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Spectral Signatures of Weak Acid Dissociation Intermediates at Cryogenic Temperatures

Prof. Radu Ion Iftimie

Département de Chimie, Université de Montréal

The existence of a broad, mid-infrared absorption ranging from 1000 to 3000 cm^{-1} is usually interpreted as a signature for the existence of protonated water networks. Herein, we use cryogenic mixtures of water and hydrogen fluoride (HF), and show experimental and computational evidence that similarly wide absorptions can be generated by a broad distribution of proton-shared and ion-pair complexes. In the present case, we demonstrate that the broadening is mainly inhomogeneous, reflecting the fact that the topology of the first solvation shell determines the local degree of ionization, and the shared-proton asymmetric stretching frequency within $H_2O{\cdot}HF$ complexes. The extreme sensitivity of the proton transfer potential energy hypersurface to local hydrogen bonding topologies modulates its vibrational frequency from 2800 cm^{-1} down to ~1300 cm^{-1}, the latter value being characteristic of solvation geometries that yield similar condensed phase proton affinities for H_2O and fluoride. By linking the local degree of ionization to the solvation pattern, we are able to propose a mechanism of ionization for HF in aqueous solutions, and to explain some of their unusual properties at large concentrations. The present findings demonstrate the existence of an additional level of complexity when interpreting the origin of broad absorptions in proton translocation systems, as they could signal the presence of un-dissociated acid groups forming an extremely strong H-bond with a solvating water molecule.

Radu Iftimie entered the Ecole Normale Supérieure (ENS, Paris, France) in 1996 via the competition reserved to foreign students; he obtained a Licence and Maîtrise (1997) there before earning a Diplôme d'Etudes Approfondies de Physicochimie Moléculaire from Université Paris XI (Orsay) in 1998. He then went on to University of Toronto to work with Jeremy Schofield on method development for computing proton transfer reactions, mostly in clusters, and completed his Ph.D. in 2003. He was then an NSERC post-doctoral fellow at New York University with Mark Tuckerman, working on method development for Car-Parrinello methods in conjunction with orbital localization methods, before taking on a position of Assistant Professor at Université de Montréal in 2005. Prof. Iftimie's research focuses on method development for new pseudopotentials that afford accurate QM/MM simulations, and proton transfer and acid dissociation reaction mechanism in water and models of water (amorphous ice for example). This last area of research involves a collaboration with Patrick Ayotte from Université de Sherbrooke.