PAHs adsorbed on interstellar ice : structures, energetics and IR spectra from a multi-method theoretical study

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Polycyclic Aromatic Hydrocarbons **(PAHs)** have had an astrophysical interest since they were proposed, in the mid-eighties, to be the carriers of the Aromatic Interstellar Bands **(AIBs),** a set of infrared (IR) emission bands observed in the [3 - 15 μm] range in many regions of the interstellar medium (ISM). In molecular clouds, some gases are condensed on dust particles and form ice mantles essentially made of water. PAHs may also condense on/in these ices and contribute to the complex grain chemistry [1]. This heterogeneous chemistry plays a fundamental role in presence of the adsorbed water, which catalyzes photochemical processes.

Although ice has been extensively investigated by IR spectroscopy [2], studies of ices containing PAHs are scarcer and have been reported recently [3]. To shed light on the unexpected role played by PAHs in cosmic ice chemistry, IR spectroscopy experiments on the cryogenic codeposition [4] of PAH and water are achieved at "Institut des Sciences Moléculaires" (Université de Bordeaux). In connection with these experiments, we are modeling **PAHs of various sizes and shapes** interacting with **various icy environments** (amorphous and crystalline) using a **multi-method approach** :

* **Molecular dynamics/force-field (MD/FF) simulations** were performed to determine the adsorption sites of PAH on ice and draw binding energy maps characterizing the variations of the PAH-ice interaction over the surface [5a].

* From the MD/FF configurations, a finite PAH-ice system was built, that can be described within the Density Functional based Tight Binding (DFTB) scheme, providing an explicit electronic structure description for such a large system. This allowed the determination of the **influence of ice interaction on the PAH ionization potential (IP)** at the DFTB level. Besides, a **relationship between interface structures** (number of interacting dangling OH) **and IP variation** was established. The theoretical results are discussed in the light of experimental data [5b].

* IR spectra of the previously determined PAH-ice structures were computed within the harmonic approximation at the DFTB level : the **influence of the adsorption of the PAH on the dangling OH mode** at the ice surface is quantified and compared to the experimental shifts.

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