Chemisorption of HCl to the MgO(001) surface: A DFT study†

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We use plane wave and embedded cluster ab initio density functional calculations to study adsorption, dissociation and diffusion of the HCl molecule on the MgO(001) surface. The two methods yield comparable results for adsorption of an isolated HCl molecule and complement each other when considering charged species and coverage effects. We find dissociative chemisorption at a coverage smaller than 0.5 monolayer with a Cl− ion electrostatically coupled to the OH− ion at the surface oxygen site. The adsorption energy of the Cl− · · · (OH)− complex is 1.5 eV and the activation energy of Cl− diffusion away from OH− is 0.6 eV. There is no significant activation energy for rotation of Cl− around the adsorption site. At rising coverage, an increase in dipole–dipole repulsion between HCl molecules leads to a lowering of the adsorption energy per HCl and a change of binding towards hydrogen-bridge type as well as a lowering of the activation energy for Cl− diffusion. OH− formed in the surface due to HCl adsorption has a stretch frequency of 3083 cm−1 with Cl− associated and 3648 cm−1 with Cl− removed.

1. Introduction

Understanding the nature of adsorption of polar molecules at oxide surfaces is important both fundamentally and for numerous technological applications. Most of the experimental and theoretical studies have been concerned with adsorption of individual water molecules and water layers. Adsorption of diatomic molecules, such as HCl and HBr, on MgO, alumina, ice and other surfaces has also been studied due to various issues pertaining to chemical processes at surfaces of atmospheric and interstellar dust particles and geochemistry (see, for example, ref. 1–3), mechanisms of photo-induced surface processes,4,5 nanochemistry6 and catalysis.7–9 Adsorption of HCl on the MgO (100) surface is perhaps one of the simplest examples of such a system. However, even the basic features of HCl adsorption, i.e. whether it is physisorption or chemisorption, whether the molecule remains intact or dissociates, how this depends on coverage, still remain controversial.

Recently Wittig et al.10,11 recorded time-of-flight (TOF) spectra of HCl scattered at the MgO(001) surface and deduced an Arrhenius activation energy for desorption of E des = 0.3 eV. On the other hand, Stark and Klubunde6 concluded that HCl and HBr molecules chemisorb at MgO nanocluster surfaces.

Interest in the adsorption behaviour of the MgO surface was motivated also by its use as an efficient nanocrystalline dehydrohalogenation catalyst.7–9 Large surface area and enhanced surface reactivity are responsible for a very high capacity of MgO to destructively chemisorb volatile organic compounds.

It was observed that the adsorption rate of HCl varies widely with temperature,7,8,12 so that chemisorption to special sites has been suggested to be the dominant adsorption mechanism.

Adsorption of HCl to another polar surface, γ-Al2O3, yields appearance of a band attributed to hydroxyl (OH−) groups at 3500 cm−1 (104.9 THz).13,14 At the same time, no band assignable to HCl was detected. This is indicative of dissociation of HCl due to adsorption. In later experimental work15 OH− groups formed at the surface were found to be mainly acidic due to OH···Cl interaction.

A study of HCl adsorption on α-Al2O316 yielded observation of a large range of desorption temperatures (300–500 K) as the signature of adsorption at sites of different adsorption energies (e.g. defect sites vs. terrace sites) without the possibility for diffusion along the surface. A constant peak desorption temperature from the Al2O3 surface at different levels of coverage was interpreted to be the signature of associative adsorption but, seemingly contradictively, the presence of OH− signals was interpreted as a sign for dissociative adsorption.

HCl adsorption on MgO has been studied theoretically by Chacon-Taylor and McCarthy.17 They used periodic Hartree–Fock calculations with the Colle–Salvetti correlation correction and predicted a relatively weak non-dissociative physisorption of HCl at the oxygen site. They reported an adsorption energy at one quarter monolayer coverage of about 0.48 eV. The predicted distance between H and O is 1.82 Å. Another physisorbed vertical configuration with chlorine bonded to a surface magnesium ion was considered, with an adsorption energy of 0.35 eV.

Both the experimental and theoretical data on HCl adsorption at the MgO(001) and alumina surfaces are not conclusive. One can look for clues in other, similar systems. In particular, water adsorption at MgO surfaces is perhaps best studied. However, the character of water adsorption remains controversial, too, as recently reviewed in ref. 18. It was also found to...
be defect related, 19–23 although adsorption to a clean surface terrace was observed at elevated vapour pressures. 21, 22 Theoretical calculations at low coverage predict weak non-dissociative physisorption 24–27 or even negative adsorption energy. 28, 29 In contrast, both H+ and OH− ions adsorb readily to the defect-free terraces.

Another polar molecule whose adsorption to the MgO(001) surface has been studied theoretically is formic acid (HCOOH). A second-order Møller–Plesset (MP2) calculation of the interaction of formic acid with a quadratic cluster of 4 × 4 MgO atoms performed by Nakatsuji et al. 30 predicts a minimum energy configuration in which the proton is dissociated from the molecule and bound to a surface oxygen ion. The adsorption energy predicted is about 2.2 eV. These cluster calculations did not include the surface Madelung potential. Recent, more accurate embedded cluster calculations 31 predict dissociative adsorption and formate ion formation at the MgO(001) terrace. A plane wave density functional calculation of this system by Szymanski and Gillan 32 demonstrated that dissociative adsorption is more favorable than molecular adsorption by about 0.3 eV. Experimentally, the dissociative adsorption of formate on MgO(001) has been demonstrated e.g. in ref. 33.

These results indicate that the character of adsorption can depend on coverage and on the particular surface site of adsorption, i.e. terrace, step, kink or a point defect, such as a vacancy. In this paper, we study the mechanism of HCl adsorption at the perfect MgO(001) surface terrace. Our periodic plane wave and embedded cluster density functional theory (DFT) simulations predict dissociative adsorption of HCl with OH− formation due to the heterolytic splitting of HCl at the surface.

The models used in this paper are described in section 2. Results are presented in section 3 and discussed in section 4.

2. Models

To study the geometric and electronic structures of individual HCl molecules and monolayers corresponding to different surface coverage on the (001) MgO surface we employed two methods: (i) periodic plane wave density functional theory (PW-DFT) at the generalised gradient approximation (GGA) level; and ii) the embedded cluster method (EC-DFT) with atomic basis sets and the B3LYP hybrid density functional. Both approaches have their advantages and limitations and largely complement each other, as discussed in e.g. ref. 34.

PW-DFT calculations were performed in two rectangular supercells containing four (001) MgO planes with surface dimension of a0(4 × 4) and a0(6 × 6) (a0 = 2.11 Å being the nearest-neighbour Mg–O distance in the bulk crystal). With a single HCl molecule in the supercell, this corresponds to a coverage of 1/8 and 1/18 of a monolayer, respectively. The vacuum gap between the slabs was set to twice the slab thickness, which is sufficient to diminish interaction between periodic images of the slab and leave sufficient space for a desorbed molecule. The two layers of MgO not facing the adsorbate were fixed to the bulk structure, while the two other layers were free to relax. We have used the VASP package 35, 36 utilising PW-DFT with the PW’91 GGA density functional by Perdew and Wang and ultrasoft pseudopotentials of Vanderbilt type, 37 as supplied by Kresse and Hafner. 38 We used an energy cutoff of 396 eV and the Γ-point only in the reduced Brillouin zone. The energy was converged to an accuracy of 0.1 eV and the forces to an accuracy of 0.05 eV Å−1.

In order to estimate the adsorption energy of a single HCl molecule (zero coverage), the energies obtained in PW-DFT calculations were corrected for a spurious dipole–dipole interaction between supercells. The correction energy was calculated using effective point charges and an algorithm due to Kantorovitch 39 with the effective charges −1.426 e at the adsorption site oxygen, 0.426 e at hydrogen as parameterised for a free OH− molecule by Saul and Catlow, 40 where e denotes the modulus of the electron charge. Formal ionic charges were used for Cl, Mg, and all other O ions.

PW-DFT calculations as just described have two principal limitations:

1. The spurious electrostatic interaction arising from the periodic boundary conditions is significant, especially in polar systems such as those considered here. In extreme cases this may lead to incorrect results even with the corrections just discussed. 34, 41

2. The self-interaction error inherent in all local and semi-local functionals (including PW’91) may lead to qualitatively incorrect predictions in systems where electronic interaction leads to the formation of localised states. 41–44

To quantify these shortcomings of the PW-DFT approach, we also used the embedded cluster method (EC-DFT) described in detail elsewhere. 34, 45–47 The setup is illustrated in Fig. 1a. A quantum cluster (QC) is embedded in a finite array of point charges located near the MgO lattice sites. The part of the ions closest to the QC (region I) is treated within the shell model. Ions of region I interact with each other and with the atoms in the QC via shell model potentials of Stoneham and Sangster. 48 The positions of cores and shells of classical ions in region I are optimised self-consistently with the ionic positions and charge density in the QC. The ions outside region I constitute region II and are represented by non-polarisable point charges fixed at their lattice sites and serve to provide a correct electrostatic potential on all ions in region I. The entire simulated system measures 19 by 19 ions along the surface and 7 ions perpendicular to the surface (i.e. about 40 × 40 × 15 Å3). In order to avoid artificial polarisation of the oxygen ions in the QC, 34, 47 the boundary of the quantum cluster Mg29O13 (Fig. 1b and c) is formed by effective core potential (ECP) Mg2+ cations. 49 The standard basis sets 6–31G* for O, Cl and H and 6–31G for Mg ions were employed. These basis sets have been validated previously in studying the electronic properties of defects at the MgO(001) surface. The electronic structure and geometry of the QC was calculated using the hybrid B3LYP density functional. 50, 51 The self-consistent embedding procedure as described in this section has been implemented in the computer program GUESS, 46 which incorporates GAUSSIAN98 52 for the electronic structure calculations.

A study of defects in an oxide surface comparing PW-DFT and cluster results has been performed previously in ref. 53 but there, pure cluster calculations (with no embedding) were used.
and the PW-DFT method was parameterised according to the cluster results. In contrast, we use EC-DFT, which models the surface more accurately than a pure cluster and compare the results of PW-DFT and EC-DFT without fitting one to the other.

3. Results

We start the discussion of our results from a brief description of surface structures obtained using both methods. As evidenced by experiments, the surface does not reconstruct, so anions and cations must retain the perfect crystal structure parallel to the surface (x and y directions) but normal to the surface (in the z direction), the symmetry is broken, so that anions and cations can have altered z-coordinates near the surface. The resulting surface relaxation and rumpling can be expressed in percentages of the lattice constant. The surface relaxation is the change $\delta d_{12}$ of the spacing $d_{12}$ between the surface and subsurface layers. It is given as a percentage of the perfect lattice spacing (half of the lattice constant) $d$

$$\delta d_{12} = \frac{d_{12} - d}{d} \times 100\%.$$  \hspace{1cm} (1)

The surface rumpling $A_1$ is defined as the difference between the z-coordinates of anions and cations, again as percentage of the ideal lattice spacing

$$A_1 = \frac{z_{\text{anion}} - z_{\text{cation}}}{d} \times 100\%.$$  \hspace{1cm} (2)

The calculated surface relaxation and rumpling parameters for MgO are $+0.81\%$ and $+3.6\%$ in PW-DFT, and $+0.05\%$ and $+2.9\%$ in EC-DFT. Relaxation and rumpling in the EC-DFT model are less reliable due to the constraint caused by the unrelaxed ions of region II and the relatively small basis set on the oxygen ions. Additionally, the surface relaxation parameter is very sensitive to the choice of $d$ (eqn (1)), which is difficult to pinpoint in EC-DFT as this method features no periodicity. Given this limitation, the obtained rumpling parameters satisfactorily reproduce earlier LDA calculations and LEED experiments on vacuum cleaved samples (see ref. 54 for a review).

In order to identify the stable adsorption configurations of the HCl molecule on the (001) MgO terrace, we examined a number of possible conformations including HCl bonding to a surface oxygen site, surface Mg site, or adsorbed over a plane interstitial site. However, our calculations predict stable adsorption only at a surface oxygen site with a formation of $\text{OH}^-$ and Cl ions in close proximity. Several configurations (abbreviated “conf.”) are found to be stable or metastable and will be discussed in the following: The symmetric, upright HCl molecule over the adsorption site oxygen (conf. (1)) is metastable and relaxes by symmetry breaking into conf. (2), corresponding to an H–Cl axis tilted in the (100) direction (towards a neighbouring magnesium ion) or into conf. (3) where the H–Cl axis is tilted in the (110) direction (towards plane interstitial position). Conf. (4) corresponds to HCl heterolytically dissociated at the crystal surface with the proton sitting on top of an oxygen and the chlorine on top of a next-nearest neighbour magnesium. Calculated configurational parameters and corresponding adsorption energies of these states are summarised in Fig. 2. PW-DFT energies are shown for the HCl coverage of 1/8 and 1/18 monolayer, respectively, as $E_{\Delta+4}$ and $E_{\Delta6+6}$. EC-DFT energies are denoted $E_{\Delta6}(\text{EC})$. We define the adsorption energy of a molecule at a surface as the sum of the calculated energies of a free molecule and a clean surface minus the calculated energy of the adsorbed molecule. Thus, a bound system has positive adsorption energy.

Most PW-DFT calculations were performed with the $a_0(4 \times 4)$ unit cell, i.e. at 1/8 monolayer coverage due to computational constraints. If not specified, this unit cell is implied for all PW-DFT results presented below. The geometries predicted by PW-DFT and EC-DFT agree very well, i.e. the PW-DFT unit cells are large enough to approximate an isolated molecule and the dipole-dipole correction yields a good extrapolation to its energy. A significant improvement is seen in the larger $a_0(6 \times 6)$ unit cell only for the subtle response of the surface ions around the adsorption site to adsorption of HCl. The distance between the proton and chlorine in the associated adsorption geometries (1)–(3) is, at between 1.70 and 2.05 Å, considerably larger than the 1.3 Å in a free molecule. The distance between the proton and the surface oxygen at the adsorption site is 1.0 Å, i.e. similar to the 0.96 Å in a free $\text{OH}^-$ molecule. The small distances of the proton to the surface oxygen and the large magnitude of the adsorption energies of above 1 eV suggest dissociative chemisorption rather than physisorption as the dominating adsorption mechanism. The proton always points away from the surface in...
order to minimise the repulsion with the magnesium ions surrounding the adsorption site oxygen.

The dissociative character of HCl adsorption is confirmed by an analysis of the electronic structure of the ground state geometry (conf. 2). Projected single-particle densities of states (DOS) obtained in PW-DFT and EC-DFT calculations are shown in Fig. 3a and b. The EC-DFT single-particle band gap of 6.3 eV (B3LYP) may be juxtaposed with the MgO surface exciton energy of 6.15–6.2 eV measured using electron-energy-loss spectroscopy55,56 (compare with a bulk MgO band gap of 7.8 eV 57). The band gap predicted by PW-DFT is much smaller at 2.6 eV. This is a well known limitation of local and semilocal (e.g. GGA) density functionals.

The adsorbed molecule does not induce states in the main band gap. However, a few low lying gap-localised and valence band resonant states are evident. Two states split from the bottom of the second and valence band (at \(\frac{\sqrt{3}}{4}0.2\) eV and \(\frac{\sqrt{3}}{4}7\) eV) are strongly localised on the oxygen adsorption site and hydrogen. These are low lying states of the OH\(_2\) molecule, which are not much perturbed by the rest of the ions. There are also two OH\(^-\) states resonant with the valence band. The state at \(-13\) eV has a strong Cl 3s character and almost zero contribution from the hydrogen ion. Three states related to Cl 3p orbitals are seen as resonances near the top of the valence band. This molecular orbital sequence confirms that, despite the fact that the adsorbed H and Cl ions are close, HCl adsorption is dissociative with the formation of an effectively positive OH\(^-\) ion and a negative Cl\(^-\) electrostatically coupled to it.

Table 1 summarises calculated ionic charges deduced from natural population analysis (NPA) of the results obtained from EC-DFT and from integration within ionic Wigner-Seitz spheres for the results of PW-DFT. Again, charges on O at the adsorption site, H and Cl consistent with dissociative adsorption are predicted by both methods.

Isosurface plots of the difference in PW-DFT charge density between a calculation with an admolecule and one without for conf. (2) are presented in Fig. 4a. In the free HCl molecule, valence electron density is shared between hydrogen and chlorine. Adsorption of HCl to the MgO(001) surface adds no such density to the clean MgO surface, as can be seen from the charge density difference plot. This means that the covalent bond between H and Cl is effectively broken. Instead, a large amount of charge density is donated from the surface oxygen to the proton indicating formation of a covalently bonded OH\(^-\) molecule. Since OH\(^-\) sits at the lattice position of an O\(^2-\) ion, it is positively charged (i.e. a hole) in the context of the crystal lattice. Chlorine carries almost a full electron charge and is bound to the OH\(^-\) adsorption site due to electrostatic attraction. The dipole due to this polarity between the OH\(^-\) hole and the Cl\(^-\) charge is responsible for the lowering of the adsorption energy per molecule at finite coverages.

Conf. (4), whose density difference plot is shown in Fig. 4b, shows a pronounced change in polarisation of the underlying oxygen crystal sublattice. As Cl\(^-\) is well separated from the OH\(^-\) hole, its charge can now cause stronger polarisation of the surrounding oxygen ions, which plays an important role in the stabilisation of this configuration. The proton also has a
more pronounced impact on the polarisation of its partner oxygen. The latter is no longer polarised laterally by chlorine, as the Cl\(^+\) charge is effectively screened by the chlorine neighbour polarisation.

Having established the structure of the stable states, we proceed with a discussion of the activation barriers. The barrier between configurations 2 and 3 gives an estimate for the rotational barrier of the Cl\(^+\) ion around the adsorption site. It is very small, at \(<0.05\) eV in both EC and PW-DFT, so Cl\(^+\) can be considered as freely rotating in a horizontal plane around the OH bond. We also calculated the barriers for the Cl\(^+\) diffusion away from the OH\(^-\) site. A direct transition between conf. (3) and conf. (4) is not viable due to the strong electrostatic repulsion between Cl\(^-\) and the surface oxygen O\(^2-\). The migration path via conf. (2) is found to be more favourable energetically. A calculation with Cl\(^-\) between nearest and next-nearest neighbour Mg\(^{2+}\) ions (i.e. between configurations 2 and 4) yields an energy less than \(0.1\) eV above the energy of conf. (4). This corresponds to a barrier of \(0.65\) eV (PW-DFT) and \(0.78\) eV (EC-DFT) for Cl\(^-\) diffusion away from the OH\(^-\) site, and \(<0.1\) eV for diffusion towards the OH\(^-\) site. The calculated dissociation energy of the HCl molecule into H\(^+\) and Cl\(^-\) at the MgO surface is \(1.8\) eV (EC-DFT). The dissociated system comprises a proton, with an adsorption energy of \(12.3\) eV and a Cl\(^-\) ion with an adsorption energy of \(1.7\) eV. Charged configurations were not simulated with the PW-DFT method due to known problems with compensation by charged backgrounds. In contrast, the adsorption energies for H\(^+\) and Cl\(^0\) are \(0.3\) and \(1.5\) eV, respectively from both the EC and PW-DFT methods.

Next we discuss the effect of HCl surface coverage on the adsorption energy. To this end, we have performed PW-DFT calculations of up to 8 HCl molecules in the \(a_0(4 \times 4)\) surface unit cell, and one molecule in the \(a_0(6 \times 6)\) unit cell. As the molecule only binds to the oxygen sites, this corresponds to coverages in the interval from \(1/18\)th monolayer (5.6%) up to a full monolayer of HCl molecules. Calculations predict adsorption energies in configuration 2 (Fig. 3) to be \(0.25, 0.83, 1.0\) and \(1.4\) eV for \(1/2, 1/4, 1/8\) and \(1/18\) monolayer, respectively.

A coverage of \(1/4\) monolayer corresponds to that modelled by Chacon-Taylor and McCarthy.\(^{17}\) Our value of \(0.83\) eV is substantially larger than the \(0.48\) eV in ref. 17. However, for \(1/4\) monolayer coverage in conf. (2), the average OH\(^-\) bond length elongates by 0.1 Å to 1.08 Å and the average H–Cl distance contracts by 0.3 Å to 1.75 Å. This indicates that HCl adsorption is more like a hydrogen-bridge bond for high coverages. Together with the tendency of Hartree–Fock to underestimate binding energies, this explains that a different geometry and physisorption were predicted in ref. 17.

### Table 1
Comparison of charges obtained from PW-DFT and EC-DFT for the tilted geometry, configuration (2). Charges are given in multiples of the positive unit charge e. It can be seen that the spherical integration charges in the first row always deviate towards positive charge compared to the NPA charges. This supports the NPA charges, as some (negatively charged) electron density is neglected for spherical integration.

<table>
<thead>
<tr>
<th>Method of calculation (population analysis)</th>
<th>Cl</th>
<th>H</th>
<th>O in OH(^-)</th>
<th>Other O</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>PW-DFT (spherical integration)</td>
<td>(-0.9)</td>
<td>0.5</td>
<td>(-1.4)</td>
<td>(-1.7)</td>
<td>1.8</td>
</tr>
<tr>
<td>EC-DFT (Mulliken analysis)</td>
<td>(-0.73)</td>
<td>0.40</td>
<td>(-1.10)</td>
<td>(-1.55)</td>
<td>1.31</td>
</tr>
<tr>
<td>EC-DFT (NPA)</td>
<td>(-0.85)</td>
<td>0.47</td>
<td>(-1.42)</td>
<td>(-1.79)</td>
<td>1.71</td>
</tr>
</tbody>
</table>
This tendency can also be seen in the binding energy of the OH\textsuperscript{-}/C\textsubscript{0} molecule, which is 2.9 eV with Hartree–Fock and 4.4 eV with B3LYP. The B3LYP result is much closer to the value of 4.9 eV we calculated with Multi-Reference Configuration Interaction (MRCI), the most accurate method we have used for this molecule (all done with basis sets at the triple zeta level).

Our results show that the coverage dependence of the adsorption energy is dominated by the dipole–dipole repulsion between the molecules which almost completely can be accounted for by Ewald summation over the molecule effective charges in the lateral directions. This is demonstrated in Fig. 6, where we have plotted the difference between the adsorption energy calculated with EC-DFT (1.54 eV, conf. 2) and PW-DFT adsorption energies per molecule at different coverages. This line is matched (taking into account error bars for the crude point charge model) by the dipole–dipole repulsion energy.

Coverage of every surface oxygen with an HCl molecule (full monolayer) results in an unstable system, i.e. upon relaxation the molecules migrate into the vacuum. However, an additional HCl molecule can be adsorbed on top of a half monolayer of HCl with an adsorption energy of 0.3 eV. The additional HCl molecule is oriented with its positive (i.e. hydrogen) end towards the underlying Cl\textsuperscript{-}/C\textsubscript{0} ion. As the lowermost proton is bonded chemically to a surface oxygen and the first and second Cl\textsuperscript{-} layer are chemically equivalent, the

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**Fig. 4** Isosurface plots of the difference in charge density between calculations of a surface with an admolecule and without. Surfaces shown match a charge density difference value of $\rho_{\text{cutoff}} = 0.56$ eÅ\textsuperscript{-3}. (a) Adsorption of an associated molecule, configuration (2). The charge density change on the far oxygen ion is due to the PBC. (b) Adsorption of a dissociated molecule, configuration (4) [Cl sits over the magnesium ion (210) from the proton adsorption site]. The apparent cutoff of the density on the leftmost O ion is due to a limitation of the plot area. More oxygen ions are polarised in (b) which partially accounts for the discrepancy between the differences in H–Cl electrostatic energy and PW-DFT energy.

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**Fig. 5** Adsorption and dissociation energies of HCl. Negative energies stand for energy gained and positive ones for energy to spend. Left side: dissociation into charged species. Right side: dissociation into neutral species.

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**Fig. 6** This comparison shows that the dipole–dipole interaction energy is the dominant contribution in the coverage dependence of the adsorption energy per admolecule. Conf. (2), dipole–dipole energies evaluated with a rigid ion model of the unit cell (hence the large error bars). The energy difference is $E_{\text{ads}}(\text{EC-DFT}) - E_{\text{ads}}(\text{PW-DFT})$, where $E_{\text{ads}}(\text{EC-DFT}) = 1.5$ eV.
Table 2  Overview of OH$^-$ mode frequencies from EC-DFT calculations. The electrostatic attraction to the associated chlorine ion softens the OH$^-$ translational and stretch modes and hardens the librational mode

<table>
<thead>
<tr>
<th>OH$^-$ in HCl on MgO terrace</th>
<th>Wavenumbers/cm$^{-1}$</th>
<th>OH$^-$ in protonated terrace</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mode</td>
<td>Translational modes</td>
<td>312–394</td>
</tr>
<tr>
<td></td>
<td>Libration</td>
<td>1007</td>
</tr>
<tr>
<td></td>
<td>Rotation</td>
<td>1021</td>
</tr>
<tr>
<td></td>
<td>Stretch</td>
<td>3083</td>
</tr>
</tbody>
</table>

proton in the middle mediates a hydrogen bond between the first and second admolecule layer.

We have used the EC-DFT method to calculate vibrational frequencies of some localised vibrational modes. Table 2 shows an overview of mode frequencies found for OH$^-$ in conf. (2) and in the protonated surface, i.e. without the associated chlorine ion. It can be seen that the non-translational modes have frequencies which are well-separated from the top of the MgO surface slab vibrational band (22 THz in shell model lattice dynamics$^{38}$). This means they are unlikely to couple strongly to the normal modes of the MgO substrate.

The electrostatic attraction of the chlorine ion softens the translational and stretch modes of OH$^-$, while it hardens the librational modes with respect to the proton without associated Cl$^-$. The changes in the intramolecular OH$^-$ frequencies are due mostly to the slight elongation of the OH$^-$ bond which makes OH$^-$ reside in the sloping part of its (approximately Morse-type) potential.

In experimental adsorption of HCl to MgO nanocrystals$^6$ at high pressure, broad bands from 3000 to 3700 cm$^{-1}$ were measured. The broad bandwidth measured indicates a wide range of OH$^-$ intramolecular distances present in the sample due to dipole–dipole repulsion and chlorine diffusion.

Chlorine readily diffuses away from the adsorption site (most likely to surface defects) at high coverage: a Cl$^-$ ion can rotate freely around its associated OH$^-$ but it can also rotate freely around an OH$^-$ ion at the neighbouring oxygen lattice position as one is likely to be available at the high coverages in these experiments, which can remove chlorine from its adsorption site. Hence, the activation energy for Cl$^-$ diffusion goes from 0.6 eV for an isolated molecule to below 0.05 eV for high coverage.

A band at 3750 cm$^{-1}$ was present prior to HCl adsorption due to surface contamination with OH$^-$. Note that these OH$^-$ species are not embedded in the surface like the one formed due to HCl adsorption at the terrace. Bands at 1600 and 1700 cm$^{-1}$ appeared on HCl adsorption which are in the region of the water bending mode (1400–1600 cm$^{-1}$, depending on isotopes). These are likely due to hydrochloric acid protonating the contaminating OH$^-$ species already present at the surface.

4. Discussion

The results presented above clearly demonstrate that at low coverage the HCl molecule adsorbs dissociatively on the MgO (001) terrace. Our DFT calculations predict adsorption of HCl to the MgO(001) surface at low coverage to be caused primarily by a chemical bond between a surface oxygen and the molecular proton. The adsorption energy in the most stable configurations, (2) and (3), is 1.5 eV. In unison with the breaking of the covalent bond between H and Cl, their distance increases to between 1.7 and 2.0 Å, compared to 1.3 Å in the free molecule. Chlorine is held at the adsorption site by its electrostatic attraction to the OH$^-$ molecule, which represents a hole in the context of the crystal. Hence HCl at the surface is chemically dissociated but electrostatically associated.

EC-DFT simulations of HCl adsorbed to the MgO(001) surface confirmed and extended our PW-DFT results. The fact that both methods using different basis sets and density functionals predict the dissociative character of the adsorption further supports our conclusions.

In comparison to molecular hydrogen, which adsorbs to MgO dissociatively only at low-coordinated special sites or vacancies$^{60–63}$ and to water, which does so at steps, vacancies or corners of nanocrystals,$^{19–23}$ HCl adsorbs dissociatively at the MgO(001) surface terrace. In this respect, HCl represents a limiting case. Out of the HX compounds, where X is a halogen ion, dissociative adsorption to the MgO(001) terrace may be hindered only for HF, which has a dissociation energy of almost 6 eV. For all other hydrohalogenic acids, dissociative adsorption is to be expected.

The adsorption energy of HCl may be viewed as consisting of the HCl vacuum dissociation energy, the protonation energy and the adsorption energy of Cl$^-$ to the proton adsorption site (Fig. 5). The accuracy of the surface protonation component determines the accuracy of the total adsorption energy. It has been determined previously by embedded cluster Hartree–Fock (HF) calculations$^{56}$ at 10.4 eV and by flame-ion mass spectrometry experiments$^{65}$ at around 10 eV. The difference between our EC-DFT result of 12.3 eV and HF can be attributed to the tendency of Hartree–Fock to underestimate binding energies and of GGA DFT to overestimate them slightly. The mixed B3LYP functional, however, is fairly reliable, as demonstrated for the OH$^-$ molecule in section 3.

The same tendencies of the methods, together with lowering of the adsorption energy due to coverage effects is responsible for the previous prediction of physisorption of HCl on MgO(001).$^{17}$

The adsorption energy of 1.5 eV predicted by our results is significantly higher than that estimated in molecular scattering experiments. Wittig et al.$^{10}$ derived an activation energy of 0.3 eV by applying the Arrhenius equation to the measured desorption rate. As we have demonstrated that the adsorption energy per HCl molecule decreases with coverage, it may be supposed that the discrepancy to our predicted adsorption energy was due to coverage. However, the experiment gives...
repeatable results for many molecular pulses, which indicates that the surface coverage remains low throughout the experiment. Due to the ratio of HCl in the molecular beam (1–2%) the surface coverage is estimated to be of the order of $10^{-3}$ monolayers HCl. Coverage can therefore be excluded as a reason for the discrepancy.

Instead we propose a dynamical mechanism: OH$^-$ at the surface has vibrational and librational frequencies well separated from the bulk phonon density of states of MgO. We argue that such spectrally and spatially localised modes are characterised by a low dissipation rate, and thus can retain vibrational excitations for a considerably long time. The smallest incident kinetic energy in the experiments of Wittig et al. corresponds to a velocity of 763 m s$^{-1}$. At an incidence angle of 15°, this corresponds to an approach velocity perpendicular to the surface of 737 m s$^{-1}$. Assuming an interaction region of 5 Å above the surface (a generous estimate, as the Madelung potential decays exponentially with distance), the molecule has about 1.35 ps to reorient, dissipate its excess energy and get trapped. If this succeeds, a chemical bond between the proton and a surface oxygen can be formed. The dissipated energy (adsorption energy + translational kinetic energy of the molecule) is likely to be initially transformed into a vibrational excitation of the OH$^-$ stretching mode. The vibrational frequencies of OH$^-$ libration and vibration (30–92 THz) are well above the maximum crystal frequency ($\omega_{\text{max}}$(MgO) = 22 THz). Therefore, excitation of these modes may survive for many pico- or even nanoseconds due to the spectral localisation of these modes. However, the activation energy for desorption of a ‘hot’ molecule is the difference between the vacuum level and the stored vibrational energy. This can significantly reduce the measured desorption energy in scattering experiments, assuming that mostly desorption of ‘hot’ molecules is observed. Accounting for the zero vibration energy of the OH$^-$ stretch mode lowers the desorption barrier by approximately 0.2 eV (1.4 eV – (0.38 eV/2) $\approx$ 1.2 eV). The desorption energy involving OH$^-$ in its first vibrational excited state would lower this energy by a further 0.3 eV, and so on.

Thermalised rotational distributions at all incident energies were previously interpreted as a sign of trapping–desorption. However, molecular dynamics predict that the collision of randomly oriented diatomic molecules with a surface should lead to such a rotational distribution naturally. The dependence of the characteristic rotational temperature on the temperature of the crystal can be ascribed to events where molecules collide with oncoming surface atoms. Overall, this demonstrates that the experimental observations in ref. 10, 11, 13–15 are not contradicting the theoretical predictions presented in this article. At special adsorption sites, such as steps and kinks, the frequency of the stretch mode of OH$^-$ should be increased due to a stronger chemical bond. This means that the OH$^-$ stretch mode is spectrally separated further from the MgO band, maintaining weak coupling. Hence, the qualitative features of the dynamics of HCl adsorbed on a step or kink oxygen should be similar to adsorption at the terrace. Low-kinetic energy, low coverage trapping–desorption experiments involving H$^{35}$Cl and D$^{35}$Cl may illuminate whether HCl molecules dissociate and recombine (in mixed combinations) at the surface prior to desorption. This would yield an unambiguous answer to the question whether molecules dissociate and whether chlorine can diffuse at the surface at long time scales.

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