Contribution ID: **37**   Type: **Contributed talk**

Vibrational Spectroscopy of Monohydrated Radical Cation Complexes

Monday 15 September 2025 17:00 (20 minutes)

In neutral bimolecular complexes, the hydrogen bond is the strongest possible intermolecular non-covalent interaction. It is well-studied with techniques such as infrared spectroscopy, due to the typical redshift in wavenumber and enhancement in the intensity of the bonded OH-stretch fundamental transition. In the present work, the monohydrated radical cation complexes $(H_2O\text{-}X)+$ are considered with X = Ar, N_2, CO_2 and N_2O. The vibrational spectra are calculated using second-order vibrational perturbation theory (VPT2) and a more advanced local mode model (LM). The VPT2 and the LM models predict redshifts of the bonded OH-stretch in hydrogen-bonded charged complexes that are an order of magnitude larger than their neutral counterparts. This can be attributed to the increased binding energies in the charged complexes. The transition wavenumber of the bonded OH-stretch in $(H_2O\text{-}Ar)^+$ predicted from our calculations agrees with the experimentally observed transition. In the sequence of the binding partners from Ar to N_2O, the calculated redshifts increase, in agreement with the increase in the binding energies. In charged radical complexes, an additional binding motif occurs through the hemi bond, which has a bond strength comparable to that of the hydrogen bond. To aid the interpretation of the experimental spectra, it is important to calculate the OH-stretch transition energies accurately for both the strongly hydrogen-bonded and hemi-bonded isomers. Such considerations are especially important because of the complicated nature of the spectra obtained for hydrated radical cation complexes, owing to the limitations in techniques such as photodissociation spectroscopy.

Keywords

Hydrogen bond: strong; Gas-phase; Theoretical calculations;

This abstract is submitted for....

HBond 2025 conference

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