FIG. 3. Temperature variation of single-particle susceptibilities.

(1) leads to the octahedral Devonshire potential and to an interaction of translations and rotations. This interaction provides an effective coupling between molecular reorientations and drives the orientational phase transition. The single-particle susceptibilities $x$ and $y$ are crucial in determining $T_c$ and affect the temperature behavior of the elastic constants.

We acknowledge most useful discussions with Professor S. Haussühl, Dr. J. M. Rowe, and Dr. J. J. Rush. B. De Raedt helped with the numerical work. Financial support was given by Interuniversitair Instituut voor Kernwetenschappen, Belgium and the Sender Freies Berlin 130 Ferroelektrika, Deutsche Forschungsgemeinschaft.


Intramolecular and Surface Vibratory Modes of Butane Adsorbed on Graphite Observed by Inelastic Neutron Scattering(a)

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(Received 16 May 1977)

Inelastic and elastic neutron scattering have been used to study the dynamics and structure of butane ($\text{C}_4\text{H}_{10}$) adsorbed on a graphitized carbon powder at 77 K. In addition to the intramolecular vibrations found in the bulk solid, new surface vibratory modes are observed. A simple model which fits the principal features of the monolayer excitation spectrum suggests an orientation of the adsorbed butane molecule and the location and strength of the bonds to the substrate.

It has been recognized for over a decade that hydrogenous films provide a wide class of adsorbates whose dynamical properties can be studied by inelastic neutron scattering.\(^{13}\) Scattered intensities sufficient to study the dynamics of submonolayer films result not only from the large incoherent cross section of hydrogen for thermal neutrons (~80 b) but also the large-amplitude molecular vibrations arising from the small atomic mass. Nevertheless, due in large part to the heterogeneity of the substrates employed, well-defined excitations generally have

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not been observed in hydrogenous films. In particular, there has been difficulty in observing surface vibratory modes associated with the loss of translational or rotational degrees of freedom of the adsorbed molecule. Either these modes are not observed at all, or a single broad band is observed, or the spectra are difficult to interpret for other reasons.

We have recently begun to use inelastic neutron scattering to study the molecular excitations of short-chain hydrocarbons adsorbed on a high-homogeneity graphitized carbon powder. We report here some of our results on butane films for which the inelastic spectra are unusually rich in structure, exhibiting new surface vibration modes as well as the intramolecular torsional modes found in the bulk solid. We demonstrate how the presence of both types of molecular excitation allows identification of the surface vibratory modes and, further, provides details of the local environment of the adsorbed species. A simple model fitting the principal features of the butane-monomolecular spectrum predicts an orientation of the adsorbed molecule and suggests the location and strength of the bonds to the substrate.

The reason for selecting butane \( \text{[C}_2\text{H}_6\text{]} \) for our initial study was that the low-energy intramolecular excitations of the bulk solid and liquid are well understood from inelastic neutron scattering. The three lowest intramolecular modes \( [\Delta E \approx 270 \text{ cm}^{-1} (33.5 \text{ meV})] \) are well separated from those at higher energy and are relatively intense since they correspond to large-amplitude torsional motion of the end methyl \( \text{[C}_3\text{H}_7\text{]} \) and methylene \( \text{[C}_2\text{H}_4\text{]} \) groups. (The molecular geometry is shown in the inset to Fig. 1.) The substrate that we have used is Carbopack B, a graphitized carbon powder with a particle size of \( \sim 50 \text{ Å} \). It was selected over Grafoil because of its larger surface area \( \sim 80 \text{ m}^2/\text{g} \) and high homogeneity, and because the molecular excitations of interest can be studied without a preferred orientation in the substrate. The adsorption isotherm for butane on a 82-g sample of Carbopack B at 273 K is shown in Fig. 1. Monolayer completion is estimated at 0.55 liter (STP), and there is an inflection point at 0.85 liter (STP) \( \sim 1.5 \) layers generally interpreted as signaling multimolecular layer formation.

The inelastic-neutron-scattering experiments were performed on the University of Missouri time-of-flight spectrometer measuring neutron energy gain. A beryllium filter produced the incident beam \( \lambda \geq 4.0 \text{ Å} \) and a Fermi chopper was positioned between the sample and the detector set at a scattering angle of 27.4°. The variation of the momentum transfer \( (1 \text{ to } 3.1 \text{ Å}^{-1}) \) over the energy range \( (32 \text{ to } 270 \text{ cm}^{-1}) \) is of little concern for the dispersionless excitations under investigation. The energy resolution of the spectrometer in this range is estimated to be 10 cm \(^{-1}\). During all the scattering measurements the sample temperature was maintained between 77 and 90 K, well below the bulk solidification temperature of butane at 135 K.

Figure 2 shows the dependence of the observed inelastic spectra on film thickness. In the bulk-solid spectrum \( \text{[Fig. 2(a)]} \), the intramolecular excitations appear only as shoulders on the high-energy side of a broad band attributed to intramolecular modes of vibration. However, the spectra change dramatically as the coverage is reduced from four layers to monolayer completion: The shoulders become resolved into a series of reproducible peaks with the appearance of a broader band centered at \( \sim 50 \text{ cm}^{-1} \). We believe the improved resolution and signal-to-noise ratio in the thin-film inelastic spectra result from a shift to lower energy of the intermolecular vibrations similar to that observed in \(^{36}\text{Ar} \) monolayers. Note that the disappearance of well-defined peaks between 1.5 and 2 layers correlates closely with the coverage at which the inflection

![Fig. 1. Adsorption isotherm of butane \( (\text{C}_2\text{H}_6) \) on Carbopack B at 273 K. Labeled points correspond to coverages of inelastic spectra in Fig. 2. The inset is a schematic diagram of the butane molecule \( (\text{C}_2\text{H}_6 \text{ symmetry}) \). The four carbon atoms \( (\bullet) \) and one hydrogen atom \( (\circ) \) from each \( \text{CH}_3 \) group are coplanar. The concentric circles \( (\bigcirc) \) represent the remaining hydrogen atoms located in two planes of four atoms each parallel to the carbon skeleton.](image)
FIG. 2. Inelastic spectra of butane adsorbed on Carbopack B at 77 K vs film thickness. Spectra of the bulk solid and the background with no butane in the cell are included for comparison. Vertical bars are drawn along constant-energy lines to facilitate comparison. The counting times shown reflect the relative intensity of the spectra.

FIG. 3. Comparison of the monolayer and calculated spectra. The background has been subtracted from the observed spectrum, and the error bars represent the statistical uncertainty since multiple-scattering effects are believed negligible. The arrows indicate the energy of the three lowest-lying modes of the bulk solid (Ref. 8). The calculated spectrum is for the two-parameter model described in the text. The inset shows the proposed orientation of butane with respect to the graphite basal plane. Only the four coplanar hydrogen atoms (C) on one side of the carbon skeleton have been included for clarity.

occurs in the adsorption isotherm.

The monolayer spectrum [Fig. 2(e)] has been repeated in Fig. 3 but with the background [Fig. 2(f)] subtracted. It can be seen that the three highest-energy peaks occur at the same energy as the intramolecular CH₃ and CH₂ torsions of the bulk solid.⁶,⁷ We should note, though, that the CH₂–CH₃ torsion lies about 30 cm⁻¹ higher than in the bulk liquid,⁶ the phase which better approximates the free molecule. Probably the most interesting feature of the monolayer spectrum is the appearance of an intense peak at 112 cm⁻¹, well below the lowest bulk mode. In addition, the band centered at 50 cm⁻¹ may contain new film-substrate modes as well as intermolecular excitations of the film.

We have found that the principal features of the monolayer spectrum can be reproduced by assuming that the plane of the butane carbon skeleton is parallel to the graphite layers as shown schematically in Fig. 3. We were led to this orientation by the adsorption isotherm, which suggests that the butane molecule occupies an area about 2.5 times that of nitrogen, and also by data¹² showing the heat of adsorption on graphite to increase in proportion to chain length in the series propane (CH₃CH₂CH₃) to hexane [CH₃(CH₂)₄CH₃]. It is a remarkable feature of this orientation that the distance of 2.5 Å between the two coplanar hydrogen atoms in adjacent CH₃ groups just calipers a carbon hexagon in the graphite basal plane. This allows the methylene hydrogens to lie in symmetry-equivalent potential wells on the basal-plane surface. For example, the CH₃ hydrogens might bond to the electron π lobes directed normal to the graphite layers as in Fig. 3 or they might lie at the center of the carbon hexagons.

To simulate these bonds, a force constant k₂ directed normal to the surface was introduced between the two CH₃ hydrogens and an infinitely massive substrate. Since coplanar CH₃ hydrogens can also lie near the graphite π lobes in the orientation of Fig. 3, a second force constant k₃ normal to the surface was introduced to each of these atoms. We assume that the butane molecule is only weakly perturbed upon adsorption so that the intramolecular force constants and atomic positions of the free molecule can be used.⁹

The normal-mode calculation shows that three new excitations occur in the constrained molecule: two rocking modes about axes in the film plane parallel and perpendicular to the chain di-
rection, respectively, and a uniform oscillatory motion of the entire molecule normal to the substrate. The energy of the rocking mode about the chain axis and the perturbation of the intramolecular torsion of the two CH₂ groups with respect to each other depend primarily on the magnitude of \( k_\nu \). A value of \( k_\nu = 0.065 \text{ mdyn Å}^{-1} \) places the rocking mode at 120 cm\(^{-1}\) in agreement with the energy of the new peak observed and matches the energy of the CH₂–CH₃ torsion with the peak at 155 cm\(^{-1}\).\(^{13}\) As expected, the energies of the CH₃ torsions depend more strongly on \( k_\nu \). We have found it necessary to use a smaller value of \( k_\nu = 0.02 \text{ mdyn Å}^{-1} \) in order to fit the observed energies of the methyl torsions, indicating that the methyl hydrogens do not interact as strongly with the graphite substrate. With these values of \( k_\nu \) and \( k_\nu \), the orthogonal rocking mode and the uniform oscillatory mode fall within the band centered at 50 cm\(^{-1}\).\(^{14}\) We suggest that they are unresolved because of the butane–butane interaction, which has been neglected in our model.

The relative intensities in the calculated spectrum of Fig. 3 are based on one-phonon annihilation by incoherent scattering assuming isotropically oriented substrate particles.\(^{14}\) The agreement between calculated and observed intensities is reasonable if allowance is made for a large background from intermolecular excitations below 85 cm\(^{-1}\). We have verified that there is worse agreement with the observed spectrum if the molecular orientation is changed so that the butane is lying on its side but with the plane of the carbon skeleton perpendicular to the surface or in the original orientation if the bonds to the substrate are localized near the butane carbon atoms instead of the hydrogens.\(^{15}\)

The picture which emerges from our model, then, is that the butane is adsorbed on the graphite basal plane with the CH₂ hydrogen atoms at equivalent sites providing the principal bond to the surface. To determine whether there is long-range order in the film, we have also performed elastic neutron diffraction on a 1.5-layer film at 81 K. We find a large enhancement of the graphite (002) peak which is consistent with the butane carbon skeleton uniformly spaced above a basal-plane surface at a distance close to the c-axis lattice constant of graphite.\(^{16}\) However, we do not observe Bragg peaks indicative of an ordered two-dimensional phase.\(^{17}\) Structural disorder may result from translations or rotations of the butane molecule about the configuration shown in Fig. 3 which preserve the two CH₂–graphite bonds.

Elastic scattering from deuterated films having a larger coherent neutron cross section should provide a more detailed description of the short-range order in the film.

In conclusion, we believe the experimental approach described here can be applied to the study of the dynamics, molecular orientation, and bonding in other hydrogenous films. The most favorable cases would seem to involve adsorption sufficiently strong that the surface vibratory modes are split off at energies higher than the intermolecular excitations. This does not appear to be the case in our preliminary measurements on ethane (CH₃CH₂) adsorbed on graphite, which might otherwise be considered a favorable system.

We thank H. Kim for helpful discussions and for providing one of the computer codes used in the normal-mode calculation. We are indebted to L. Passell, J. P. McTague, J. S. King, E. O. Schlemper, S. A. Werner, and T. Wolfram for their continued advice and encouragement.

\(^{13}\) Work supported by the University of Missouri Research Council and the University of Missouri Research Reactor Facility.

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\(^{16}\) S. Todireanu, Nuovo Cimento Suppl. 5, 543 (1967).


\(^{24}\) Supelco, Inc., Bellefonte, Pa. 16823. Carbopack B is similar to Graphon previously manufactured by the
Probing Magnetism by Photoelectric Currents

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(Received 6 June 1977)

Measurements on the antiferromagnet Fe₃O₄ demonstrate that threshold photoelectric currents plotted vs. temperature yield the spin correlation function of a thin sheet at the surface. The data support an interpretation based on a magnetic final-state effect. Similar phenomena are expected to occur in many magnetic materials.

Information on effective exchange fields $H_{\text{eff}}$ in magnetic materials is obtained by using the magnetic moment $\mu$ of a nucleus or an unfilled electronic shell as a probe and finding the frequency of an alternating field that induces transitions between the Zeeman levels. We show in this Letter that photoemission from a localized magnetic shell with spin $S$ can also yield information on $H_{\text{eff}}$. This arises because on removing one electron by absorption of a photon $S$ changes and one can have transitions with $S'_{\text{(initial)}} - S'_{\text{(final)}} = \pm \frac{1}{2}$. There is then a magnetic contribution of $\pm \mu H_{\text{eff}}$ to the kinetic energy $E_{\text{kin}}$ of the photoelectron which is a few meV only, but as will be shown, can actually be observed. The novel feature of measuring $H_{\text{eff}}$ by photoemission is that information on magnetism in a thin sheet of material at the surface is obtained, by virtue of the small escape depth of photoelectrons. There are two other methods to measure surface magnetism, namely spin-polarized photoemission and field emission, and exchange scattering in low-energy–electron diffraction (LEED). The first one is limited to ferromagnets and ferrimagnets, and special cases of antiferromagnetism. The second one applies to antiferromagnets only and seems to be very difficult due to the smallness of exchange scattering compared to Coulomb scattering. Both types of experiments are very complex, yet we show here that a spin–spin correlation function of the surface can also be obtained by simply measuring photoelectric currents.

In Fig. 1 we show the photoelectric yield $Y$ (number of photoelectrons per incident photon) for Fe₃O₄, which is an antiferromagnet with a Néel temperature $T_N \approx 193$°K and crystallizes in the NaCl structure. $Y$ rises steeply near the photoelectric threshold $\Phi$ and reaches a flat region with some structure at higher photon energies $\hbar\omega$. A single crystal grown by the Czochralski technique with $x \approx 0.91$ was used. The defects are primarily tetrahedral cation interstitials which are frozen in regularly at $T < 400$°K. The measurements were made on surfaces obtained by cleaving crystals in ultrahigh vacuum (UHV). The LEED pattern showed that a (100) surface had actually been obtained. The samples were then transported in UHV from the LEED spectrometer to the photoemission apparatus, where they are held in place by a temperature-controlled gripper.

Figure 2 shows the temperature dependence of