

Conformational Dynamics and Finite-Temperature Infrared Spectra of Water Clusters adsorbed on Polycyclic Aromatic Hydrocarbons

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Polycyclic Aromatic Hydrocarbons (PAHs) have raised growing interest since the discovery in the mid-eighties of the Aromatic Infrared Bands, a set of mid-IR emission bands observed in many regions of the interstellar medium, and assigned to a population of PAHs [1]. Despite many experimental and theoretical studies, no specific PAH molecule has been identified yet.

Most published theoretical spectra of PAH-derived species are computed in the harmonic approximation. However, interstellar spectra are emission spectra from species heated by UV-photons. Describing the effect of internal energy on the IR spectra is a current theoretical challenge. In our group, we study PAHs with adsorbed cations, molecules and clusters of astrophysical interest such as Si⁺ [2], Fe⁺ [3] and (H₂O)_n (n>1) [4]. Studies with water clusters are also relevant for the chemistry of the atmosphere as PAHs are precursors of soot.

In order to describe the effect of internal energy on the structures and IR spectra of these large and floppy species, a method of choice is to perform on-the-fly Born-Oppenheimer Molecular Dynamics simulations with an electronic structure described with Density Functional Tight Binding (DFTB) in its Self-Consistent-Charge (SCC) form. Finite-temperature IR spectra are obtained computing the dipole moment autocorrelation function. We will present the analysis of conformational dynamics for several (H₂O)_nC₂₄H₁₂ (n=2-8) complexes in the temperature range 10-300 K. The temperature dependence of the IR spectra will be discussed, and the signatures for finite-size effects, such as the edge-coordination of the water clusters on the PAH, will be shown in particular.

References

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