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Abstract

We have calculated adsorption energies for N_2O on the MgO (001) surface using periodic DFT calculations with the B3LYP functional and subsequent dispersion correction. Additionally a wavefunction-based correlation treatment at the MP2 level was performed. While the B3LYP calculation failed to find a bond state, both the dispersion corrections and the MP2 treatment result in a significantly better description. The best agreement with experiment is obtained with a dispersion correction via the D3 scheme. The calculated binding energies are very similar for adsorption with the nitrogen or the oxygen end towards the surface, while calculated vibrational frequencies of adsorbed N_2O match the experimental values better when assuming an O-down adsorption structure.

1. Introduction

Physisorption processes are of great importance in many fields of surface chemistry and physics. The resulting abundance of experimental data has created a high demand for fast and accurate computational methods which yield reliable results that can help to interpret the experiments. Density functional theory (DFT) is a computationally cheap and in many cases accurate method for the investigation of solid systems, however, standard density functionals often underestimate electron dispersion effects. Grimme has suggested a systematic scheme to circumvent this problem by incorporating an empirical dispersion correction with London-type R^{-6} dependency into common density functionals [1, 2]. The importance of an explicit treatment of dispersion has been demonstrated for adsorption on MgO [3, 4] and on other surfaces alike [5, 6].

In this study, we investigate the contribution of electron dispersion to the binding energy of nitrous oxide (N_2O) on magnesium oxide (MgO). Earlier

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computational studies indicate that this seemingly simple system cannot easily be described with standard DFT calculations. Since magnesium oxide is known to catalyse the decomposition of nitrous oxide [7], several computational studies have investigated the decomposition process [8, 9, 10, 11, 12]; two among them address adsorption energies. Scagnelli *et al.* found that N_2O does not bind to the (001) surface of MgO [12]. Xu *et al.*, however, observed binding of N_2O with either the O-end or the N-end pointing towards the surface with adsorption energies of -190 and -220 meV, respectively [11]. Both studies combine embedded cluster models of MgO with DFT calculations using the B3LYP functional and basis sets of comparable quality.

We use fully periodic models for the investigation of the N_2O/MgO(001) system, which are not prone to finite system effects and allow for an investigation of coverage effects. Dispersion correction is included via the D2 scheme, proposed by Grimme in 2006 [1], as well as the more recent D3 scheme [2]. For comparison, and in order to validate the results obtained with empirical corrections, we also calculated adsorption energies using Møller-Plesset perturbation theory at the second order (MP2).

2. Computational Details

We performed periodic DFT calculations with the B3LYP functional as implemented in the programme package CRYSTAL09 [13, 14]; other functionals were also tested but they performed worse (LDA, PBE) or very similar (PBE0) to the B3LYP functional. In CRYSTAL09, the Kohn-Sham equations are solved in reciprocal space by constructing Bloch functions from Gaussian type atomic basis functions. Eigenvectors are calculated for a limited number of k points in the first irreducible Brillouin zone, followed by an extrapolation for intermediate k vectors. This Pack-Monkhorst net was constructed by taking 8 equidistant points along each lattice vector. For the Gilat net, which is used in the calculation of the Fermi energy and the density matrix, the number of points in each direction was doubled. The numerical accuracy strongly depends on the cutoff criteria for the exact evaluation of the bielectronic integrals, which is controlled by the parameter set TOLINTEG (cf. CRYSTAL09 manual [14]). We set the tolerances for Coulomb overlap, Coulomb penetration, exchange overlap and the first exchange pseudo-overlap to 10^{-8} and the tolerance for the second exchange pseudo-overlap to 10^{-16}, which corresponds to a significant improvement of the default values.

In periodic calculations, overlap of basis functions on neighbouring atoms can lead to numerical difficulties. Therefore, for Mg and O we applied basis sets that were especially designed for solids, namely polarised valence triple zeta basis sets where the 2s and 2p functions have identical exponents but independent coefficients [15, 16]. For the N_2O molecule, correlation consistent basis sets from the polarised valence double zeta series by Dunning were employed [17].

Adsorption was modelled by constructing a slab of MgO—periodic in the x and y direction—with two (001) surfaces and symmetrically placing nitrous

oxide atop cations on both surfaces of the slab. Different coverages were simulated by occupying all, half or one quarter of the surface cations in the unit cell, and adsorption with either the O-end or the N-end pointing towards the surface was considered. In the structure optimisations, all ions in the slab and the atoms in the molecules were allowed to fully relax, keeping the dimension of the unit cell fixed.

Within the Counterpoise scheme [18], interaction energies of a surface (s) with an adsorbant (ads) are defined as

$$E_{\mathrm{int}} = \frac{1}{N}\{E(\mathrm{s}+\mathrm{ads}) - E(\mathrm{s}+\mathrm{GF}_{\mathrm{ads}}) - E(\mathrm{ads}+\mathrm{GF}_{\mathrm{s}})\},$$

where GF stands for "ghost functions", which account for the basis set superposition error (BSSE). $E(\mathrm{s}+\mathrm{ads})$ is obtained in a structure optimisation while for $E(\mathrm{s}+\mathrm{GF}_{\mathrm{ads}})$ and $E(\mathrm{ads}+\mathrm{GF}_{\mathrm{s}})$ the structure is fixed. All three terms, also the energy of the molecule, correspond to periodic calculations. N is the number of adsorbants per periodic unit cell.

In principle, the interaction energy is not suitable for comparison with experiment, since the energy of the non-interacting reference state is estimated too high, leading to interaction energies that are too attractive. To calculate the adsorption energy with respect to the *free* surface and molecule, the energetic effect of structural relaxation needs to be considered. For each component, the relaxation energy can be calculated as

$$\Delta E_{\mathrm{rel}} = E_{\mathrm{opt}} - E_{\mathrm{fix}}.$$

Here E_{opt} is the energy of the component in its equilibrium structure and E_{fix} is the energy of the component in the adsorption structure, but isolated from the other component and without ghost functions. In case of the adsorbant, these calculations are not periodic. We have calculated the relaxation correction for many of the adsorption structures which are presented in the next section and found that it is of the order of 10 meV or even smaller. Therefore, we will neglect this correction in the following and simply refer to the interaction energy as adsorption energy.

Vibrational frequencies for the adsorbed N_2O molecule were calculated at the gamma point [19, 20]. These calculations also allow us to quantify the difference in zero point energy of the free and the adsorbed molecule, which we found to be around 20 meV per N_2O molecule. This term has to be be added to the adsorption energy and therefore leads to a weakening of the physisorption bond. Since we have only evaluated vibrational energies at the B3LYP level, all adsorption energies given in this paper will be without zero point energy correction, so that values from different methods can be compared consistently.

Grimme-type dispersion correction introduces an extra term to the total energy. Within the D2 scheme [1], this is calculated from a pair sum over all atoms which decays with R^{-6} dependency:

$$E_{\mathrm{DFT+D}} = E_{\mathrm{DFT}} - \frac{1}{2}\sum_{A\neq B} s_6 \frac{C_6^{AB}}{R_{AB}^6} \cdot f_{\mathrm{damp}},$$

where f_{damp} is a damping function for short distances. Recently Grimme has proposed a new scheme, referred to as D3 [2], which includes a term with R^{-8} dependency and a three-body term. Furthermore, the form of the damping has been revised [21]:

$$E_{\mathrm{DFT+D}} = E_{\mathrm{DFT}} - \frac{1}{2}\sum_{A\neq B}(s_6\frac{C_6^{AB}}{R_{AB}^6 + f_{\mathrm{damp}}^6} + s_8\frac{C_8^{AB}}{R_{AB}^8 + f_{\mathrm{damp}}^8}) - E^{(3)}$$

The two schemes also differ in the dispersion parameters. For both D2 and D3, we have adopted the parameter set proposed by Grimme in the original publications, references [1] and [2, 21], respectively. The D2 scheme is implemented in CRYSTAL09 for both energy and gradient calculations so that it can be employed in structure optimisations. For the D3 scheme, only single point calculations were performed.

MP2 corrections were computed using the periodic Local MP2 (LMP2) method implemented in the CRYSCOR programme [22], using the structures optimised at the DFT level. The same basis set as described above for DFT calculations was used for the Hartree-Fock (HF) part, while augmented $d-$type polarisation functions have been added to enrich the virtual space according to a dual basis set scheme [23, 24]; the exponents of such d functions were taken from the molecular aug-cc-pVDZ basis set. There is experience that this approach provides good LMP2 results even with moderately large basis sets, as seen in the context of the evaluation of cohesive energy of molecular crystals [25] and of nanostructures [26]. Domains have been defined by using the DEFDOM2 keyword in CRYSCOR input (cf. CRYSCOR manual [27]), and consist of the sole N_2O atoms for occupied orbitals sitting on that molecule, while for Wannier functions centered on the oxygen atoms of the slab domains included the oxygen itself and the nearest neighbouring Mg atoms. Bielectronic integrals were evaluated differently according to their distance from the reference cell: Up to 8 Å, the density fitting procedure was employed [28] in its direct space formulation [29] and using a valence triple zeta level auxiliary basis with mixed Poisson- and Gaussian-type functions. From 8 to 12 Å, integrals were calculated via multipolar expansion up to hexadecapoles. More distant integrals were accounted for by Lennard-Jones extrapolation [22]. Larger calculations were run using the parallelised development version of the CRYSCOR code [25].

3. Results and Discussion

Bulk and Clean Surface

As a first step, we have done a structure optimisation for bulk magnesium oxide, which crystallises in the sodium chloride structure (space group 225). B3LYP calculations yielded a lattice parameter of 4.232 Å, which is in good agreement with the experimental value of 4.203 Å measured by Hazen at 77 K [30]. With the optimised cell parameter we have constructed periodic slabs for the surface calculations. Only the (001) surface was considered in this study

since the other low-index surfaces are significantly higher in energy. The thickness of the slabs was assessed based on surface rumpling and the Mulliken charges of the ions in the middle of the slab; both criteria were converged for slabs of seven layers.

Some of the adsorption calculations presented in the following section include structure optimisations at the B3LYP+D2 level. For those cases, it is necessary to use a lattice constant optimised with D2 correction, which we found to be 4.166 Å.

Adsorption energy

In table 1 we present adsorption energies, together with selected structure parameters, of N_2O adsorption on the MgO (001) surface, for different coverages and orientations of the N_2O molecule. All entries in one row refer to the same structure, which has been optimised with the B3LYP functional. Additionally to the B3LYP adsorption energy we give the results of subsequent dispersion correction via the D2 and D3 scheme. For comparison, we also included results from single-point MP2 corrections, based on restricted Hartree-Fock (RHF) calculations. All results in table 1 neglect the effects of zero-point energy and relaxation, which would add approximately +20 meV and +10 meV, respectively, to all values; we refer to the previous section for details.

The optimised structures are shown in figure 1. At full coverage, the molecules are perpendicular to the surface, while they tilt towards the surface (in direction of another cation) for half and quarter coverage. An exception is the coverage 0.25 for N-down adsorption with a nearly perpendicular adsorption structure. To test the reliability of this structure, we have repeated the calculation with a different initial structure, where the molecule is already slightly tilted (for the other calculations, the initial structure was perpendicular). Indeed, this calculation resulted in a tilt angle of 39.9°. However, the corresponding adsorption energy is almost identical to the one given in table 1. This indicates that adsorption with the nitrogen end down is very insensitive to the tilt angle. O-down adsorption, on the other hand, seems to favour a tilted conformation.

The experimental adsorption structure has been discussed in some detail by Heidberg and Redlich [31]: They describe the formation of a $(2\sqrt{2} \times \sqrt{2})\mathrm{R}45\,^\circ$ superstructure, where two molecules tilt towards different directions on the surface. The tilt angle is not given, but assumed to be around 27° in analogy to the system CO_2 on MgO, which behaves very similarly. The superstructure cannot be reproduced by our calculations because we only consider one molecule per surface unit cell. However, we have attempted to model the reconstruction in a separate set of calculations with N_2O slabs with up to four molecules per unit cell (*without* MgO surface), but even here the molecules always stay parallel. This is most likely due to the difficulty of DFT calculations in modelling the dipole and quadrupole moment of N_2O, which are responsible for superstructure formation. This difficulty also leads to an inadequate repulsion between the N_2O molecules, which probably prevents them from tilting at full coverage.

Generally, it might be problematic to rely on the structures optimised with B3LYP in the single-point B3LYP+D and MP2 calculations, especially since

B3LYP fails to find a bond state. Therefore, we have performed a few structure optimisations at the B3LYP+D2 level. We found no significant differences to the results presented above, neither for the structure nor for the adsorption energy. It would be desirable to compare to structures optimised at the D3 or MP2 level, but unfortunately D3 and MP2 gradients have not been implemented in the programs CRYSTAL09 and CRYSCOR, yet.

Turning to the adsorption energies, we first note that calculations at the B3LYP level predict that N_2O does not bind to the MgO (001) surface, which is in agreement with the cluster calculations by Scagnelli *et al.* [12]. Including dispersion correction, negative binding energies were found of around -170 meV for the D2 scheme and -250 meV for the D3 scheme (the lower binding energy for full coverage, O-down, will be discussed below). The D3 results are in very good agreement with the experimentally observed value of -230 meV by Lian *et al.* [32].

In the case of CO adsorption on MgO, the DFT+D results could be improved by rescaling the dispersion parameters, both in case of D2 [3] and D3 [33]. These rescaled dispersion corrections result in lower binding energies than corrections with the standard parameter sets, which overestimate the binding of CO to MgO. In our N_2O/MgO calculations, neither the D2 nor the D3 correction overestimates the binding energy, so that the rescaled parameter sets do not seem a sensible alternative. However, we note that both Civalleri *et al.* [3] and Ehrlich *et al.* [33] used larger basis sets, which might lower the binding energy also for N_2O adsorption, and thus lead to overbinding in case of B3LYP+D3.

The MP2 level predicts adsorption energies that are significantly smaller than the B3LYP+D values. A likely reason for this shortcoming is the size of the basis set, which affects MP2 more severely than DFT and DFT+D. Therefore, we have repeated the MP2 calculations with an augmented basis set (see last column of table 1). This decreased the binding energies, but a discrepancy of around 100 meV to the experimental value remains. Even larger basis sets might fix this problem, however, periodic MP2 calculations with the present basis set are already at the verge of the computational resources at hand. The large computational cost is also the reason why augmented MP2 calculations were omitted for coverage 0.25.

Despite the underestimation of the binding energy, the MP2 level is generally considered to be more accurate than the B3LYP+D level since it does not rely on semiempirical parameters. Therefore, we believe the MP2 results can serve as a reference for the relative stability of different adsorption structures. Indeed, the MP2 level and the B3LYP+D level predict the same general trends, that is, the adsorption energies for different orientations and coverages are very similar, with the exception of O-down adsorption at full coverage. We note that the significant difference of around 50 meV of this structure to all other is present only after the dispersion or MP2 correction and not in the original B3LYP or RHF values (the latter are not shown in table 1).

In case of the dispersion correction, these results might be understood from the dispersion coefficients of nitrogen and oxygen, which are 1.23 and 0.70, respectively, at the D2 level [1]. Therefore, terms containing nitrogen contribute

	bond dist. [Å]	tilt angle	B3LYP [meV]	+D2 [meV]	+D3 [meV]	RHF+MP2 [meV]	MP2,aug. [meV]
θ=1 (N)	2.716	0.0°	14	-153	-223	-75	-113
θ=0.5 (N)	2.682	36.4°	21	-166	-251	-80	-120
θ=0.25 (N)	2.594	1.4°	-4	-173	-249	-88	-
θ=1 (O)	2.784	0.0°	33	-107	-156	-40	-71
θ=0.5 (O)	2.558	52.6°	20	-176	-260	-88	-137
θ=0.25 (O)	2.545	47.7°	7	-177	-258	-83	-

Table 1: Adsorption energy for one N_2O molecule on the (001) surface of MgO for different coverages, calculated with the B3LYP functional, Grimme-type dispersion correction (parameter sets D2 and D3) and RHF with MP2 perturbation. For each row, the structure has been optimised with the B3LYP functional; the molecule-surface distance and the tilt angle are given. Negative energies indicate bond states.

stronger to the dispersion than terms containing oxygen. As a result, if the atom closest to the surface is nitrogen, the position of the other two atoms has only a small influence on the total dispersion correction, so they are rather insensitive to the tilt angle. However, if the atom closest to the surface is oxygen, bringing the other two atoms closer to the surface results in a much stronger energy gain. The correlation contributions of the MP2 calculation cannot be interpreted as easily, but they fully support the finding that O-down adsorption is more sensitive to the tilt angle.

The above considerations strongly suggest that perpendicular adsorption of N_2O on MgO is not stable at least for O-down adsorption. Therefore, it is sensible to compare only the results for θ=0.5 and 0.25, which predict on the B3LYP+D3 and the MP2 level that O-down adsorption is more stable than N-down adsorption by 10 meV. Within the error margins of the calculations, these values can be considered identical. In experiment, an energy difference of this magnitude should allow for co-adsorption of both species at temperatures of 60 K [32] and 80 K [31].

Vibrational modes

We have calculated vibrational frequencies of the symmetric (ν_1) and antisymmetric (ν_3) valence-stretching modes of the free and adsorbed N_2O molecules at the B3LYP level. For the free molecule these two modes have frequencies of 1339 and 2337 cm^{-1}, respectively. In table 2, we present the frequency shifts for adsorbed N_2O, calculated for the same structures that where discussed in the previous section (see figure 1).

Similar to the calculated values for the adsorption energy, there is no significant difference between the different coverages for N-down absorption, which implies that the frequency is insensitive to the tilt angle. For O-down adsorption, the frequency shifts for θ=1 differ from θ=0.5 and θ=0.25, which reflects the difference in binding energy. In line with the argumentation of the previous section, we consider the results for lower coverages to be more reliable. Comparing the frequency shifts of N-down and O-down adsorption, we find that,

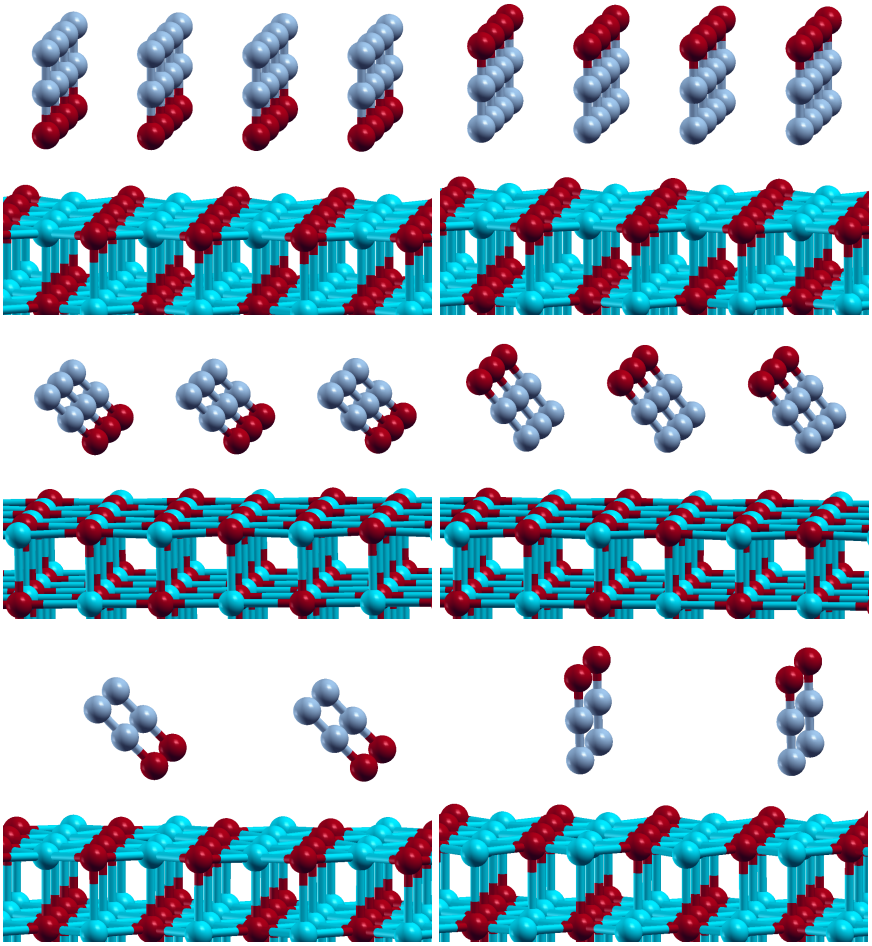

Figure 1: Adsorption structures of N_2O on the MgO (001) surface, calculated on the B3LYP level. Blue-grey globes are nitrogen, red globes oxygen and turquoise globes magnesium atoms or ions. Note that the surface unit cell for $\theta = 0.5$ (middle row) is rotated by 45° with respect the calculations at $\theta = 1$ (left row) and $\theta = 0.25$ (right row).

	N-down			O-down			experiment
	θ=1	θ=0.5	θ=0.25	θ=1	θ=0.5	θ=0.25	($\theta \approx$1)
$\Delta\nu_3$	77.1	61.3	68.8	69.1	30.8	34.4	12[32]; 6 and -7[31]
$\Delta\nu_1$	15.3	21.3	19.5	23.3	3.0	3.8	-10[32]

Table 2: Frequency shift of antisymmetric and symmetric stretching vibration, $\Delta\nu_3$ and $\Delta\nu_1$, relative to free N_2O molecule calculated at the B3LYP level. Experimental values are given for comparison. A positive value denotes a blue-shift.

in contrast to the calculated adsorption energies, they do differ significantly, so that they might serve as a means to distinguish the two adsorption structures.

Traditionally, ν_1 is expected to be red-shifted for O-down adsorption [34], while a blue-shift indicates N-down adsorption, and ν_3 always shows a blue-shift. Indeed, experiments with N_2O on α-Cr_2O_3 [35] and TiO_2 [34] show two different adsorption-species with these shift-patterns. For N_2O on MgO, ν_3 is reported to be blue-shifted [32, 31] and ν_1 is reported to be red-shifted by 10 cm^{-1} [32], which indicates O-down absorption [2]. Our calculation yields a blue-shift of ν_1 even for O-down adsorption, but for low coverages it is significantly smaller than the blue-shift in case of N-down adsorption. Also the blue-shift of ν_3 is better described by O-down adsorption, where it is overestimated by 20 cm^{-1}, compared to an overestimation of 60 cm^{-1} for N-down absorption.

4. Summary

Our periodic calculations showed that the B3LYP level is not suitable to describe physisorption of N_2O on the MgO (001) surface. Including an empirical dispersion correction improved the results significantly; the recently published D3 scheme performs better than the D2 scheme, yielding adsorption energies which are close to the experimentally observed value. MP2 calculations at the feasible level of accuracy underestimate the adsorption energy, but serve as a valuable tool for the verification of the B3LYP+D results, as they give qualitatively the same results.

No significant difference in binding energies between the N-down and the O-down conformation was found, as long as the molecules are tilted with respect to the surface. In a comparison of calculated with experimental vibrational frequencies, we found the best agreement for a tilted conformation with the oxygen end down.

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[2]The correlation-field splitting of the antisymmetric mode observed by Heidberg and Redlich [31] cannot be reproduced in our calculations, since all adsorbed molecules in the considered structures are symmetry-equivalent.

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