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The structure and spectroscopy of monolayers of water on MgO: An *ab initio* study

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The structure and energetics of a monolayer of water on a perfect MgO substrate is investigated by *ab initio* calculations. Several minima in the potential energy surface were found including both physisorbed and chemisorbed states in which one third of the water molecules were dissociated. In the more stable of the physisorbed states, the water molecules were not all parallel to the surface, but some showed hydrogen bonding with surface oxygen ions. Even in the physisorbed state, the geometry of these surface H-bonded water molecules were distorted relative to the bulk. One of the stable chemisorbed states was the same as that found in earlier work by Giordano *et al.* [Phys. Rev. Lett. **81**, 1271 (1998)]. Two more stable chemisorbed structures were found in which strong hydrogen bonds to the hydroxide ions in the water layer were formed. The existence of different minima appears to be the result of a subtle interplay between hydrogen bonding between adsorbed species and with the surface oxide ions. Harmonic vibrational frequencies were determined for both a chemisorbed and a physisorbed states and spectroscopic features which should discriminate between chemisorbed and physisorbed states are identified. © 2000 American Institute of Physics. [S0021-9606(00)30932-1]

I. INTRODUCTION

Thin films of one or a few monolayers of water on clean MgO surfaces have been extensively studied by both experiments and computation. The reason for this wide interest is that the interaction of water with MgO is of geophysical and atmospheric interest. In spite of this extensive body of work the structure of a monolayer of water on MgO is not known for certain. Recent work has shown that the potential energy surface is extremely complex, and involves the interplay between several competing interactions: adsorbate–adsorbate hydrogen-bonding substrate–adsorbate hydrogen bonding, and in addition partial dissociation of water molecules.

In this paper we present results of careful *ab initio* geometry optimizations which gave two types of minima in the potential energy surface, namely physisorbed minima with undissociated water molecules and chemisorbed minima in which at least some of the water molecules are dissociated. We have determined a complete set of vibrational frequencies for both a physisorbed and a chemisorbed state.

The interpretation of theoretical and experimental results is a controversial issue. It has been commonly accepted that water adsorbs molecularly on the perfect (100) surface and that at temperatures around 200 K dissociative adsorption (chemisorption) occurs only in presence of surface defects. Low energy electron diffraction (LEED) and helium scattering (HAS) experiments^{1–3} show a water monolayer with $p(3\times 2)$ structure formed between 185 K and 220 K structure physisorbed on the perfect MgO surface. These two experi-

mental techniques do not give any information about the positions of the hydrogen atoms, and so give no direct evidence for the presence or absence dissociation. The adsorption isotherms are found to be completely reversible even at these low temperatures, which suggests that the water molecules are physisorbed rather than chemisorbed. This interpretation is supported by some classical calculations^{4–6} in which the physisorbed state was found to be flat and stabilized by intermolecular H-bonds. Recently some *ab initio* calculations showed spontaneous dissociation in a monolayer of water on the perfect surface,^{7–9} although earlier calculations¹⁰ showed that single adsorbed water molecules only dissociated at defect sites.

In principle infrared spectroscopy can give information about dissociation. Although experiments¹¹ showed the presence of hydroxide groups on a MgO substrate after desorbing the water molecules, it is difficult to say whether these are on defects or on perfect surfaces. The technical difficulties in preparing perfect MgO for experiments¹² are considerable. In another study using RAIRS, the lack of signals for the O–H bond was interpreted as evidence that the monolayer was flat and that there were no dissociated molecules.¹³

An important question to be answered is whether there is a physisorbed state with a monolayer of water molecules on a perfect MgO (100) surface and if so whether it is flat and how large the barrier to dissociation and chemisorption is. We find two minima corresponding to stable physisorbed states, one flat and the other (lower in energy) twisted, but the barrier to dissociation is not high.

II. TECHNICAL DETAILS OF THE CALCULATIONS

The calculations have been performed in the framework of density-functional theory, pseudopotentials and plane-

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TABLE I. Energies of configurations obtained after energy minimization. The values are given for one surface unit cell (6 water molecules) and are relative to that of the “Marseilles” configuration evaluated using the same computational conditions.

Geometry	Energy difference/ mHa	Energy difference/ kJ mol ⁻¹	Method
Dissociated:			
Marseilles	0	0	<i>k</i> and Γ ; BFGS
asymmetric	-7.2	-18.8	Γ , BFGS
flat	-12.4	-32.4	Γ , BFGS
Physisorbed:			
twisted	24.64	64.68	Γ , accurate BFGS
twisted	23.1	60.5	<i>k</i> points, 0 K MD
flat	30.0	78.6	<i>k</i> points, 0 K MD

wave basis sets. We used the finite-electronic temperature method of Alavi *et al.*¹⁴ (FEMD) which allows the use of a large MD time step. In this method, a free energy functional is optimized, yielding at self-consistency the electronic free energy. This method can handle partial occupation of states at the Fermi level, and is also conveniently implemented with *k*-point sampling of the electronic states in the Brillouin zone of the supercell. Both these issues (partial occupation and *k*-point sampling) may be of relevance in small systems with dissociating bonds, and one aim of this work is to investigate the dependence of the results on these parameters.

In all cases the system consisted of 6 water molecules lying on a slab of three or four layers of (100) planes of MgO. The surface unit cell corresponds to a 3×2 structure.

The size of the simulation box for both the four and three layer simulations was $L_x=8.94$ Å, $L_y=5.96$, and $L_z=17.88$ so that the thickness of the vacuum between the water layer and the bottom layer of the image slab of MgO is equal to about 9 Å for the 4 layer system and 11 Å for the 3 layer simulations. The water molecules and the first layer of MgO were not fixed, while the other two or three layers were fixed in the ideal lattice structure.

A Troullier–Martins¹⁵ pseudopotential was used to describe the oxygens, a local pseudopotential was used for the hydrogen, and for magnesium the pseudopotential in the form developed by Gonze *et al.*¹⁶ was used. The plane wave cut off was 60 Rydberg. The BLYP density functional with gradient corrections was used as it seems to give the best results for H-bonded systems.¹⁷

We investigated the importance of a number of calculation variables to see how sensitive the structure and energy differences of the minima were. These were the number of layers of MgO used in total and the number allowed to move; the number of *k* points; the cutoff and the pseudopotential. Calculations were performed using a *k* point mesh of 2×2×1 or a simple Γ -point sampling in order to test possible effects due to the two different approaches and to speed the calculation time. The optimized structures using the two schemes were very similar and this can be taken as a justification of the use of Γ point sampling in the 3×2 cell. There is a small change in the energy differences between minima obtained in the two methods (see Table I).

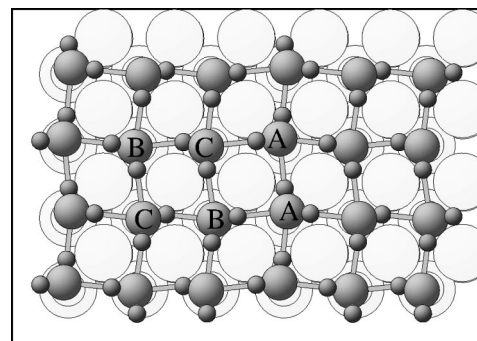


FIG. 1. Top view of the flat physisorbed structure. The top view shows four surface unit cells, each of which contain six water molecules related in pairs by a glide plane. The distinct molecules are labeled A, B, and C. The large open circles represent oxide ions and the smaller open circles magnesium ions. Note that all the molecules are connected by hydrogen bonds (drawn if $r_{\text{HO}} < 2.2$ Å) and that the water oxygen atoms sit above the magnesium ions.

III. STRUCTURES AT MINIMA

A. Physisorbed structures

As a starting point for the *ab initio* geometry optimization, we used a classical optimized configuration (supplied by Hoang^{1,18}). In this structure there is an adsorbed monolayer of water molecules lying in a plane on a slab of four layers of MgO and ordered in a 3×2 structure. The local energy minimum was located using the BFGS algorithm.¹⁹ When the forces acting on the nuclei of the nonfixed atoms are reduced to the order of 10⁻³ a.u. it was followed by a low temperature molecular-dynamics run to confirm that a minimum had been found. The resulting structure (the “flat physisorbed structure”) is shown in Fig. 1. Compared to the structure obtained using a classical intermolecular potential¹ the pattern of oxygen atoms is somewhat more distorted and the separation between the oxide surface plane and the water plane has increased from 3.99 bohr to about 4.45 bohr. In this structure there is a complete two-dimensional network of hydrogen bonds within the monolayer of water molecules (see Fig. 1 and Table II). The oxygen of each water molecule is above a magnesium ion.

However a more stable physisorbed structure (about 7 mHa or 18 kJ mol⁻¹ lower in energy per surface unit cell) was found by heating the system to 600 K, doing a short molecular dynamics run and quenching the result. This did not lead to a chemisorbed state, but to one in which two of the six water molecules had rotated so that they were hydrogen bonded to the surface. We shall refer to this state as the twisted physisorbed state; its structure is shown in Fig. 2. Like the flat physisorbed structure it also has a glide plane perpendicular to the long axis of the 3×2 surface unit cell which is consistent with the LEED observations. The hydrogen bond network within the plane (see Fig. 2) is no longer as extensive, but there are also short, strong hydrogen bonds (see Table II) between the twisted water molecules and surface oxide ions. The gain in energy is presumably the result of the strength of these hydrogen bonds to the oxide ions which are stronger hydrogen bond acceptors than are water molecules. There are a number of “free” OH bonds which do not form H-bonds and which tend to point away from the

TABLE II. OH bond lengths and hydrogen-bond distances. A, B, and C are intact water molecules; *c* is a OH[−] ion in the adsorbed layer while *d* is a dissociated proton bonded to a surface oxide ion.

Configuration	Molecule	$r(\text{OH})/\text{\AA}$	$r(\text{H}\cdots\text{O})^a/\text{\AA}$	
Physisorbed (twisted)	A	0.96
	A	1.04	1.58	to surface oxide ion
	B	0.96
	B	0.98	1.93	to A
	C	0.97
Physisorbed (flat)	C	0.97	1.96	to another B
	A	0.97	2.16	to B
	A	0.97	2.04	to A
	B	0.97	2.00	to C
	B	0.97	1.97	to another C
Dissociated (Marseilles)	C	0.97	2.09	to B
	C	0.97	2.00	to another B
	A	0.96
	A	0.98	2.05	to surface oxide ion
	B	1.01	1.57	to <i>c</i> (OH [−])
Dissociated (asym.)	B	0.96	2.13	to A
	<i>c</i> (OH [−])	0.96
	<i>d</i> (HO _{MgO})	1.00	1.65	to C
	A(1)	0.97	2.11	to B
	A(1)	0.99	1.83	to A(2)
	A(2)	0.97	2.11	to A(3)
	A(2)	1.01	1.59	to <i>c</i> (1) (OH [−])
	A(3)	0.96
	A(3)	1.01	1.60	to <i>c</i> (2) (OH [−])
	B	0.96
	B	1.01	1.65	to ion <i>c</i> (2)
	<i>c</i> (1)	0.96
	<i>c</i> (2)	0.96
	<i>d</i> (1)	1.01	1.59	to <i>c</i> (2) (OH [−])
	<i>d</i> (2)	0.99	1.75	to <i>c</i> (1) (OH [−])
Dissociated (flat)	A	0.97	2.19	to A
	A	1.00	1.70	to <i>c</i>
	B	1.10	1.57	to <i>c</i>
	B	0.96
	<i>c</i>	0.96
	<i>d</i>	0.98	1.92	to <i>c</i>

^aHydrogen bonds are recorded if $r(\text{H}\cdots\text{O}) < 2.2 \text{\AA}$.

oxide surface. We shall see that the stretching frequencies of these bonds are high. The OH bond lengths and the Mulliken charges on the protons also respond to the presence or absence of H-bonding. The OH bond lengths range from 1.04 Å for the bond in the A molecule which hydrogen bonds to the surface oxide ion to 0.96 Å for “free” OH bonds. The corresponding Mulliken charges are reduced from about 0.5*e* to 0.4*e* for the proton in the strong hydrogen bond. Table II gives the OH and corresponding hydrogen bond lengths in all the configurations we examined.

LEED experiments with tensor LEED analysis¹ locate the positions of the oxygen atoms to accuracies of ±0.15 Å in *x* and *y* and ±0.05 Å in *z*. No information is obtained concerning proton positions. The differences between our physisorbed positions and the positions from the LEED analysis are about four times as large as the quoted experimental errors, with the main error being in the *z* coordinate.

Although this structure is certainly an energy minimum (the vibrational analysis described in Sec. IV gives real fre-

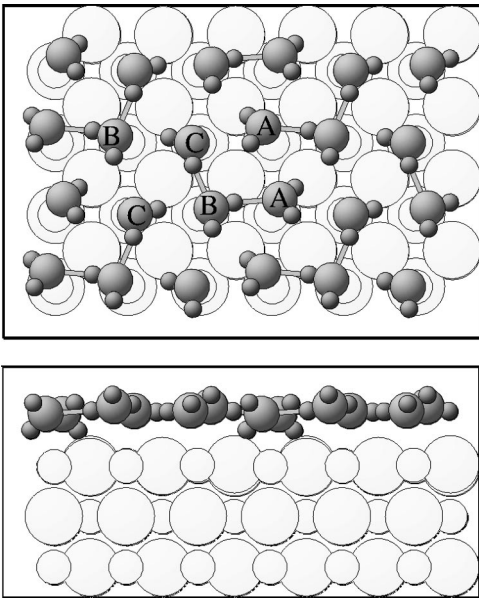


FIG. 2. Two views of the physisorbed configuration. The top view shows four surface unit cells, each of which contain six water molecules related in pairs by a glide plane. Note that molecules of type A form hydrogen bonds to the surface oxide ions and that there is much less hydrogen bonding within the water layer than in the flat structure.

quencies), the barrier to dissociation is not high. A molecular dynamics run was performed at 300 K starting from the physisorbed state. After a short time (70 fs) one of the waters (labeled A in Fig. 2) that was originally hydrogen bonded to a surface oxygen, transferred a proton to the surface. In an apparently concerted motion a water molecule (B) that was donating a hydrogen bond to the molecule that was about to dissociate moved away from the surface into an overlayer. As a result it made a stronger hydrogen bond to A. This process in which a single proton was transferred broke the glide plane symmetry. The maximum potential energy during this run was 50.2 mHa above the initial energy of the physisorbed minimum. Assuming a thermal contribution of $\frac{1}{2}kT$ per degree of freedom (the harmonic contribution) this gives an estimate of a barrier height of about 9 mHa or 0.24 eV. This is almost 10*kT* at 300 K. After a further period of 150 fs a second proton was transferred to the surface, but not from the second molecule labeled A in the original structure. This new chemisorbed structure did show any further signs of proton transfer when the trajectory was run on for a further period of 500 fs. The final configuration from this run was quenched.

B. Chemisorbed states

Giordano *et al.*⁷ found a chemisorbed state in which two of the six water molecules had donated protons to oxide ions in the surface, and which maintains the glide plane. We shall refer to this chemisorbed structure as the Marseilles structure. It is different from the structure obtained from quenching our MD run, which we shall refer to as the asymmetric dissociated structure as it has no glide plane. We also obtained a further low energy structure (the “flat” dissociated structure) from a short molecular dynamics run starting from

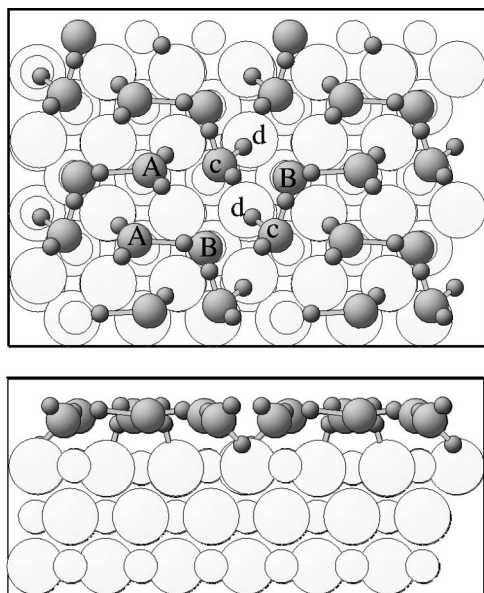


FIG. 3. Two views of the Marseilles dissociated configuration. A and B are intact water molecules, while *c* is a hydroxide ion and *d* is the proton which has dissociated and chemisorbed on the surface. There is a glide plane relating molecules with the same labels. Note the two dissociated protons are bonded to the oxide ions in the surface and the hydroxide ion *c* is twisted out of the surface. The hydrogen bonds from molecules A to surface oxide ions are shown in the side view.

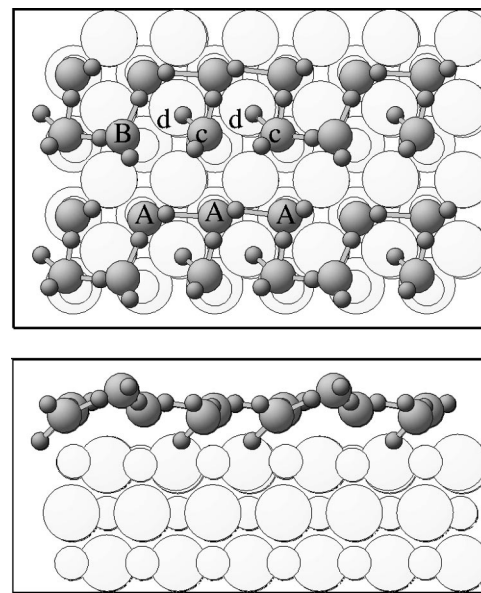


FIG. 4. Two views of the asymmetric dissociated configuration. The hydroxide ions are labeled *c* and the dissociated protons *d*. Molecule B lies above the plane of the adsorbed water (see side view) and hydrogen-bonds strongly with one of the hydroxide ions. As there is no glide plane, the three molecules labeled A are not related by symmetry. Note the pattern of hydrogen bonding which leads to a striped structure. Compared to the Marseilles configuration there is more in-plane hydrogen bonding.

the Marseilles structure. We have investigated and compared the properties of these three structures. The asymmetric structure is more stable than the Marseilles structure by 7 mHa, but as it has no glide plane it is not consistent with the experiments. The flat dissociated structure is more stable than the Marseilles structure by 12.4 mHa and has a glide plane.

Using Giordano *et al.*'s configuration as input (with a small scaling due to the fact that we used a lattice constant of 2.99 Å rather than 3.01 Å for MgO) we confirmed that the Marseilles structure was indeed a minimum with our choice of density functional and other technical parameters. The energy of this state is considerably lower than that of the physisorbed state (by 60 kJ mol⁻¹).

The structure is shown in Fig. 3. The hydrogen bond network has been almost completely disrupted although the two of the three hydrogen bonds that remain are exceptionally short and strong (see Table II). The hydroxide group in the monolayer is a strong hydrogen bond acceptor and accepts such bonds from both the dissociated proton and one of the water molecules. The remaining water molecule (A) does not hydrogen bond to the hydroxide ion, but twists so that it can hydrogen bond to the surface oxide ion.

We shall see that the facts that both this structure and the twisted physisorbed have water molecules with "free" OH bonds and that the surface hydroxyl groups are not free, but take part in hydrogen bonding, is important for understanding the vibrational spectra. The agreement of the dissociated structure with the LEED experimental results are of similar quality to the physisorbed structure, so one cannot use the LEED results to discriminate between these structures.

The asymmetric dissociated structure is shown in Fig. 4.

It is similar to the Marseilles structure in having one-third of the water molecules dissociated. Comparing the two chemisorbed structures, the most notable points of difference are the relative positions of the dissociated molecules and the protons on the surface relative to the 2×3 surface unit cell. The top view of the asymmetric structure shows stripes of adsorbed water molecules and hydroxide ions separated by troughs without water molecules. This is the result of the lack of hydrogen bonding between alternate rows and is facilitated by the fact that one row contains two OH⁻ groups and a water molecule which has moved into an overlayer and which hydrogen bonds strongly to one of the hydroxide ions.

The lowest energy structure (the flat dissociated structure) was obtained by performing a molecular dynamics run starting from the Marseilles configuration at 600 K followed by a quench. The main difference between this structure and the Marseilles structure is that there is more hydrogen bonding within the plane of adsorbed molecules. Figure 5 shows the structure. Comparing this with the "Marseilles" structure (Fig. 3) we see that the main difference is that the A molecules are planar rather than twisted so that each forms a strong hydrogen bond to the OH⁻ ion and a weak one to the other A molecule rather than just a hydrogen bond to the surface oxide ion. The bond lengths and hydrogen bond distances are given in Table II. It seems that the energy of these second two structures are stabilized because of strong hydrogen bonding to the hydroxyl group formed by dissociation.

When trying to decide on the structure of the chemisorbed state, it is instructive to realize that, in fact, many partially dissociated structures in which protons are transferred to the surface can be constructed. A more extensive study of this question is underway. For the present we simply

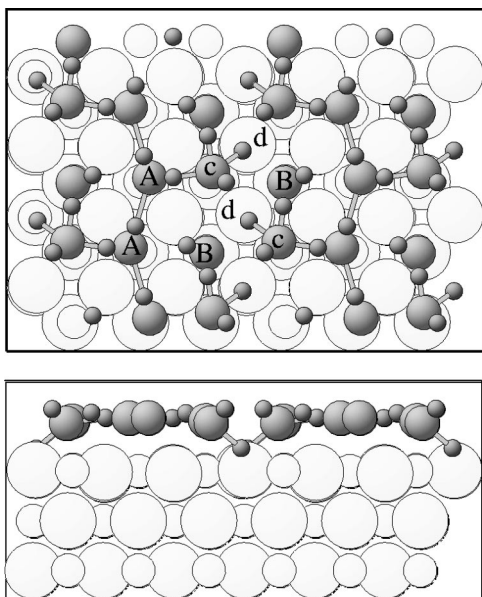


FIG. 5. Top view of the flat dissociated configuration which is the lowest energy structure found. This structure has a glide plane and also has more in-plane hydrogen bonding than the Marseilles configuration.

note that once a pair of water molecules have dissociated, it is exceedingly unlikely on the time scale of the simulations that other dissociated minima are visited. It is entirely possible, therefore, that the global minimum has not been found.

IV. VIBRATIONAL FREQUENCIES

The vibrational frequencies were determined by using the vibrational analysis option of the CPMD code. In this method, the dynamical matrix is obtained numerically by computing the changes in forces on ions with finite (both positive and negative) displacements along all Cartesian coordinates of a specified set of atoms. In order to investigate the coupling between the surface MgO atoms and the water molecules, we considered displacements of atoms in the water molecules those in the top layer of MgO. In practice this meant moving 30 atoms, and therefore 180 force calculations. The dynamical matrices and vibrational frequencies of two states were determined. The two states chosen were the twisted physisorbed configuration and the Marseilles dissociated configuration. These two states were chosen as they are consistent with the LEED observation of a glide plane. Later we found the flat dissociated state which also has a glide plane and is lower in energy. As vibrational analysis takes considerable computation and the distinctive spectral features of the dissociated state are associated with the surface hydroxyl groups which are still present, we did not repeat the analysis. In both the states analyzed all the eigenvalues of the Hessian matrix were positive, confirming that they are local minima of the potential energy surface.

Figure 6 shows the spectra presented in a number of different ways. At the top the density of vibrational states is shown for the two configurations while below are approximate representations of the predicted infrared spectra with polarizations parallel and perpendicular to the surface. Let us examine first the density of states which was constructed by

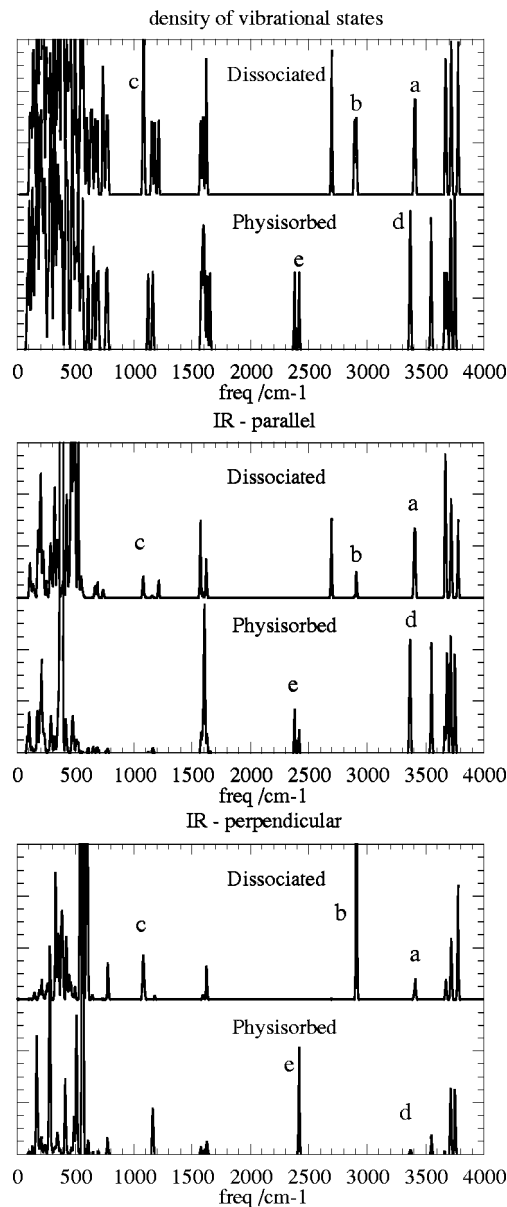


FIG. 6. Harmonic vibrational frequencies of the dissociated and physisorbed monolayers. The top part shows the density of states while below are approximate representations of the IR activity. These figures show fundamental harmonic frequencies and all lines are shown with the same width (5 cm^{-1}), so they should be treated as schematic and will differ from observed spectra. The transitions labeled a–e are characteristic of physisorbed and chemisorbed states; the assignments are given in Table III.

applying a Gaussian broadening of 5 cm^{-1} to the calculated harmonic frequencies of the normal modes. The modes below 800 cm^{-1} are substrate modes and external modes of the motion of water molecules relative to each other and to the surface. The modes at about 1100 cm^{-1} involve the stretching of the hydrogen bond to the surface or wagging of the surface hydroxide group formed by dissociation, the modes at about 1600 cm^{-1} are water bending modes and the high frequency modes are O–H stretching modes. These groups of modes are similar in both physisorbed and dissociated species. The modes that are distinct are labeled a–e in the figure and their assignments are given in Table III. It is clear that the changes in spectra provide good discrimination be-

TABLE III. Vibrational modes that discriminate between physisorbed and dissociated structures. In the physisorbed state OH_s is the water OH bond which is hydrogen-bonded to the surface while in the dissociated state the surface OH is the hydroxyl group formed by the dissociated proton and an oxide ion on the surface.

Mode	Frequency/cm ⁻¹		Assignment	Activity
	H ₂ O	D ₂ O		
PHYSISORBED	(twisted)			
d	3550	2571	symmetric stretch	IR par (s)
d'	3545	2564	symmetric stretch	IR par
e	2416	1775	OH···O _s stretch-in phase	IR perp;IR-par(wk);R
e'	2376	1747	OH _s stretch-out of phase	IR par(wk)
DISSOCIATED	(Marseilles)			
a	2907	2127	surface OH stretch in-phase	IR perp-(s) IR-par(wk);R
a'	2890	2113	surface OH stretch out-of-phase	
b	2697	1976	mixed OH stretch	
b'	2693	1973	mixed OH stretch	IR-perp;R
c	1089	787	surface OH wag	
c'	1081	783	surface OH wag	
c''	1078	780	surface OH wag in-phase	IR-par;IR perp

tween physisorbed and dissociated states. However the distinctive features are not the highest frequency modes, which arise from stretching of water OH bonds which are not or very weakly hydrogen bonded, for example, the free OH bond in molecules A. In the physisorbed state the distinctive transitions labeled (e) at about 2400 cm⁻¹ arise from stretching the OH bonds in the A molecules which are H-bonded to the surface. We have seen in the previous section that these bonds are stretched and the corresponding H-bond is unusually short. In the dissociated state on the other hand the distinctive transitions arise from the hydroxyl groups on the surface and the hydroxide ions in the monolayer. The stretching frequencies of these are at about 2900 cm⁻¹ and 2700 cm⁻¹ respectively. These frequencies are much lower than for free hydroxide ions due to hydrogen bonding. The wagging vibrations of the surface hydroxyl groups at 1080 cm⁻¹ are also distinctive.

The polarized infrared spectra shown below have been constructed from the vibrational density of states using estimated intensities obtained by placing fixed charges on the nuclei. It is difficult to calculate accurate infrared intensities even though the changes in electron densities are available because of the use of periodic boundary conditions.²⁰ However these approximate intensities show the effects of symmetry and provide a reasonable guide. In a real spectrum effects of anharmonicities would lead to combination bands and overtones. The line widths are likely to vary widely from peak to peak. Such effects are not included in these spectra. The frequencies calculated using density functionals with gradient corrections are usually reliable to $\pm 5\%$. However it must be emphasized that we have no information about the vibrational linewidths, so that the spectra shown in the figure may be misleading as hydrogen-bonded hydroxide vibrations tend to be broad.

Spectra were also constructed in a similar way for D₂O on MgO. These look very similar to the ones shown for H₂O, but with the frequencies appropriately scaled. Frequencies for the modes (a) to (e) are given in Table III.

V. DISCUSSION

What can we conclude about the state of water on MgO (100)? These calculations suggest that the potential energy surface for the system is complex with many minima. These fall into two types, physisorbed and dissociated states. The barrier to dissociation of the twisted physisorbed states is low enough that it was found to dissociate in 100 fs in a molecular dynamics run at 300 K. Whether it is sufficiently stable at cryogenic temperatures to be the observed phase at 200 K is not clear.

In all the dissociated states that we have located so far, two out of the six molecules in the 3×2 unit cell are dissociated transferring a proton each to hydroxylate the surface. An important factor in the stabilization of these states is the formation of strong hydrogen bonds from undissociated water molecules to the OH⁻ in the adsorbed water layer. This suggests that the maximum number of dissociated water molecules is likely to be 50%. The stability of the physisorbed phases is a subtle balance between the maintenance of the hydrogen bond network within the water layer and the formation of hydrogen bonds to the oxide ions in the surface layer which are stronger hydrogen bond acceptors.

Our results, while consistent with other *ab initio* calculations, indicate that the problem of finding the lowest energy structure has not yet been solved. The observed reversibility of the adsorption isotherms has been interpreted as evidence for the existence of a physisorbed state, and we find such states. However a sufficiently low barrier to dissociation could also account for the observations. The spectroscopic data is also not clear cut. The vibrations that have been observed so far are not in the regions where our data suggests that vibrational spectra can distinguish between physisorbed and chemisorbed structures. Clearly further experimental and theoretical work is needed.

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