

Collective Excitations in Ethane Monolayers Adsorbed on Graphite (0001) Surfaces

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(Received 17 April 1984)

Inelastic incoherent neutron spectra below 4.1 THz have been obtained for the $\sqrt{3} \times 4$ "herringbone" and $\sqrt{3} \times \sqrt{3}$ "on-end" monolayer phases of ethane adsorbed on graphite basal planes. One-phonon cross sections calculated independently with empirical atom-atom potentials make possible identification of the collective vibrational modes observed and reproduce qualitatively the rather different spectra of the two phases.

PACS numbers: 68.30.+z, 63.20.Dj

Inelastic neutron scattering (INS) is one of the few probes presently available for investigating the low-frequency collective excitations of adsorbed monolayers. As first demonstrated for ^{36}Ar adsorbed on exfoliated graphite,¹ energy-loss peaks corresponding to zone-boundary longitudinal and transverse phonons of a monolayer can be observed and their intensity interpreted quantitatively. Because of the weak neutron-film interaction, experiments are limited to high-surface-area substrates, in contrast with inelastic electron² and He atom³ scattering which have recently been used to investigate the lattice dynamics of adsorbates on single-crystal surfaces. While a polycrystalline substrate precludes direct measurement of the adsorbate dispersion relations,² INS offers several advantages over these other probes: (1) Neutron-phonon cross sections can be calculated relatively easily; (2) selection rules are absent; (3) ultrahigh vacuum is not required; and (4) there is high sensitivity to the motion of light atoms such as hydrogen. The last feature greatly facilitates observation of librational modes of adsorbed hydrocarbons in which H atoms at the molecule's extremities undergo large-amplitude displacements.

While collective modes have been observed in a variety of hydrocarbon monolayers,⁴ interpretation of the INS spectra has been severely hampered by uncertainty in the monolayer structure, particularly the molecular orientations. We have recently overcome this difficulty in INS experiments on ethane (C_2H_6) adsorbed on graphite (0001) surfaces. By combination of elastic neutron scattering⁵ with low-energy electron diffraction,⁶ two of the monolayer structures of this system have been solved. The S_1 phase [Fig. 1(a)] found at coverages ≤ 0.8 layers has a commensurate $4 \times \sqrt{3}$ unit cell containing two molecules which lie on their sides in a herringbone pattern. It is similar to other herringbone structures which have been found for monolayers

of N_2O_2 ,⁷ N_2 ,⁸ and $\text{Fe}(\text{CO})_5$ ⁹ physisorbed on graphite. The S_3 phase [Fig. 1(b)] occurring at higher coverages has a $\sqrt{3} \times \sqrt{3}$ commensurate structure in which the single molecule per cell

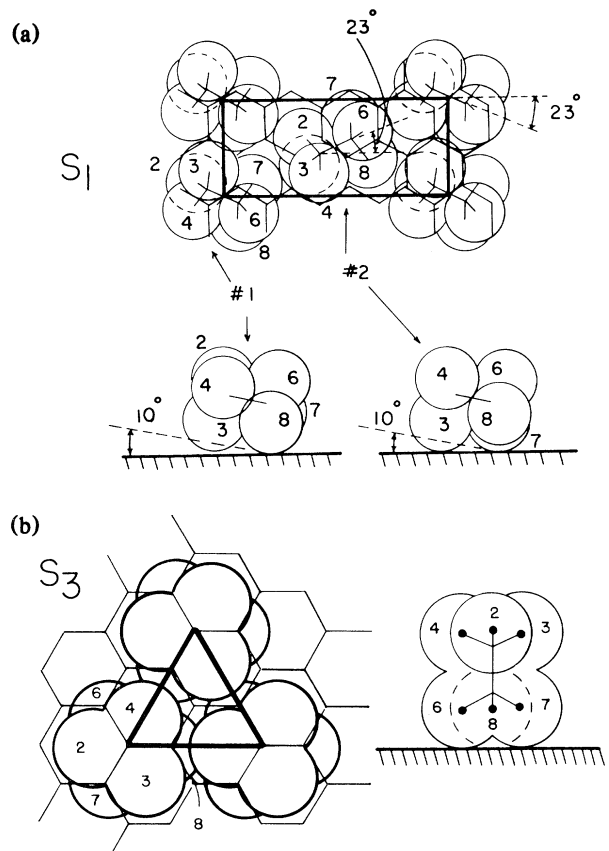


FIG. 1. Ethane monolayer structures showing projection of the unit cell on the graphite (0001) surface and orientation of the molecules with respect to the surface for (a) the S_1 phase and (b) the S_3 phase. The location of the unit cells on the graphite basal plane is that inferred from potential energy calculations in Refs. 5 (S_1) and 9 (S_3).

stands on a methyl tripod. The same structure has been inferred for submonolayer methane on the graphite (0001) surface.¹⁰ Thus both ethane phases provide prototypical monolayer structures of a rigid¹¹ rod-shaped molecule whose collective excitations can be investigated by INS. In addition, the C_2H_6 /graphite system has the advantage that reliable empirical atom-atom potentials are available^{12,13} for calculation of both the monolayer structure and the lattice dynamics. We report here our initial results identifying collective translational and librational modes in the S_1 and S_3 ethane phases by comparison of observed and calculated INS spectra. A more detailed description of this work is in preparation.¹⁴

INS spectra were obtained with the Mitsubishi triple-axis spectrometer at the University of Missouri Research Reactor Facility. The spectrometer was operated in an energy-loss mode with a fixed incident energy of 33 meV and at a constant momentum transfer $\vec{Q} = \vec{k}_f - \vec{k}_i$. Use of the Cu(200) reflection for both monochromating and analyzing crystals and 40' collimation throughout gave an instrumental resolution width (full width at half maximum) of 0.4 THz (1.8 meV) in the energy transfer range $0.5 \leq \Delta E \leq 4.1$ THz. The samples consisted of a Grafoil¹ substrate having a surface

area of $\sim 20 \text{ m}^2/\text{g}$. Two different sample cells were used, one for \vec{Q} parallel and the other for \vec{Q} perpendicular to the Grafoil sheets (there is some preferential orientation of the graphite c axes perpendicular to the sheets). All spectra presented here were measured at a temperature of 10 K by placing the cells in a closed-cycle helium refrigerator. They have been corrected for the energy dependence of the analyzer reflectivity.

The neutron energy-loss spectra at $Q = 4.0 \text{ \AA}^{-1}$ for the ethane S_1 "herringbone" and S_3 "on-end" phases are shown in the upper panels of Figs. 2 and 3, respectively. The spectra for the two phases are qualitatively different. However, for the S_1 phase and to a lesser extent S_3 , little difference is observed between spectra in the \vec{Q} parallel and perpendicular configurations. This suggests that most of the available surface area is contributed by smaller particles which are oriented isotropically.¹⁵ We shall assume an isotropic particle distribution in the analysis which follows.

Our lattice-dynamics calculations for the two ethane phases were performed on zero-temperature structures obtained by minimizing the potential energy of a monolayer cluster of rigid ethane molecules. Pairwise atomic C-C, C-H, and H-H potentials of the form $E = Ar^{-6} + B \exp(-\alpha r)$ with

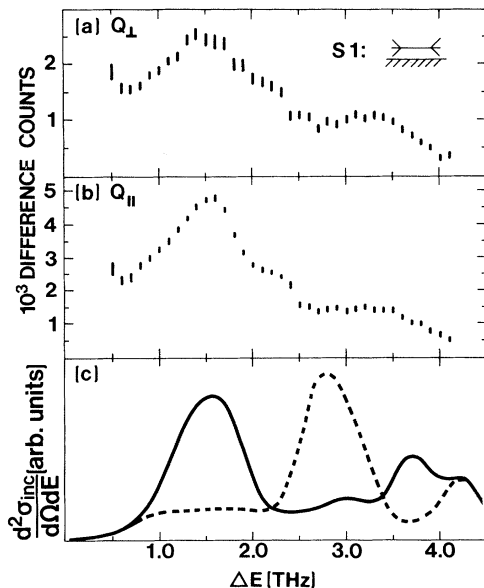


FIG. 2. Neutron energy-loss spectra of the S_1 monolayer ethane phase at 10 K for the momentum transfer \vec{Q} (a) perpendicular and (b) parallel to the Grafoil sheets. (c) Calculated one-phonon cross sections for the S_1 phase with (solid curve) and without (dashed curve) the coupling of librational and translational modes as described in the text.

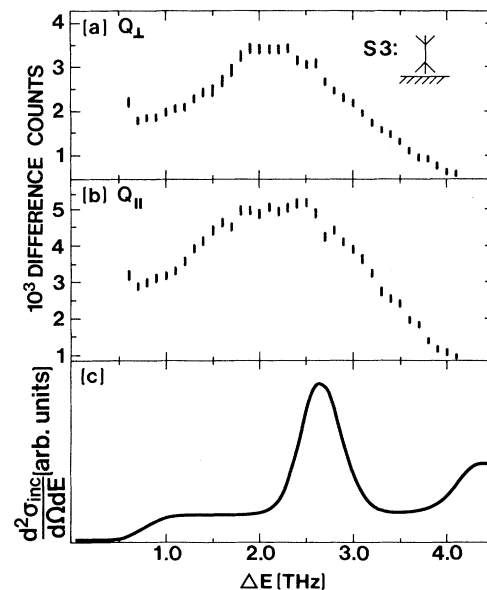


FIG. 3. Neutron energy-loss spectra of the S_3 monolayer ethane phase at 10 K for the momentum transfer \vec{Q} (a) perpendicular and (b) parallel to the Grafoil sheets. (c) Calculated one-phonon cross section for the S_3 phase. A weak band predicted at 4.3 THz lies just beyond the observed spectra.

Kitaigorodskii's¹³ values for A , B , and α were used to represent the intermolecular and molecule-substrate interactions. The (0001) graphite surface is simulated by a single honeycomb layer of carbon atoms since deeper layers are beyond the cutoff lengths of the potentials.¹² During the energy minimization procedure, the S_1 and S_3 unit cells are constrained to have rectangular and hexagonal symmetry, respectively. The calculations yield the same molecular orientations inferred experimentally⁵ but lattice constants for the two phases which are a few percent smaller than for the commensurate structures observed. The effect of the cluster incommensurability on the calculated INS spectra is believed to be small. It is the zone-boundary modes which dominate the one-phonon cross section,¹ and their frequencies are determined primarily by intermolecular forces and the average molecule-substrate interaction rather than the lateral forces of registry.

The procedure for representing the potential energy of the film in terms of intermolecular interactions and for calculating the dynamical matrix was similar to that developed for three-dimensional (3D) molecular crystals.¹⁶ Consistent with the cutoff lengths of the potentials, the intermolecular interactions include nearest and next-nearest couplings for the rectangular S_1 structure but only nearest-neighbor interactions for the hexagonal S_3 phase. Each molecule is coupled to the substrate by six force constants corresponding to its three rotational and three translational degrees of freedom.¹² Force constants for both the intermolecular and molecule-substrate interactions are explicitly calculated by use of the empirical potentials so that, with the exception of the coupling described below, there are no adjustable parameters.

We have calculated the incoherent cross section for one-phonon creation using the standard formula given by Marshall and Lovesey.¹⁷ This expression was spherically averaged, as appropriate for an isotropic substrate. All coherent scattering was neglected because of the dominance of the incoherent scattering from hydrogen, and the Debye-Waller factor for each H and C atom was set equal to zero. To obtain the cross section for each phase, half of the 2D Brillouin zone was sampled with a uniform mesh of 800 points.

The inelastic cross section for the S_1 phase is shown by the dashed curve in Fig. 2(c) after folding of it with the instrumental resolution function. It is dominated by a broad band at ~ 2.8 THz contributed mainly by two modes: the translation of the molecules normal to the surface and the libration

about a symmetry axis perpendicular to the C-C bond and parallel to the surface [see Fig. 1(a)]. The agreement with the observed spectra is poor with the calculated peak position a factor of 2 higher than that of the intense band observed at ~ 1.5 THz. Rather than assume large errors in the force constants calculated for both the translational and librational modes, we have investigated the effect of a coupling between them. Such a coupling appears plausible since the large distance of the CH_3 groups from the librational axis could result in a dependence of the librational restoring forces on the molecular height above the surface. The solid curve in Fig. 2(c) represents the best fit to the observed spectra which could be obtained by adjusting this coupling constant. The coupling splits the band at 2.8 THz into two peaks, the more intense of which reproduces well the band observed at 1.5 THz except for the shoulder observed at ~ 2.3 THz. The weaker peak predicted at 3.7 THz is at somewhat higher energy transfer than the band observed at 3.2 THz [better resolved in the \bar{Q} -perpendicular spectrum, Fig. 2(a)]. Little dispersion is calculated¹⁴ for these coupled modes indicating their local character. On the other hand, the weak mode at 3.0 THz involving translational motion parallel to the surface is strongly dispersed. This mode together with the libration about the surface normal (4.2 THz) are unaffected by the coupling.

The spectrum calculated for the ethane S_3 phase is shown in Fig. 3(c). In this more densely packed structure in which the molecules stand on end, the librational modes are predicted to occur at higher frequency than in the S_1 phase. The dominant mode calculated in the energy-transfer range investigated is the molecular vibration normal to the surface at 2.6 THz. The predicted peak is narrower and slightly higher in frequency than the single band observed in both \bar{Q} configurations.¹⁸

In summary, the sensitivity of INS to large-amplitude motion of H atoms allows investigation of low-frequency librational and translational modes of ethane physisorbed on graphite which are difficult to observe by other surface spectroscopies. Calculations of the one-phonon cross sections based on empirical atom-atom potentials permit mode identification and account for the qualitatively different spectra found for the two ethane monolayer phases. Moreover, they suggest that an essential feature of the herringbone phase dynamics is a coupling of the lowest-frequency librational mode to the vibratory mode normal to the surface. We intend to investigate whether the quantitative agree-

ment between the observed and calculated INS spectra can be improved by use of empirical potentials which more accurately reproduce the monolayer structures. We also plan INS experiments on other hydrocarbon monolayers for which the molecular orientations are known.

This work was partially supported by the National Science Foundation Grants No. DMR-7905958 and No. DMR-8304366, a grant of the Petroleum Research Fund administered by the American Chemical Society, a Dow Chemical Company Grant of the Research Corporation, and a grant from the Danish Natural Science Foundation.

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¹¹For the excitations of interest here [$\Delta E \leq 4.1$ THz (17 meV)], the ethane molecule can be regarded as rigid since the lowest intramolecular mode is the methyl torsion at 8.7 THz (36 meV).

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¹⁵This is consistent with the results of Ref. 1 indicating at least $\frac{2}{3}$ of the Grafoil surface area to be isotropically oriented.

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¹⁸Calculations (Ref. 14) suggest that the large width of the band observed in the \bar{Q} -parallel configuration [Fig. 3(b)] may be due to the enhancement of translational modes parallel to the surface which is neglected in our isotropic substrate approximation. Also, we cannot exclude the possibility of multiple-scattering effects which become more severe as the coverage is increased.