

Water molecule complex study: experiment and *ab initio* calculations of rovibrational levels and dissociation energy

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Spectrum of the water molecule is of fundamental importance for a various applications. It is also used as a benchmark for spectroscopic calculation methods. We have performed a comprehensive experimental and theoretical study of highly-lying rovibrational levels and the lowest dissociation energy threshold for the water molecule and its isotopologues. The initial measurements and calculations performed for the main isotopic species, H₂¹⁶O molecule [1-3], have been subsequently extended to HD¹⁶O and other isotopologues.

Energies of rovibrational levels, as well as dissociation energy, have been calculated using *ab initio* methods. For experimental measurement of these values, a multi-resonance vibrational overtone excitation scheme has been employed. This technique offers a several orders of magnitude higher excitation efficiency than that of a direct absorption approach, allowing a promotion of a significant fraction of water molecules to the energy region as high as above the lowest dissociation threshold. In addition to this the state-selective nature of the multi-step excitation facilitates rotational assignment of the accessed states, making the determination of the dissociation energy very precise. In the latest work [4], this experimental approach was used to determine the lowest dissociation energy, D_0 , for the water isotopologue HD¹⁶O as $41239.7 \pm 0.2 \text{ cm}^{-1}$ and to improve D_0 for H₂¹⁶O to $41145.92 \pm 0.12 \text{ cm}^{-1}$. *Ab initio* calculations, which include a systematic basis set and the electron correlation convergence studies, relativistic and Lamb shift effects, as well as corrections beyond the Born–Oppenheimer approximation, agree with the measured values within 1 and 2 cm⁻¹, respectively. In addition to this, the D_0 values for other five major isotopologues of water molecule were predicted. In particular, D_0 for H₂¹⁸O was predicted to be 41154.2 cm^{-1} which was lately measured in Laboratoire de Chimie Physique Moléculaire, EPFL, validating the predicted value within 1 cm⁻¹ [5].

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