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Two-layer film of $Fe(CO)_5$ adsorbed on a (0001) graphite plane: Mössbauer studies

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A comparison between bulk and films of $Fe(CO)_5$ adsorbed on graphite shows that dynamical anomalies which occur at ~110, ~155, and ~180 K have in both forms similar effects on the Mössbauer parameters. The origin of these transitions is briefly discussed. In the 2.3-layer film, anomalous clustering of the film results in coexistence of solid bulk and a compressed monolayer; consequently, the film displays a novel behavior of the Mössbauer quadrupole splitting.

The wetting of a substrate by a liquid or a solid has recently become a topic of increasing attention.[1] Of particular interest is the way in which a film approaches the bulk three-dimensional (3D) state in the process of layer-by-layer growth. In this context a complete wetting is a layer-by-layer condensation on the substrate up to coexistence with bulk. Incomplete wetting corresponds to a formation of a *limited* number of adsorbed layers up to bulk coexistence. Actually, little is known on the multilayer growth, structure, and dynamical behavior of adsorbed layers of nonspherical molecules on graphite. Such films exhibit structural phase transitions which do not occur in adsorbed layers of spherical molecules.[2,3]

A recent study has been published on the structure and phase transitions of $Fe(CO)_5$ (iron pentacarbonyl or IPC) submonolayers adsorbed on (0001) graphite plane.[4] The study presents a model for the monolayer structure and transitions at low temperatures inferred from neutron-diffraction and Mössbauer experiments. As in other similar cases there are reasons to believe that it may be interesting to follow the behavior of these nonspherical IPC molecules in films thicker than one monolayer.

In the present paper we report results from Mössbauer experiments on anomalies of dynamical origin observed in a 2.3 layer film of IPC adsorbed on graphite. The results are compared with those obtained from bulk and thinner films. The motivation for using IPC as a Mössbauer probe for layering film of increasing thickness stems from a recent x-ray study that shows IPC films on graphite basal plane to be an extreme example of incomplete wetting, in which a single solid monolayer coexists with bulk particles.[5] In these films *anomalous layering* has been observed which is believed to be associated with particularly interesting dynamical behavior of adsorbed molecules. We use Mössbauer spectroscopy which has been proven to be a sensitive tool for observation of changes in translational and rotational motions of the adsorbed molecules in the neighborhood of phase transitions.[6,7]

The IPC is liquid at room temperature with melting temperature $T_m = 252$ K. A bulk sample was cooled slowly below melting and Mössbauer study has been carried out at various temperatures. For $Fe(CO)_5$ as adsorbate, a stack of 40 Grafoil squares, $20 \times 20 \times 0.25$ mm^3 each, served as a substrate.[8] This arrangement enabled two configurations of Mössbauer measurements; one with the direction of the γ propagation vector parallel to the common plane of the Grafoil sheets, and the other perpendicular to it.[6] Calculations based on the directional distribution of graphite crystallites in Grafoil show that for not too high diffusion rates ($\sim 10^{-7}$ cm^2/s) these two directions of measurement are easily distinguishable.[9] The Grafoil stack was first cleaned by heating in vacuum for 5 h at 950 °C and then transferred under helium gas atmosphere to the Mössbauer transmission cell. The effective adsorption area of the stack was then determined by measuring the nitrogen vapor pressure isotherm. The film samples were prepared by introduction of IPC vapor into the cell following room-temperature adsorption vapor pressure isotherm to the desired coverage. The details on this procedure are described elsewhere.[6] Unity coverage was defined to be a complete monolayer having the $\sqrt{7} \times \sqrt{21}$ structure described in Ref. 4. The appropriate temperature of the Mössbauer cell was achieved by liquid-nitrogen-controlled flow around the sample holder. In this Brief Report we restrict ourselves to a film 2.3-layer thick which is a representative example for all IPC films thicker than one monolayer. Due to a high freezing temperature and low vapor pressure at room temperature it is difficult to control the adsorption of IPC films thicker than three monolayers. A constant acceleration spectrometer and a 20-mCi Rh:^{57}Co gamma source were used for all measurements. The geometry limited the counting rate at 600 counts/min at each velocity channel. At each channel $\sim 2 \times 10^6$ counts were accumulated for reasonably reliable data analysis. Four Lorentzians were allowed to fit each of the spectrum. No *a priori* restrictions were imposed on linewidths, energies, or intensities of these Lorentzians. For bulk and low surface coverages the fit produced two Lorentzians; but for coverages thicker than a two-monolayer film, two pairs of Lorentzians were required for a best fit to the observed spectrum: one of the two pairs resulted in spectral parameters (quadrupole splitting and line positions) identical to those of bulk.[10]

One of our principal results derived from the Lorentzian fits involves the spectral intensity of the resonance dips. For thin samples, these intensities are proportional to the resonance cross section. This condition holds for all of the bulk and adsorbed film samples we have studied. Applying standard techniques for subtraction of nonresonant background radiation we obtained the results shown in Fig. 1(b). In this figure the Mössbauer spectral intensity is shown as a function of temperature for a bulk sample

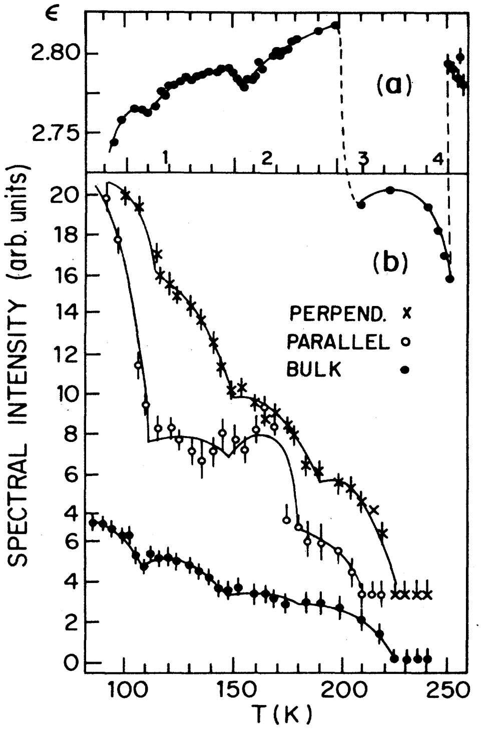

FIG. 1. (a) The dielectric constant $\epsilon(T)$ of bulk $Fe(CO)_5$ (from Ref. 21). (b) The temperature variation of the Mössbauer spectral intensity of 2.3-layer film in the perpendicular and parallel configurations and for bulk.

and for the 2.3-layer film adsorbed on graphite, recorded perpendicular and parallel to the sample plane. The temperature dependence of the intensity in the parallel configuration is exceptionally anomalous, particularly at $T_1 \simeq 110$ K, $T_2 \simeq 155$ K, and $T_3 \simeq 180$ K. It is interesting to elucidate that the temperature variation of the spectral intensity for the 2.3-layer film qualitatively displays similar anomalies as seen in bulk solids and films thicker than one monolayer, and similar to anomalies also observed in submonolayer films below their two-dimensional melting temperature.[4] The origin of these anomalies will be discussed below.

The other interesting experimental result is the temperature dependence of the quadrupole splitting (QS) presented in Fig. 2(b) for the 2.3-layer film and for the bulk IPC. Even though anomalies in QS and Mössbauer spectral intensity for the different samples appear at similar temperatures, the temperature *variation* of the QS for the 2.3-layer film is markedly different from that observed in thinner adsorbed IPC films and in bulk. In the analysis of submonolayer Mössbauer spectra, only one quadrupole split doublet could be resolved and the temperature dependence of it QS is rather regular [see Fig. 2(a)]. For more than one monolayer and below two-layer films the Mössbauer lines narrow when a transition is approached, but the resolution is not sufficient and in practice only one doublet can be fitted at each temperature to the spectrum. In the analysis of the 2.3-layer film, however, a distinction between two doublets could be made, clearly indicating two nonequivalent sites [lines α and β in Fig. 2(b)].

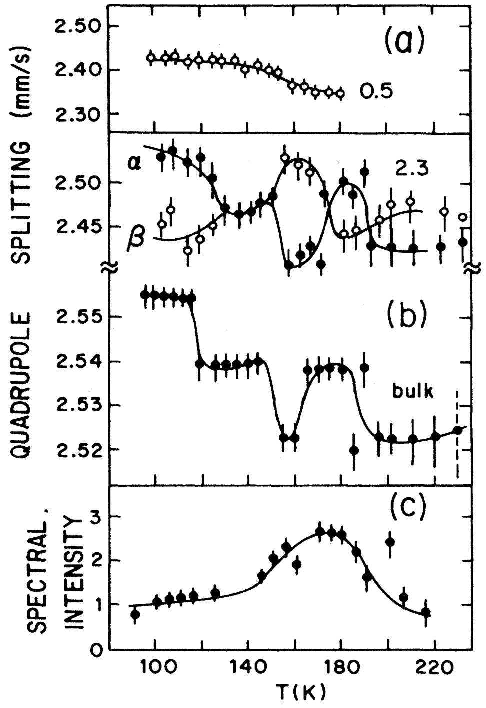

FIG. 2. (a) The Mössbauer quadrupole splitting in $Fe(CO)_5$ molecules adsorbed as 0.5-layer films on the graphite basal plane. (b) The quadrupole splitting for the 2.3-layer film (upper panel) and for bulk. For the 2.3 film one of the two pairs of spectra was assigned to bulk (α line) and the other to the adsorbed layer (β line). (c) Temperature variation of the Mössbauer spectral intensity of the quadrupole splitted doublet assigned for bulk.

The electric field gradient at the iron nucleus (which results in the QS observed in the Mössbauer spectrum) is mostly independent on the environment of the molecule[11,12] except for effects such as charge fluctuations[13,14] and possible *static* configurational distortions:[15] IPC is a nonrigid molecule which displays a QS susceptible to molecular deformation.[10] At liquid-nitrogen temperature the QS in bulk is 2.57 mm/s,[11] and is usually believed to be temperature independent. Static distortions of the IPC molecules, however, result in slight reduction in the QS to 2.51 mm/s.[15]

For IPC molecules adsorbed on (0001) graphite basal plane the QS is slightly smaller than that expected in bulk molecules.[15] Consequently, we assigned the pair of Lorentzians with the larger splitting to the bulk component in the 2.3 film spectrum and the other pair represents the molecules in the adsorbed monolayer film. The solid lines α and β through the experimental points in Fig. 2(b) illustrate the results of this model. The temperature dependence of QS for one of the doublets [line α in Fig. 2(b)] follows pretty well the QS temperature variation for the bulk sample [lower panel in Fig. 2(b)]. Comparison of this novel variation of the QS for the 2.3-layer film with that of the bulk sample suggests that one of the two doublets can possibly represent the bulk particles which we have found to coexist with a compressed monolayer film of IPC molecules adsorbed on the graphite basal plane. This assignment is also further justified by the temperature dependence of the spectral intensity of the doublet assigned to the bulk [Fig. 2(c)]: Since the intensity is proportional to the number of molecules in the phase represented by a particular Mössbauer spectrum, its temperature dependence shows that the amount of bulk *solid* increases as the temperature is raised. These experimental results suggest that when transition temperature $T_3 \simeq 180$ K is approached the relative amount of bulk in the film increases at the expense of the adsorbed layer film. Toward 200 K this *solid* bulk component disappears. This behavior is rather abnormal when compared with classical substances such as ethylene on graphite:[16] Ethylene is in the state of incomplete wetting at low temperatures and one observes a monotonic *decrease* in the amount of coexisting bulk component with increasing temperature.

Our Mössbauer results are in full agreement with recent low-temperature synchrotron x-ray diffraction measurements[5] which show qualitatively that in IPC films on graphite of thickness larger than one monolayer there is a mixture of bulk and *compressed* monolayer film. At $T < 173$ K, the IPC forms a polycrystalline monolayer on the graphite basal plane; from x-ray results it is inferred that the monolayer has been compressed into an incommensurate phase. The density of this phase is $\sim 15\%$ larger than that of the commensurate phase.[5] At 175 K this phase melts and becomes a fluid monolayer. Part of the 2.3-layer film forms bulk. At 175 K, the x-ray results show that the amount of bulk increases in expense of the monolayer. The bulk is now in the form of isotropic particles of monoclinic IPC. At $190 \text{ K} < T < 230$ K the bulk transforms into a fluid. Consistent with these results, the distinction between two doublets in the Mössbauer spectra from the 2.3-layer film clearly indicates the existence of two nonequivalent sites. Comparison of the novel variation of the QS for the 2.3-layer film with that displayed by a bulk solid suggests that one of the two doublets can possibly be associated with the bulk sites in the film;[17] the other doublet displays the spectrum of molecules adsorbed on graphite.

We now focus on the origin of other anomalies superimposed on the temperature dependence of the spectral intensity and QS. The following discussion is based on many known molecular and intramolecular properties of the IPC, such as its configuration,[18] vibrational modes,[19] and induced electric dipole moment.[20] The temperature dependence of the dielectric constant $\epsilon(T)$ in solid bulk of IPC (Ref. 21) between 90 and 260 K displays several anomalies [Fig. 1(a)]. The IPC molecule has no *static* dielectric constant: $\epsilon(T)$ is associated with the induced electric dipole moment due to intramolecular configurational fluctuations.[19,20] It is then reasonable to associate the anomalies observed in $\epsilon(T)$ to molecular dynamics.

The first anomaly is observed at $T_1 \simeq 110$ K. This anomaly is discussed in a separate report;[7] evidence on intramolecular exchange among CO groups[22] at T_1 may result in this first anomaly in $\epsilon(T)$. The dynamical nature of this anomaly results in irregular "V-shape" temperature dependence of the Mössbauer spectral intensity[23] followed by a drop in the QS (Figs. 1 and 2).

The second anomaly in $\epsilon(T)$ is observed at $T_2 \simeq 155$ K. Mössbauer spectral intensity displays an anomaly in this temperature range in bulk and adsorbed films (s): This anomaly is observed in both perpendicular and parallel configurations [Fig. 1(b)]. The QS drops sharply, and recovers at higher temperatures. At T_2 the monolayer films experience an orientational disordering transition.[4]

$T_3 \simeq 170$–180 K is the melting point of the two-dimensional films of IPC on graphite.[4] The 2.3-layer film, however, displays an anomalous *delayering* at this temperature,[5] and an anomaly in $\epsilon(T)$ is observed.

$T_m \simeq 252$ K is the melting point of *bulk* IPC. At T_m no Mössbauer signal could be observed due to diffusional motions; the system responds with strong changes in $\epsilon(T)$.

The novel behavior of the quadrupole splitting at T_1 through T_3 [Fig. 2(b)] is a response to intramolecular configurational dynamical changes. These configurational changes may be precursors to the observed transitions at T_i. As noted in previously reported cases, intramolecular structural changes associated with the rotation of NH_3 in $Fe(NH_3)_6Cl_2$, and the glass transition in a $FeCl_2$ frozen water solution[24] were shown to be associated with the release of rotational modes in the molecule. In this respect is should be interesting to study the detailed temperature variation of the intramolecular fundamental modes in $Fe(CO)_5$. This can make it possible to determine whether the observed anomalies actually originate in intramolecular motions.

As a consequence of the suggested interpretation of the experimental data it seems that the intramolecular dynamical changes found in adsorbed IPC molecules result in extremely small stable deformations compared to $Fe(CO)_5$ molecules in the liquid state, and that the constituents of the system (substrate-monolayer-bulk) are dynamically coupled in some way.

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