

Nonadiabatic fragmentation of H_2O^+ and isotopomers

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Synopsis The $\text{H}_2\text{O}^+(\tilde{B}^2\text{B}_2)$ and $\text{HDO}^+(\tilde{B}^2\text{B}_2)$ non-adiabatic fragmentation is studied using wavepacket propagation on four coupled electronic states. Fragment ratios are obtained and compared with photodissociation experiments. The isotopic effects and non-Franck-Condon initial conditions are also explored and compared with experimental data.

Collisions of electrons, photons and ions on molecular targets can lead to the formation of molecular ions in different electronic states, which can decay by emitting radiation or by fragmentation. In two recent studies [1, 2], we have addressed the dynamics of the excited water cation $\text{H}_2\text{O}^+(\tilde{B}^2\text{B}_2)$, which could be formed when a $1b_2$ electron of the molecule is removed in a sufficiently sudden ionization collision [3].

For this study, potential energy surfaces (PES) and non-adiabatic couplings (NAC) were obtained from multireference configuration interaction wavefunctions. The integration of the time-dependent Schrödinger equation was carried out using the GRID-TDSE package [4], and we considered two initial conditions: a Franck-Condon wave packet (FCWP), corresponding to the ground vibrational state of H_2O , and a vibrationally excited wave packet (VEWP), a excited vibrational state of the adiabatic $\tilde{B}^2\text{B}_2$.

In this calculation, we consider the propagation of the initial wavepacket into the PES corresponding to the electronic states \tilde{X} , \tilde{A} , \tilde{B} and \tilde{C} , which are connected by non-adiabatic couplings. The initial wave packet in \tilde{B} undergoes a strong transition to \tilde{A} in a few femtoseconds due to a conical intersection (CI) between the corresponding PES. The wave packet lands in \tilde{A} with an important excitation of the bending mode. The molecule is then driven towards the linear geometry, where states \tilde{A} and \tilde{X} are degenerate and connected via a Renner-Teller coupling, which allows the population of the ground state \tilde{X} . The fragmentation can take place either through the energy transfer from the bending to the stretching motion in the \tilde{A} state, leading to the dissociation into $\text{OH} + \text{H}^+$, or, after the Renner-Teller

transition, in the \tilde{X} state, leading to the dissociation into $\text{OH}^+ + \text{H}$. Our calculation supports the experimental branching ratios of Tan *et al.* [5] (starting with a FCWP) and those of Harbo *et al.* [6] (starting with a VEWP).

Fragmentation branching ratios for isotopomers HDO^+ and D_2O^+ have also been considered. As illustrated in Fig. 1, substitution of H by D favors the production of molecular ions against of atomic ones, in agreement with experimental data [7].

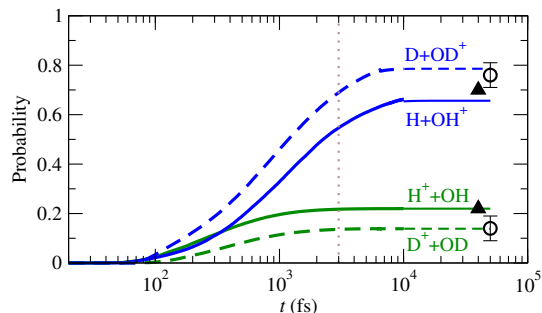


Figure 1. Fragmentation probabilities of D_2O^+ and $\text{H}_2\text{O}^+ \tilde{B}$. Lines: present results; experimental data: circles [7] and triangles [5].

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References

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