

## Structure of Physisorbed Molecules on an Oxide Surface from Potential Calculations and Dynamical Low-Energy Electron Diffraction Analysis: Acetylene on MgO(100)

D. Ferry,<sup>1</sup> P. N. M. Hoang,<sup>2</sup> J. Suzanne,<sup>1</sup> J.-P. Bibérian,<sup>1</sup> and M. A. Van Hove<sup>3</sup>

<sup>1</sup>CMRC2-CNRS,\*, Département de Physique Faculté des Sciences de Luminy, Case 901, 13288 Marseille Cedex 9, France

<sup>2</sup>Laboratoire de Physique Moléculaire (URA-CNRS 771), Faculté des Sciences La Bouloie, Université de Franche-Comté, 25030 Besançon Cedex, France

<sup>3</sup>Materials Sciences Division, Lawrence Berkeley National Laboratory, University of California, Berkeley, California 94720  
(Received 19 November 1996)

Semiempirical potential calculations have been combined with a dynamical low-energy electron diffraction analysis to determine the complete structure of molecules physisorbed on an oxide surface, namely, acetylene ( $C_2H_2$ ) adsorbed on MgO(100) at  $T = 88$  K. This allows determination of the adsorption sites and the molecule-molecule and molecule-substrate distances. The results are consistent with molecules that lie almost parallel to the surface in a herringbone structure. Neither molecule nor substrate exhibits significant distortions, due to the weak physisorption. [S0031-9007(97)03254-7]

PACS numbers: 68.55.Jk, 34.20.Gj, 61.14.Hg

Molecular adsorption, including physisorption, on oxides is of special importance for catalysis, since oxides play major roles both as active catalysts and as supports for metallic catalyst particles [1]: Zeolites, in particular, have attracted much attention [2]. While strong metal-support interactions remain under extensive study [3], there is a need for studying surfaces that are accessible to a wider range of surface science techniques, primarily external single-crystal surfaces [4]. MgO provides a most favorable model oxide crystal for this purpose: It is itself used as a support in catalysis. It is furthermore used as support for the growth of high- $T_c$  superconductors. MgO provides high-quality single-crystal surfaces while it is also available as uniform powder on whose large surface area molecular adsorption can be studied with neutron diffraction. Calculations [5], as well as low-energy electron diffraction (LEED) dynamical analyses [6,7] and medium-energy ion scattering analysis [8], have shown that the bare MgO(100) surface is only slightly perturbed from its bulk structure. Molecular adsorbates bearing strong dipole or quadrupole moments have been investigated on this surface. They are good probes of the surface electric field and have been used to evaluate the effective ionic charge  $q^* = q/e$  of the surface ions [9]. This effective charge is about  $\pm 1.2$ , in agreement with theoretical models [10]. Acetylene has a strong quadrupole moment which is expected to interact strongly with the surface electric field gradient and give a molecular arrangement with strong quadrupole-quadrupole interactions. LEED adsorption isotherms on MgO(100) surfaces [11] as well as volumetric isotherms on powders [12] have provided adsorbate-substrate and adsorbate-adsorbate interaction energies which have been compared to semiempirical potential calculations [11]. However, the detailed equilibrium structure given by the theoretical model must still be confronted with experimental results. The dynamical analysis of LEED intensities provides a unique way to obtain the complete structure: molecular ad-

sorption sites, molecule-substrate distance, and orientation, in addition to any relaxation within the molecules and the substrate. However, this analysis requires an approximate knowledge of the monolayer structure to start with, since it is a perturbationlike method. This is the reason why our approach combines the results of semiempirical theoretical modeling with a fully dynamical analysis of LEED intensities. This is the first application of such LEED analysis to physisorbed molecules on any substrate in the case where the interactions which determine the geometry of the adsorbed layer are predominantly of an electrostatic nature. Unlike chemisorption, where molecules can be strongly perturbed and eventually dissociated, physisorption leaves the adsorbed molecule relatively undistorted. Furthermore, we have a unique opportunity to compare the calculations and the LEED analysis to neutron diffraction experiments of  $C_2D_2$  on MgO [12], where a classical kinematical analysis of diffracted intensities can be achieved. However, the neutron diffraction technique does not allow determination of either the epitaxial relation between the substrate and the overlayer or the molecule-surface distance. Hence our work provides additional details on the acetylene monolayer/MgO(100) system.

In this Letter we present the main results. Details will be presented elsewhere [13].

The experimental apparatus and sample preparation have been described elsewhere [14]. Acetylene was adsorbed at 88 K and  $P = 4 \times 10^{-8}$  mbar on an in situ cleaved MgO single crystal to give one monolayer coverage. The resulting overlayer structure produced a sharp LEED pattern [11] which is consistent with a  $(2 \times 2)$  symmetry in agreement with previous neutron diffraction measurements for adsorption on powders [12]. The  $(1/2, 0)$  and  $(0, 1/2)$  spots are missing at normal incidence, consistent with two orthogonal glide planes [11]. LEED intensity versus electron energy measurements [ $I(V)$  curves] were performed for the  $(1,0)$ ,  $(1,1)$ ,

(1/2, 1/2), (3/2, 1/2), (2,0) and (2,1) reflections under the temperature and pressure conditions indicated above and, at normal incidence, using a video camera connected to an Apple Mac II Cx computer; the energy range 50–300 eV was used in the analysis.

Calculations with semiempirical potentials have been performed to determine the equilibrium structure of the acetylene monolayer [11]. The interaction potentials  $V_{MS}$  between a  $C_2H_2$  molecule and the MgO substrate and  $V_{MM}$  between two adsorbate molecules are written as a sum of three contributions: electrostatic, induction, and dispersion repulsion. The total interaction potential  $V$  between a  $C_2H_2$  adlayer and the MgO substrate is then a sum of pairwise interactions:

$$V(\vec{r}, \vec{\Omega}) = \sum_i \left[ V_{MS}(\vec{r}_i, \vec{\Omega}_i) + \frac{1}{2} \sum_j V_{MM}(\vec{r}_i, \vec{\Omega}_i, \vec{r}_j, \vec{\Omega}_j) \right]. \quad (1)$$

The quantities  $\vec{r}_i$  and  $\vec{\Omega}_i$  define the position of the center of mass and the orientation of the  $i$ th  $C_2H_2$  molecule with respect to an absolute frame ( $\vec{x}, \vec{y}, \vec{z}$ ) tied to the substrate, the  $\vec{x}$  and  $\vec{y}$  axes being in the surface plane as shown in Fig. 1. The orientation is defined by the azimuthal and polar angles  $\Phi$  and  $\theta$  between the C-C molecular axes and the  $\vec{x}$  and  $\vec{z}$  axes, respectively. The molecules and the substrate are assumed to be undeformable. In the present work, two different values of the effective ionic charge of the surface ions have been taken:  $\pm 1.2$  and  $\pm 2$ . The latter value,  $q^* = \pm 2$ , corresponds to a totally ionic MgO crystal, whereas the former value,  $\pm 1.2$ , has been determined, as mentioned above, from experiments [9] and theoretical calculations [10]. No temperature effects are introduced in the model. Hence the calculations represent the system at  $T = 0$  K. However, the potential barriers

to translation or rotation at the absorbing site are high enough to prevent dramatic changes in molecule positions at the temperature of our experiment [11]. Furthermore, in the present work, the use of the potential calculations is primarily to obtain an approximate structure to start the tensor LEED analysis. Consistently, the results of the LEED analyses will give us valuable information in the accuracy of the potential calculations.

The calculations of the minimum energy configuration are performed for various situations. We first consider a single  $C_2H_2$  molecule adsorbed on MgO(001) and determine the minimum potential energy surface experienced by this molecule when it moves above the MgO surface. The next step concerns the monolayer structure determination. The minimization procedure [14] consists of a numerical search for the potential minimum  $V_{(n \times m)}^{\min}(\vec{r}, \vec{\Omega})$  associated with a  $(n \times m)$  unit cell containing  $s$  molecules, with respect to the  $5s$  degrees of freedom. Many cells have been considered [11]. The most stable calculated geometry corresponds to the  $(2 \times 2)$  phase containing two molecules, as shown in Fig. 1. The molecular center of mass is located above Mg atoms. The first molecule lies at the origin of the drawn unit cell with its molecular axis parallel to the surface plane ( $\theta = 0^\circ$ ) and rotated by  $\Phi = 60^\circ$  with respect to the  $\vec{x}$  axis. The second molecule is located at the center of the unit cell with its molecular axis also parallel to the surface plane but azimuthally rotated by  $\Phi = 120^\circ$  with respect to the  $\vec{x}$  axis. The  $z$  distances between the center of mass of each molecule and the MgO(100) surface are identical and depend on the value of the effective surface charge, as shown in Table I. Our calculations show that the molecule-substrate interactions are dominant. The competition between the dispersion-repulsion and electrostatic contributions is always dominated by the electrostatic terms in the molecule-molecule and the molecule-substrate interactions. It is interesting to note that these calculations lead to two glide planes, in agreement with neutron diffraction experiments [12]. These glide planes are also consistent with our LEED observations, where  $(h/2, 0)$  and  $(0, k/2)$  reflections with  $h$  and  $k$  odd are missing.

To analyze the LEED  $I(V)$  curves and thereby determine atomic positions from experiment, we used an automated tensor LEED method, which includes all multiple scattering in a convergent manner and allows fitting many unknown atomic coordinates in the system [15]. No structural symmetry was assumed in the analysis. The positions in three dimensions of all carbon atoms and all Mg and O atoms in the topmost oxide layer within a  $(2 \times 2)$  unit cell were optimized by fitting to experiment using Pendry's  $R$  factor [16], representing  $3 \times 12$  coordinates (in addition to the muffin-tin zero level). Hydrogen was ignored as usual in LEED for H-containing molecules, being a weak electron scatterer. It should be pointed out that optimization

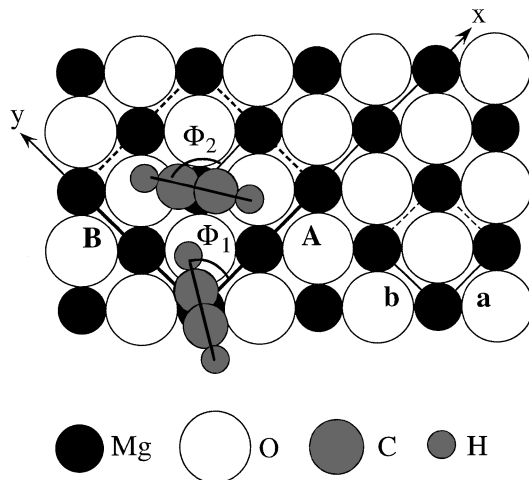


FIG. 1. The structure of the  $(2 \times 2)$  acetylene monolayer adsorbed on MgO(100). See Table I for the coordinates of the center of mass of the molecules and orientation angles determined from potential calculations and from dynamical analysis of LEED intensities.

TABLE I. Positions of the center of mass in Å and orientation of acetylene molecules determined from tensor LEED analysis of experimental data at 88 K (this work), from neutron diffraction (ND) at 150 K [12], and calculated from semiempirical potential calculations [11]. The height  $z$  is measured from the nuclear plane of the outermost MgO layer. The two calculated  $z$  values are for effective charges of  $\pm 1.2$  and  $\pm 2$ , respectively. See Fig. 2 and text for definitions of  $\Phi$  and  $\theta$ . Neutron experiments cannot give either adsorption sites or molecule-surface distances.

Molecule	$x$	$y$	$z$	$\Phi$	$\theta$
1 LEED	$0.22 \pm 0.10$	$-0.16 \pm 0.10$	$2.50 \pm 0.05$	$67^\circ \pm 10^\circ$	$108^\circ \pm 5^\circ$
ND	?	?	?	$45 \pm 15^\circ$	$90^\circ \pm 15^\circ$
Theory	0.00	0.00	2.49/2.39	$60^\circ$	$90^\circ$
2 LEED	$2.79 \pm 0.10$	$3.06 \pm 0.10$	$2.50 \pm 0.05$	$118^\circ \pm 10^\circ$	$89^\circ \pm 5^\circ$
ND	?	?	?	$135 \pm 15^\circ$	$90^\circ \pm 15^\circ$
Theory	2.98	2.98	2.49/2.39	$120^\circ$	$90^\circ$

of the Pendry  $R$  factor leads to a fit on the LEED diffracted peak positions but not on their relative intensities.

The  $I(V)$  curves for the (1,0), (1,1), and (1/2,1/2) reflections are shown in Fig. 2. We obtain the lowest

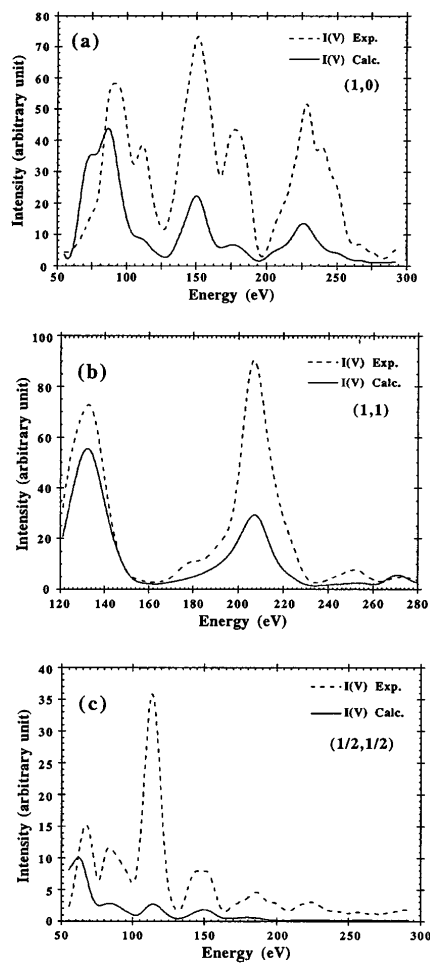


FIG. 2. LEED  $I$ - $V$  curves for a  $(2 \times 2)$  acetylene monolayer on MgO(100) at  $T = 88$  K and  $P(\text{C}_2\text{H}_2) = 4 \times 10^{-8}$  mbar. (a) (1,0) reflection, (b) (1,1) reflection, (c) (1/2,1/2) reflection. Dashed lines: experiment; full lines: tensor LEED best fit.

Pendry  $R$  factor, 0.14, when we take a molecule-surface distance equal to 2.49 Å. Within the accuracy of the tensor LEED method [15] the results from the LEED analysis are in good agreement with the optimized semiempirical model as shown in Table I: molecules lying almost parallel to the surface in a herringbone configuration above Mg atoms with azimuthal orientations relative to the  $\vec{x}$  axis of  $\Phi_1 = 67^\circ \pm 10^\circ$  and  $\Phi_2 = 118^\circ \pm 10^\circ$ ; the first molecule is found to have its C-C axis slightly tilted by  $18^\circ \pm 5^\circ$  (i.e.,  $\theta = 108^\circ \pm 5^\circ$ ) with respect to the surface plane, whereas the second molecule axis is parallel to the surface (i.e.,  $\theta = 89^\circ \pm 5^\circ$ ). The height of the center of gravity of the molecules is  $2.5 \text{ Å} \pm 0.05 \text{ Å}$  above the mean nuclear plane of the top MgO layer, in good agreement with the calculations for an effective charge  $q^* = \pm 1.2$ . This top MgO layer shows small distortions on the scale of 0.05 Å, which, however, are below the accuracy of the LEED analysis and also do not satisfy the glide plane symmetries that can be expected to exist. Therefore, they are interpreted to represent noise from the analysis. Similarly, the carbon positions lead to a C-C distance of  $1.2 \text{ Å} \pm 0.05 \text{ Å}$  compared to 1.18 Å for an undistorted molecule. These values are within the uncertainty of the analysis and are thus consistent with molecules that are undistorted with respect to the gas phase. Indeed, undistorted molecules are expected in the case of physisorption. Hence the good values that we obtain for the C-C distance is a good check of the accuracy of our data. It should be pointed out that the LEED dynamical analysis with the electron beam at normal incidence leads to an accuracy on atom positions which is less in the plane parallel to the surface than to that in the perpendicular direction [15]. In Table I we have also reported the results from the neutron experiments analysis [12]. They are consistent with a  $(2 \times 2)$  unit cell with two molecules which are mutually perpendicular and making an angle  $\Phi$  of  $45^\circ$  and  $135^\circ$  with  $\vec{x}$  axis. One sees that, within the experiment uncertainties, the agreement with semiempirical potential calculations and our

LEED analysis is rather good. However, these neutron experiments cannot give the molecule adsorption site positions nor the molecule-surface distance. Hence our analysis gives a better description of the monolayer acetylene/MgO(100) system.

The value 2.5 Å of the molecule-substrate distance that we have found for acetylene/MgO(100) is somewhat smaller than the distance 2.81 Å between (100) planes of the low temperature phase of bulk acetylene, where the molecule arrangement is close to that in the acetylene monolayer on MgO [17]. Acetylene adsorbed onto another ionic substrate NaCl(100) has been studied by polarized infrared (IR) spectroscopy [18]. The IR spectra could be qualitatively explained by a bilayer structure, where molecules in each layer are tilted by about 10° from the surface plane direction. The authors proposed qualitatively that molecules within the first layer are located over Na ions and parallel to the Na-Na rows to form T-shaped, hydrogen-bonded pairs. The second layer is half-filled, and molecules are parallel to each other and parallel to Cl-Cl rows. No quantitative experimental determination of the molecule-surface or molecule-molecule distances was made in these IR experiments. Recent Hartree-Fock calculations performed for monolayer acetylene on NaCl(100) have given a molecule-surface distance of 2.74 Å [19].

We have tested a molecule-surface distance 2.39 Å found by the calculations for an effective charge of ±2. The *R* factor is 0.2 which is larger than that for the distance 2.49 Å corresponding to the effective charge ±1.2. Our tensor LEED analysis shows definitively a convergence towards 2.5 Å, consistent with the value ±1.2 of the surface effective charge as proposed in previous experiments of NH<sub>3</sub> adsorbed on the same MgO(100) substrate [9]. Finally, we have tried to put the molecules above oxygen ions with the same orientational parameters and molecule-surface distance given by the calculations. The tensor LEED analysis leads to a *R* factor of 0.47, indicating that this adsorption site is not favorable.

As shown in Table I, our semiempirical potential calculations and dynamical analysis of LEED intensities agree rather well with the structure and adsorption sites of the acetylene molecules on the MgO(100) surface. The small tilt ( $\theta = 108^\circ$ ) of the C-C axis of one of the acetylene molecules is different from  $\theta = 90^\circ$  found in the calculations. Also, the tensor LEED analysis indicates a small displacement ( $\approx 0.2$  Å) of the center of mass of the molecules. Since we estimate our experimental uncertainties to be about 0.1 Å on the molecule positions, we believe that the molecule displacement from the Mg sites is meaningful. The small differences between experiments and calculations can be explained either by inaccuracies in the potential used or by the fact that the calculations correspond to  $T = 0$  K, whereas our experiment is performed at 88 K. It is particularly important to notice that these

results are also consistent with neutron diffraction experiments performed on very uniform MgO powders formed of small cubes presenting (100) faces only [12]. Since our experiment approach is the first to provide a complete quantitative description of the geometry of a molecule, namely, acetylene, physisorbed on oxide or ionic surfaces, it provides a starting point for exploring the detailed bonding of other molecules on these surfaces and to test the validity of semiempirical potential parameters.

M. A. V. H. is most grateful for a position as Visiting Professor during time spent at Marseille. M. A. V. H. was supported in part by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

\*Also associated with Université de la Méditerranée and Université Aix-Marseille 3.

- [1] G. A. Somorjai, *Chemistry in Two Dimensions* (Cornell University Press, Ithaca, New York, 1981).
- [2] W. O. Haag, in *Zeolites and Related Microporous Materials: State of the Art 1994*, edited by J. Weitkamp, H. G. Karge, H. Pfeifer, and W. Hölderich, Studies in Surface Science and Catalysis Vol. 84b (Elsevier, New York, 1994).
- [3] S. J. Tauster, *Acc. Chem. Res.* **20**, 389 (1987).
- [4] V. E. Henrich and P. A. Cox, *The Surface Science of Metal Oxides*, (Cambridge University Press, Cambridge, England, 1994).
- [5] J. Goniakowski and C. Noguera, *Surf. Sci.* **323**, 129 (1995).
- [6] D. L. Blanchard, D. L. Lessor, J. P. LaFemina, D. R. Baer, W. K. Ford, and T. Guo, *J. Vac. Sci. Technol. A* **9**, 1814 (1991).
- [7] D. Ferry, J. Suzanne, V. Panella, J. P. Biberian, A. Barbieri, and M. A. Van Hove, *J. Vac. Sci. Technol.* (to be published).
- [8] J. B. Zhou, H. C. Lu, T. Gustafsson, and P. Häberle, *Surf. Sci.* **302**, 350 (1994).
- [9] M. Sidoumou, V. Panella, and J. Suzanne, *J. Chem. Phys.* **101**, 6338 (1994).
- [10] S. Russo and C. Noguera, *Surf. Sci.* **262**, 245 (1992).
- [11] D. Ferry, J. Suzanne, P. N. M. Hoang, and C. Girardet, *Surf. Sci.* **375**, 315 (1997).
- [12] J. P. Coulomb, Y. Lahrer, M. Trabelsi, and I. Mirebeau, *Mol. Phys.* **81**, 1259 (1994).
- [13] D. Ferry, P. N. M. Hoang, J. Suzanne, J.-P. Bibérian, and M. A. Van Hove (to be published).
- [14] P. N. M. Hoang, C. Girardet, M. Sidoumou, and J. Suzanne, *Phys. Rev. B* **48**, 12 183 (1993).
- [15] M. A. Van Hove, W. Moritz, H. Over, P. J. Rous, A. Wander, A. Barbieri, N. Materer, U. Starke, and G. A. Somorjai, *Surf. Sci. Rep.* **19**, 191 (1993).
- [16] J. B. Pendry, *J. Phys.* **43**, 937 (1980).
- [17] H. K. Koski and E. Sandor, *Acta Crystallogr., Sect. B* **31**, 350 (1975).
- [18] S. K. Dunn and G. E. Ewing, *J. Phys. Chem.* **96**, 5248 (1992).
- [19] A. Allouche, *Surf. Sci.* (to be published).