Neutron-Scattering Study of Ethylene Motions on Graphite Surfaces

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Quasielastic and inelastic, incoherent scattering of neutrons has been used to probe the diffusional and vibrational motions of ethylene molecules on graphite basal-plane surfaces. The experimentally observed dynamical response is found to agree reasonably well with molecular-dynamics simulations of ethylene films under similar conditions of coverage and temperature.

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Elastic, coherent scattering of neutrons is often employed to investigate the structures of gas films adsorbed on exfoliated-graphite substrates.[1] In some of these films, i.e., those composed of hydrogen-containing molecules, inelastic, incoherent neutron scattering can also be used to probe the surface motions of the molecules.[2] We have recently applied this technique to ethylene molecules on graphite basal-plane surfaces and would like to report here some of our observations relating to the overlayer dynamical response.

Concurrent with our measurements, Nosé and Klein undertook to make a series of molecular-dynamics calculations for the ethylene-on-graphite system under similar conditions of coverage and temperature.[3] Their computer simulations were invaluable as guides to the interpretation of many features of our experimental data.

Ethylene, C_2H_4, is a planar molecule with carbon-carbon distance 1.338 Å, carbon-hydrogen distance 1.093 Å, and hydrogen-carbon-hydrogen angle 117.2°. X-ray[4] and neutron[5] diffraction measurements have identified a liquid and at least two (and possibly three) solid monolayer phases of ethylene on graphite. We studied the dynamics of the liquid phase and two of the solid phases, the high-density (HD) and low-density (LD) solids, but because of space limitations only the dynamics of the liquid and the LD solid phase (a triangular-lattice solid with a nearest-neighbor spacing of 4.65 Å and a melting temperature of 68 K) will be discussed here. A more complete description of the measurements is planned for a later time. Configuration-energy calculations suggest that the molecules in the LD solid have their carbon-carbon axes aligned parallel to the surface and that the molecular planes are tilted away from the surface at an angle of about 35° as shown in the inset to Fig. 2. Steric hindrances to molecular rotations do not appear to be excessive in this arrangement. Indeed, no experimental evidence of further orientational order has been found in the LD phase, even at temperatures as low as 4 K.

The use of neutrons as a molecular-dynamics probe depends on the fact that hydrogen has an unusually large (and almost entirely incoherent) scattering cross section. Thus in a molecule like ethylene the hydrogen atoms will contribute the greatest part of the scattering. Moreover, this scattering, being incoherent, will directly reflect, in its spectral distribution, the motions of the hydrogen atoms and, thereby, the motions of the molecules. Such scattering processes are most conveniently described by a cross section of the form[6]

$$\frac{d^2\sigma}{d\Omega\, d\omega} = N\frac{k_f}{k_i}\,\frac{\sigma_{\text{inc}}}{4\pi}S_{\text{inc}}(\vec{Q},\omega), \tag{1}$$

where N represents the number of scatterers (H atoms) in the beam, $\vec{k}_i$ and $\vec{k}_f$ are the wave vectors of the incident and scattered neutrons, $\sigma_{\rm inc}$ is the incoherent scattering cross section, the scattering vector $\vec{Q} = \vec{k}_i - \vec{k}_f$, the energy transfer $\hbar\omega = (\hbar^2/2m)(k_i^2 - k_f^2)$ with m being the mass of the neutron, and, finally, $S_{\rm inc}(\vec{Q},\omega)$ is the incoherent dynamic structure factor, i.e., the Fourier transform of the self-correlation function $G_s(\vec{r},t)$ which is the probability that if a particle is at the origin at time $t=0$ it will be at the position $\vec{r}$ at time t. $S_{\rm inc}(\vec{Q},\omega)$ describes the dynamical response of the scatterer. We will be interested in both diffusional and vibrational motions. As far as diffusion is concerned, rotational and translational processes will have to be treated separately since they lead to somewhat different types of quasielastic scattering. Librational and translational components of the vibrational motions, on the other hand, will not have to be similarly separated since the inelastic scattering they produce is of the same basic form.

Considering first rotational diffusion, there are two cases in which the dynamic structure factor has a relatively simple analytic form: diffusion around a single axis [one-dimensional (1D)diffusion] and diffusion in which the motions of the particles take place on the surface of a sphere (3D diffusion). For the 1D case[7]

$$S_{\rm inc}(Q,\omega) \sim J_0^2(Qa\sin\theta)\delta(\omega) + \frac{2}{\pi}\sum_{n=1} J_n^2(Qa\sin\theta)\left[\frac{n^2 D_{\rm ro}}{(n^2 D_{\rm ro})^2 + \omega^2}\right], \tag{2}$$

the J 's representing Bessel functions, $\vec{a}$ being the radius of rotation, θ the angle between $\vec{Q}$ and $\vec{a}$, and $D_{\rm ro}$ the rotational-diffusion constant. In the 3D case[7]

$$S_{\rm inc}(Q,\omega) \sim j_0^2(Qa)\delta(\omega) + \frac{1}{\pi}\sum_{l=1}(2l+1)j_l^2(Qa)\left\{\frac{l(l+1)D_{\rm ro}}{[l(l+1)D_{\rm ro}]^2 + \omega^2}\right\}, \tag{3}$$

with the j 's here being spherical Bessel functions, a the radius of gyration, and the other quantities having the same meanings as before. The expression for two-axis rotation is too complicated to reproduce here.

Translational diffusion is adequately represented in the small-Q limit by a dynamic structure factor of the form[6]

$$S_{\rm inc}(Q,\omega) \sim \frac{1}{\pi}\frac{D_{\rm tr}Q^2\sin^2\theta}{(D_{\rm tr}Q^2\sin^2\phi)^2 + \omega^2}, \tag{4}$$

with ϕ being the angle between $\vec{Q}$ and the surface normal and $D_{\rm tr}$ the diffusion constant for translational motions.

It is evident from Eqs. (2) and (3) that at low rotational-diffusion frequenices the scattering is effectively elastic but as $D_{\rm ro}$ increases, weight is taken from the elastic part of the scattering and redistributed among a series of increasingly broader Lorentzian terms. Also note that the weighting is Q dependent, the quasielastic part increasing relative to the purely elastic part as Q grows larger. Translational diffusion, by comparison, produces a simple, quasielastically broadened spectrum of width $2D_{\rm tr}Q^2$ at small values of Q. This difference in response is a reflection of the fact that it is assumed here that the rotational diffusion is taking place within a restricted volume and the self-correlation function $G_s(\vec{r},t)$, therefore, remains finite as $t\to\infty$, while in the translational case $G_s(\vec{r},\infty)=0$ since the translational motions are not similarly limited.

Finally, we will want to consider the inelastic scattering which arises from vibrational motions. Under the assumption of excitation by the neutron of a single vibrational quantum, a convenient form of the dynamic structure factor for comparison with molecular-dynamics calculations is[8]

$$S_{\rm inc}(\vec{Q},\omega) \sim \frac{Q^2\exp\{-[2W_{\rm H}(\vec{Q}) - (h\omega/k_{\rm B}T)]\}}{3\omega^2} f_{\rm H}(\omega), \tag{5}$$

where $\exp[-2W_{\rm H}(\vec{Q})]$ is the hydrogen-atom Debye-Waller factor, and $f_{\rm H} \equiv (2\pi)^{-1}\int_{-\infty}^{\infty} dt\exp(-i\times\omega t)\langle\vec{V}_{\rm H}(0)\cdot\vec{V}_{\rm H}(t)\rangle$ is the Fourier transform of the hydrogen-atom velocity autocorrelation function, assumed—in first approximation—to be independent of crystallographic direction.[9]

Our measurements were made with an isotropic powder sample consisting of ethylene films adsorbed on the basal-plane surfaces of slightly compressed, exfoliated graphite. A separate, nitrogen-adsorption-isotherm measurement was used to determine the surface area of the substrate. All neutron scans were made on a triple-axis spectrometer operated in the constant-Q mode: the quasielastic scans with k_i fixed at

1.55 Å^{-1} and the inelastic scans with k_f fixed at 2.67 Å^{-1}. As is usual in this type of experiment, the scattering from the adsorbed films was obtained by taking the difference between counts with and without the ethylene in the sample cell.

Rotational diffusion is most easily identified with neutrons by setting the spectrometer to accept only elastically scattered neutrons and monitoring the temperature dependence of the scattered intensity at a fixed value of Q. In this way the point at which the rotational-diffusion rate becomes rapid enough to make the scattering significantly nonelastic will appear as a rapid falloff in the scattered intensity. (With our instrumental resolution we are sensitive to values of $D_{\text{ro}} > 10^{10}$ sec^{-1}). The scattering from the LD solid showed such a drop at 30 K; in fact the drop was so abrupt that by 45 K the intensity had decreased to half the 30 K value, seemingly indicating an orientational disordering transition. Since we have not been able to find any experimental evidence of orientational order in this phase, we are led to suspect that it is one in which the molecules are pinned by the incommensurate substrate into a state of "frozen-in" orientational disorder at low temperatures. Configuration-energy calculations lend support to this conclusion.

The Q dependence of the elastic scattering from the LD phase at a temperature of 60 K is shown in Fig. 1(a). Because of the finite energy resolution of the spectrometer, not all of the nonelastic scattering is actually excluded in such a scan which thus represents an upper limit to the purely elastic part of the scattering. Also plotted in the figure are solid lines indicating the Q dependence expected for the 3D- and (powder-averaged) 1D-type rotational-diffusion processes discussed earlier. The observed rotational diffusion falls roughly between the 1D and 3D limits, consistent with the calculations of Ref. 3 where rotations in the LD phase at higher temperatures are predicted to occur about both the carbon-carbon molecular axis and an axis normal to the carbon-carbon axis and in the molecular plane.

To obtain a more comprehensive view of the ethylene diffusional motions, we measured the Q dependence of the quasielastic scattering in the LD solid phase at 60 K and in the liquid phase at 90 K. Representative spectra are plotted in Fig. 1. In the 60-K data both a central elastic peak and broad, quasielastic wings characteristic of rotational-diffusive motions appear. At 90 K, in the liquid phase, the spectrum is markedly different: The central peak is noticeably broadened—indicating translational diffusive motions— while the rotational part has become so broad as to appear as an almost flat background.

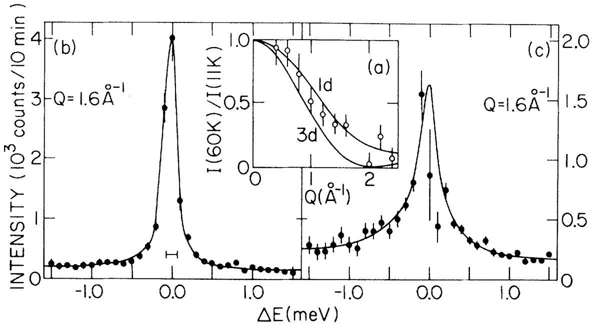

FIG. 1. (a) Q dependence of the elastic scattering from the LD solid phase at 60 K normalized to the scattering at 11 K. The solid lines are intensity profiles calculated for 1D and 3D rotational diffusion. (b) Quasielastic scattering from the LD solid phase at 60 K. The solid line was calculated under the assumption of 2D rotational diffusion with $D_{\text{ro}}(\text{C}-\text{C}) = 3.3\times10^{11}$ sec^{-1} and $D_{\text{ro}}(\perp) = 2.5\times10^{10}$ sec^{-1}. (c) Quasielastic scattering from the liquid phase at 90 K. The solid line was calculated under the assumption of translational diffusion with $D_{\text{tr}} = 2.0\times10^{-5}$ cm^2 sec^{-1}. The double-ended horizontal line indicates the spectrometer resolution.

For the LD solid phase at 60 K the calculations of Ref. 3 predict for rotations about the carbon-carbon axis a rotational-diffusion constant of 3.1×10^{11} sec^{-1} and for rotations about the axis normal to the carbon-carbon axis and perpendicular to the molecular plane a diffusion constant of 3.0×10^{10} sec^{-1}. In the liquid phase of the same density at 90 K the translational-diffusion constant is calculated to be 2.8×10^{-5} cm^2 sec^{-1}. Fitting our 60-K spectra with an orientationally-averaged dynamical structure factor for 2D rotational diffusion about the carbon-carbon axis and an axis normal to the substrate surface (not the same axis used in the molecular-dynamics calculations) we obtained $D_{\text{ro}} = 3.3\times10^{11}$ sec^{-1} for carbon-carbon axis rotation and $D_{\text{ro}} = 2.5\times10^{10}$ sec^{-1} for rotations normal to the substrate surface. Terms up to $l = 3$ were included in the analysis. An equivalent analysis of the 90-K spectra verified the expected Q^2 dependence of the line width. From the small-Q spectra we obtained $D_{\text{tr}} = 2.0\times10^{-5}$ cm^2 sec^{-1}. The solid lines in Figs. 1(b) and 1(c) are our fits to the data. Agreement of the calculated diffusion constants with the experimentally determined values is within expectations.

Turning from the quasielastic to the inelastic scattering, we show in Fig. 2 the neutron energy-loss spectrum obtained at $Q = 3.0$ Å^{-1} from the LD

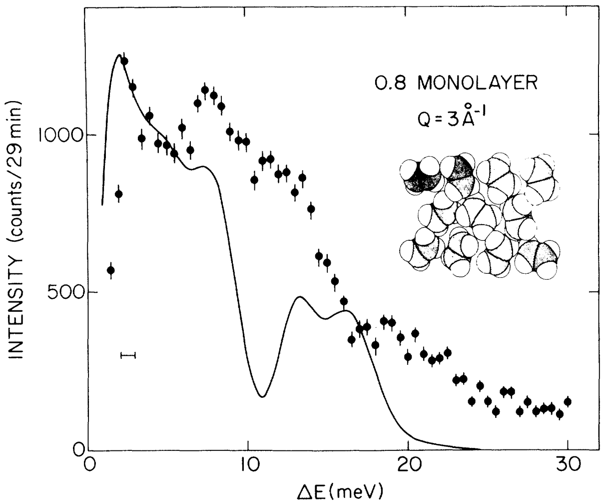

FIG. 2. Inelastic spectrum from the LD solid at 11 K. The inset shows a top view of the orientationally disordered molecular arrangement suggested by configuration-energy calculations, the double-ended line indicates the spectrometer resolution, and the solid line is the single-excitation spectrum predicted by molecular-dynamics calculations.

solid at a temperature of 11 K. All of the dynamical response appears to be concentrated in a region extending from roughly 1 to slightly above 20 meV. Inspection shows a close correspondence between the positions of peaks in the experimental spectra and regions where the calculations of Ref. 3 predict peaks in the density of vibrational states. Thus the peaks at 2 and 8 meV fall near the energies expected for in-plane and out-of-plane translations while the shoulders at 12 and 18 meV are close to the energies at which peaks in the density of states are predicted for librations about axes respectively perpendicular and parallel to the carbon-carbon axes of the molecules. Also shown in the figure is a solid line representing the single-excitation spectrum obtained from the molecular-dynamics calculations of Ref. 3 using $S_{\mathrm{inc}}(\vec{Q},\omega)$ as given by Eq. (5). It has been arbitrarily normalized to match the data in the region between 4 and 5.5 meV. The response both below ~ 1 meV and above 6 meV is not altogether correctly predicted; the former because a smooth substrate is assumed and the latter because neither multexcitation contributions to the scattering nor multiple scattering processes are included in the simulations. Nevertheless, each feature of the experimetal spectrum appears to have its counterpart in the predicted density of states—a correspondence we view as highly satisfactory.

Finally, a comment is in order concerning what appears to be a cutoff in the dynamical response below 1 meV. This could derive from a small-wave-number phonon gap brought about by film-substrate interactions. Estimates showing the lateral variation of the film-substrate interaction potential to be about 1 meV tend to support this interpretation.

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[1] J. P. McTague, M. Nielsen, and L. Passell, in *Chemistry and Physics of Solid Surfaces,* edited by R. Vanselow and W. England (CRC Press, Boca Raton, Fla., 1979), Vol. III, p. 439.

[2] H. Taub, H. R. Danner, N. P. Sharma, H. L. McMurray, and R. M. Brugger, Phys. Rev. Lett. **39**, 215 (1977); P. Thorel, J. P. Coulomb, and M. Bienfait, Surf. Sci. Lett. **114**, L43 (1982).

[3] S. Nosé and M. L. Klein, following Letter [Phys. Rev. Lett. **53**, 818 (1984)].

[4] M. Sutton, S. G. J. Mochrie, and R. J. Birgeneau, Phys. Rev. Lett. **51**, 407 (1983).

[5] S. K. Satija, L. Passell, J. Eckert, W. Ellenson, and H. Patterson, Phys. Rev. Lett. **51**, 411 (1983).

[6] W. Marshall and S. W. Lovesey, *Theory of Thermal Neutron Scattering* (Oxford Univ. Press, London, 1971).

[7] W. Press, *Single Particle Rotations in Molecular Crystals,* Springer Tracts in Modern Physics, edited by G. Höhler, Vol. 92 (Springer, Berlin, 1981), p. 28.

[8] H. Boutin and S. Yip, *Molecular Spectroscopy with Neutrons* (MIT Press, Cambridge, Mass., 1968).

[9] B. Hudson, A. Warshel, and R. G. Gordon, J. Chem. Phys. **61**, 2929 (1974).