Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

"Formation of coronene:water complexes: FTIR study in argon matrices and theoretical characterization"

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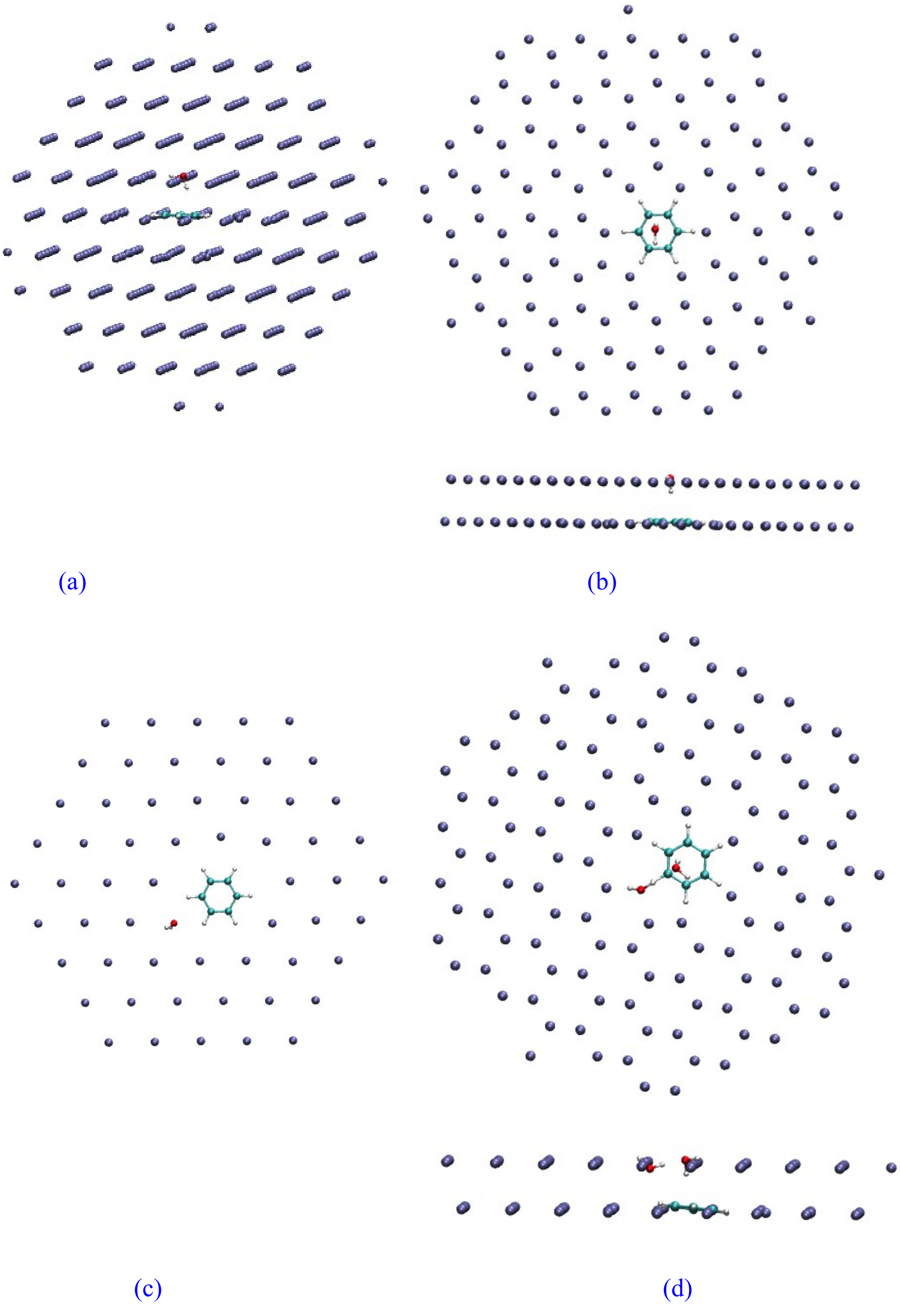
Table S1 and Figures S1 – S5

Figure S1: DFTB/FF optimised geometries of $(C_6H_6)(H_2O)/Ar$ ((a,b), 425 Ar atoms) and $(C_6H_6)(H_2O)_2/Ar$ ((c,d), 424 Ar atoms)


(a) (b) (c) (d)

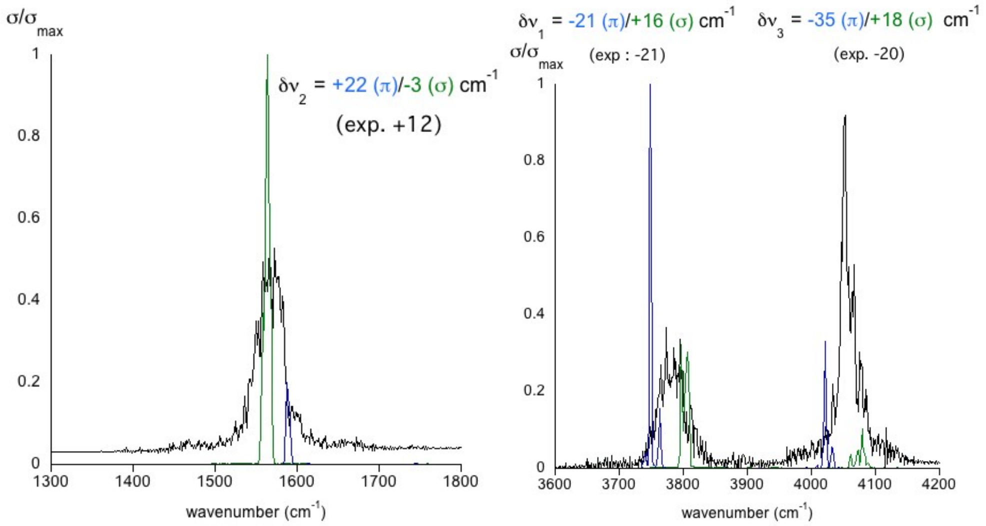


Figure S2. Simulated (BOMD/DFTB/FF) water bands in the $(C_6H_6)(H_2O)$/Ar complexes (green : σ complexes, blue: π complexes) vs (H_2O)/Ar (black lines). Left panel: bending mode, Right panel: stretching modes. The fact that there are several bands for a given mode is due to slightly different orientations of the water molecule, a typically observed matrix effect. This is not seen in the harmonic spectra as it is a purely dynamic effect. $\delta\nu = \nu$ (H_2O in $(C_6H_6)(H_2O)$/Ar) – ν (H_2O/Ar).

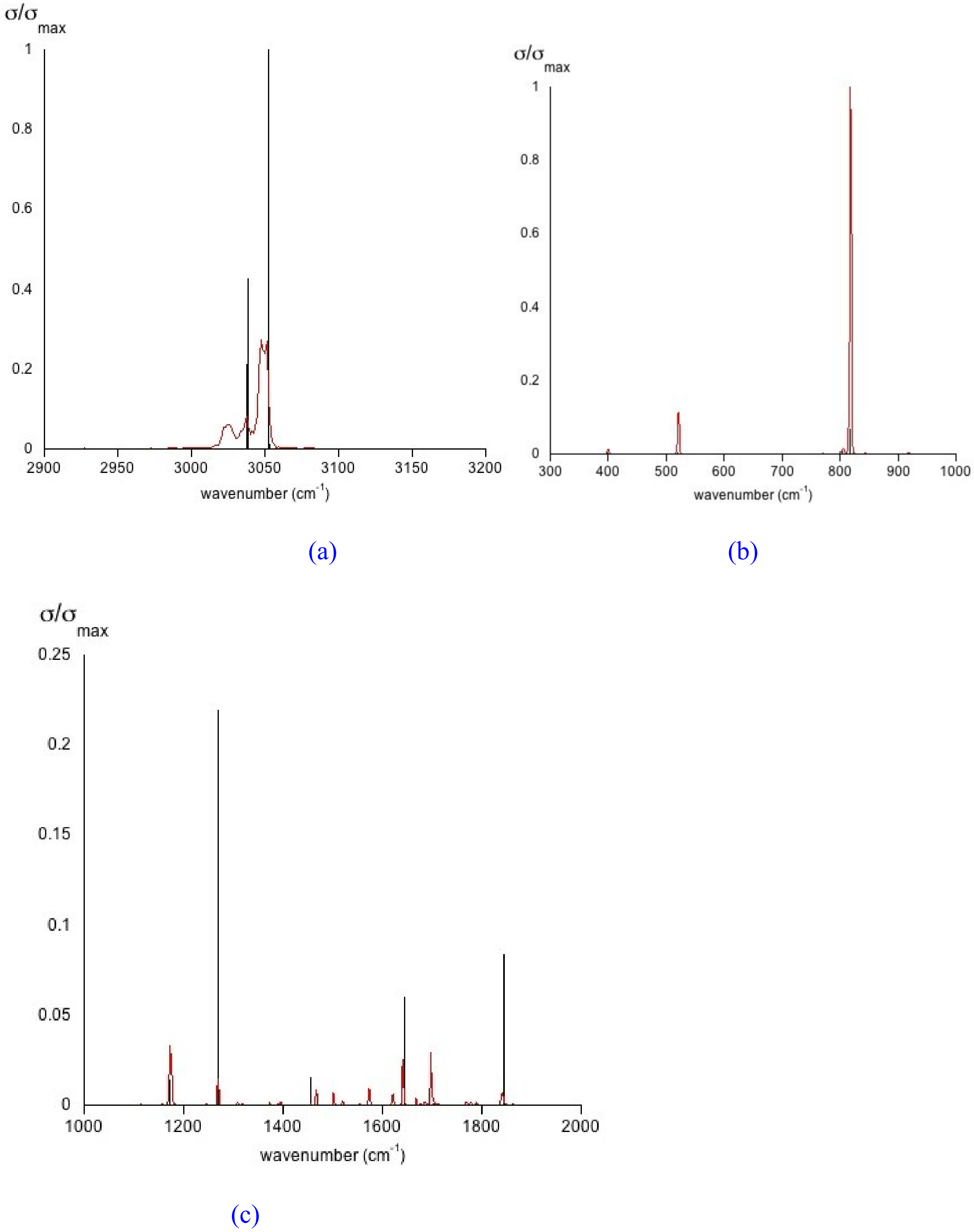
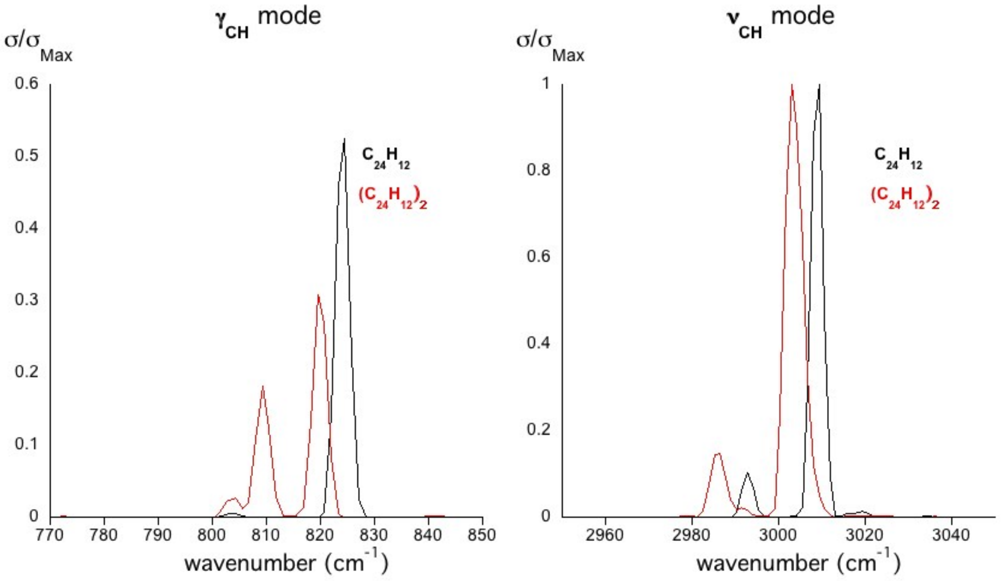


Figure S3: Computed harmonic (black) and finite-temperature (red, at 10 K) spectra of $C_{24}H_{12}$/Ar computed with the DFTB/FF potential.



(A) (B)

Figure S4: Simulated spectra (BOMD/DFTB) at 10K of coronene monomer and dimer in the coronene mode regions γ_{CH} (A), and ν_{CH} (B).

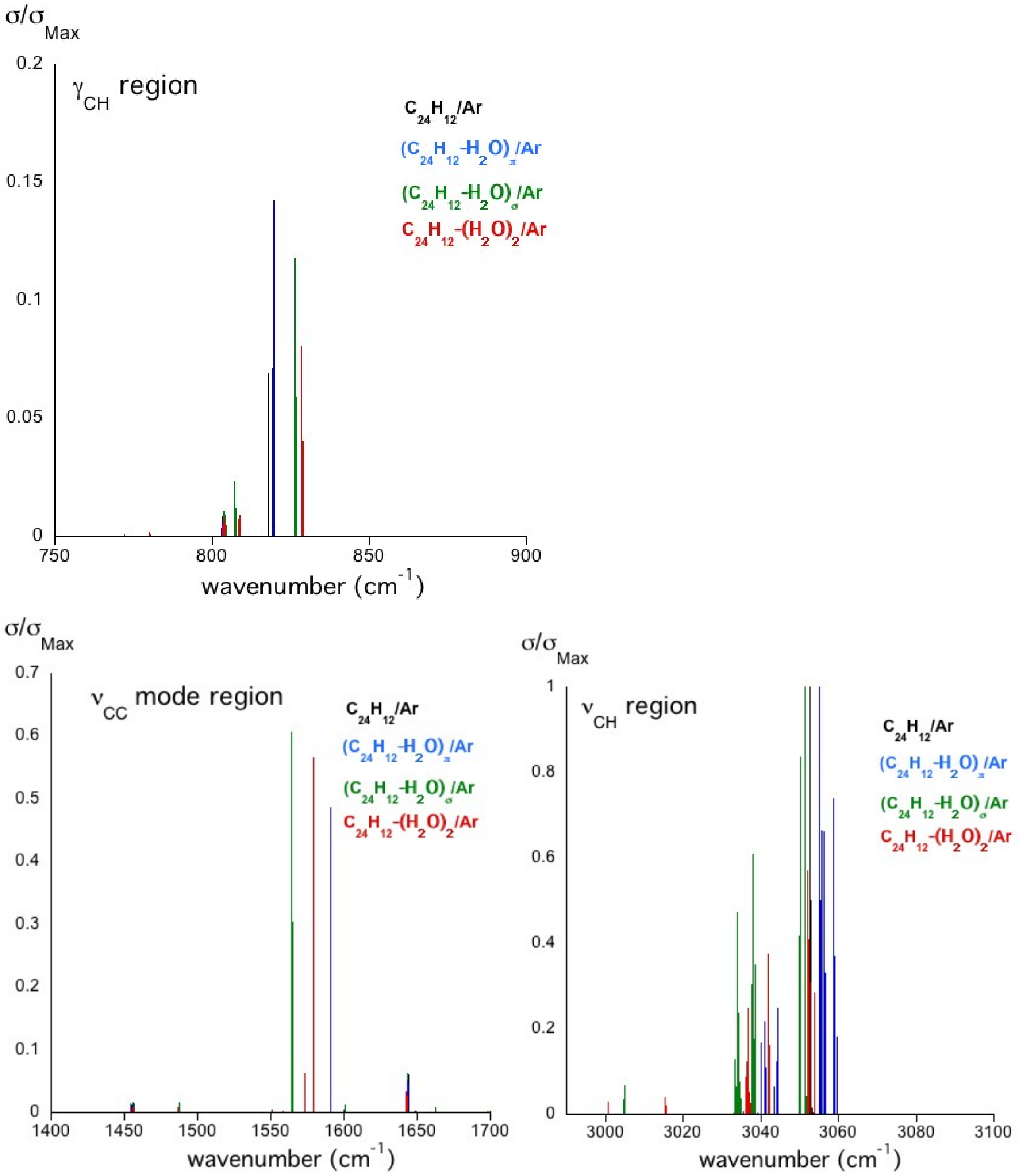


Figure S5: **Computed harmonic spectra of $C_{24}H_{12}$/Ar and $(C_{24}H_{12})(H_2O)_{1,2}$ complexes in the ν_{CH}, ν_{CC} and γ_{CCH} vibration regions, at the DFTB/FF and DFTB levels of theory respectively.**

$C_{24}H_{12}$/Ar (DFTB)		$C_{24}H_{12}$ (DFTB)			$C_{24}H_{12}$ (DFT, scaling factor 0.958, from Langhoff [16])			
wavenumber (cm^{-1})	Intensity (km/mol)	wavenumber (cm^{-1})	Intensity (km/mol)	mode	wavenumber (cm^{-1})	Intensity (km/mol)	mode	symmetry
137	0.06	116	0.01	δCCC oop	123	5	δCCC oop	
(115)	(0.003)							a2u
400	1	396	0.4	δCCC ip	378	3	δCCC ip	e1u
519	1	518	0.6	δCCC oop	549	28	δCCH oop	a2u
771	0.01	774	0	γCH	774	13	δCCH ip	e1u
803	1	802	0.8	δCCH ip	802	0.15	δCCC ip	e1u
818	24	823	22	γCH	864	175	γCH	a2u
1172	5	1167	4	δCCH	1140	6	δCH	e1u
1268	38	1264	41	δCCH	1214	1	δCH	e1u
1455	3	1452	3	νCC+δCCH	1312	24	δCH	e1u
1644	10	1639	10	νCC	1387	0.5	δCH+νCC	e1u
1701	0.4	1694	0.05	νCC	1495	1	δCH+νCC	e1u
1845	14	1838	13	νCC	1603	13	δCH+νCC	e1u
3038	75	2992	75	νCH	3042	8	νCH	e1u
3053	350	3008	350	νCH	3064	142	νCH	a2u

Table S1: harmonic spectra (positions, intensities and assignment) of coronene in Ar matrix, in the gas phase, and DFT values (gas phase) from ref 16. One can see that the assignment of bending modes is difficult based on both DFB and DFT harmonic calculations.