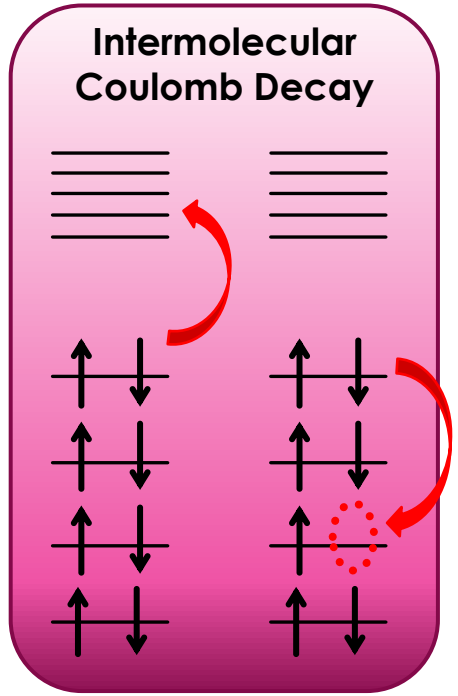

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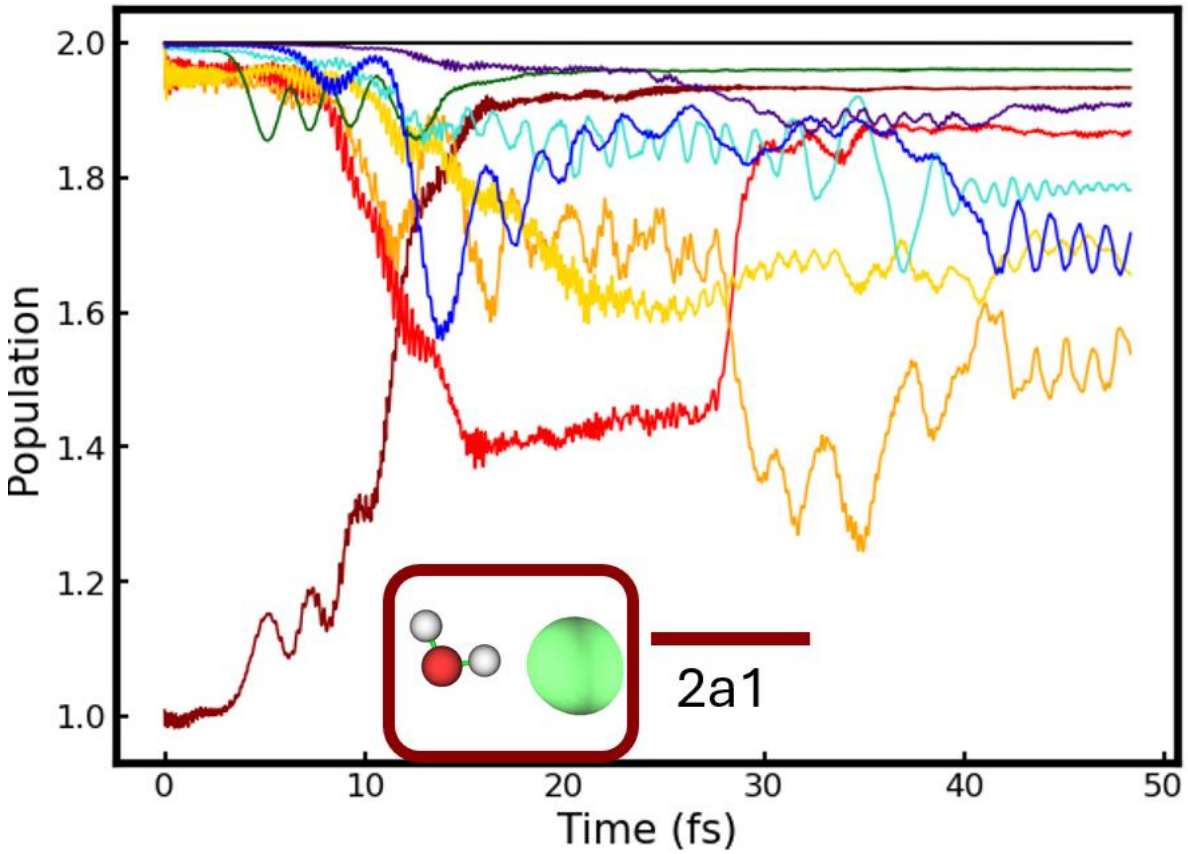

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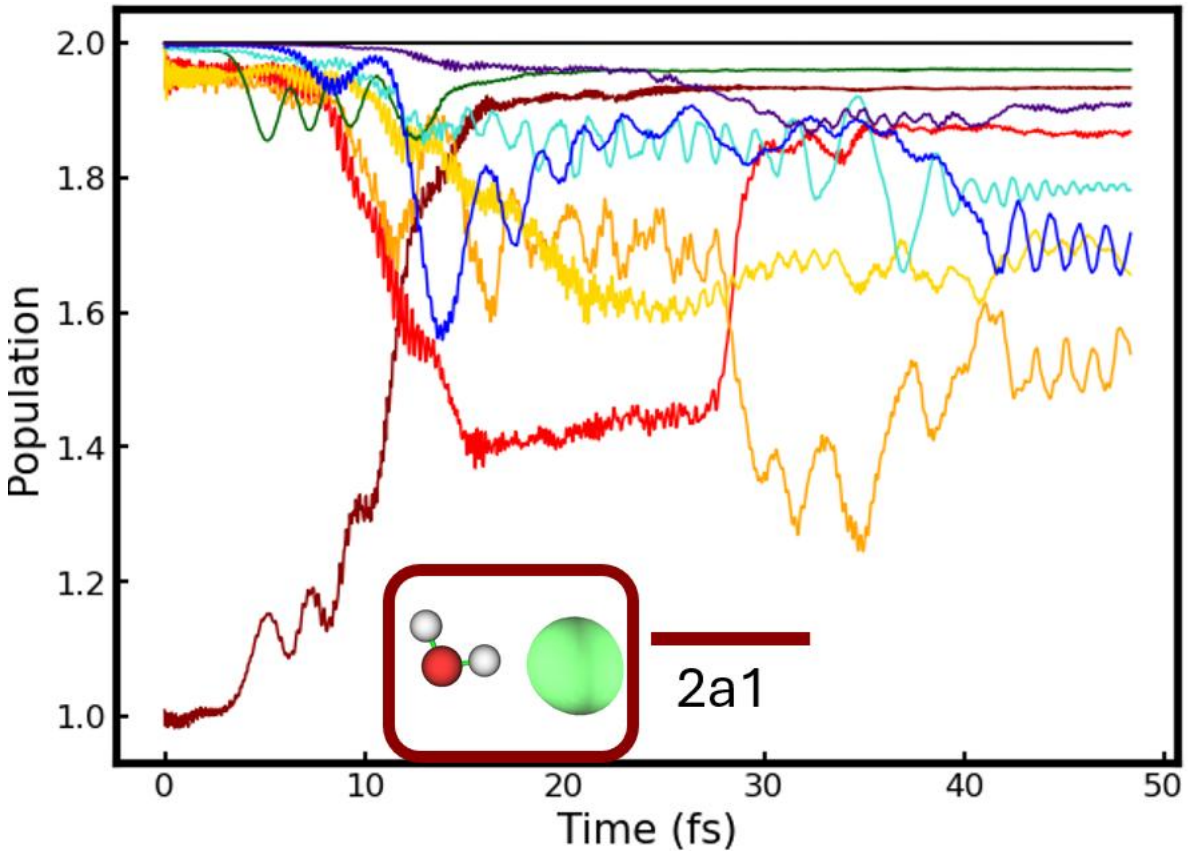

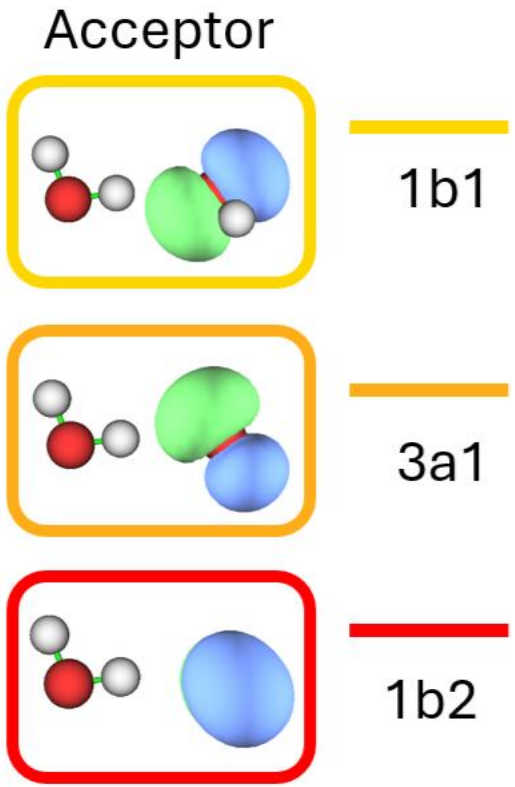

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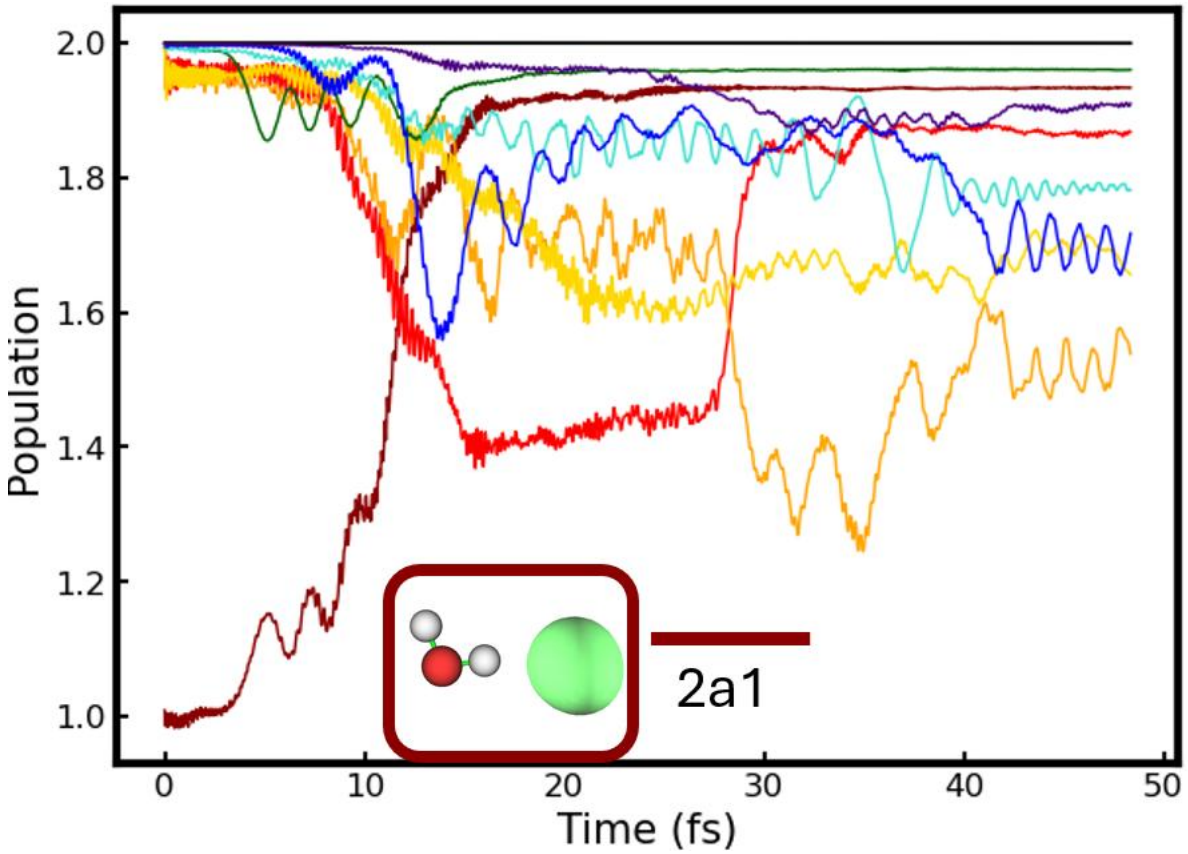

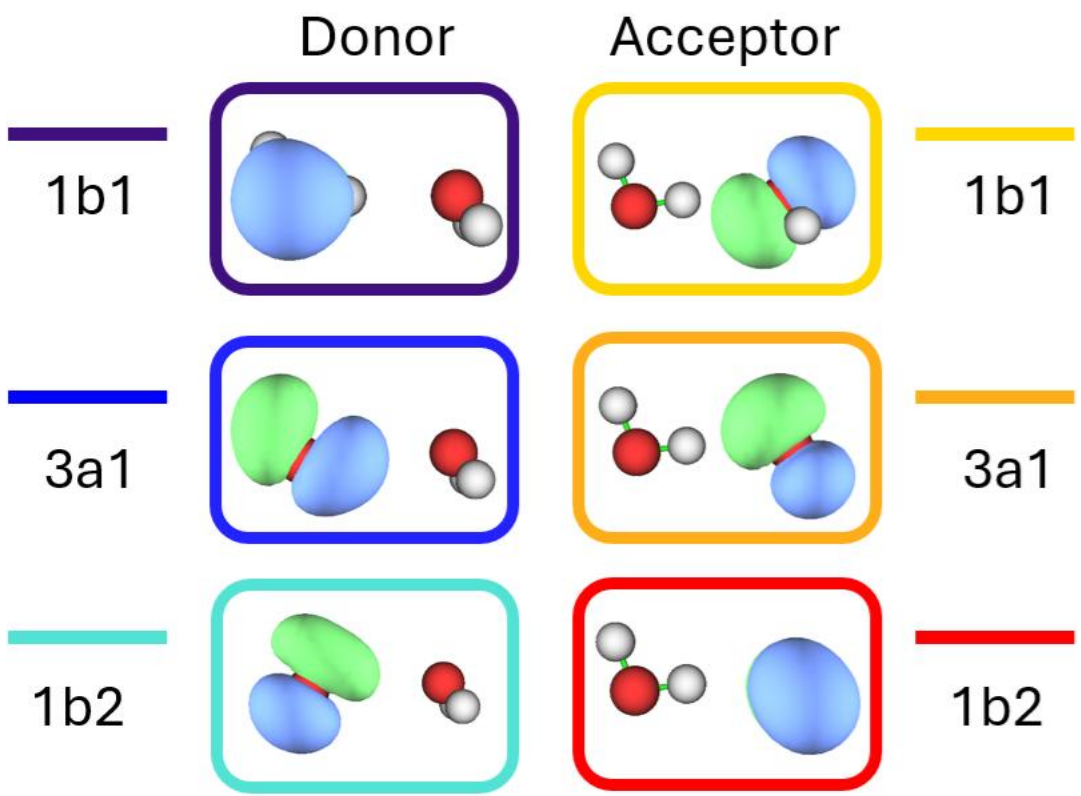

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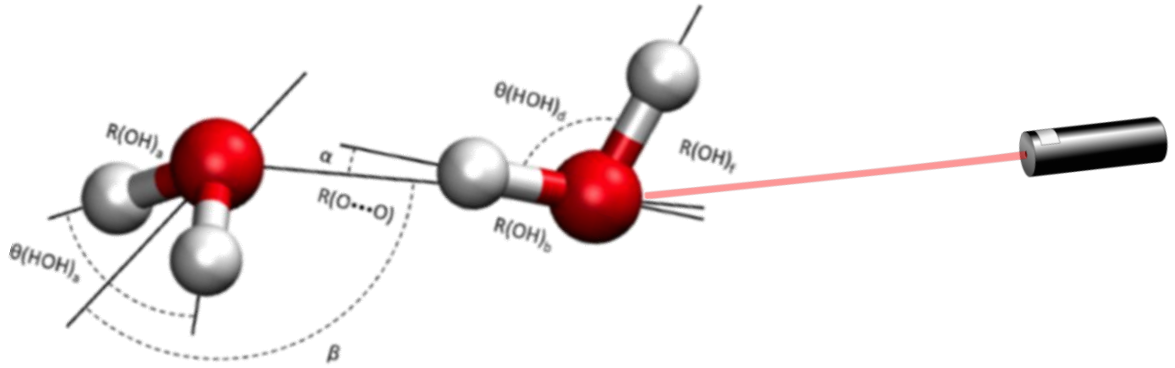

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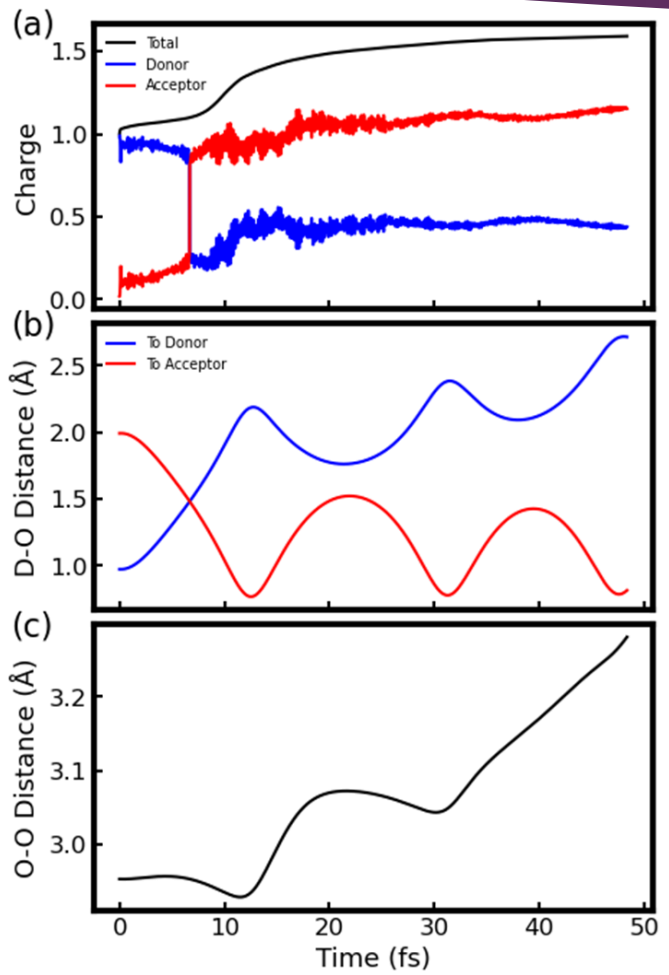

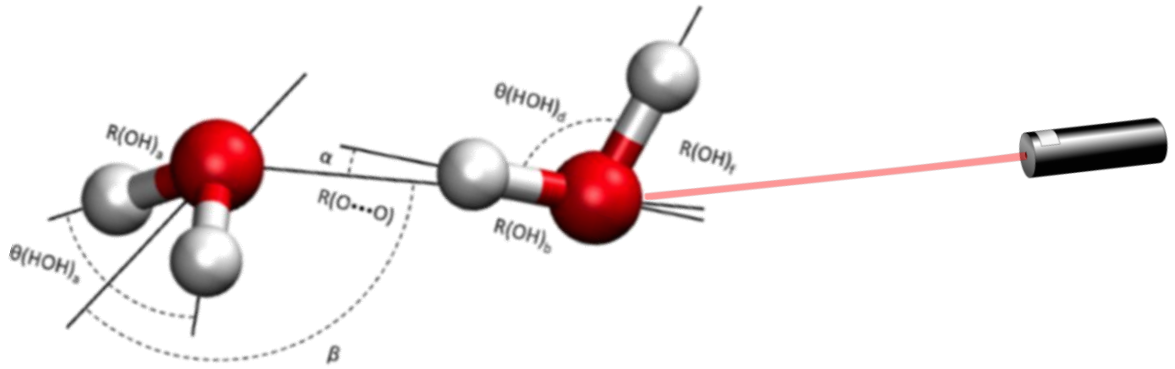

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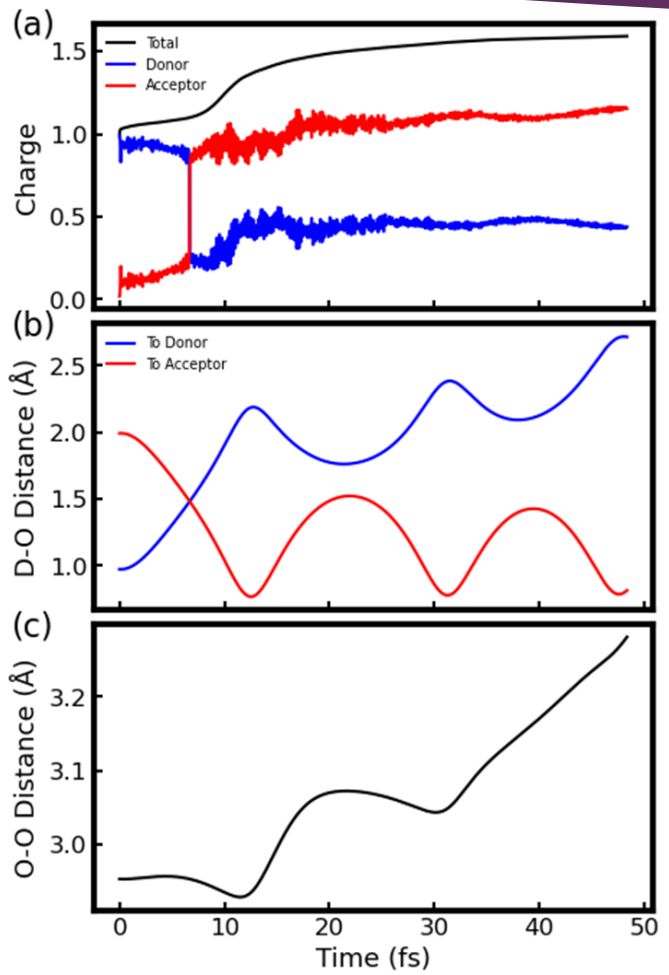

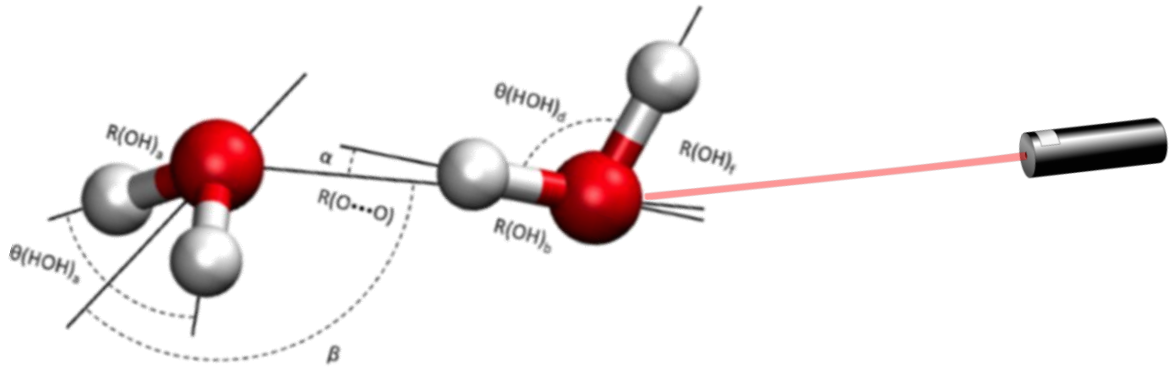

$$D_2O + DOD^{+*} \xrightarrow{PT} D_3O^+ + OD^* \xrightarrow{Auger} D_3O^+ + OD^+$$

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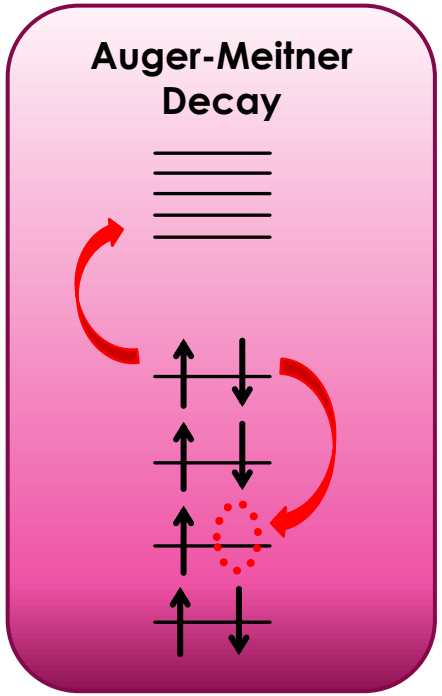
Acceptor



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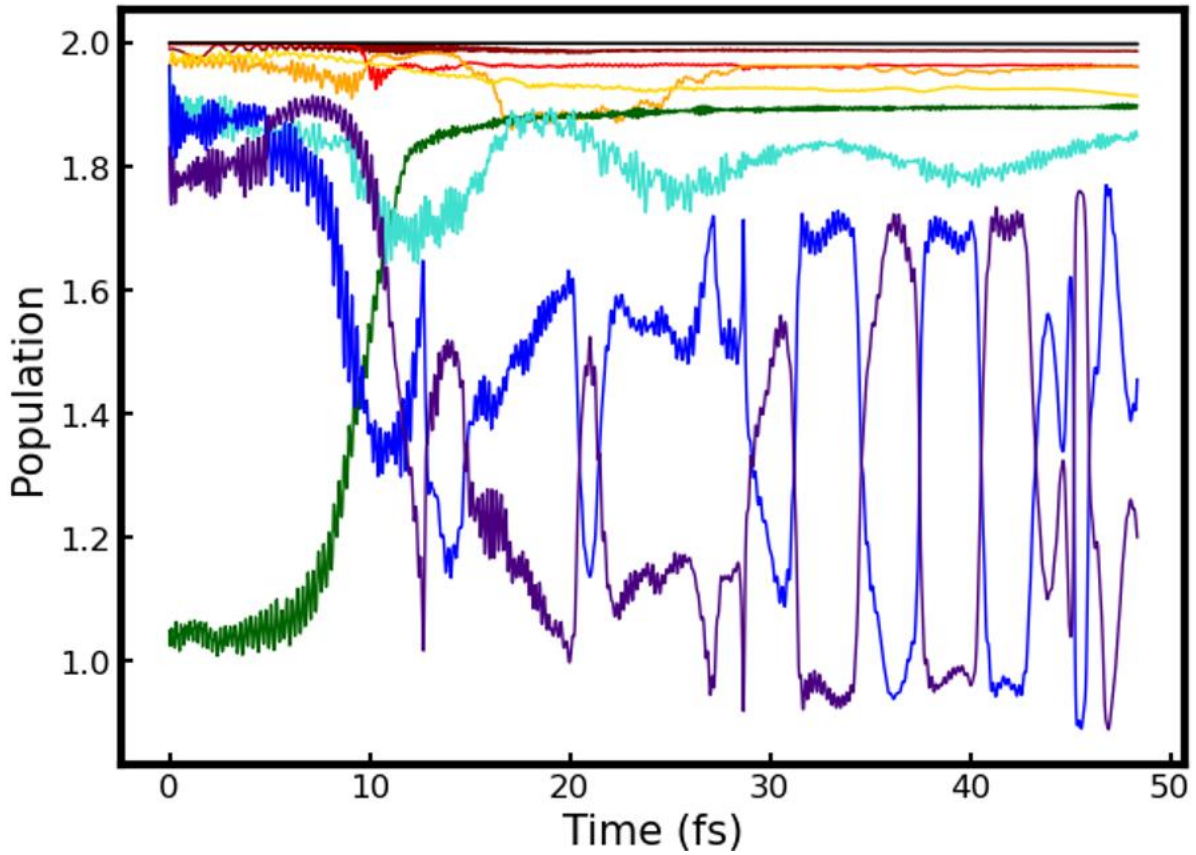

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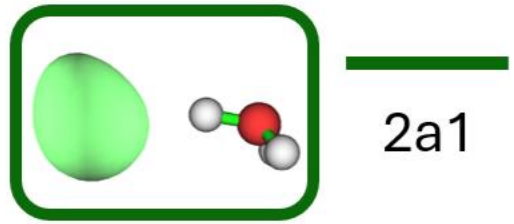

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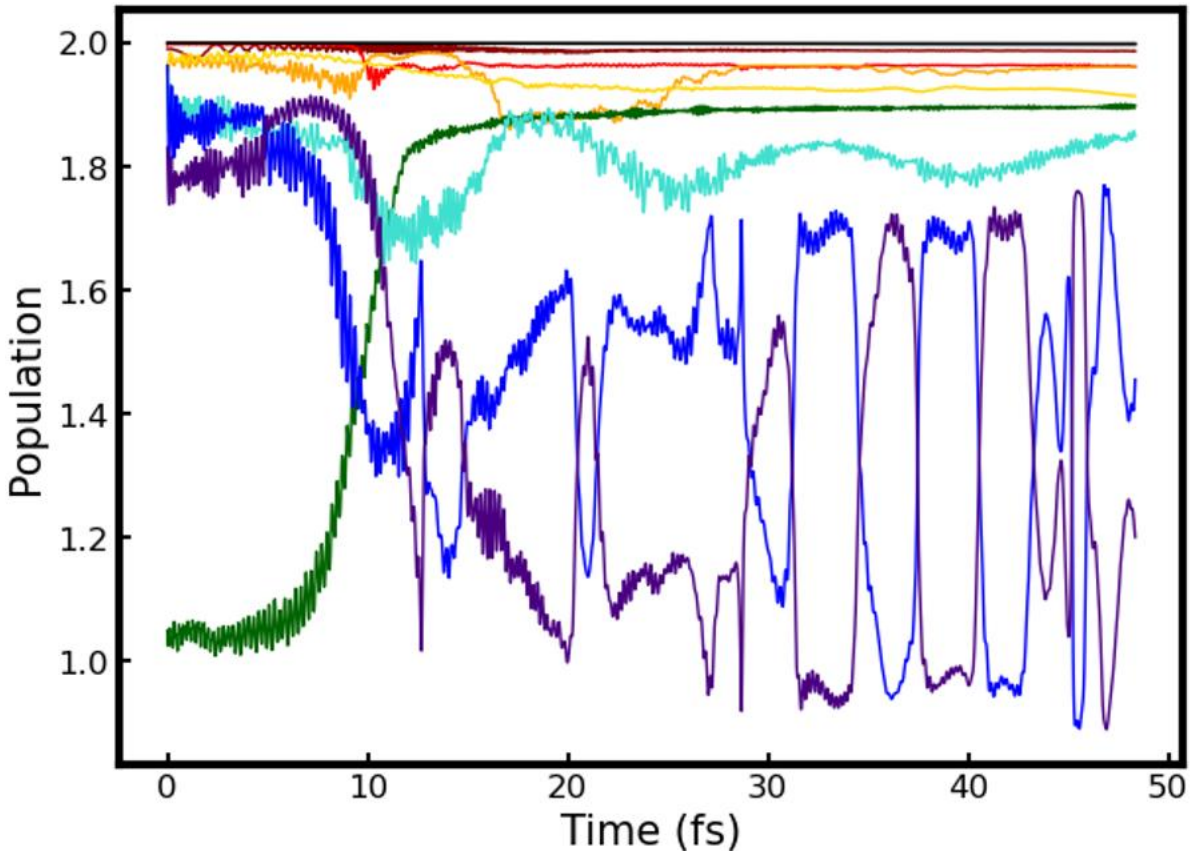

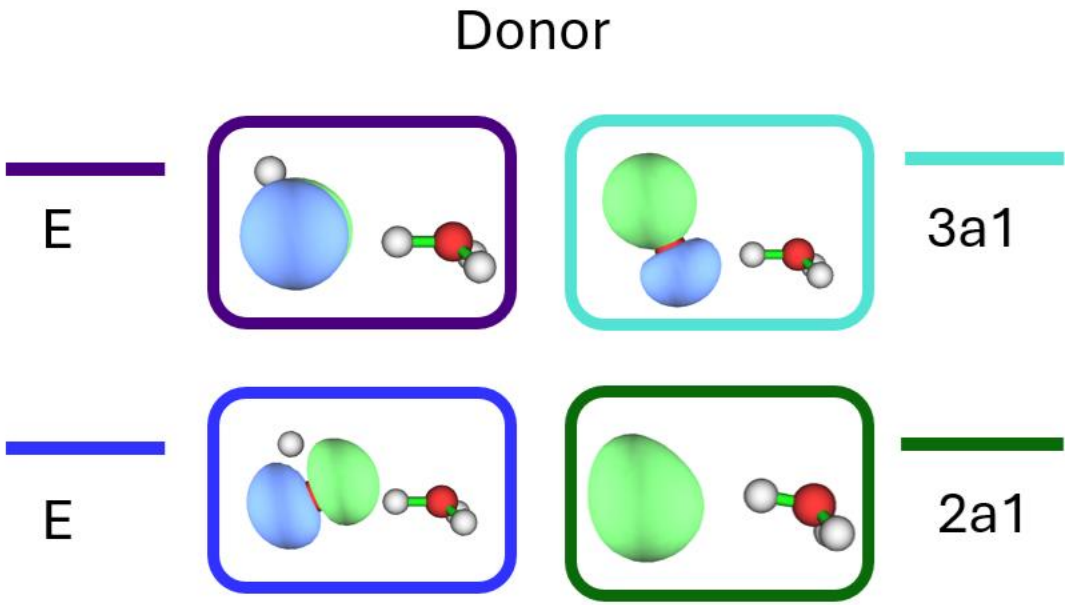

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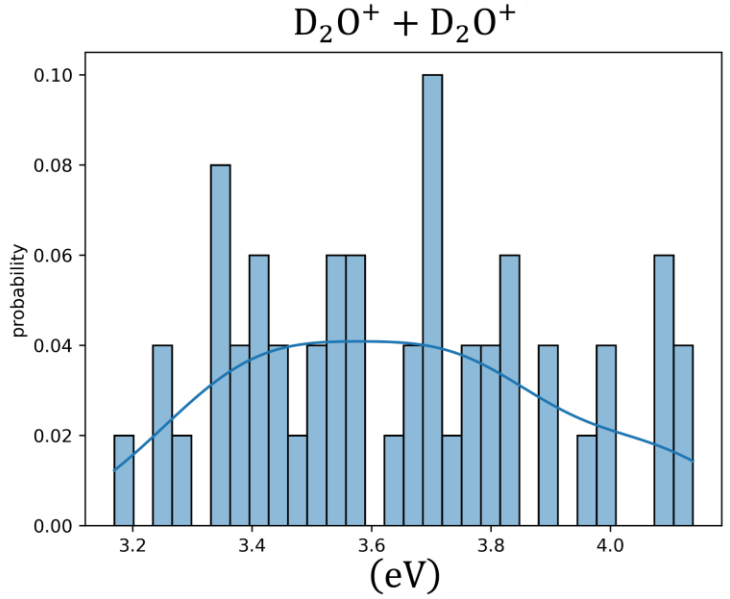
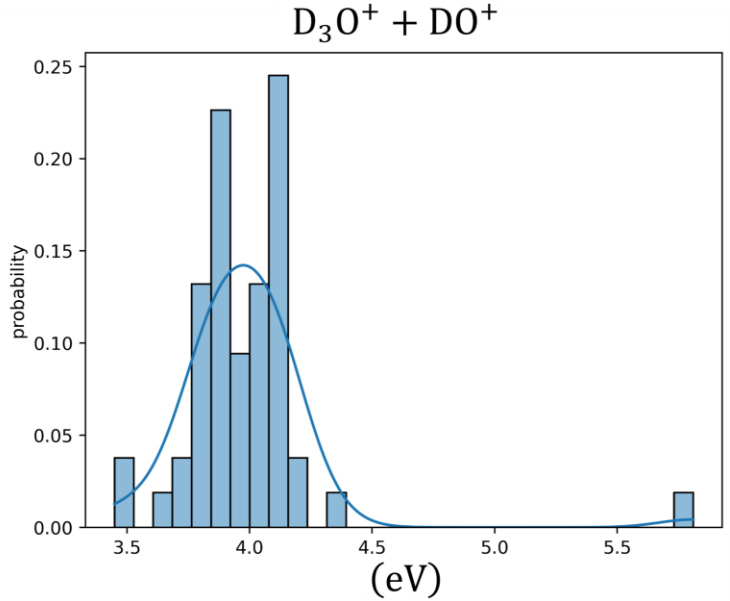
- From BOMD we predict final fragmentation products and kinetic energy release (KER) of the fragments





Credit to Dr. Yi-Siang Wang

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- We predict a new plausible mechanism for ICD within water dimers in the case of proton donor excitation consistent with our experimental collaborators and the literature

Acknowledgements

- Project members: Yi-Siang Wang, Matthew Rohan
- Code developers: Matthew Rohan, Mikhayla Clothier
- Our code called TIDES is currently available on github, plans to implement our methodology directly into PSI4 are underway.