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Binding energies of ethanol and ethylamine on interstellar water ices: synergy between theory and experiments - Electronic Supplementary Information

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1 Details on the calculation of the binding energy

As the key quantity of this work is the BE(0), its evaluation via computational modelling requires a certain number of steps defining separate contributions to the binding energy (see Table 1 for their meaning).

The interaction energy ΔE is defined by:

$$\Delta E = E_P(S \cdot \cdot \mu // S \cdot \cdot \mu) - E_P(S // S) - E_M(\mu // \mu) \quad (1)$$

ΔE contains all the contributions (deformation and lateral interactions, *vide infra*) implicitly. In the following, we disentangle all the quantities relevant for the building up of the final ΔE , starting from the geometry deformation terms:

$$\delta E_S = E_P(S // S \cdot \cdot \mu) - E_P(S // S) \quad (2)$$

$$\delta E_\mu = E_M(\mu // S \cdot \cdot \mu) - E_M(\mu // \mu) \quad (3)$$

The lateral interaction energy E_L is due to the interactions experienced by each adsorbate with its images on the replicated unit cells. This term becomes particularly relevant for high adsorbate coverage, as the distances between adsorbate molecules in neighbour cells will become shorter with increasing coverage. Here, we are interested in minimizing the E_L term, to arrive at a ΔE representative of the sole interaction between the adsorbate and the ice surface. This requires the adoption of a large enough unit cell to minimize the E_L term.

$$E_L = E_P(\mu // S \cdot \cdot \mu) - E_M(\mu // S \cdot \cdot \mu) \quad (4)$$

An important contribution to the ΔE is the deformation-free interaction energy, $\Delta E^* = \Delta E - \delta E_S - \delta E_\mu - E_L$, defined as:

$$\Delta E^* = E_P(S \cdot \cdot \mu // S \cdot \cdot \mu) - E_P(S // S \cdot \cdot \mu) - E_P(\mu // S \cdot \cdot \mu) \quad (5)$$

It represents the interaction between the adsorbate and the surface in their already deformed geometry, i.e., ΔE^* does not account for the cost of the geometry deformation. We also need to correct for the basis set superposition error (BSSE), which arises because we are using a finite basis set of localized functions.

$$BSSE(S) = E_P(S \cdot \cdot [\mu] // S \cdot \cdot \mu) - E_P(S // S \cdot \cdot \mu) \quad (6)$$

$$BSSE(\mu) = E_P([S] \cdot \cdot \mu // S \cdot \cdot \mu) - E_P(\mu // S \cdot \cdot \mu) \quad (7)$$

Therefore, the deformation-BSSE-free interaction energy, that is $\Delta E^\# = \Delta E^* - BSSE$, is given by:

$$\Delta E^\# = E_P(S \cdot \cdot \mu // S \cdot \cdot \mu) - E_P(S \cdot \cdot [\mu] // S \cdot \cdot \mu) - E_P([S] \cdot \cdot \mu // S \cdot \cdot \mu) \quad (8)$$

The energy we are interested in is the Counterpoise-deformation-corrected interaction energy, $\Delta E^{CP} = \Delta E - BSSE$, also defined as:

$$\Delta E^{CP} = \Delta E^* + \delta E_S + \delta E_\mu + E_L - BSSE(S) - BSSE(\mu) \quad (9)$$

By convention, the BE is simply the opposite of ΔE^{CP} as:

$$BE = -\Delta E^{CP} \quad (10)$$

In order to properly compare the computed BE with the experimental data, we have to correct the electronic BE for the zero point energy (ZPE) contribution. As the temperatures of a dense cloud are close to 10 K, the ZPE correction already accounts for the largest thermal contribution to the final enthalpy. The ZPE correction is computed by the set of harmonic frequencies computed for the adsorbate, the free surface and the adsorbate/surface complex. From each ZPE contribution we obtain $\Delta ZPE = ZPE(S \cdot \cdot \mu // S \cdot \cdot \mu) - ZPE(S // S) - ZPE(\mu // \mu)$, from which we define the final binding energy BE(0) at 0 K, as:

$$BE(0) = BE - \Delta ZPE \quad (11)$$

2 Calculation of the pre-exponential factor

In order to obtain E_{des} from the sub-monolayer and monolayer depositions of $\text{CH}_3\text{CH}_2\text{OH}$ and $\text{CH}_3\text{CH}_2\text{NH}_2$ on the bare gold substrate, a mathematical model developed by Chaabouni *et al.*¹,

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Table 1 Contributions to the binding energy and details of each calculation. Periodic refers to an energy evaluation within the periodic boundary conditions, therefore defining an energy per unit cell content. Molecular refers to a standard molecular calculation.

Contribution	Explanation	Type of calculation
$E_P(S//S)$	Periodic, energy of the optimized surface	Optimization
$E_M(\mu//\mu)$	Molecular, energy of the optimized molecule	Optimization
$E_P(S\cdot\mu//S\cdot\mu)$	Periodic, energy of the optimized adsorption complex	Optimization
$E_P(S//S\cdot\mu)$	Periodic, energy of the surface in the optimized complex	Single point
$E_P(\mu//S\cdot\mu)$	Periodic, energy of the molecule in the optimized complex	Single point
$E_M(\mu//S\cdot\mu)$	Molecular, energy of the molecule in the optimized complex	Single point
$E_P(S\cdot[\mu]//S\cdot\mu)$	Periodic, energy of the surface in the optimized complex with the molecule ghost functions	Single point
$E_P([S]\cdot\mu//S\cdot\mu)$	Periodic, energy of the molecule in the optimized complex with the surface ghost functions	Single point
ZPE ($\mu//\mu$)	Molecular, vibrational frequencies and thermochemistry of the molecule	Frequency
ZPE ($S//S$)	Periodic, vibrational frequencies and thermochemistry of the surface	Frequency
ZPE ($S\cdot\mu//S\cdot\mu$)	Periodic, vibrational frequencies and thermochemistry of the complex	Frequency

based on the Polanyi-Wigner equation, was employed to fit the experimental results. One of the parameters that enter in the model is the pre-exponential factor, which was calculated with an equation derived from the transition state theory, established by Tait *et al.*² and recommended in Minissale *et al.*³:

$$A_{\text{TST}} = \frac{k_B T}{h} \frac{A}{\Lambda^2} \frac{\sqrt{\pi}}{\sigma h^3} (8\pi^2 k_B T_{\text{peak}})^{3/2} \sqrt{I_x I_y I_z} \quad (12)$$

In this equation, k_B is the Boltzmann constant, h is the Planck constant, and A is the surface area per adsorbed molecule, i.e., the inverse of the number of surface sites per unit area, fixed at 10^{-19} m^2 . The thermal wavelength of a molecule (Λ) depends on its atomic mass, and on the temperature of the maximum of the desorption T_{peak} . It corresponds to 21.8 pm for $\text{CH}_3\text{CH}_2\text{OH}$, and 22.4 pm for $\text{CH}_3\text{CH}_2\text{NH}_2$. The symmetry factor σ is the number of different but indistinguishable rotational configurations of the species. Both ethanol and ethylamine belong to the C_s symmetry point group, and accordingly the value of σ is fixed to 1. The principal moments of inertia I_x , I_y , and I_z , of the molecules are taken from the CCCBDB database* at the highest theory level available (namely, QCISD/aug-cc-pVTZ): for ethanol, $I_x = 14.348 \text{ amu } \text{\AA}^2$, $I_y = 53.736 \text{ amu } \text{\AA}^2$, and $I_z = 61.769 \text{ amu } \text{\AA}^2$; for ethylamine, $I_x = 14.348 \text{ amu } \text{\AA}^2$, $I_y = 53.736 \text{ amu } \text{\AA}^2$, and $I_z = 61.769 \text{ amu } \text{\AA}^2$.[†] The temperature T is taken to be equal to T_{peak} , approximating the temperature dependence of A_{TST} with a constant value calculated at T_{peak} .

3 Basis sets

The single point calculations needed for the determination of the BE(0) were performed at B3LYP-D3(BJ) level of theory, combined with an Ahlrichs triple zeta valence quality basis set supplemented with a double set of polarization functions, hereafter A-VTZ*. The basis sets used for H, C, N, and O, are printed in the following.

Hydrogen A-VTZ* basis set		
1	4	
0	0 3 1.0 1.0	
	34.0613410	0.60251978E-02
	5.1235746	0.45021094E-01
	1.1646626	0.20189726
0	0 1 0.0 1.0	
	0.32723041	1.0000000
0	0 1 0.0 1.0	
	0.10307241	1.0000000
0	2 1 0.0 1.0	
	0.8000000	1.0000000
Carbon A-VTZ* basis set		
6	11	
0	0 5 2.0 1.0	
	8506.0384000	0.53373664E-03
	1275.7329000	0.41250232E-02
	290.3118700	0.21171337E-01
	82.0562000	0.82417860E-01
	26.4796410	0.24012858
0	0 1 2.0 1.0	
	9.2414585	1.0000000
0	0 1 0.0 1.0	
	3.3643530	1.0000000
0	0 1 0.0 1.0	
	0.87174164	1.0000000
0	0 1 0.0 1.0	
	0.36352352	1.0000000
0	0 1 0.0 1.0	
	0.12873135	1.0000000
0	2 4 2.0 1.0	
	34.7094960	0.53300974E-02
	7.9590883	0.35865814E-01
	2.3786972	0.14200299
	0.81540065	0.34203105
0	2 1 0.0 1.0	
	0.28953785	1.0000000
0	2 1 0.0 1.0	
	0.10084754	1.0000000
0	3 1 0.0 1.0	
	1.6000000	1.0000000
0	3 1 0.0 1.0	
	0.4000000	1.0000000

* NIST Computational Chemistry Comparison and Benchmark Database, NIST Standard Reference Database Number 101 Release 22, May 2022, Editor: Russell D. Johnson III. <http://cccbdb.nist.gov/>

† <https://cccbdb.nist.gov/calcmomint1x.asp> (accessed Apr 8, 2024)

Nitrogen A-VTZ* basis set		
7 11		
0 0 5 2.0 1.0		
11913.4167560		-0.52297017365E-03
1786.7213834		-0.40428404036E-02
406.59012834		-0.20772715125E-01
114.92525065		-0.81183137849E-01
37.105883422		-0.23871497395
0 0 1 2.0 1.0		
12.971676198		1.0000000
0 0 1 0.0 1.0		
4.7302291164		1.0000000
0 0 1 0.0 1.0		
1.2525184258		1.0000000
0 0 1 0.0 1.0		
0.51260071231		1.0000000
0 0 1 0.0 1.0		
0.17939714002		1.0000000
0 2 4 3.0 1.0		
49.218758392		0.55526953476E-02
11.348935304		0.38054617957E-01
3.4285088246		0.14941412242
1.1799512559		0.34898187368
0 2 1 0.0 1.00		
0.41726122577		1.0000000
0 2 1 0.0 1.00		
0.14295131280		1.0000000
0 3 1 0.0 1.0		
2.000000		1.0000000
0 3 1 0.0 1.0		
0.5000000		1.0000000

Oxygen A-VTZ* basis set		
8 11		
0 0 5 2.0 1.0		
15902.6474590		0.51499803703E-03
2384.9537829		0.39819764428E-02
542.71957182		0.20476971922E-01
153.40407874		0.80262367915E-01
49.545716140		0.23766839947
0 0 1 2.0 1.0		
17.339649897		1.0000000000
0 0 1 0.0 1.0		
6.3303355272		1.0000000000
0 0 1 0.0 1.0		
1.6995882201		1.0000000000
0 0 1 0.0 1.0		
0.68954491271		1.0000000000
0 0 1 0.0 1.0		
0.23936028181		1.0000000000
0 2 4 4.0 1.0		
63.270524011		0.60709205960E-02
14.623312295		0.41947688723E-01
4.4489518003		0.16156883988
1.5281513180		0.35682779292
0 2 1 0.0 1.0		
0.52997315870		1.0000000000
0 2 1 0.0 1.0		
0.17509445998		1.0000000000
0 3 1 0.0 1.0		
2.4000000		1.0000000
0 3 1 0.0 1.0		
0.6000000		1.0000000

Notes and references

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