



European XFEL Theory Seminar

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Vibrational Spectroscopy and Dynamics of the Hydrated Proton by Full-Dimensional Quantum Mechanics

Protonated water clusters $[H(H_2O)_n]^+$ constitute the basic units that explain the structural and dynamical features of the hydrated proton in water. Embedded in biological and materials structures, these clusters mediate proton mobility, e.g. across membranes, and hence play an important role in charge transport phenomena.

Therefore, over the years and until today, the infrared (IR) spectroscopy of $[H(H_2O)_n]^+$ clusters has been investigated in great detail in the gas phase mostly using action spectroscopy techniques [1]. In parallel, different kinds of theoretical approaches have been applied in order to reproduce and assign those spectra. Protonated water clusters are characterized by their large fluxionality and anharmonicity, with several equivalent potential energy minima connected by shallow barriers, and by marked resonance phenomena among their vibrational modes.

To date, only calculations based on the MCTDH approach were able to reproduce the IR spectrum of the Zundel cation ($n=2$) in the full spectral range extending from 0 to 4000 cm^{-1} and could assign all of its most prominent spectral features[2,3].

In this contribution, we will discuss and review the key aspects of the linear IR spectroscopy of the Zundel cation ($n=2$). We will discuss our latest results on pump-probe spectra of this species and will present as well preliminary results on the complete IR spectrum of the Eigen cation ($n=4$), whose gas-phase spectrum has been recently measured [4], and for which an accurate potential energy surface is available [5]. The Eigen cation is 33-dimensional. Coping with this large dimensionality in a set of internal coordinates that faithfully describe their flexibility and couplings over the complete spectral range requires of various state-of-the-art technologies: automatic analytic derivation of kinetic energy operators, efficient fitting of potential energy surfaces to product form by Monte-Carlo approaches, and last but not least, the multilayer extension of MCTDH to cope with the highly dimensional quantum mechanics problem.

[1] J.M. Headrick et al., Science 308, 1765 (2005) DOI: 10.1126/science.1113094

[2] OV, F. Gatti, H.-D. Meyer, Angew. Chem. Int. Ed. (VIP) 46, 6918 (2007) DOI: 10.1002/anie.200702201

[3] OV, F. Gatti, H.-D. Meyer, Angew. Chem. Int. Ed. (VIP) 48, 352 (2009) DOI: 10.1002/anie.200804646

[4] T.K. Esser et al., J. Phys. Chem. Lett. 9, 798 (2018) DOI: 10.1021/acs.jpcclett.7b03395

[5] Q. Yu, J.M. Bowman, J. Phys. Chem. A 123, 1399 (2019) DOI: 10.1021/acs.jpca.8b11603

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