PCCP

ARTICLE TYPE

Cite this: DOI: 00.0000/xxxxxxxxx

Predicting accurate binding energies and vibrational spectroscopic features of interstellar icy species. A quantum mechanical study. Electronic Supplementary Information

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Binding energy calculations

The interaction energy, $\Delta E,$ between a molecule and the surface is computed as

$$\Delta E = E(SM//SM) - (E_m(M//M) + E(S//S))$$
(1)

where E(SM//SM) is the potential energy of a fully relaxed cell containing the slab S and the adsorbate molecule M, E(S//S) is the potential energy of a full relaxed cell of the slab alone, and $E_m(M//M)$ is the potential energy of the isolated molecule. For an accurate BE determination in a periodic calculations *posteriori* corrections need to be added. They include the deformation energy of the surface and the molecule, the lateral interaction between the molecules of adjacent unit cell that result from the use of a periodic system, and the correction of the basis set superposition error (BSSE) that arises when truncated basis set is used. The definition of these terms are

$$\delta E_S = E(S//SM) - E(S//S) \tag{2}$$

for the slab deformation energy, where E(S//SM) is the potential energy of the slab in the geometry where it interacts with the adsorbed molecule.

$$\Delta E_M = E_m(M//SM) - E_m(M/M) \tag{3}$$

for the molecule deformation energy, where $E_m(M//SM)$ is the molecular energy of the molecule frozen in the geometry it is adsorbed to the surface.

$$\Delta E_L = E(M//SM) - E_m(M/M) \tag{4}$$

for the lateral interaction energy, where E(M//SM) is the potential energy of the unit cell that only contains the molecule frozen in the geometry it is adsorbed to the surface. The BSSE was cor-

rected using the *CounterPoise* (CP) method^{1,2}. Defined as

$$\Delta E^{BSSE} = BSSE(S) + BSSE(M) \tag{5}$$

where

$$BSSE(S) = E(S[M]//SM - E(SM//SM)$$
(6)

$$BSSE(M) = E([S]M//SM) - E(SM//SM)$$
(7)

where the species (molecule or slab) in the square parenthesis is the one which basis functions are included in the calculations without the atoms (the 'ghosted' species). The corrected interaction energy is

$$\Delta E^{CP} = E^* - \Delta E^{BSSE} + \delta E_S + \Delta E_M + \Delta E_L \tag{8}$$

where ΔE^* is the deformation free energy:

$$\Delta E^* = E(SM//SM) - (E(M//SM) + E(S//SM))$$
(9)

The corrected BE, BE, is ΔE^{CP} with the opposite sign.

$$BE = -\Delta E^{CP} \tag{10}$$

Zero-point-energy (ZPE) corrections were be calculated and applied to the BE,

$$\Delta ZPE = ZPE(SM) - ZPE(S) - ZPE(M)$$
(11)

where ZPE(SM), ZPE(S) and ZPE(M) are the zero-point energies of the species/surface complex, the surface, and the molecule, respectively. Accordingly, the result of the ZPE correction is the estimate enthalpy of the system at 0K:

$$BE(0) = BE - \Delta ZPE \tag{12}$$

The relative error of the BE

The relative error of the BE(0) averages for each adsorbed species were calculated in the following way:

$$\delta(\%) = \left| \frac{BE(0)^B - BE(0)^F}{BE(0)^B} \right| \cdot 100$$
(13)

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Table 1 Vibrational modes of the target species in their gas-phase state obtained computationally and experimentally, and the resulting scaling factors for each mode.

| Species (mode) | Gas phase experimental frequencies | Gas phase calculated frequencies | Scaling factors |
|---|------------------------------------|----------------------------------|-----------------|
| NH ₃ (sym. def.) | 950 | 1044.10 | 0.90987 |
| NH ₃ (asym. def.) | 1627 | 1676.26 | 0.97061 |
| NH ₃ (sym. stretch.) | 3337 | 3456.42 | 0.96545 |
| NH ₃ (asym. stretch.) | 3444 | 3575.3 | 0.96328 |
| CH ₃ OH (CO stretch.) | 1033 | 1035.52 | 0.99757 |
| CH_3OH (CH_3 rock.) | 1060 | 1078.46 | 0.98288 |
| CH ₃ OH (CH ₃ rock.) | 1165 | 1168.64 | 0.99689 |
| CH_3OH (OH bend.) | 1345 | 1371.74 | 0.98051 |
| CH ₃ OH (CH ₃ def.) | 1455 | 1497.22 | 0.97180 |
| CH ₃ OH (CH ₃ def.) | 1477 | 1480.02 | 0.99796 |
| CH ₃ OH (CH ₃ def.) | 1477 | 1509.62 | 0.97840 |
| CH ₃ OH (CH ₃ stretch.) | 2844 | 2988.39 | 0.95168 |
| CH ₃ OH (CH ₃ stretch.) | 2960 | 3032.83 | 0.97599 |
| CH ₃ OH (CH ₃ stretch.) | 3000 | 3107.89 | 0.96529 |
| CH ₃ OH (OH stretch) | 3681 | 3814.4 | 0.96503 |
| CO ₂ (CO stretch.) | 2349 | 2386.48 | 0.98429 |
| OCS (CO stretch.) | 2062 | 2103.32 | 0.98035 |
| CO (CO stretch.) | 2143.2 | 2201.86 | 0.97336 |
| CH ₄ (asym. bend.) | 1306 | 1342.61 | 0.97273 |
| CH ₄ (asym. stretch.) | 3019 | 3130.59 | 0.96435 |

where $BE(0)^B$ is the average obtained in this work and $BE(0)^F$ is the average obtained by Ferrero *et al.*³.

The ZPE correction scaling factors

The scaling factor for the zero-point energy correction for **all the adsorbed species** was calculated by finding the linear regression between *BE* and *BE*(0). The result is shown in 1, with a comparison with the scaling the general result of Ferrero *et al.*³.

Scaling factors for the spectral features

For each molecule, the gas phase frequencies were computed. The calculations accounted for their symmetry, in order to exclude the analogues vibrations resulting from symmetry. The scaling factors were calculated with respect to experimental values taken from the Computational Chemistry Comparison and Benchmark Data Base (CCCBD)⁴. The formula for the scaling factor was

$$s = \frac{v_{exp}}{v_{comp}} \tag{14}$$

Data extracted from the CCCBD is given in the Table 1 along with the calculated frequency and the corresponding modes, and the calculated scaling factors.

References

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- 3 S. Ferrero, L. Zamirri, C. Ceccarelli, A. Witzel, A. Rimola and P. Ugliengo, *Astrophys. J.*, 2020, **904**, 11.
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Fig. 1 Linear regression between BE and BE(0) values computed in present work (blue line), and applying the scaling factor proposed by Ferrero *et al.*³ (green line).