Intramolecular Rotational Phase-Transition in Bulk and Adsorbed $Fe(CO)_5$ on (0001) Graphite *

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Mössbauer spectroscopy results on bulk iron pentacarbonyl $Fe(CO)_5$ and as adsorbate on (0001) graphite display a sharp transition at ~ 110 K related to intramolecular hindered rotations of CO-ligands, with no associated structural changes. The hysteresis in the temperature dependence of the quadrupole splitting and the abrupt change in the spectral intensity suggest a cooperative first-order phase transition.

1. Introduction

Intramolecular rearrangements and motion of large molecular groups, like CH_3 and NH_3 in solids play an important role in determining their macroscopic properties and have been the subject of numerous investigations. Phase transitions accompanied by anomalies in intramolecular motions are common to a large number of materials composed of large molecules [1–6]. Recently, using Mössbauer spectroscopy and X-ray diffraction, we have found interrelation between intramolecular motion and phase transitions in solid tetramethyltin, $Sn(CH_3)_4$ whether in bulk form or in the form of as adsorbed films [7]: bulk and adsorbed films of this molecule as well form lattice structures different from each other, but nevertheless show similar dynamical anomalies at practically the same temperature. This fact, together with available experimental data on possible modes of molecular motions in $Sn(CH_3)_4$ lead us to suggest that the observed dynamical anomalies are intramolecular in origin.

The motivation for this study is to find if dynamical anomalies of intramolecular origin can exist in other materials, knowing to have anomalous "Debye-Waller" behavior. Among the substances known to be dynamically very active is the iron pentacarbonyl (IPC), $Fe(CO)_5$. X-ray diffraction studies [8] of solid IPC bulk have shown that it has a trigonal bipyramid configuration with the carbon atom of each CO group bonded to the iron. Infrared and Raman studies [9] show that many intramolecular modes are possible, which involve C–O stretchings and bendings. NMR results [10] on this molecule suggest the existence of some intramolecular exchange with $\lesssim 1$ kcal/mol barrier between non-equivalent axial and equatorial carbonyl groups. This exchange process takes place in IPC molecules in their solid state and persists through quite a large temperature range. The exchange mechanism in this type of molecules was first suggested by Berry (Berry pseudorotation) [11, 12].

Previous neutron diffraction studies [13] on IPC monolayers adsorbed on the (0001) graphite basal plane have shown no evidence of neither structural non orientational transitions up to 150 K. In contrast to neutron diffraction results, an anomaly in the temperature behavior of Mössbauer spectral intensity and bulk dielectric constant was found at $T_R \simeq 110$ K [14]. The anomaly was associated with intramolecular rotational activities. In this report we present some details on Mössbauer measurements of the 110 K anomaly in bulk and adsorbed films of IPC on (0001) graphite plane. We show that at ~ 110 K the solid IPC undergoes a first-order phase transition, characterized by a hysteresis in the temperature dependence of the quadrupole splitting and abrupt change of the Mössbauer spectral area. The phase-transition is associated with a change in the intramolecular rotational motions.

II. Experimental

For the Mössbauer experiments on bulk IPC the liquid was encapsulated in a disk-shaped cell with Mylar windows. The effective absorber thickness was kept low enough to avoid saturation effects. Adsorbed

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film samples were prepared by following the adsorption vapor pressure isotherms of IPC to the desired coverage on an area-calibrated Grafoil stack [15]. Unity coverage was defined as a complete IPC monolayer of the commensurate $(\sqrt{7} \times \sqrt{21})19^\circ$ phase [13]. Prior to adsorption the Grafoil was baked at 900 °C for several hours under high-vacuum conditions and transferred into the Mössbauer cell in an He atmosphere glove box. The design of the cell allowed the gamma rays to pass in either direction parallel or perpendicular to the Grafoil sheets. The Mössbauer spectra were recorded using a 20 mCi: ^{57}Co gamma source in a transmission configuration. A conventional constant accelaration Mössbauer spectrometer was used. The appropriate temperature of the adsorption cell was achieved by a liquid nitrogen cryostat, stabilized to ± 0.1 °C by a commercial temperature controller. The Mössbauer spectra display a well-resolved quadrupole splitted doublet which was analyzed using two independent Lorentzian fits. Line positions, width, quadrupole splitting and background corrected spectral intensity were determined.

III. Results and Discussion

Figure 1 illustrates the temperature variation of the Mössbauer spectral intensity for a bulk sample and for adsorbed IPC films with three different surface coverages. From these results it is apparent that the Mössbauer spectral intensity in the perpendicular direction (Fig. 1 b) is consistently larger than that parallel to the surface (Fig. 1 a) inferring differences in the mean squared displacement of the adsorbed molecules between the measured directions. An estimate from the temperature dependence of the spectral intensity [16] in the perpendicular direction provides a binding energy of ~ 8 kcal/mole for the IPC molecule to the graphite substrate.

The observed spectral intensity is a complicated function of temperature and appears to be quite different from the regular exponential Debye behavior. In the temperature range of our experiment a substantial and sharp drop in the spectral intensity is seen at $T_R \simeq 110\,K$; moreover it becomes more pronounced as the film coverage increases. Since we observe the same anomalous behavior in bulk, it is possible that this dynamical anomaly is of intramolecular origin. To support the latter assumption, no structural changes have been detected by neutron diffraction studies [13] below 150 K neither in bulk nor in adsorbed IPC films; we consequently believe that the reason for the anomaly in the Mössbauer spectral intensity at ~ 110 K is a result of a cooperative rotational phase transition.

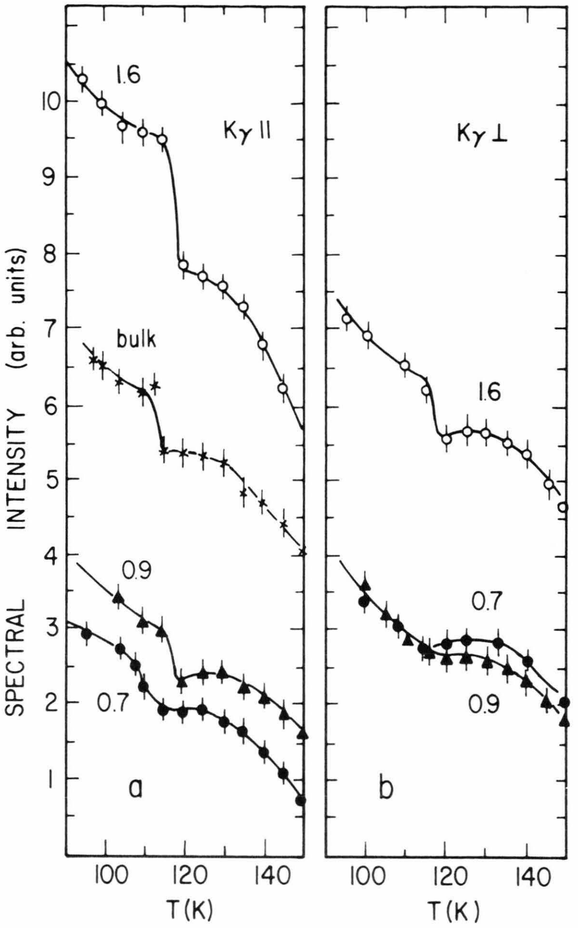

Fig. 1. The temperature variation of the Mössbauer spectral intensity for 0.7, 0.9, and 1.6 layer films a) in the parallel configuration with the gamma k-vector parallel to the graphite basal plane and b) in the perpendicular configuration. Bulk results are shown in (a).

Usually, anomalies in Mössbauer spectral intensity indicate a transition associated with dynamical changes in the mean-squared displacement of the Mössbauer atom. The dynamical disorder which causes the drop in the Mössbauer spectral intensity can be either of translational or rotational nature. The resonance Mössbauer fraction in molecular solids is determined by both the translational and librational lattice modes. A Mössbauer dynamical anomaly will be observed if for any reason these phonons or librons will experience a change either of their frequency or in their distribution across the transition. It is believed that such libronic modes are stable below a certain transition temperature T_R [17]. Model calculations show that there is a coupling between the librons and phonons and that at the temperature T_R the reduction in the libron frequency (in which the Mössbauer atom does not participate) is followed by a certain reduction in the phonon frequency [17]. In this case the mean squared displacement of the Mössbauer atom increases and consequently the transition results in a drop in the spectral area.

An other interesting anomaly in the Mössbauer spectrum close to the transition temperature T_R is observed in the temperature linewidths behavior of both quadrupole doublet components π and σ. Figures 2a and 2b display the temperature dependence of the linewidth in bulk and 1.6-layer film of IPC, respectively. For the 1.6-layer film and IPC submonolayers as well, the π and σ lines have the same width at a given temperature and display the same temperature dependence. For the bulk sample, however, the π and σ linewidths at given temperature are different. A study on the effect of anisotropic diffusion on the linewidths of quadrupole-split spectra shows [18] that in some cases the broadenings of the π and σ lines are expected to be equal only for single crystals; for polycrystals, however, unequal broadening is predicted.

The temperature dependence of the linewidths shows line narrowing as the transition temperature T_R is approached. After recovery to the initial value another narrowing is observed as the temperature increases further and the orientational-disordering transition is approached [19]. The line-narrowing at the transition temperature T_R can be attributed to motional narrowing [20]: It is possible that an increase of CO-ligand motion about the Mössbauer Fe-atom can result to some degree in relaxation of quadrupole fields with consequent averaging of local strains and other inhomogeneities. As a result the linewidth decreases.

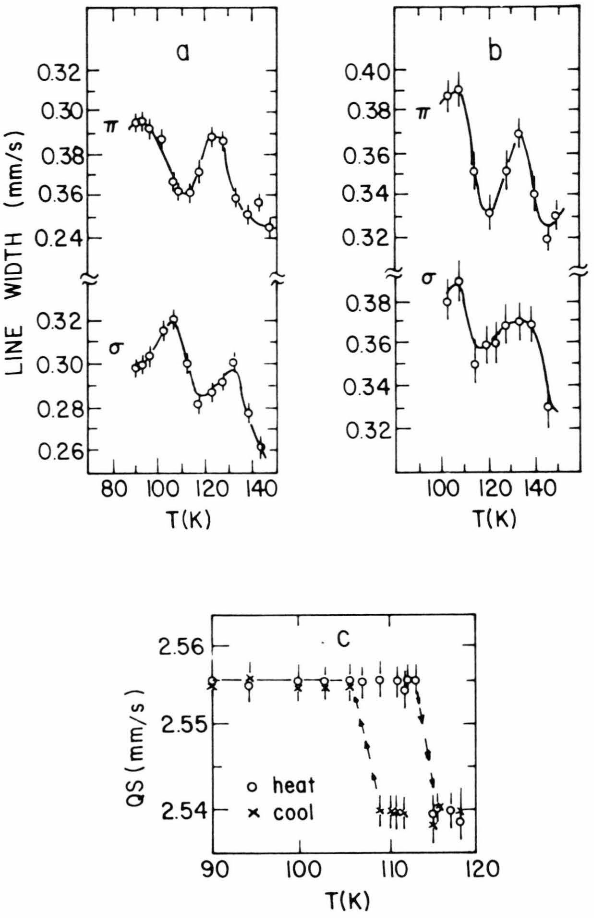

Fig. 2. a) The temperature dependence of the π and σ linewidths for the bulk sample. b) The temperature dependence of the π and σ linewidths for the 1.6 layer film. c) The temperature dependence of the quadrupole splitting on cooling and heating the Fe(CO)$_5$ bulk sample.

Based on the results described above, we can describe the dynamical behavior of the IPC molecule. The transition at $T_R \simeq 110$ K is associated with "rotational" motion of the CO-ligands. At temperatures below T_R, the CO-groups vibrate about their equilibrium position with some intramolecular exchange between axial and equatorial positions [10]. As T_R is approached, the CO-groups are released and a smooth rotational motion starts about the C_3 axis of the molecule [10]. Such a rotation causes an intramolecular average change in the equatorial charge-distribution toward a slightly more symmetric arrangement. From this charge-redistribution the isomer shift is effected as well. Since this rotational transition is not accompanied by structural changes, the effect on the isomer shift is expected to be extremely small. Fluctuations in the charge-distribution are associated with fluctuations in the electric field gradient and a slight drop in the quadrupole splitting is apparent at the transition temperature T_R (Figure 2c). The temperature dependence of the quadrupole splitting in Figure 2c displays hysteresis through cooling and heating of the bulk sample. The observation of hysteresis and the sharpness of the transition together with the anomalous behavior of the bulk dielectric constant [14] indicate a cooperative first-order rotational transition. The transition at T_R is somewhat blurred for the adsorbed mono and submonolayer films samples (see Fig. 1a) due to additional hinderence of the CO group rotation caused by the exchange with the graphite substrate. However, it is possible that this transition is a bulk property, and its existence in the 1.6 layer film and higher coverages agrees with X-ray and neutron diffraction results [21] which indicate that for high coverages part of the adsorbed IPC molecules forms bulk.

The effectiveness of Mössbauer spectroscopy was shown here when used as a dynamical probe to acquire information complementary to other experimental techniques. It will, however, be interesting if the sharp transition at ~ 110 K will be observed in bulk and adsorbed films of IPC molecules by other techniques as well.

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