

Structural study of C₂D₆ thin films adsorbed on MgO (100)

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The structure of C₂D₆ thin films adsorbed on high homogeneous MgO (100) powder surface have been investigated by means of neutron diffraction techniques at 10 K. Neutron diffraction spectra have been recorded for three different coverages. Two bi-dimensional solids S₁ and S₂ have been determined, respectively for a coverage $\theta = 0.7$ layer and $\theta = 1.2$ layer. In agreement with LEED measurement, the S₂ phase presents the commensurability $C(\sqrt{2} \times \sqrt{2})R45^\circ$ with the MgO (100) surface. The S₁ phase also presents a commensurate structure with the substrate lattice but its commensurability is weaker than that of S₂. The (2D) solid phase, measured at an intermediate coverage $\theta = 1.0$ layer is a mixture of S₁ and S₂. For both solid phases, unit cell, location and orientation of molecules within are determined. The commensurate cell of the S₁ solid with the MgO (100) surface is given.

Keywords: Neutron diffraction spectra, Bi-dimensional phase, Commensurate structure

1 Introduction

The study of structural and dynamic properties of thin films of ethane (C₂D₆) adsorbed on graphite has been the subject of numerous research works¹⁻⁵. At the monolayer coverage region, three condensed phases S₁, S₂ and S₃ have been identified and their structures have been determined. The structure of the intermediate phase S₂ has been the most difficult to establish.

Paradoxically, the study of the structure of the ethane monolayer film adsorbed on MgO (100) surface presents the same difficulties. The structure of the C₂D₆ adsorbed phases on MgO has been studied in order to complete a previous thermodynamic study⁶ where thermodynamic characterisations of the first and the second layers of ethane adsorbed on MgO are presented. A preliminary interpretation of a set of neutron diffraction spectra measured at 10 K for three different coverages has been given⁷.

Independently, LEED measurement has been performed to determine the structure of the ethane monolayer film adsorbed on MgO monocrystal⁸. To interpret the diffraction patterns of the low coverage over layer, Sidoumou *et al.*⁸ have taken into account the neutron diffraction spectrum reported⁷ and measured at 10 K for 0.7 layer of ethane adsorbed on MgO. What seems absurd and incomprehensible is the fact that they have not seen the peak located at

1.67 Å⁻¹. Obviously conclusions based on incomplete data can only be erroneous. Both the experimental and calculation findings related to the S₁ structure⁸ are not considered reliable. Their results for the S₂ structure and the coexistence of two phases S₁ and S₂ are found to be interesting.

The last attempt to establish the structure of monolayer films of ethane adsorbed on MgO is that of Arnold *et al.*⁹. In addition to the thermodynamic investigation of the three stabilized layers of ethane on MgO, a neutron diffraction spectrum measured at 4.2 K for a coverage corresponding approximately to one complete layer is represented⁹. But no conclusion is advanced on the structure and this seems especially evident since the phase they probed is a mixture of two phases.

With the aim to establish the structures of the two ethane monolayer phases (unit cell, position and orientation of the molecules within) the neutron diffraction patterns are re-examined and reported⁷.

2 Experimental Details

The neutron diffraction experiments were performed with a two-axis spectrometer G6-1, equipped with a multi-detector and cryostate allowing temperature variation from 2 to 300 K, located at Léon Brillouin Laboratory, Saclay, France. The multi-detector subtended a scattering angle 2θ of 80° and

the incident neutron wavelength is $\lambda = 4.725 \text{ \AA}$. The sample consisted of MgO powders, prepared by burning Mg ribbons in a controlled atmosphere as described¹⁰. Such powders are essentially formed of micro-cubes delimited by the (100) faces. An isotherm of CH₄ measured at 77 K is used firstly as a probe of the homogeneity of our substrate and secondly to calibrate our sample. The completion of the monolayer was taken to be the inflexion point of the isotherm plateau ($Q_{ads} = 19.3 \text{ cm}^3 \text{ STP}$ for the used sample). In Figs 1-3, the measured difference spectra (with and without adsorbate) are represented by crosses (x) and the solid curves represent the profile of the calculated relevant crystallographic structure factors. Such structure factors are calculated explicitly from the nuclear position of each atom in the unit cell. The thermal motion of the nuclei around their equilibrium position is assumed to be small enough at 10 K and is accounted for by a Debye-Waller factor $\exp(-Q^2 \langle u^2 \rangle)$ where the mean square displacement $\langle u^2 \rangle = 0.01 \text{ \AA}^2$ is taken to be the same for all nuclei.

The overlap of Bragg peaks results from the asymmetric Roland and Tompa line shape of the peaks, the dimension of the two dimensional (2D) crystallites $L = 300 \text{ \AA}$ and the finite Q resolution of the spectrometer.

3 Neutron Diffraction as Technique of Thin Films Structure Study

Neutron diffraction scattering and low energy electron diffraction (LEED) can be considered as two complementary techniques used in structural study of physisorbed films, while LEED experiments give the (2D) unit cell and the epitaxial relation of the adsorbed films structures with the surface substrate. The neutrons whose interaction with matter is so weak that it do not perturb the adsorbed film, allow investigation of positional and orientational order of adsorbed molecules in the unit cell.

By measuring the neutron diffraction spectrum and the difference spectrum (with and without adsorbate), one can deduce:

- (1) The position and orientation of molecules in the unit cell by peaks intensities comparison,
- (2) The range order along each peak direction from the full width at middle height of the peak (FWMH).
- (3) The parameters (a, b, γ) of the (2D) unit cell from scattering vectors position, which mean that the

accuracy of the unit cell parameters depends on the peaks number.

Generally, more than one cell indexed the observed peaks and there the information given by LEED experiments is of major interest to determine the unit cell. Other data like molecular size or the area occupied by an adsorbed molecule in the monolayer film and deduced from measured isotherms are also important.

4 Results and Discussion

The structures of the C₂D₆ thin films condensed on the MgO (100) surface have been investigated by means of neutron diffraction experiments. The spectra measured at $T = 10 \text{ K}$ and for $\theta = 0.7$ layer, 1.0 layer and 1.2 layer are showed in Fig. 1, respectively. The positions of the observed peaks do not vary considerably from one coverage to the other giving then the impression that the condensed phases have the same structure with a simply evolution in the molecules orientation as the coverage increases. Such interpretation has been abandoned after the publication of the LEED experiments⁸ since the observed structure, presenting the commensurability $C(\sqrt{2} \times 2\sqrt{2})R45^\circ$ with the MgO (100) surface, cannot index the peaks observed on the lower coverage spectrum, namely $Q_{11} = 1.43 \text{ \AA}^{-1}$. To determine the structure of the low density condensed

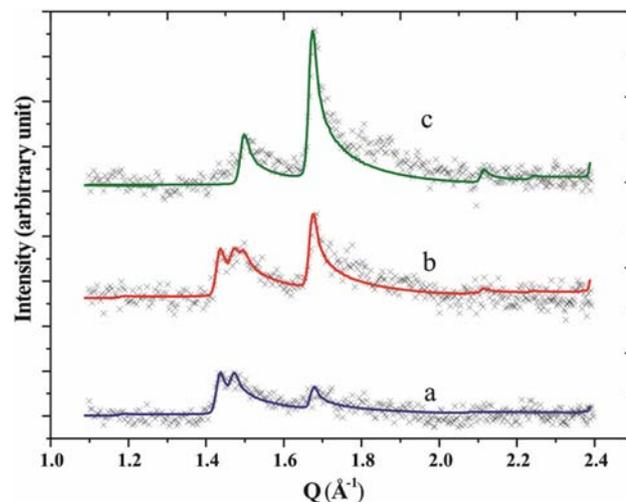


Fig. 1 — Neutron diffraction spectra of C₂D₆ adsorbed on MgO (100) surface at $T = 10 \text{ K}$, (a) 0.7 layer, (b) 1.0 layer and (c) 1.2 layer. Crosses correspond to experimental data while full lines represent the computed diffraction profiles calculated with parameters given in Table 1. The spectrum measured at the intermediate coverage is a mixture of the two others

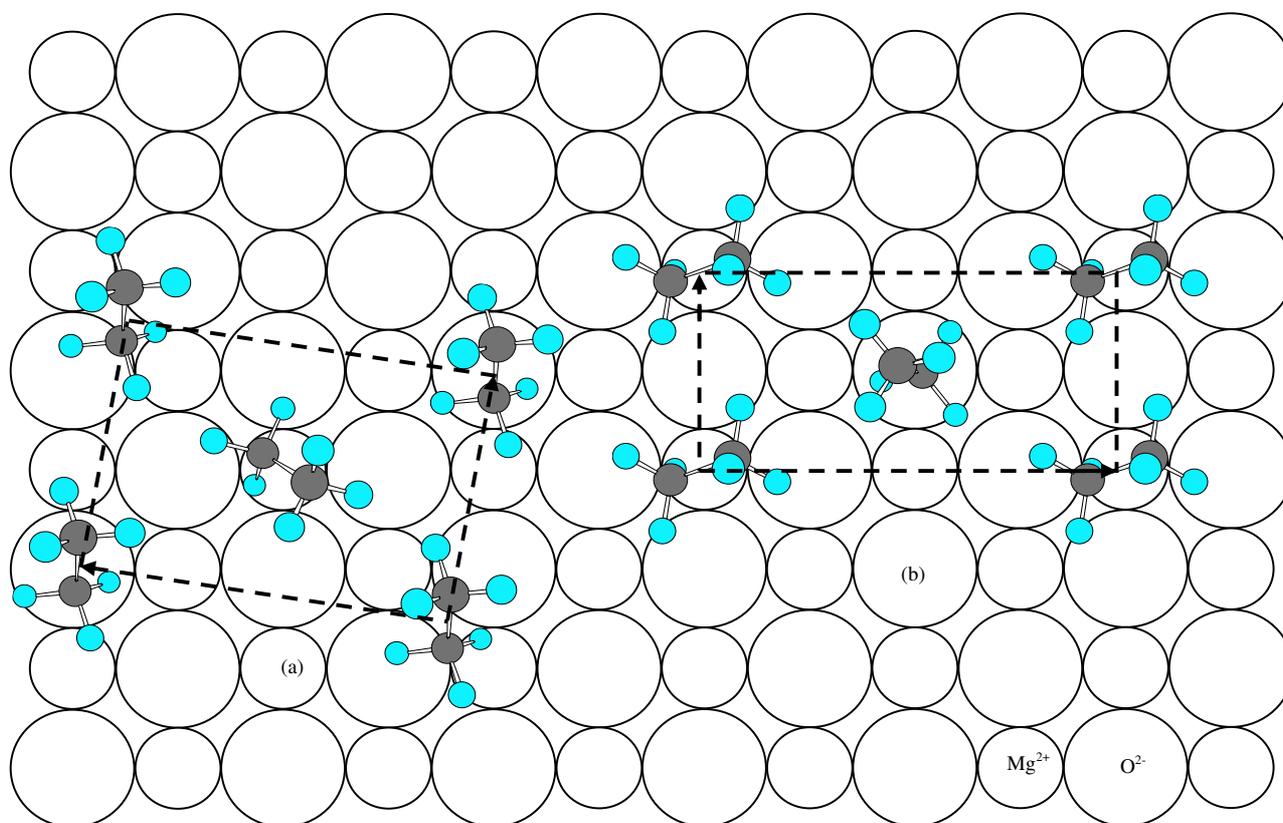


Fig. 2 — Schematic representation of the unit cell: (a) solid (S_1) measured at $\theta=0.7$ layer and (b) solid (S_2) corresponding to $\theta=1.2$ layer. The open circles correspond to the MgO (100) surface

phase, S_1 , the unit cells allowing the indexation of the three observed peaks are considered.

An additional criterion used here to choose the unit cell is the area $\sigma_{C_2H_6} = 19.9 \text{ \AA}^2$ occupied by a single molecule of C_2H_6 adsorbed in the monolayer film on MgO, deduced from adsorption isotherms of C_2D_6 and CH_4 measured separately on the same sample⁶ of MgO at comparable reduced temperature

$$\frac{T_c}{T_c(3D)} \approx 0.37, \text{ where } T_c(3D) \text{ is the bulk critical}$$

temperature. The unit cell giving the best fit of the measured spectrum is a quasi-rectangular centered one containing two molecules with different orientations [Fig. 2(a)].

Figure 3 shows the ethane adsorbed quantity⁶ variation along the plateau is larger than that of the methane isotherm. At the upper region of the plateau, corresponding approximately to $\theta = 1.2$ layer, the density of the C_2H_6 adsorbed phase is comparable to that of CH_4 at the monolayer completion. Knowing that the CH_4 crystallize in a $C(2 \times 2)$ structure¹¹, the

area occupied by a molecule of C_2H_6 in the solid phase S_2 should be similar to that of CH_4 , namely 17.72 \AA^2 . Effectively, the neutron diffraction spectrum measured at $\theta = 1.2$ layer is close to that calculated by considering a $C(\sqrt{2} \times 2\sqrt{2})R45^\circ$ unit cell containing two molecules. A representation of this unit cell is given in Fig. 2(b).

For both condensed phases S_1 and S_2 , the structural parameters (a , b , γ) of the unit cell are given in Table 1. The molecules position and orientation in the unit cell are also indicated. The structures of the S_1 and S_2 condensed phases correspond to a packing and an area per molecule close to that of a (101) and (011) planes of bulk ethane, respectively. The (2D) condensed phase with intermediate density is considered as a mixture of S_1 and S_2 and the neutron diffraction spectrum measured at 1.0 layer is well fitted by considering $0.57S_1 + 0.43S_2$.

The spectrum published⁹ is probably measured at coverage slightly different from that we denote 1.0 layer in the present paper. The principal peaks

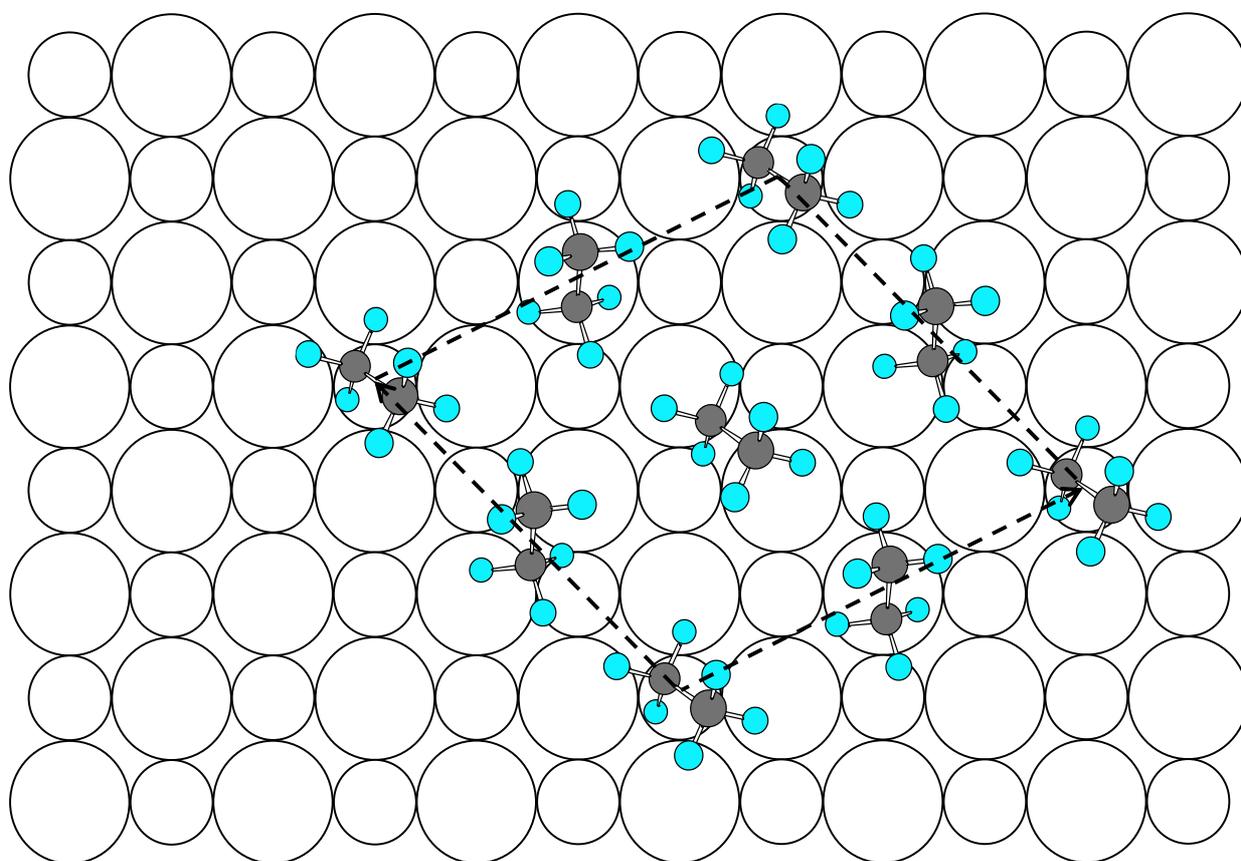


Fig. 3 — Schematic representation of the commensurate cell ($a=9.42\text{\AA}$, $b=8.94\text{\AA}$, $\gamma=108.43^\circ$) proposed for the (S_1) solid

Table 1 — Structural parameters of the unit cell, positions and orientations of the molecules. θ and φ are respectively the polar and azimuthal angles. ψ describes the rotation of the C₂H₆ molecule around the C—C axis

(2D) solid	Coverage (layer)	Unit cell parameters			Molecules position			Molecules orientation		
		$a(\text{\AA})$	$b(\text{\AA})$	$\gamma(^{\circ})$	$x(\text{\AA})$	$y(\text{\AA})$	$z(\text{\AA})$	$\theta(^{\circ})$	$\varphi(^{\circ})$	$\psi(^{\circ})$
S_1	0.7	5.31	7.513	91.58	0	0	0	47	66.58	80
					2.655	3.755	0	47	6.58	80
S_2	1.2	8.42	4.21	90	0	0	0	60	20	10
					4.21	2.105	0	-20	-20	85

$Q_{11}=1.43 \text{ \AA}^{-1}$, $Q_{1-1}=1.47 \text{ \AA}^{-1}$ and $Q_{20}=1.67 \text{ \AA}^{-1}$ are identical to what we have recorded at that coverage. The additional peaks $Q_{21}=2.11 \text{ \AA}^{-1}$ and $Q_{30}=2.24 \text{ \AA}^{-1}$ observed in the spectrum of Arnold *et al.*⁹ can be indexed by the S_2 solid unit cell. These latter peaks are not distinguishable in our difference spectrum due to the apparatus resolution' which is quite different from that of the spectrometer they used.

In the two different condensed phases, S_1 and S_2 , the molecules orientation seems to be governed by the quadrupole-quadrupole interaction as in the (3D) bulk solid.

By reproducing the (2D) unit cell on the MgO (100) surface, it is noted that the structure of the lower density (2D) condensed phase (S_1) is commensurate with the substrate lattice. The proposed commensurate cell with parameters are (9.42\AA ; 8.94\AA ; 108.43°), contains four molecules. The commensurability of such structure with the MgO (100) surface lattice is given in the matricial representation as

$$\begin{pmatrix} a \\ b \end{pmatrix} = \begin{pmatrix} 3 & -1 \\ 0 & 3 \end{pmatrix} \begin{pmatrix} a_s \\ b_s \end{pmatrix}$$
 where $a_s = b_s = 2.98 \text{ \AA}$ are the dimension of the MgO (100) surface square unit cell

(Fig. 3). A supplementary indication of such commensurability comes from the stability of the (2D) adsorbed phase in a relatively wide range of temperature⁷ $10\text{ K} < T < 58\text{ K}$ (not represented here).

The structure of C_2D_6 thin films condensed on MgO has been investigated by means of neutron diffraction technique at 10 K. From the neutron diffraction spectra measured at three different coverage, it has been inferred that the two dimension solid phases observed on both sides of the monolayer completion have a commensurate structure with MgO (100). Such structures are auto determined since they compare well with (101) and (011) planes of bulk ethane.

On the other hand, the molecules orientations seem to be governed by the quadrupole-quadrupole interaction. Despite the small value of the C_2H_6 quadrupole moment, -0.65 esu , the relevant interaction persists in the (2D) films. The spectrum recorded at an intermediate coverage ($\theta = 1.0$ layer) of ethane adsorbed on MgO (100) surface is well reproduced by considering a mixture of the two other condensed phases. Such situation has been encountered when studying the C_2D_2 -graphite system^{6,7}.

A further indication of the commensurability of the ethane thin films adsorbed on MgO comes from the stability of the solid phase⁶ (2D) in a wide temperature range $T \leq 55\text{ K}$. This value is in good agreement with that given in Ref. 12. The heat of adsorption $Q_{\text{ads}}(1) = 4.70\text{ kcal/mol}$ is close to that given by Arnold *et al*¹². $Q_{\text{ads}}(1) = 4.3\text{ kcal/mol}$.

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