Singlet and triplet states dissociation of doubly charged HDO, H2O

Serge Martin, Li Chen, Richard Bredy, Jérôme Bernard, A. Cassimi

Singlet and triplet states dissociation of doubly charged HDO, H_2O and D_2O as a function of internal energy

XXIX International Conference on Photonic, Electronic, and Atomic Collisions (ICPEAC2015) IOP Publishing
Journal of Physics: Conference Series **635** (2015) 032080 doi:10.1088/1742-6596/635/3/032080

Singlet and triplet states dissociation of doubly charged HDO, H_2O and D_2O as a function of internal energy

S. Martin*[1], L. Chen*, R. Brédy*, J. Bernard* and A. Cassimi†

* Institut Lumière Matière, UMR5306 Université Lyon 1-CNRS, Université de Lyon 69622 Villeurbanne cedex, France

† CIMAP, GANIL Université de Caen, Bd. H. Becquerel, Caen, France

Synopsis The fragmentation of HDO^{2+}, H_2O^{2+} and D_2O^{2+} is reported as a function of the excitation energy. The doubly charged ions were prepared selectively to triplet or singlet excited states in collisions with F^+ and H^+ at 3 keV, respectively. For HDO^{2+} the isotopic ratio, ratio of probabilities for the two dissociation channels $OD^+ - H^+$ over $OH^+ - D^+$, was estimated to be 4.5 ± 0.8 using H^+ and 3.8 ± 0.8 using F^+ projectiles. Results are compared with recent calculations.

Fragmentation of doubly charged water or heavy water ions has been studied with a large variety of excitation methods using photons, electrons, slow or fast ion impact. Two-body and/or three-body dissociation schemes have been predicted in theoretical calculations for each molecular energy state. For HDO^{2+} the isotopic ratio defined as the ratio of probabilities for the two dissociation channels $\frac{OD^+-H^+}{OH^+-D^+}$ was calculated to be 8.6 for the ground triplet state. For the first and second singlet states the ratios were found to be 3 and 15.7, respectively [1]. These calculations showed a strong dependence on the energy and the multiplicity of the HDO^{2+} molecular state.

In this work, we investigated the fragmentation of HDO^{2+}, H_2O^{2+} and D_2O^{2+} prepared selectively to singlet or triplet state due to the spin conservation rule using $H^+ + M \rightarrow H + M^{2+}$ (singlet states) or $F^+ + M \rightarrow F + M^{2+}$ (triplet states) collisions at 3 keV. M represents the mixture of HDO, H_2O and D_2O. Excitation energies of singlet and triplet states of the doubly charged parent ions with respect to the neutral ground state have been measured for different dissociation channels using the CIDEC method [2]. The doubly charged parent ions were identified by analyzing the correlation between the charged fragments. For HDO^{2+}, $OD^+ - H^+$ is the dominant dissociation channel for both multiplicities. For this channel the excitation energy of HDO^{2+} parent ion was measured to be 42.2 ± 0.5 eV and 40.7 ± 0.3 eV in H^+ and F^+ collisions. The isotopic ratio was estimated to be 4.5 ± 0.8 using H^+ and 3.8 ± 0.8 using F^+ projectiles. For F^+ projectiles the discrepancy between the measured and the theoretical isotopic value suggests that the initial vibrational and rotational states of neutral HDO play an important role in the dissociation dynamics of the doubly ionized molecules. The good agreement between the measured excitation energy and the calculated electronic energy levels indicates that the molecules are prepared to electronic excited states by electron capture directly from inner orbitals without vibrational energy deposition. This is also confirmed by our KER (kinetic energy release) measurements which are comparable to values obtained in photon ionization.

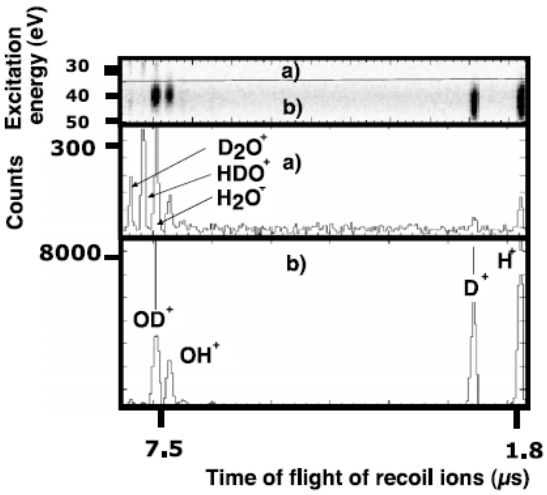

Figure 1. $H^+ + M \rightarrow H + M^{2+}$ (singlet states) collisions. Top panel: excitation energy (E_{exc}) versus time of flight of the recoil ions. (a) Mass spectrum for $E_{exc} < 34$ eV. (b) Mass spectrum for $E_{exc} > 34$ eV.

References

[1] B. Gervais *at al* 2009 *J. Chem. Phys.* **131** 024302

[2] S. Martin *at al* 2015 *J. Chem. Phys.* **142** 094306

[1] E-mail: smartin@univ-lyon1.fr