



6 February 2002

**CHEMICAL  
PHYSICS  
LETTERS**

Chemical Physics Letters 352 (2002) 318–322

www.elsevier.com/locate/cplett

## Evidence for partial dissociation of water on flat MgO(1 0 0) surfaces

Y.D. Kim <sup>a</sup>, R.M. Lynden-Bell <sup>b,\*</sup>, A. Alavi <sup>c</sup>, J. Stulz <sup>a</sup>, D.W. Goodman <sup>a</sup>

<sup>a</sup> Department of Chemistry, Texas A&M University, College Station, TX 77842-3012, USA

<sup>b</sup> Atomistic Simulation Group, School of Mathematics and Physics, The Queen's University, Belfast BT7 1NN, UK

<sup>c</sup> University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK

Received 12 November 2001; in final form 7 December 2001

### Abstract

Ab initio calculations of the density of states for adsorbed monolayers of water on a MgO(100) surface are compared with metastable impact electron spectra (MIES) and ultraviolet photoelectron spectra (UPS). The calculations confirm the suggested assignments and in particular show that there is good evidence that some, but not all, molecules have dissociated to hydroxide ions. Density of state calculations are shown for configurations with no dissociated molecules, one third of the molecules dissociated and half the molecules dissociated; the agreement with experiment is best for the configuration with one third of the molecules dissociated. © 2002 Published by Elsevier Science B.V.

### 1. Introduction

Although it has been long postulated that water is physisorbed on a defect-free (1 0 0) magnesium oxide surface, ab initio calculations [1–3] suggest that configurations in which at least a proportion of the water molecules is dissociated is energetically preferred. Additional calculations [4] have shown that the barrier to dissociation is very small, countering the argument that reversible adsorption implies that water is physisorbed. A recent study [5] using metastable impact electron spec-

troscopy (MIES) suggests partial dissociation. In this Letter we report experimental and theoretical data that are consistent with water being partially dissociated within the first monolayer on MgO. The calculations allow us to identify the contributions of various molecular orbitals corresponding to OH<sup>-</sup> species and water molecules on the surface.

### 2. Technical details of the calculations

In earlier work we found several low energy potential minima [8] which are consistent with 2 × 3 surface unit cell with glide planes deduced from LEED observations [6,7]. The configurations used for analysis in the present work were taken

\* Corresponding author. Fax: +44-2890-241958.

E-mail address: r.lynden-bell@qub.ac.uk (R.M. Lynden-Bell).

from these earlier calculations. Four energy-minimised structures were used. One of these was the  $2 \times 3$  physisorbed state found by Delle Site et al. [3]; two were low energy states found in an exhaustive search for low energy minima which satisfied the experimental symmetry and which had one third of the molecules dissociated (configurations bz2 and by2 from [8]) and the final configuration used had one half the molecules dissociated in a  $2 \times 2$  surface unit cell [8].

The technical details of the calculations are given in our earlier papers [3,8]; to understand the analysis described in this Letter it suffices to say that the calculations were performed in a plane wave basis with density functional theory and the Kohn–Sham orbitals and eigenvalues obtained. These orbitals were then projected onto valence atomic orbitals on each atom and the eigenvalues and coefficients of the projected eigenfunctions used for further analysis.

The Kohn–Sham density of states or eigenvalue spectrum can then be analysed into contributions from different types of orbital on different atoms (e.g., p orbitals on oxygen atoms in hydroxide ions or hydrogen orbitals on undissociated water molecules). In order to show the results graphically, the spectra were computed by broadening the weighted eigenvalues with a Lorentzian function of width 0.5 eV.

The energy zero of the Kohn–Sham eigenvalues must be found from a separate calculation, since the energy given in the program is the energy relative to the average potential in the simulation box. The desired energy, however, is that relative to the potential at large distances from the slab. This potential was found by plotting the average potential as a function of distance from the slab. Unfortunately it is quite noisy in regions of low electron density (due to the way in which the BLYP gradient corrections are computed) and there is an uncertainty of 1.5 eV in the absolute positions of the eigenvalues and the calculated spectra.

### 3. Experimental

Experiments were carried out in an ultrahigh vacuum (UHV) system with a base pressure of

$10^{-10}$  Torr. This system is equipped with LEED, temperature programmed desorption (TPD), Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), MIES and ultraviolet photoelectron spectroscopy (UPS). MIES and UPS were measured simultaneously using a cold-cathode discharge source, that provides both ultraviolet photoelectrons and metastable He 23S ( $E^* = 19.8$ ) atoms with thermal kinetic energy. Metastable and photon contributions to the signal were separated by time-of-flight using a mechanical chopper. MIES/UPS data were acquired with an incident photon/metastable beam at  $45^\circ$  with respect to the surface normal in a constant pass energy mode using a double pass cylindrical mirror analyser. In the following spectra, all binding energies are referred to the Fermi level of Mo(100).

MgO(100) films on a Mo(100) substrate were prepared by deposition of Mg in an  $O_2$  atmosphere of  $10^{-7}$  Torr at a sample temperature of 600 K. Subsequently, the sample was annealed at 1150 K. The thickness of the MgO(100) films was estimated to be ca. 15 ML. It is noteworthy that by employing techniques such as LEED, MIES, and CO adsorption experiments, we have found that annealing to 1150 K is essential to create a flat and very well-ordered MgO(100) surface. The fact that there is no CO adsorption on these MgO film at 90 K shows that there is no exposed metallic surface [9].  $D_2O$  (Aldrich 99.9%) was purified by several freeze–pump–thaw cycles and was dosed via back filling the chamber.

## 4. Results and discussion

### 4.1. Comparison of experimental and calculated spectra

Fig. 1 shows UPS spectra (above) and MIES spectra (below) at a number of coverages. In each part of the figure the calculated density of states for monolayer coverage is shown underneath the experimental spectra. The solid line is the density of states of the adsorbed monolayer of water in which one third of the molecules are dissociated and the dashed line is the density of states arising from the substrate. The four experimental curves

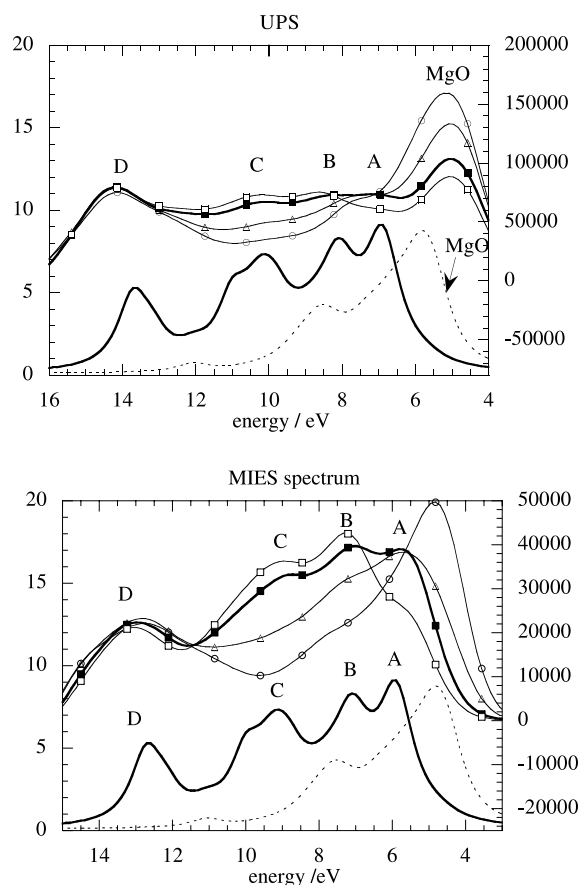


Fig. 1. Above: UPS spectra of water on MgO at coverages of 0 L (circles), 0.5 L (triangles), 1.4 L (filled squares) and 2.4 L (open squares). The highlighted curve corresponds to monolayer coverage (1.4 L). Immediately below the calculated densities of states are shown for the MgO substrate (dashed line) and for an adsorbed ( $2 \times 3$ ) monolayer with one third of the molecules dissociated (solid line). Below: The corresponding MIES spectra. Note that in both types of spectrum features B and C grow with increasing coverage; A first appears and then decreases.

shown correspond to coverages of 0, 0.5, 1.4 and 2.4 Langmuir (L). According to TPD [5], the formation of the  $D_2O$  first monolayer completes at  $D_2O$  exposures of 1.3–1.4 L; the data for monolayer saturation are highlighted in bold.

The MIES technique probes only the outermost layer on the surface while the UPS technique is sensitive to a number of layers near the surface. This difference arises from the different penetrating powers of the probes – namely excited helium at-

oms in the MIES technique and ultraviolet photons in the UPS technique.

In both MIES and UPS spectra, new features (A, B and C) appear as the coverage of water is increased, while the feature with least ionisation potential (marked MgO) decreases in intensity. Feature D seems to be independent of coverage in both types of spectrum. The peak (labelled MgO) at about 5 eV is assigned to the oxygen 2p orbitals of the MgO substrate. The corresponding density of states is shown (as a dashed line) underneath the spectra. Note that this peak disappears from the MIES spectrum at a coverage of about 1.4 L (bold curve) which corresponds to a coverage of one monolayer. As the coverage increases above a monolayer, peak A decreases in intensity, while peaks B and C become more prominent. Accordingly peak A is assigned to dissociated  $D_2O$  in the first monolayer and peaks B and C to undissociated water molecules [5]. As shown below, these assignments are fully supported by our calculations. Peak D is somewhat puzzling. Although this feature is believed to contain a contribution from water, its intensity is independent of coverage in both MIES and UPS. It is likely that this band is due to secondary electrons which swamp the water contribution. In UPS, the secondary electrons come from the substrate. In MIES, they may originate from both water and the substrate.

There are three further points to be made in the discussion of the comparison of the calculated density of states with the MIES and UPS spectra. Firstly the Kohn–Sham eigenvalues do not, strictly speaking, correspond to the one electron ionisation energies even in the absence of orbital relaxation; Koopman's theorem only applies to the highest Kohn–Sham eigenvalue. However Görling [10] has shown that differences in Kohn–Sham eigenvalues provide a first order estimate of excitation energies. Secondly, orbital relaxation may well occur. In spite of these caveats the Kohn–Sham density of states probably gives a good semi-quantitative estimate of the ionisation spectrum of this system in the valence region, especially in view of the agreement with the experimental spectra. Finally, the peaks in the two experimental spectra appear to be shifted relative to each other by about

1 eV. As explained above the energy zero for the calculated densities of states is uncertain by  $\pm 1.5$  eV, and the calculated spectra have been shifted by amounts differing by about 1 eV in the two parts of the figure to give the best comparison.

#### 4.2. Degree of dissociation

Fig. 2 shows the densities of states for the four different configurations with zero, one third (two examples) and one half the molecules dissociated. There are significant differences between the densities of states with different fractions of the water dissociated. In particular, peaks A and E are absent if there is no dissociation and are considerably more intense if half the molecules are dissociated. The experimental spectra do not reach the region of the oxygen 2s states (peaks E and F), but the agreement between the experimental MIES spectra in the region of 0–15 eV and the calculated density of states from a configuration (bz2) with one third of the molecules dissociated suggests that this is

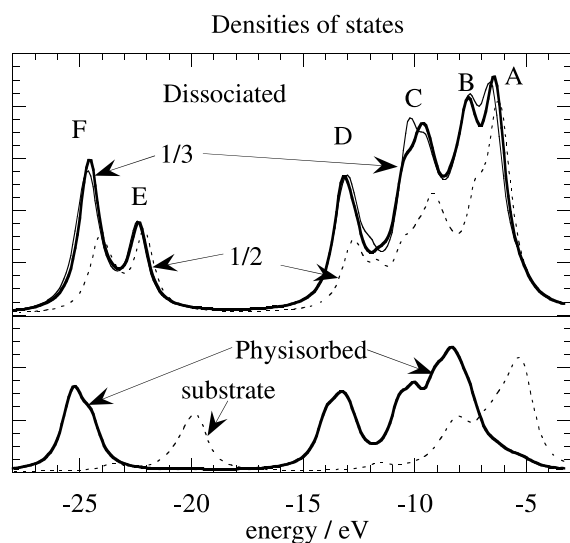


Fig. 2. Calculated densities of states for partly dissociated configurations (above) and non-dissociated configurations (below). In the upper part the continuous lines correspond to energy-minimised structures with one third of the molecules dissociated (bold line 'bz2', thin line 'by2' structures) while the dashed line corresponds to an energy-minimised structure with half the water molecules dissociated. In the lower part the dashed line shows the density of states for the substrate (MgO).

the observed degree of dissociation. This supports earlier calculations [1,2].

The density of states from the oxide ions in the substrate is also shown (dashed line in the lower part of the figure). The orbitals of these ions are less tightly bound than the corresponding water or hydroxide orbitals.

#### 4.3. Assignment of bands

Fig. 3 shows the contribution of different components to the bz2 density of states. The dashed line is the contribution arising from the hydroxide ions formed by dissociation, while the thin lines show the contributions from different components of the water orbitals. These support the following assignments of the bands:

- A: OH –  $\pi$  – as only O(2p) orbitals from OH<sup>-</sup> contribute.
- B: H<sub>2</sub>O – b<sub>1</sub> – as only O(2p) orbitals from H<sub>2</sub>O contribute.
- C: H<sub>2</sub>O – a<sub>1</sub> – as O(2s), O(2p) and H orbitals from H<sub>2</sub>O contribute.
- C shoulder: OH –  $\sigma$  – as O(2p), O(2s) and H orbitals from OH<sup>-</sup> contribute.
- D: H<sub>2</sub>O – b<sub>2</sub> – as H and O(2p) orbitals on H<sub>2</sub>O contribute, but O(2s) do not.
- E: OH –  $\sigma$  as – O(2s) from OH is the main contribution.

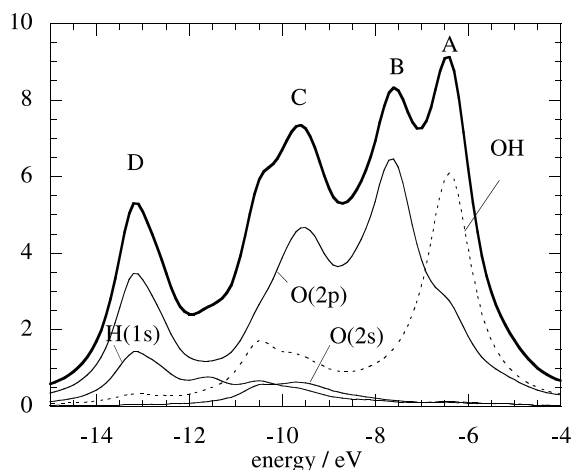


Fig. 3. Contributions from different types of orbital to the overall density of states in the 'bz2' configuration.

F:  $\text{H}_2\text{O} - a - 1 - a$  as O(2s) from  $\text{H}_2\text{O}$  is the main contribution.

## 5. Conclusion

The combination of calculated and experimental spectra described in this paper provides strong evidence that adsorption of 1.4 L water on a clean, flat MgO surface leads to a mixed monolayer in which one third of the molecules is dissociatively adsorbed and two thirds remain undissociated. Further dosing of water leads to multilayer formation of undissociated water molecules on top of the ( $\text{D}_2\text{O} + \text{OD}$ ) mixed monolayer. As the MIES spectrum is only sensitive to the outermost layers, the OD feature (band A) disappears. In the UPS spectrum, this band becomes swamped by the  $\text{D}_2\text{O}$  features which increase in intensity with increasing coverage. Our data do not give strong evidence as to whether the lowest multilayer remains dissociated or not. There is, however, independent evidence [11] that the multilayer grows over a stable ( $\text{D}_2\text{O} + \text{OD}$ ) mixed monolayer. It could be argued that the surface properties of a thin film (about 45 Å) of MgO on a metal differ from those of a surface of a cleaved MgO crystal, for example because of the effect of the conducting layer on the electrostatic energy of the dissociated molecule. We estimate the order of magnitude of the additional

stabilisation of a dissociated molecule with charges separated by 3 Å to be  $10^{-2}$  meV or  $10^{-3}$  kJ/mol, which is negligible.

## Acknowledgements

We acknowledge financial support from the Department of Energy, Basic Energy Sciences, Division of Chemical Sciences, and EPSRC (grants GR/K20651 and GR/L08427).

## References

- [1] L. Giordano, J. Goniakowski, J. Suzanne, Phys. Rev. Lett 81 (1998) 1271.
- [2] M. Odelius, Phys. Rev. Lett 82 (1998) 3919.
- [3] L. Delle Site, A. Alavi, R.M. Lynden-Bell, J. Chem. Phys. 113 (2000) 3344.
- [4] L. Giordano, J. Goniakowski, J. Suzanne, Phys. Rev. B 62 (2000) 15406.
- [5] Y.D. Kim, J. Stultz, D.W. Goodman, J. Phys. Chem. B, in press.
- [6] D. Ferry, S. Picaud, P.N.M. Hoang, C. Girardet, L. Giordano, B. Demirdjian, J. Suzanne, Surf. Sci. 409 (1998) 101.
- [7] C. Xu, D.W. Goodman, Chem. Phys. Lett. 265 (1997) 341.
- [8] R.M. Lynden-Bell, L. Delle Site, A. Alavi, Surf. Sci. 496 (2002) L1–L6.
- [9] Y.D. Kim, J. Stultz, D.W. Goodman, Surf. Sci., submitted.
- [10] A. Görling, Phys. Rev. A 54 (1996) 3912.
- [11] B. Demirdjian, J. Suzanne, D. Ferry, J.P. Coulomb, L. Giordano, Surf. Sci. 462 (2000) L581.