

Isotope Effect in D₂O Negative Ion Formation in Electron Transfer Experiments: DO – D Bond Dissociation Energy

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Negative ion formation in electron transfer processes mediated by collision of neutral potassium atoms with bare H₂O and D₂O molecules have been thoroughly investigated for the first time employing experimental and theoretical methodologies. The time-of-flight mass spectra recorded in a wide range of collision energies from 29 to 630 eV in the lab frame, yield ions assigned to OH⁻/OD⁻, O⁻ and H⁻/D⁻ with no evidence of parent anion formation. The branching ratios show a relevant energy dependence with important isotope effect in case of D₂O relative to H₂O especially in the intermediate/higher collision energies. The most intense fragment anions in the whole energy range investigated have been assigned to OH⁻/OD⁻ in contrast to dissociative electron attachment experiments. The electronic state spectroscopy of H₂O and D₂O has been further investigated by recording potassium cation energy loss spectra in the forward scattering direction at 205 eV impact energy (lab frame), with quantum chemical calculations for the lowest-lying unoccupied molecular orbitals in the presence of a potassium atom supporting mostly of the experimental findings. The collision dynamics was further investigated from the character of the singly excited (1b₂⁻¹) molecular orbital and doubly excited states.¹

References

1. S. Kumar, M. Hoshino, B. Kerkeni, G. García, and P. Limão-Vieira, *J. Phys. Chem. Lett.* **14**, 5362 (2023), and references therein.