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# Theoretical core spectroscopy of molecules interacting with ice surfaces

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## Résumé

Ice is everywhere in the environment and plays an essential role as a catalyst for reactions between atmospheric trace gases. The uptake of halogenated molecules to ice has been proposed to have a major impact on geo-chemical cycles, human health and ozone depletion in the stratosphere [1]. X-ray photoelectron spectroscopy (XPS) [2], serves as a powerful technique to delineate the elemental composition of interacting molecular systems due to its surface sensitivity. Given the existence of complex physico-chemical processes such as adsorption, desorption, and migration within the ice matrix, it is important to establish a theoretical framework to determine the structural and electronic properties (electron binding energies, chemical shifts, etc) of these molecules or species under different conditions such as temperature and concentration. The focus of this work is to construct an embedding framework employing DFT and WFT to model and interpret photoelectron spectra of adsorbed halogenated species on ice surfaces at the core level with the highest accuracy possible.

We utilize a theoretical approach to determine the electron binding energies of adsorbed halide (HCl) and its ion (X<sup>-</sup>, Cl<sup>-</sup>), which has been suggested to cause perturbation in the hydrogen bonding network of the liquid-like layer on ice [3]. We construct model systems consisting of the halide/halide ion adsorbed on different (H<sub>2</sub>O)<sub>n</sub>-clusters (n = 8, 50, 100, 150 and 200). The structure used is obtained through classical molecular dynamics (CMD) simulation with a force field. For the interpretation of XPS spectra, the core energy shift is of relevance and the interaction of molecules needs to be modeled in a relativistic manner [4]. In this respect, the core-electron binding energies of the adsorbed halide ion are explored through the exact 2-c SR/SO-X2CAMF CVS-EOM-IP-CCSD and approximate 2-c SR/SO-ZORA through the SAOP model.

We show that the use of fully quantum mechanical embedded method to treat solute-solvent systems is computationally efficient, yet accurate enough to determine the electronic properties of the solute system (halide ion) as well as the long-range effects of the solvent environment (polar ice). The results of our calculations add further information to the debate on the long-range effects of water molecules on ionic systems.

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**Mots-Clés:** core spectroscopy, CVS, EOM, IP, CCSD, embedding