

# The vibrational signatures of polyaromatic hydrocarbons on an ice surface

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**Abstract.** We use quantum chemical techniques to model the vibrational spectra of small aromatic molecules on a proton-ordered hexagonal crystalline water ice (XIh) model. We achieve a good agreement with experimental data by accounting for vibrational anharmonicity and correcting the potential energy landscape for known failures of density functional theory. A standard harmonic description of the vibrational spectra only leads to a broad qualitative agreement.

**Keywords.** astrochemistry, line: identification, ISM: molecules, methods: numerical

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## 1. Introduction

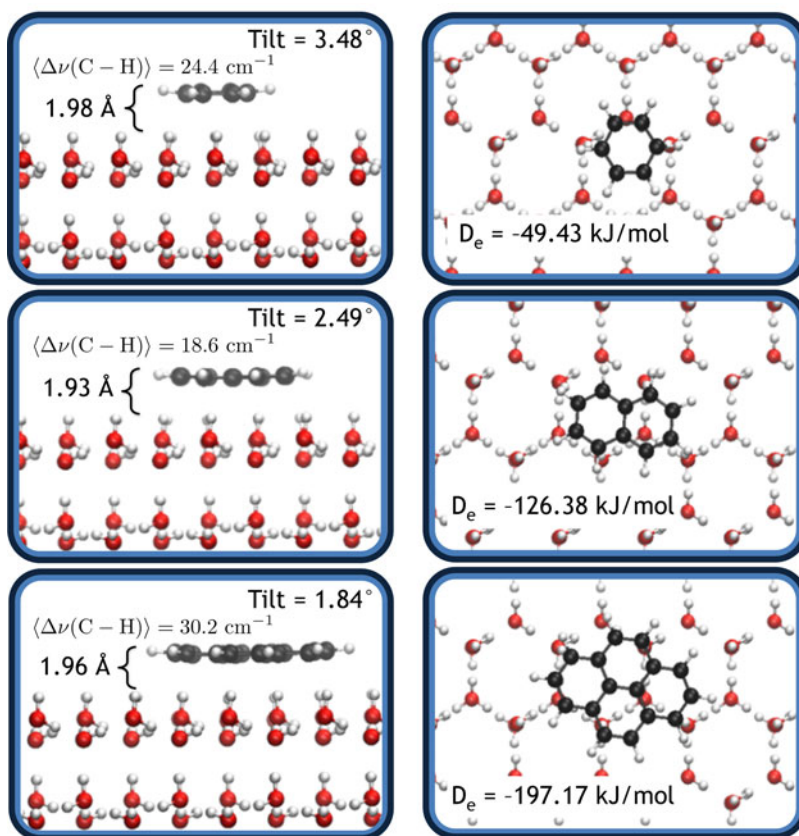
Several studies have suggested that the unidentified infrared (UIR) bands could be from carbonaceous origin and correspond to aromatic C–C and C–H vibrations (Hony *et al.* (2001) and references herein). Those (polycyclic) aromatic hydrocarbon molecules (PAH) are known to adsorb on ice covered dust grains (see Bouwman *et al.* (2010)). However, adsorption modifies the PAH vibrational spectra thus rendering gas-phase spectral data less suitable for their identification. Theoretical predictions of molecular IR bands can be used to bridge this gap but reliable data can only be obtained through robust anharmonic corrections (see Benoit (2004)). Unfortunately, there are only limited attempts to model a quantum anharmonic treatment of adsorbed molecules on surfaces. Our feasibility study investigates deposition and vibrations of small aromatic molecules on ferroelectric proton-ordered hexagonal crystalline water ice (XIh).

## 2. Method

All calculations are performed using CP2K V4.1 (cp2k.org) with semi-periodic (XY) density functional theory at the PBE-D3/TZV2P-MOLOPT-GTH level of theory. The ice surface model is a 26.9535 Å × 23.3424 Å × 14.67162 Å slab of ferroelectric ice XIh containing 288 H<sub>2</sub>O molecules (minimum energy structure from Hirsch and Ojame (2004)). Anharmonic calculations are performed using pvsfcf (pvsfcf.org) and extrapolated CCSD(T) calculations are performed using orca v3.0.3 (Neese (2012)).

## 3. Results

Fig. 1 shows the optimised adsorption geometries of benzene, naphthalene and pyrene on the surface of water ice XIh. All three molecules hover at about 2 Å above the ice surface (1.98 Å, 1.93 Å and 1.96 Å, respectively). The tilt angle is very small for all 3 molecules, consistent with the flat adsorption geometry seen in scanning-tunnelling microscopy studies (Wan and Itaya (1997)) and simulations (Michoulier *et al.* (2018)). The binding energies for each molecule (see Fig. 1) increases with molecule size, likely



**Figure 1.** Adsorption geometry, average vibrational C–H band shift,  $\langle \Delta\nu(\text{C-H}) \rangle$ , and binding energy,  $D_e$ , for benzene (top), naphthalene (middle) and pyrene (bottom) molecules on proton-ordered ferroelectric hexagonal water ice XIh, computed at the PBE-D3/TZV2P-MOLOPT-GTH level of theory. We define the binding energy as  $D_e = E_{\text{opt}}^{(\text{molecule}+\text{ice})} - E_{\text{opt}}^{(\text{molecule})} - E_{\text{opt}}^{(\text{ice})}$ , where  $E_{\text{opt}}$  is the PBE-D3 energy of the optimal geometry. Note that we only allow the topmost layer of water molecules to relax during geometry optimisations.

due to the increased number of weak  $\pi$ -hydrogen bonds between water molecules and aromatic adsorbate. Assuming an average bond energy of  $-15.08$  kJ/mol (Takatani *et al.* (2010)), we can estimate that benzene, naphthalene and pyrene form 3.3, 8.4 and 13.1 hydrogen bonds to the surface, respectively.

Finally, we compute the average harmonic vibrational shift for the C–H band for the adsorbed molecules (see  $\langle \Delta\nu(\text{C-H}) \rangle$  in Fig. 1). The results deviate significantly from the observed frequency shifts for both benzene (31%, Hagen *et al.* (1983)) and pyrene (412%, Bernstein *et al.* (2005)), but are in fortuitous agreement for naphthalene (7% deviation, Sandford *et al.* (2004)). Direct scaling of the harmonic vibrational frequencies (Kesharwani *et al.* (2010)) would not improve results in this case as it applies to both isolated and adsorbed molecules. To estimate anharmonicity effect, Table 1 shows a selection of C–H vibrational frequencies for isolated benzene. We also correct known deficiencies of PBE-D3 by using a hybrid CCSD(T)/CBS surface (Benoit (2015)). The harmonic approximation fortuitously performs well for modes 7 and 13 but the anharmonic calculation on the same PBE-D3 potential lead to much lower frequencies, indicating that

**Table 1.** Selected C–H stretch vibrational transitions for isolated benzene in  $\text{cm}^{-1}$ . Comparison between harmonic, anharmonic (PBE-D3 and hybrid [CCSD(T)/CBS & PBE-D3]) and experimental data (Christiansen *et al.* (1998)). Anharmonic results are obtained using iterative active-space selection vibrational configuration interaction (VCIPSI-PT2, Scribano, & Benoit (2008)).

Mode	Harmonic	Anharmonic		Exp.
		PBE-D3	Hybrid	
2 [A <sub>1g</sub> ]	3115	3003	3074	3074
7 [E <sub>2g</sub> ]	3090	2927	3031	3057
13 [B <sub>1u</sub> ]	3080	2953	3056	(3057)
RMSD	33	104	15	–

PBE-D3 underestimates bond strength. However, once we correct the single mode surface with CCSD(T)/CBS, we obtain a very satisfactory agreement with experimental frequencies.

#### 4. Conclusions

Including anharmonicity for a corrected potential energy surface improves the description of the vibrations of benzene. Harmonic results for PAH on ice only provide a broad agreement for the vibrational shifts. Extending the approach outlined here offers a route towards a more accurate description for vibrations of adsorbed molecules on surfaces.

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