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Role of dispersive interactions in the CO adsorption on MgO(001): periodic B3LYP calculations augmented with an empirical dispersion term

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Empirically dispersion corrected B3LYP method (i.e. B3LYP-D) is demonstrated to give excellent results for structure, adsorption energy and vibrational frequency shift for the CO molecule adsorbed on the MgO(001) surface, a system considered a challenge for current density functional methods. A periodic approach was adopted to model the interaction using a three-layer slab model. For the B3LYP-D* method an interaction energy of -13.1 kJ/mol is computed at low-coverage in very good agreement with experimental evidence (-12.6 kJ/mol) as well as a positive CO vibrational shift of 10 cm^{-1} to be compared with the experimental value of 14 cm^{-1}.

Introduction

Dispersive forces are particularly relevant when dealing with adsorption processes that take place at the external (inner) surface of bulk (microporous) inorganic, organic and hybrid materials. In the ab initio modeling of such processes density functional theory (DFT) methods[1] have been extensively used. However, it was demonstrated that they badly fail to adequately describe dispersive interactions[2] in molecular adducts but also, recently, in adsorbate/inorganic surface interactions. As an example, we refer the reader to the very recent work by Bredow and co-workers[3] (see also reference therein). Different strategies have recently been proposed to improve current DFT methods to deal with dispersion from full ab-initio[4, 5] to semiempirical approaches. Among the latter, the inclusion of empirical London-type terms has been the subject of a renewed interest and several attempts have been reported to use pair-wise attraction terms of the form $-f(R)C_n/R^n$ (n=6,7,8,…) for both molecular complexes[6-13] and extended systems[14-19]. The proposed corrections differ in the form of the damping function $f(R)$ and the atom-atom dispersion coefficients C_n.[20]

In the present work, adsorption of CO on penta-coordinated Mg at the (001) surface of MgO, which has proven to be a difficult case for DFT, has been considered as a case study for benchmarking the augmentation of the B3LYP method with an empirical dispersion correction. Such system can also be viewed as a prototype system to investigate the role played by dispersion forces in the interaction of small molecules on inorganic surfaces. In the last few decades, CO/MgO(001) has been the subject of numerous studies, and we refer the reader to the very recent work by Illas and co-workers [21] for a review of published theoretical results and experimental data. It was shown that both standard and newly developed exchange-correlation functionals give results that are not completly satisfactory. Despite the highly ionic nature of the surface, Ugliengo and Damin[22] using a B3LYP+MP2 mixed scheme within a periodic ONIOM-like approach have shown that the dispersive interactions are quite relevant being almost a half of the binding energy (7.0 kJ/mol vs 12.6 kJ/mol).

Here, we adopt the empirical $-f(R)C_6/R^6$ correction to DFT methods recently proposed by Grimme[8, 9] for molecular systems. Grimme defined a general set of parameters and used an optimized scaling factor to adjust the dispersion correction for each DFT method. This treatment has proved to be successful in dealing with small and large molecular adducts.[23, 24] Very recently we adopted it in combination with the B3LYP hybrid method[25-28] (hereafter referred as B3LYP-D) and assess the trasferability of such a model to the case of molecular crystals[14] and layered minerals, namely $Mg(OH)_2$, $Ca(OH)_2$ and kaolinite[19]. It was proved that the best results are obtained when a modification of the original parameterization is adopted (hereafter referred to as B3LYP-D*) according to a proposal by Hobza and co-workers[11]. In the present work, we also compare the B3LYP method with the corresponding empirically augmented versions both in the original parameterization B3LYP-D and the modified B3LYP-D* one. The Grimme empirical model has been implemented in the CRYSTAL06 code[29], a periodic ab initio program based on an atom-centered Gaussian-type basis set.

Computational details

All B3LYP, B3LYP-D and B3LYP-D* calculations have been carried out by using a development version of the periodic ab-initio code CRYSTAL06[29]. According to Grimme's proposal[9], an atom-atom additive damped empirical potential of the form $-f(R)C_6/R^6$ were used to include long-range dispersion contributions to the computed ab initio DFT total energy and gradients at the B3LYP (ref) level of theory:

$$E_{B3LYP\text{-}D} = E_{B3LYP} + E_{Disp} \quad (1)$$

where E_{Disp} is the empirical term

$$E_{Disp} = -s_6 \sum_{\mathbf{g}} \sum_{ij}{}' f_{dmp}(R_{ij,\mathbf{g}}) \frac{C_6^{ij}}{R_{ij,\mathbf{g}}^6} \quad (2)$$

Here, the summation is over all atom pairs and **g** lattice vectors with the exclusion of the $i=j$ contribution (i.e. self interaction) for **g**=0, C_6^{ij} is the dispersion coefficient for the pair of atoms i and j, s_6 is a scaling factor that depends on the adopted DFT method (i.e. s_6=1.05 for B3LYP) and $R_{ij,\mathbf{g}}$ is the interatomic distance between atoms i in the reference cell and j in the neighbouring cells at distance |**g**|. A cutoff distance of 25.0 Å was used to truncate the summation over lattice vectors which corresponds to an estimated error of less than 0.02 kJ/mol on computed interaction energies with respect to larger cutoffs. A damping function was used to avoid near-singularities for small interatomic distances:

$$f_{dmp}\left(R_{ij,\mathbf{g}}\right) = \frac{1}{1+e^{-d\left(R_{ij,\mathbf{g}}/R_{vwd}-1\right)}} \quad (3)$$

where R_{vdW} is the sum of atomic van der Waals radii and d determines the steepness of the damping function (d=20)[9]. The role of the damping functions is crucial and will be further discussed below. Van der Waals radii and atomic C_6 coefficients were taken from Table 1 of ref. [9]. From the latter, the C_6^{ij} dispersion coefficients were computed by using a geometric mean.

At variance with the B3LYP-D method originally proposed by Grimme, the B3LYP-D* set the s_6 scaling factor to one while rescaling the R_{vdW} atomic van der Waals radii by 1.05.[14]

For ionic solids the use of the atom-derived C_6 coefficients, as tabulated by Grimme[9], is questionable. However, their trasferability can be assessed by considering the correct prediction of the MgO lattice parameter as an internal check. Computed data are: B3LYP: a=4.243 Å; B3LYP-D: a=4.175 Å and B3LYP-D*: a=4.211 Å to be compared with the experimental values of 4.203 Å determined at 77 K[30] and 4.184 Å obtained after correction for the zero-point anharmonic expansion[31]. B3LYP-D gives a slightly underestimated lattice constant while the B3LYP-D* value is slightly overestimated. In both cases a very good agreement is observed with respect to reference data thus confirming the goodness of the assumption made in the present work.

Calculations were carried out by using a TZVP basis set on Mg and O atoms of the slab model as previously adopted by Ugliengo and Damin[22]. For the CO molecule, two different basis sets were investigated, namely: a TZ2P and a QZV2P basis set as devised by Ahlrichs and co-workers[32] with the latter being quite effective to reduce the BSSE. In addition, to further reduce the BSSE, the basis set of the slab model was enriched by using a QZVP basis on Mg and O of the top-most layer in combination with the QZV2P basis set for CO.

The level of accuracy in evaluating the Coulomb and exchange series is controlled by five thresholds[29], for which values of 10^{-7}, 10^{-7}, 10^{-7}, 10^{-7}, 10^{-14} were used for the Coulomb and the exchange series. The DFT exchange-correlation contribution is evaluated by numerical integration over the cell volume[33] with a (75,974) pruned grid[29]. The condition for the SCF convergence was set to 10^{-8} on the energy difference between two subsequent cycles. A shirinking factor of 8 was used to sample the irreducible Brillouin zone for MgO bulk that results in 25 k-points for the slab model.

First, a full relaxation of the MgO lattice parameter was performed at each level of theory, then a 3-layer slab model was created and a fixed-cell relaxation of the atomic coordinates by means of analytical energy gradients[34-36] carried out. Finally, a CO molecule was added perpendicularly on top of a Mg atom in a 1×2 surface coverage and atomic positions relaxed. At the B3LYP-D* level, within a supercell approach, two lower coverages were investigated, namely: 1×4 and 1×8, to arrive close to an isolated adsorbed molecule. Similar models were adopted by one of us in a previous study[37] and we refer to that work for further details.

For the geometry optimisation[38] default algorithms and convergence criteria were adopted[29]. After adding the CO molecule the residual symmetry was maintained during the whole optimisation process.

The interaction energy was computed as:

$$\Delta E = E(slab/ads) - E(slab) - E(mol) \quad (4)$$

where *E(slab/ads)* is the total energy of the CO/MgO(001) three-layer unit cell, *E(slab)* is the total energy of the slab model alone and *E(mol)* is the total energy of the isolated CO molecule in the gas phase. Computed data were corrected for the BSSE through the counterpoise method[39]. Computed interaction energy was zero-point vibrational energy (ZPVE) corrected by adding the ZPVE obtained from vibrational frequencies of the intermolecular vibrations of the adsorbed CO molecule plus the variation of the CO stretching frequency computed at the Γ point, within the harmonic approximation[33]. Comparison with a full calculation show that this assumption leads to an average error of less than 0.4 kJ/mol.

Table 1 Computed results for CO adsorbed on a MgO(001) as compared to available experimental data. Distances in Å, interaction energies in kJ/mol, and harmonic vibrational frequencies in cm^{-1}.

	B3LYP	B3LYP-D	B3LYP-D*	Exp.
Coverage	1×2	1×2	1×2	
BS CO	TZ2P	TZ2P	TZ2P	
d(Mg···CO)	2.578	2.512	2.489	
ΔE(CPC)	-1.6	-17.9	-16.4	
[BSSE]	[7.2]	[6.8]	[7.3]	
$\Delta H^0(0)$	0.93	-15.4	-13.8	-12.6[b]
$\Delta\omega_h$[a]	9	10	11	14[c]

[a] Free ω_h(CO)=2203 cm^{-1} with TZ2P basis set. [b] Ref. [40]. [c] Ref. [41].

Results and Discussion

As clearly reported in references [42] and [21], the value for the adsorption energy of CO on the clean and defect-free MgO(001) surface has taken more than 20 years to reach a final consensus. Recent experiments from thermal desorption spectra on a vacuum-cleaved MgO(001) crystal[40] and variable

temperature IR spectrometry on sintered MgO microcrystals[41] agree to each other yielding values of 12.6 kJ/mol and 11 kJ/mol, respectively. Here, to assess the B3LYP method augmented with the empirical dispersion term and for consistency with the work of Illas and co-workers[21], we will refer to the value of -12.6 kJ/mol. Note that this value corresponds to the dissociation energy from the vibrational ground state so that includes the zero-point vibrational energy (ZVPE). At variance with ref. [21] here we consistently include the ZVPE contribution to the interaction energy for a direct comparison with the experimental dissociation energy.

Also, for comparison, the CO stretching frequency shift is available from FTIR spectroscopy measurements.[41] A blue-shift of 14 cm^{-1} (with respect to a gas-phase value of 2143 cm^{-1}) is observed for low-coverage adsorption that decreases to 7 cm^{-1} when increasing the surface coverage. In the present work, the experimental shift is compared with the calculated one at harmonic level.

Despite this is an apparently simple system that may not appear of broad practical importance, no such accurate experimental data are available for adsorption on other alkaline earth metal oxides. Therefore, the interaction of CO with MgO(001) is definitely a useful benchmark in the study of adsorbed species and to validate the present computational method.

First we discuss results for the B3LYP method without and with the inclusion of the empirical dispersion term as obtained for a 1×2 surface coverage. Computed results are reported in Table 1.

B3LYP yields a largely underestimated BSSE corrected interaction energy, in agreement with previous theoretical findings[21, 37, 43], resulting in a repulsive dissociation energy. The inclusion of the dispersion correction dramatically improves the computed binding energies. Results for both B3LYP-D and B3LYP-D* are in nice agreement with experiment with a deviation of less than +3.0 kJ/mol, well within the well-known chemical accuracy (1 kcal/mol). The dispersion correction amounts to about 15 kJ/mol on average. This value is roughly twice the dispersion contribution computed by Ugliengo and Damin[22] at the MP2 level of theory but it confirms the dominant role of dispersive interactions for CO interacting with MgO(001).

The comparison between the two dispersion augmented methods shows that B3LYP-D* gives an even more striking accord with experimental $\Delta H^0(0)$. The BSSE corrected dissociation energy is -13.7 kJ/mol to be compared with the experimental value of -12.6 kJ/mol. Note that the inclusion of the full ZVPE contribution reduces the computed dissociation energy to -13.3 kJ/mol, even closer to experiment.

As expected, the dispersion contribution leads to Mg···CO distances shorter than the uncorrected B3LYP. This also corresponds to a slight decrease of the CO distance of the order of 10^{-4} Å. It must be noted that, unexpectedly, the Mg···CO distance for B3LYP-D* is smaller than that for B3LYP-D, despite the latter gives a larger binding energy. A deeper analysis of the results shows that the B3LYP-D* dispersion correction is smaller than the B3LYP-D one but it is proportionally larger at shorter Mg···CO distances. This effect is due to the role of the damping function and it seems related to the rescaling of the atomic van der Waals radii.[44]

All methods predict a positive CO frequency shift in agreement with experiment, although results are sligthly underestimated with respect to the 14 cm^{-1} reported by Zecchina and co-workers[41]. Interestingly, while the inclusion of the empirical dispersion is crucial for the interaction energy it does not affect significantly the predicted frequency shifts. This was also pointed out by some of us for the vibrational properties of layered materials[19]. It seems that although the dispersion correction markedly influences the interaction energy it does not affect so much the second derivative of the energy with respect to atomic positions (i.e the force constants).

Overall results indicate that the B3LYP-D* method performs very well and it will be adopted for further investigating the interaction of CO with MgO(001).

So far, the comparison with experiment is quite good. However, present calculations refer to a rather high surface coverage (i.e. 1×2) whereas experimental data were measured for a low-coverage CO monolayer. Hence, in the following, we studied lower surface coverages as in ref. [37], at the B3LYP-D* level. Calculated binding energies and vibrational shifts are reported in Table 2.

Mg···CO distances are roughly independent from the coverage. $\Delta H^0(0)$ slightly increases from -13.7 to -14.0 kJ/mol when lowering the surface coverage because of the balance between the lateral interactions between CO molecules (repulsive and short-ranged), and the dispersion contribution (always attractive and long-ranged).

The effect of surface coverage on the CO frequency shift results in a decrease from 11 to 8 cm^{-1} when reducing the coverage. This is in contradiction with the increase of the binding energy. Furthermore, experimental findings[41] indicate that the CO shift increases from 7 cm^{-1} at high-coverage to 14 cm^{-1} at low-coverage. The reason for this discrepancy may be attributed to the imposed perpendicular orientation of the CO molecule on the surface when there is a evidence from experiment of a tilted conformation.

As a further refinement, we explored the basis set dependence of computed results. First, with the 1×2 coverage, the basis set of the CO molecule was enriched to QZV2P and, then, also for the top-most layer of the MgO slab model a QZVP basis set was employed. The purpose was twofold: (i) to investigate the influence of the basis set and (ii) to analyze the role of the BSSE. The latter could be quite relevant because it gives a spurious binding energy which summed to the always attractive dispersion contribution tends to overestimate the interaction. While the BSSE is usually removed from the binding energy it still affects the predicted equilibrium structure. Therefore, it is important to reduce it as much as possibile to avoid errors in the computed geometries (i.e. underestimated adsorbate/surface distances).

Results are also gathered in Table 2. Computed Mg···CO distances are the same for all basis sets thus showing that

BSSE does not influence the structure. Also, binding energies appear to be less sensitive to the basis set size, for both uncorrected and BSSE corrected values. Notably, the BSSE shows a sizeable reduction from 7.3-8.0 to 4.5 kJ/mol only when the basis set of both CO and the top-most MgO layer are enriched.

Finally, with the largest basis set, a reduction of the coverage from 1×2 to 1×8 was attempted. The calculated $\Delta H^0(0)$ is -13.1 kJ/mol in closer agreement with the experimental dissociation energy (see Table 2). Due to the cost of the calculation the CO frequency shift is not available. A rough estimation can be obtained by considering the effect of the surface coverage and basis set size. A $\Delta\omega_h$ of some 10 cm^{-1} can be estimated, not far from the 14 cm^{-1} experimental value. It is worthy to note that the dispersion contribution is now 10 kJ/mol in reasonable agreement with 7 kJ/mol as predicted by Ugliengo and Damin[22].

Table 2 Computed results at the B3LYP-D* level for CO adsorbed on a MgO(001) three-layer slab model at different surface coverage and with different basis sets as compared to available experimental data. Distances in Å, interaction energies in kJ/mol, and harmonic vibrational frequencies shifts in cm^{-1}.

	B3LYP-D*						Exp.[c]
Coverage	1×2	1×4	1×8	1×2	1×2	1×8[b]	
BS CO	TZ2P	TZ2P	TZ2P	QZV2P	QZV2P[a]	QZV2P[a]	
d(Mg···CO)	2.489	2.467	2.486	2.478	2.488	2.488	
ΔE(CPC)	-16.4	-17.0	-16.8	-16.0	-16.2	-15.8	
[BSSE]	[7.3]	[7.8]	[7.7]	[8.0]	[4.5]	[4.6]	
$\Delta H^0(0)$	-13.8	-14.1	-14.0	-13.3	-13.5	-13.1	-12.6[d]
$\Delta\omega_h$[c]	11	9	8	12	13		14[e]

[a] QZVP basis set on Mg and O of the top-most layer. [b] Single-point energy calculation on the relaxed geometry as for the 1×2 coverage.

[c] Free ω_h(CO) is 2203 and 2202 cm^{-1} for the TZ2P and QZV2P basis sets, respectively. [d] Ref. [40]. [e] Ref. [41].

Conclusions

In the present work, the benchmark CO/MgO(001) system have been investigated with the B3LYP method augmented with an empirical dispersion term. Results are remarkably improved from the pure B3LYP when the empirical correction term is included. The role of the dispersion interactions in the adsoption of CO has been shown to be crucial for energetics (more than 10 kJ/mol with largest basis set) whereas it is less relevant for CO vibrational shifts. Also, the role of surface coverage and the effect of the basis set size (up to QZV2P basis set) have been investigated to arrive at a closer comparison with reference experimental data.

The comparison between B3LYP-D and B3LYP-D* shows that the former tends to overestimate the dispersion correction. This confirms that the modification of the original Grimme's parameterization proposed by some of us for molecular crystals[14] can be trasferred to other systems as well, even for inorganic systems such as hydroxides, clays[19] and oxides.

In conclusion, B3LYP-D* results for both interaction energy and CO frequency shift are in very satisfactory agreement with experiment. Our best computed results are $\Delta H^0(0)$=-13.1 kJ/mol and $\Delta\omega_h \cong 10$ cm^{-1} versus experimental data of -12.6 kJ/mol[40] and 14 cm^{-1}. [41]

B3LYP-D* results also agree with most recent "mixed" and pure post-HF theoretical calculations of Ugliengo and Damin[22] with the B3LYP+MP2 periodic ONIOM-like scheme and extrapolation towards the complete basis set limit (ΔE(CPC)=-13 kJ/mol) and Qin[45] obtained using a CI embeddeding method (ΔE(CPC)=-10.5 kJ/mol and $\Delta\omega_h$=19 cm^{-1}). It must be noted that those results did not include the ZVPE contribution and, thence, are both underestimated. A full periodic post-HF calculation would be desirable for comparison. In this respect, recent advances in the development of a periodic LMP2 scheme seem rather promising[46].

With respect to recent DFT calculations, present interaction energies are also superior to results obtained by Valero et al.[21] using a cluster approach and the hybrid M06-family of functionals[47] that show an overestimation of more than 50% compared to experiment.

In perspective, this work shows that the theoretical characterization of adsorbed species can be significantly improved when the B3LYP-D* method is adopted. Due to its simplicity, this is of paramount relevance for the study of adsorption processes in which dispersion interactions are crucial. For instance, in the case of either more complex systems, such as aromatic molecules on the surface of various materials (e.g. pollutants on soils[48] or organic molecules on metals[49, 50]) or hydrocarbons in zeolites[17, 51], or very weak interactions such as for hydrogen storage in microporous materials.

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Notes and references

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