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Dispersion corrected DFT calculations for the adsorption of N_2O on MgO

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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 wave function-based correlation treatment at the MP2 level was performed. Whilst 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, whilst 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 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 [8–12]; 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 the 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 the 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

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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

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

where GF stands for “ghost functions”, which account for the basis set superposition error (BSSE). $E(\text{s}+\text{ads})$ is obtained in a structure optimisation whilst for $E(\text{s}+\text{GF}_{\text{ads}})$ and $E(\text{ads}+\text{GF}_{\text{s}})$ 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

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

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 the 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 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:

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

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]:

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

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 [1,2,21], 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, whilst 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. Experience shows 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, whilst for Wannier functions centred 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 the Lennard–Jones extrapolation [22]. Larger calculations were run using the parallelised development version of the Cryscor code [25].

3. Results and discussion

3.1. 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.

3.2. 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