

Cr₈O₄(O₂CPh)₁₆ Magnetic Molecules at Air-Water Interfaces

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Introduction

Magnetic molecules with intramolecular magnetic exchange interactions that are strong relative to intermolecular ones are of interest because of both their unique fundamental magnetic properties and their potential technological applications [1]. Typically organometallic based, these “molecular magnets” consist of two or more 3d or 4f magnetic ions coupled by electronic superexchange interactions, and they can be more than 10 nm in size. The controllable size and geometries of the magnetic ions are of fundamental importance to testing our understanding of magnetic interactions and have already led to the discovery of the quantum tunneling effect of magnetic spins [2].

Herein we present our structural study of a 2-D Langmuir film formed by the magnetic molecule Cr₈O₄(O₂CPh)₁₆ [3]. The antiferromagnetic Cr₈O₄ cubane core is similar to the compound described by Atkinson et al. [3] containing two coupling constants *J*. This molecule is readily soluble in CHCl₃ and possesses a hydrophobic outer shell composed of 16 phenyl rings, making it a potential monolayer former when spread on water surfaces. Such monolayers can be subsequently transferred to solid surfaces by employing the Langmuir-Blodgett (LB) technique to form well-defined multilayer systems. Control of their arrangement on solid surfaces is an important step leading to potential applications of these molecular magnets in electronic or magnetic devices.

Materials and Methods

The Cr₈O₄(O₂CPh)₁₆ compound was prepared according to the method described in the literature [3, 4]. Langmuir monolayers were prepared on pure water (Milli-Q apparatus, Millipore Corp., Bedford, MA; resistivity, 18.2 M Ωcm) in a temperature-controlled Teflon® trough maintained at 18-20°C in a gas-tight aluminum container. Surface pressure was measured with a microbalance by using a filter-paper Wilhelmy plate. To reduce incoherent scattering from air and to slow down film deterioration caused by oxidation resulting from the production of radicals by the intense synchrotron beam, the monolayer was kept under a He environment during the x-ray measurements.

In situ grazing incidence x-ray diffraction (GIXD) experiments were carried out on the newly built liquid surface diffractometer on the 6-ID-B beamline at the APS. A downstream Si double-crystal monochromator selects the x-ray beam at the desired energy ($\lambda = 1.5498 \text{ \AA}$). The

highly monochromatic beam is deflected onto the liquid surface to the desired angle of incidence with a Ge(111) crystal. During the GIXD experiments, the angle of the incident beam with respect to the surface is fixed below the critical angle for total reflection.

Results

During the GIXD experiments, the angle of the incident beam with respect to the surface is fixed below the critical angle for total reflection. Figure 1 shows diffraction patterns from the monolayer at various points along the isotherm. At finite pressures, GIXD scans in the range of $0.05 \text{ \AA}^{-1} \leq Q \leq 2.0 \text{ \AA}^{-1}$ revealed a prominent peak centered at $Q_{xy} \approx 0.428\text{-}0.465 \text{ \AA}^{-1}$, with a full width at half maximum (FWHM) that is much broader than the resolution of the diffractometer ($\sim 0.01 \text{ \AA}^{-1}$) characteristic

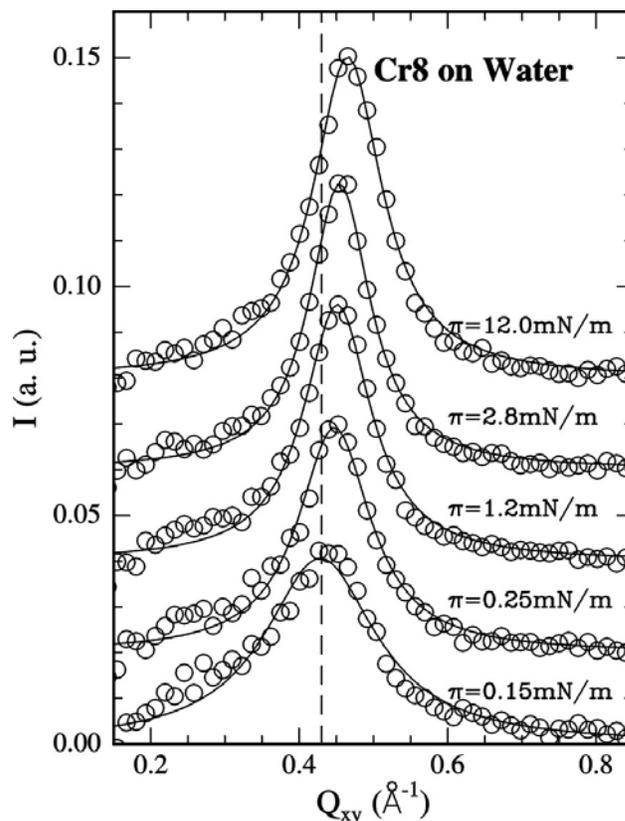


FIG. 1. In-plane diffraction at grazing angles of incidence from a Cr8 monolayer at the air-water interface.

of short-range order (SRO). For a molecular area $A_{iso} = 265 \text{ \AA}^2$ (extracted from the isotherm), the peak position center at $Q_{xy}^0 \approx 0.428 \text{ \AA}^{-1}$ corresponds to a d-spacing $2\pi/Q_{xy}^0 \approx 14.9 \text{ \AA}$, which is slightly smaller than the estimated molecular diameter. The observation of a single Bragg peak in the diffraction pattern suggests that SRO is either of hexagonal or square symmetry. The assumption of hexagonal or square SRO corresponds to an average nearest-neighbor (NN) distance $a_{Hex} = 17.2 \text{ \AA}$ or $a_{Square} = 14.9 \text{ \AA}$. The diameter of the molecule that determines NN distance is governed by the largest edge-to-edge distance between phenyl groups $R \approx 17\text{-}18$ and therefore indicates that the 2-D system is compressible and liquidlike to at least 5 mN/m .

Rod scans along the surface normal at the 2-D Bragg reflection were conducted to determine the form factor of the diffracting objects and to provide another measure for film thickness. Two such rod scans at $\pi = 4.2$ and 8 mN/m are shown in Fig. 2 (similar rod scans were observed at higher surface pressures). Quantitatively, the intensity along the rod of the 2-D Bragg reflection can be analyzed in the framework of the distorted wave Born approximation (DWBA) by using $I \propto |t(k_{z,i})|^2 |F(Q_z)|^2$, where $t(k_{z,i})$ is the Fresnel transmission function [5, 6], which gives rise to the enhancement around the critical angle, as seen in Fig. 2. Here, it is assumed that the molecule can be approximated by a homogeneous sphere of radius R with a structure factor as follows:

$$F(Q_z) = [\sin(Q_z R) - Q_z R \cos(Q_z R)] / (Q_z R)^3 \quad (1)$$

The solid lines in Fig. 2 represent the best fit to the data, yielding an R of 6.2 ± 0.5 at 4.2 mN/m and 6.7 ± 0.5 at 8 mN/m . The value for R that is extracted from the rod scan represents an average effective radius of the electron density of a Cr8 molecule. At low pressures, this thickness, together with the reflectivity, shows that the film consists of a single layer. However, at surface pressures higher than $\sim 5 \text{ mN/m}$, the average film thickness extracted from the reflectivity is approximately twice that extracted from the rods. Whereas the reflectivity indicates the formation of a second layer, the rod scan analysis shows that the second layer does not contribute to the Bragg reflection observed. This finding suggests that the second layer is extremely disordered, lacking even SRO, as a result of the fact that the second layer is incomplete.

Discussion

The π -A isotherm, x-ray reflectivity, and GIXD variations (width and peak position and rod scan) with compression all imply the formation of a monolayer at the air-water interface at surface pressures that are smaller than $3\text{-}5 \text{ mN/m}$. The monolayer is disordered with a liquidlike structure factor and correlation lengths that extend over a few molecular distances. The electron density profile extracted from the reflectivity suggests that

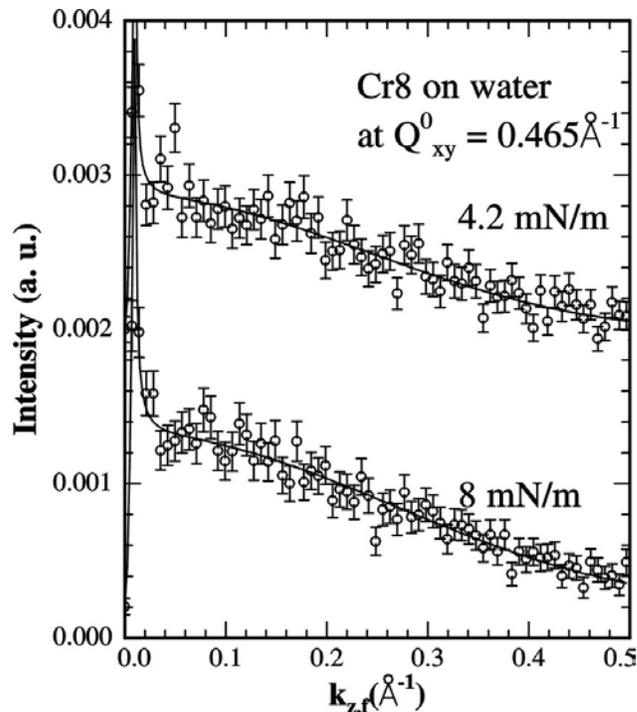


FIG. 2. Rod scans along the surface normal at the position of the 2-D peak shown in Fig. 1.

the film is highly hydrated. As the pressure increases above $\sim 5 \text{ mN/m}$, the film becomes incompressible, and a second but inhomogeneous layer is formed on the first one. This second layer does not contribute to the 2-D Bragg reflection observed from the monolayer, implying that it is highly disordered and lacking SRO.

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