

Ab initio description of the fragmentation of $\text{H}_2\text{O}^+(\tilde{B}^2\text{B}_2)$

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Synopsis A quantum-dynamical study of the fragmentation of $\text{H}_2\text{O}^+(\tilde{B}^2\text{B}_2)$ is carried out by using wave packet propagations on *ab initio* potential energy surfaces connected by nonadiabatic couplings assuming a Franck-Condon initial wave packet from the ground state of the water molecule. The simulations indicate that a conical intersection between the $\tilde{B}^2\text{B}_2$ and $\tilde{A}^2\text{A}_1$ states of H_2O^+ allows the transfer of 80% of the initial wave packet within 30 fs, while the Renner-Teller coupling between the $\tilde{A}^2\text{A}_1$ and $\tilde{X}^2\text{B}_1$ states determines the fragmentation branching ratios in the ps timescale.

The single ionization of water molecules by collisions with photons, electrons or ions leaves H_2O^+ in several possible electronic states: $\tilde{X}^2\text{B}_1$, $\tilde{A}^2\text{A}_1$ and $\tilde{B}^2\text{B}_2$. The first two states are obtained after removal of one electron from the two highest occupied molecular orbitals of H_2O , and the corresponding cations do not fragment; however, the energy of the third state lies above the dissociation limits of the first two ones in a large fraction of geometry configurations, and it undergoes predissociation.

In a recent work [1], we have carried out a grid-based wave packet time-propagation in several potential energy surfaces (PESs), including nonadiabatic transitions between them. Both PESs and nonadiabatic couplings have been obtained *ab initio* in a set of $50 \times 76 \times 73$ grid points in Jacobi coordinates (R, r, θ) . By considering four *ab initio* PES, and the corresponding nonadiabatic couplings, we have studied the fragmentation dynamics of water ions, assuming they are formed through Franck-Condon transitions from the ground state of the water molecule. Our simulations show that, within 10 fs, most of the initial wave packet in \tilde{B} is transferred through a conical intersection to \tilde{A} . On the other hand, the inclusion of the Renner-Teller coupling between the $\tilde{A}^2\text{A}_1$ and $\tilde{X}^2\text{B}_1$ states at linear geometries produces fragmentation branching ratios that nicely reproduce the experimental values of [2].

We have also considered an alternative fragmentation mechanism that involves spin-orbit transitions from both \tilde{B} and \tilde{A} states to the repulsive $\text{H}_2\text{O}^+(\tilde{a}^4\text{B}_1)$ state. This path leads to a small ion production due to the small fraction of the wave packet that explores the relevant crossing regions in the PESs, and the small coupling.

Figure 1(a) displays the time evolution of the

populations of the \tilde{X} , \tilde{A} and \tilde{B} electronic states of H_2O^+ within the grid studied, for $K = 1$, with K the quantum number corresponding to the projection of the total angular momentum along the internuclear axis at linear geometry configurations. Figure 1(b) shows the probabilities of formation of the different ions and radicals.

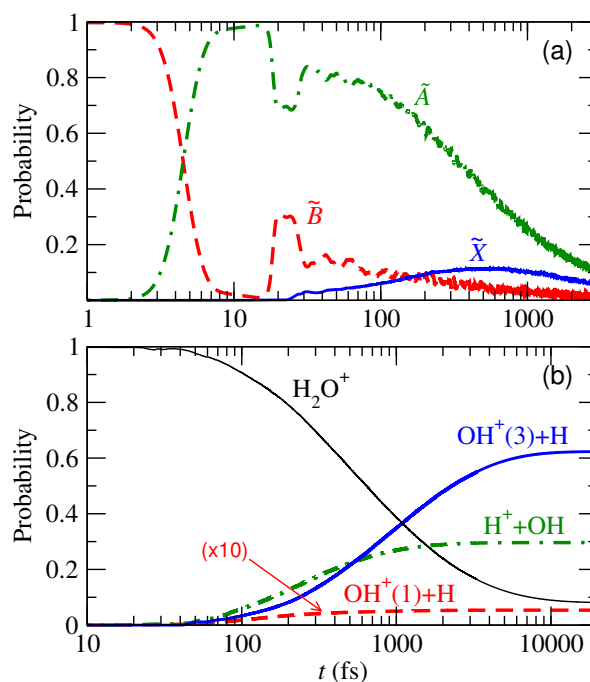


Figure 1. Time evolution of (a) the populations of $\tilde{X}^2\text{B}_1$, $\tilde{A}^2\text{A}_1$ and $\tilde{B}^2\text{B}_2$ electronic states of H_2O^+ and (b) probability of production of the different fragments.

References

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