

# A non-adiabatic wave packet study of the post-collisional fragmentation of $\text{H}_2\text{O}^+$

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**Synopsis** We present a wave packet study of the fragmentation of  $\text{H}_2\text{O}^+$  and  $\text{HDO}^+$  in the  $\tilde{B}^2\text{B}_2$  electronic state. The calculated fragmentation branching ratios show good agreement with photodissociation experiments and with the isotopic dependence of fragmentation after ionization by collisions of  $\text{H}_2\text{O}$  with multicharged ions.

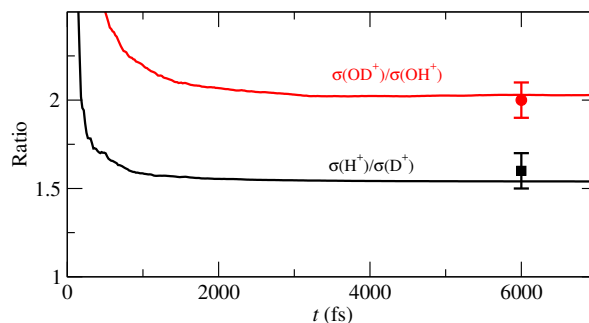
In a previous paper [1], we have carried out a wave-packet-propagation calculation to study the fragmentation of the water cation on the  $\tilde{B}$  state. The initial condition of our calculation was a Franck-Condon wave packet (FCWP), obtained by vertical ionization of the ground vibrational state of  $\text{H}_2\text{O}$ . The calculation employed the GRID-TDSE package [2] modified in order to incorporate non-adiabatic transitions, to solve time-dependent Schrödinger equation. In that work we showed that the dissociation mechanism involves non-adiabatic transitions to the states  $\tilde{A}$  and  $\tilde{X}$ . The transition  $\tilde{B}-\tilde{A}$  takes place in a few femtoseconds in the vicinity of the conical intersection (CI) between the corresponding potential energy surfaces. When the wave packet approaches the linear configuration, the states  $\tilde{A}$  and  $\tilde{X}$  are degenerate and connected via a Renner-Teller coupling, which populates 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, leading to the dissociation into  $\text{OH}^++\text{H}$ . A stringent test of the method is provided by the comparison with the photodissociation experiments of Harbo *et al.* [4], who measured the ratio between the cross sections for production of the fragments  $\text{OH}+\text{H}^+$  and  $\text{OH}^++\text{H}$  in a crossed-beam experiment where  $\text{H}_2\text{O}^+$  was irradiated with a 532 nm (2.33 eV) laser, obtaining

$$\gamma = \frac{\sigma(\text{OH}+\text{H}^+)}{\sigma(\text{OH}^++\text{H})} = 1.3 \pm 0.3 \quad (1)$$

In order to simulate this experiment, we have run the wave packet calculation starting from the vibrational wavefunction of  $\tilde{B}$  electronic state with energy 2.30 eV. The wave-packet propagation leads to a similar result,  $\gamma_{\text{exc}} = 0.97$ , in contrast to the Franck-Condon value  $\gamma_{\text{FC}} = 0.31$  [5, 1]. We have found that the dissociation mechanism from the excited vibrational state is similar to that from the FCWP, but in the former case fragmentation takes place fast after

transition to the state  $\tilde{A}$ , which hinders the transition to  $\tilde{X}$  and the ensuing fragmentation into  $\text{OH}^++\text{H}$ .

We have also considered the isotopic dependence of the fragmentation branching ratios by carrying out wave packet calculations for the isotopomers  $\text{HDO}^+$  and  $\text{D}_2\text{O}^+$ . With respect to the particular case of the fragmentation of  $\text{HDO}^+$ , time of flight coincidence experiments [3] of collisions of  $\text{H}^+$  and  $\text{F}^{7+}$  with water molecules have pointed out a strong preference of breaking the OH bond for both single and double ionization of water molecules. We have carried out the non-adiabatic dynamical calculation of the fragmentation of this isotopomer to study the bond cleavage preference. The good agreement of our results with the experimental ones is illustrated in Fig. 1.



**Figure 1.** Comparison of the bond cleavage preference results with the experimental ones [3].

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## References

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