

Rotational transitions in monolayer molecular solids

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We have measured the NMR spin-lattice relaxation time and second moment for ethylene and methane monolayers adsorbed on a graphite substrate. Coverages were in the low-density-solid region. Substantial rotational mobility (apparently isotropic) is found for both systems at temperatures below the freezing transition. Some or all of this mobility is lost in a second, rotational transition for ethylene at about 35 K and for methane at about 17 K.

The phases and phase transitions exhibited by monolayer molecular films adsorbed on highly uniform substrates have been the subject of considerable interest in recent years. Much of the work has been concentrated on determining the lattice structure of the various solid phases and in studying the melting transitions from these solids. In only a few cases have the rotational dynamics been studied.¹⁻³ This has largely been due to the low sensitivity of most experimental probes to the degree of rotational mobility in the film. Nuclear magnetic resonance spectroscopy offers one probe with a high sensitivity to the rotational motion. It is for this reason that, since its inception, NMR has been widely used to study rotational motion in bulk molecular solids.⁴ Recent NMR work on ethylene⁵ and methane⁶ monolayers, as well as neutron and x-ray scattering experiments (see Refs. 7-9 and references contained therein), have carefully mapped out the melting transition for these systems. In the case of methane a search was made for a rotational transition in connection with the commensurate-incommensurate transition¹⁰ but none was found. In this paper we present low-temperature NMR measurements on these two systems. We find that the molecules in the solid retain isotropic rotational mobility to temperatures well below the melting point. This mobility (or a portion of it) is lost in a second transition at about 35 K for ethylene and 17 K for methane.

The sensitivity of NMR to molecular motion comes from the dependence of the spin-lattice relaxation time T_1 and the observed second moment of the resonance line m_2 on the correlation time.¹¹ The correlation time τ_c is the time it takes for the surroundings of a nucleus to change significantly. The time between rotational jumps or jumps from one lattice site to another are examples. When τ_c is short, T_1 is long and m_2 is small. As τ_c increases, in our case due to a decrease in temperature, m_2 increases while T_1 decreases, passing through a minimum when $\tau_c \approx 1/\omega_0$ where ω_0 is the Larmor frequency. A further increase in τ_c brings an increase in T_1 and a continued increase in m_2 . Finally, when $\tau_c > (M_2)^{-1/2}$ where M_2 is the second moment for infinite τ_c (the "rigid lattice" value), m_2 becomes constant, equal to M_2 . Since $(M_2)^{1/2} \ll \omega_0$ the minimum in T_1 occurs at a shorter correlation time, and therefore a higher temperature, than the onset of a constant m_2 .

It is possible for the molecular motion to be character-

ized by more than one τ_c . A molecule may jump between lattice sites with a different correlation time than for rotational jumps. If the correlation times are sufficiently different each will give rise to a separate minimum in T_1 as a function of temperature, while m_2 will increase in a steplike manner, the value at each step reflecting the degree of mobility left in the system. For example, the molecules may form a solid in which they retain rotational mobility, with m_2 rising to a value given by an infinite translational τ_c but a short rotational τ_c . Then at a lower temperature the rotational motion may freeze out, with m_2 rising still higher to the value for rigid molecules.

Our proton relaxation time measurements were performed using a coherent, pulsed, NMR spectrometer operating at 24 MHz. A $\pi/2$ pulse length was 8 μ s; the receiver dead time following a pulse was 30-40 μ s. The Grafoil (Union Carbide Corp.) substrate was prepared by a 12-h bakeout at 1000°C under vacuum, after which it was sealed in a Macor (Corning Glass Works) sample cell. Thin teflon sheets between the Grafoil pieces provided electrical insulation. Care was taken to keep all hydrogen-containing materials away from the NMR coil so that only the adsorbed molecules would contribute to the signal. With no adsorbate present there was no detectable proton NMR signal.

The substrate surface was calibrated by a nitrogen isotherm at 77 K, identifying the beginning of the small sub-step near monolayer completion as indicating a registered $\sqrt{3} \times \sqrt{3}$ film. We assign this quantity of *any* gas unit coverage, $x=1.0$. For the cell used here a registered monolayer consisted of 4.38 cm³ STP gas, or about 4.7×10^{20} protons. This gave a signal-to-noise ratio before signal averaging of about 3 at 77 K. Thermometry was provided by a carbon thermometer mounted directly on the sample cell and calibrated against a platinum resistance thermometer.

The data collected were the spin-lattice relaxation time using a π - τ - $\pi/2$ inversion recovery pulse sequence and the decay of the free induction signal following a $\pi/2$ pulse. The free induction decay (FID) was found to be fitted best by a Gaussian function. For Gaussian decay the second moment can be obtained directly from the slope of the natural log of the FID versus t^2 . The anisotropic magnetic susceptibility of the graphite substrate creates significant field inhomogeneity, setting a lower limit on m_2 . We report m_2 values only at temperatures where they fall

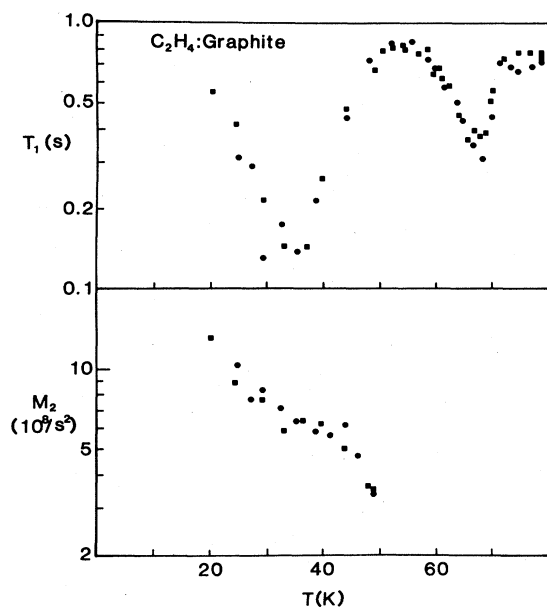


FIG. 1. Spin-lattice relaxation time and second moment for ethylene on Grafoil. Coverages are $x=0.65$ (●) and 0.74 (■).

above this substrate-imposed limit. Since our interest here is in phases where the motion is restricted, resulting in large values of m_2 , this is not a serious problem.

The coverages were chosen to be in regions of the phase diagram where the film forms a self-bound solid phase. For ethylene, coverages of $x=0.65$ and 0.74 were measured, both well within the incommensurate low-density-solid phase^{5,7,8} (lattice spacing 4.65 \AA), while for methane

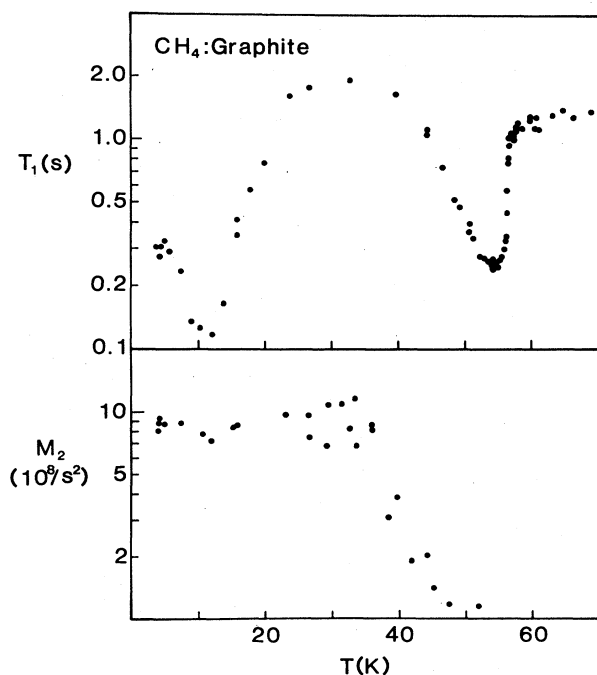


FIG. 2. Spin-lattice relaxation time and second moment for methane on Grafoil. Coverage is 0.70 .

a coverage of $x=0.70$ falls in the region of the $\sqrt{3} \times \sqrt{3}$ registered solid⁹ (lattice spacing 4.26 \AA). The results of the measurements are shown in Figs. 1 and 2. For both molecules qualitatively similar behavior is observed. As the temperature is lowered a minimum in T_1 is found, followed by the beginning of an increase in m_2 , and finally a second minimum in T_1 .

The existence of two T_1 minima is a clear indication that the motion of the molecules is characterized by two correlation times which pass through the value $\tau_c \approx 1/\omega_0$ at quite different temperatures. We associate the high-temperature minimum in T_1 with the loss of translational mobility upon freezing, as discussed elsewhere^{5,6} and the low-temperature minimum with a reduction of rotational mobility at the rotational transition, and will refer to the associated correlation times as the translational τ_c and the rotational τ_r .

Turning to the second moment data, we note that for both molecules m_2 first begins to increase at a temperature above the rotational T_1 minimum. Thus, this initial increase in m_2 must be associated with the translational correlation time. In the case of methane, m_2 increases with decreasing temperature until it reaches a value of $9 \times 10^8 \text{ S}^2$ at about 35 K , after which it remains constant. Thus below 35 K the translational correlation time has become sufficiently long that we observe the value of m_2 corresponding to an infinite translational τ_c . To explore the type of motion which might remain in this solid it is necessary to calculate the second moment which would be observed for particular motions and compare it with the data. The spherical shape of the methane molecule suggests that rotation in the solid might be quite easy. Assuming isotropic reorientation the contribution to the second moment from intramolecular interactions is negligible due to motional averaging. However, because the centers of mass of the molecules are fixed in a lattice, the intermolecular contribution is not fully averaged. For rotating molecules it is difficult to calculate the intermolecular contribution to the second moment exactly. A simple and reasonably accurate approximation is to treat the intermolecular interaction as if the nuclei in neighboring molecules were separated by a fixed distance equal to the distance between molecular centers.¹² Doing this for methane with a separation of 4.26 \AA results in a value for m_2 of $10.9 \times 10^8 \text{ S}^2$, in agreement with the observed value within the uncertainty of the approximations involved. Single-axis rotation about one of the C_3 axes, which does not fully average the intramolecular interaction, gives a calculated m_2 of $71.3 \times 10^8 \text{ S}^2$, much larger than observed. Thus we conclude that below the freezing point the methane molecules execute isotropic rotation. The low-temperature minimum in T_1 shows that at least some of this rotational motion is subsequently lost. (Note that the rotational T_1 minimum comes at a temperature well below the incommensurate-to-commensurate transition, confirming the conclusion¹⁰ that this transition does not involve a change in rotational mobility.) The fact that no further increase in m_2 is observed indicates that the rotational correlation time never gets sufficiently long to affect m_2 .

For ethylene molecules a somewhat different variation

of m_2 with temperature is found. While m_2 for ethylene also begins to increase at a temperature above the rotational T_1 minimum, this increase continues to temperature well below this minimum. Thus it is likely that some of this increase is associated with each of the two correlation times. A careful inspection of the m_2 data in the region between 32 and 42 K reveals a small plateau with a value of m_2 of about $6 \times 10^8 \text{ S}^2$. This plateau extends to temperatures above the rotational T_1 minimum and must therefore be the value of m_2 obtained for a infinite-translational correlation time. We can again calculate the value of m_2 expected for various motions. For isotropic rotation we calculate a value of $6.4 \times 10^8 \text{ S}^2$; for single-axis rotation about an axis perpendicular to the carbon-carbon axis we calculate $9 \times 10^8 \text{ S}^2$ to $66 \times 10^8 \text{ S}^2$, depending on the angle of the rotation axis with respect to the molecular plane; for single-axis rotation about the carbon-carbon axis we calculate $32 \times 10^8 \text{ S}^2$. The good agreement for isotropic rotation leads us to favor this picture. However, the uncertainty of the calculation and the scatter of the data do not completely rule out the possibility of single-axis rotation about an axis perpendicular to the carbon-carbon axis.

Below 32 K, m_2 again begins to increase. This is below the temperature of the rotational T_1 minimum so we suspect that this change in m_2 is associated with a loss of rotational mobility. By 20 K, m_2 has increased to $13 \times 10^8 \text{ S}^2$ and the decay of the FID has become so rapid that a large fraction of the signal is lost in the dead time of our receiver. For this reason we report no data below 20 K. We speculate that the increase in m_2 continues, but the increasingly rapid free induction decay makes it im-

possible for us to determine the true low temperature m_2 . Thus our picture is that between the freezing transition and the rotational transition the monolayer forms a solid in which the molecules undergo rapid reorientation, probably isotropic. Some or all of this rotation is then frozen out at about 35 K.

If the change in rotational mobility occurs via a simple thermal activation, the minimum in T_1 plotted against $1/T$ would be symmetric, with the slope on either side of the minimum giving the activation energy. If, on the other hand, an abrupt transition occurs a discontinuity in T_1 would be found, as is observed for both systems when the translational mobility changes abruptly upon freezing. For methane the low-temperature T_1 data as a function of $1/T$ bear a strong resemblance to the data at the freezing transition, with a discontinuity at about 17 K. This suggests that there is an abrupt transition in the rotational mobility. The transition temperature agrees very well with estimates based on a Monte Carlo simulation¹³ and is consistent with quasielastic neutron scattering results¹⁴ which showed the disappearance of tunneling levels at about 20 K. Further measurements are planned in an effort to more completely determine the nature of the loss of rotational mobility for these systems.

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