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The Structure and Dynamics of Methane Adsorbed on Graphite [and Discussion]

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The structure and dynamics of methane adsorbed on graphite

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The application of neutron scattering techniques to the study of methane physisorbed on graphite is described.

Two types of adsorbent have been used, graphitized carbon blacks of high and low surface area, and an exfoliated graphite.

Neutron diffraction has been used to determine the structure of the adsorbed layer at low temperatures, part of the phase diagram, and the distance of the methane molecule from the surface. Below a monolayer the methane molecules occupy a triangular lattice with a $\sqrt{3} \times \sqrt{3}$ structure in register with the underlying basal plane that forms the surface of graphite. Just above a monolayer, the lattice contracts out of register with the surface. The molecule–surface distance (carbon to surface) is found to be 3.30 ± 0.05 Å.

Incoherent neutron elastic scattering spectra give the frequencies of the vibrational modes of the adsorbed layer. The frequencies of both whole molecule displacements and torsional motions are found to be similar for directions perpendicular and parallel to the surface, at about 100 and 70 cm^{-1}, respectively.

Rotational tunnelling transitions have been observed in the range 0–200 μeV (0–1.6 cm^{-1}) corresponding to hindered rotation in a potential field of trigonal symmetry. The two types of barrier to rotation are estimated to be 150–200 cm^{-1} high.

All of the experimental parameters are compared with values calculated from atom–atom potentials by using different empirical parameters.

Introduction

The structure and dynamics of adsorbed monatomic and monomolecular layers are currently of interest (Dash 1975). This paper presents a progress report on recent neutron diffraction and spectroscopic measurements of the properties of methane adsorbed on the basal planes of graphite, and exemplifies the type of novel information on such systems that may be obtained by neutron methods (White *et al.* 1978).

The methane–graphite system follows a B.E.T. type II isotherm (Thomy & Duval 1970) characteristic of an adsorbate that completely 'wets' the surface of the adsorbent and therefore forms a monomolecular layer at suitable temperatures and pressures. Elsewhere we have described corresponding experiments on the ammonia–graphite system where the surface–molecule interaction is rather weak and which follows a B.E.T. type III isotherm (Bomchil *et al.* 1979*a*; Gamlen *et al.* 1979). This is characteristic of an adsorbate that does not 'wet' the surface and that shows no tendency at all to form a monolayer. The experiments described in this paper are part of an attempt to find microscopic models for the two-dimensional physical and chemical behaviour of molecules in the monolayer next to the surface.

Materials, methods and thermodynamic properties

For the two types of experiment reported here, methane was used for the incoherent inelastic scattering experiments because of the high incoherent scattering cross section of protons, and deuteromethane (from Merck, Sharp and Dohme) for the diffraction experiments because of the high coherent scattering from deuterons. The relative contributions to the scattering of adsorbate and adsorbent have been summarized by Marlow *et al.* (1977, 1978) and White *et al.* (1978). Three different substrates were used, a high surface area (Vulcan III, 71 $m^2 g^{-1}$) and a low surface area (Sterling FT-G(2700), 11 $m^2 g^{-1}$) graphitized carbon black, both obtained from the National Physical Laboratory and described by Everett *et al.* (1974); and a partly orientated exfoliated graphite (Papyex, *ca.* 20 $m^2 g^{-1}$, mosaic spread *ca.* 30°) obtained from Le Carbone Lorraine (described by Coulomb *et al.* 1977).

The substrates, contained in welded aluminium 'cans' suitable for the neutron experiments, were outgassed for at least 12 h at 10^{-6} mmHg† and 350 °C immediately before the experiment. A background run of the scattering from the sample and container was always recorded before volumetric dosing of the surface with methane. This dosing was done slowly without any physical disturbance of the sample other than the changes in temperature required for complete annealing of the adsorbed layer. Annealing was carried out at temperatures where the methane molecules were known to have a liquid-like mobility (50–100 K). The coverages given in this work were calculated from the quoted surface areas of the adsorbents and a molecular area of 15.7 $Å^2$ for methane.

Preliminary neutron diffraction experiments from strongly diffracting samples were made with the Curran powder diffractometer at the Atomic Energy Research Establishment, Harwell, with an incident neutron wavelength of 2.63 Å‡. For weak reflexions and for studies of the temperature and coverage dependence of the peaks, the high flux diffractometer D1B at the Institut Laue–Langevin was used (Institut Laue–Langevin 1977). The incident flux and wavelength were 9×10^5 neutrons $cm^{-2} s^{-1}$ and 2.4 Å. D1B has a multidetector, making it possible to record the whole pattern at once. Typically, with this instrument, it took 12 h to record a pattern from a 5 g sample at a coverage of 0.5 monolayers.

Neutron inelastic scattering experiments were also done at the Institut Laue–Langevin. Neutron energy loss spectra in the range 0–30 meV (0–240 cm^{-1}) at momentum transfers 1–5 $Å^{-1}$ were recorded on the rotating crystal time of flight spectrometer, IN4, at a resolution of $\Delta E/E$ of 5%. At lower energies, 0–5 meV (0–40 cm^{-1}), the cold neutron time of flight spectrometer, IN5, was used at a resolution of 20 μeV. The back scattering spectrometer, IN10, was used for energy transfers in the range 0–40 μeV (0–0.3 cm^{-1}) with a resolution of 1 μeV (0.008 cm^{-1}).

The methane–graphite system has been extensively studied by classical methods, and adsorption isotherms for many different carbon blacks have been determined over a wide range of temperature (Steele 1974; Thomy & Duval 1970). The isotherm shows the initial formation of a monolayer at low partial pressures of methane followed by multilayer deposition at higher pressures. For particularly homogeneous surfaces, discontinuities in the isotherm show the presence of different phases in the monolayer domain. These have been fully discussed by Thomy & Duval. Attempts to calculate the isosteric heat of adsorption from models of intermolecular forces have been made and are summarized by Steele.

† 1 mmHg ≈ 133.3 Pa. ‡ 1 Å = 10^{-10} m = 10^{-1} nm.

A fundamental difficulty in model calculations of isosteric heats is that there is neither a theoretical nor an empirical basis for the selection of parameters that characterize the molecule–surface potential. The problem is discussed at length by Steele (1974), and one of the aims of the present work is to produce a self-consistent potential that will describe accurately the structure and dynamics of adsorbed phases.

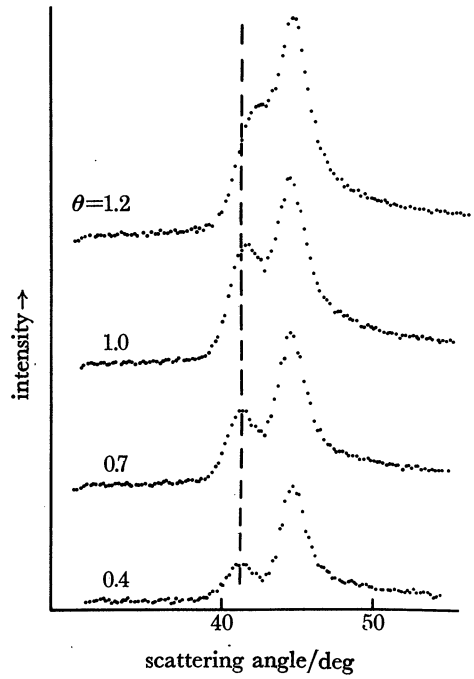

FIGURE 1. Diffraction patterns from methane-d_4 adsorbed at various coverages on Vulcan 111 at 20 K. The background patterns have been subtracted. The incident neutron wavelength was 2.4 Å. θ denotes coverage (see text).

STRUCTURAL STUDIES OF METHANE ADSORBED ON GRAPHITE

(a) *The two-dimensional lattice*

Figure 1 shows part of the neutron diffraction pattern from CD_4 adsorbed on Vulcan III at coverages (θ) between 0.4 and 1.2 monolayers and at a temperature of 20 K. Each pattern is the scattering remaining after subtraction of the background scattering from Vulcan III alone. At all coverages there are two peaks. The one at higher angle coincides with the (002) reflexion from the graphite basal planes and, as we shall discuss below, is associated with interference between the scattering from the adsorbed monolayer and from the basal planes. The lower angle peak at 41.4° (θ = 0.4, λ = 2.4 Å) can only arise from diffraction by the absorbed layer of CD_4.

The asymmetry of the lower angle peak is characteristic of diffraction from a collection of randomly orientated two-dimensional lattices (Warren 1941). The low-angle edge is directly related to the methane–methane distance in the layer. For coverages between 0.4 and 0.9 this lattice parameter is 4.26 Å, consistent with a $\sqrt{3} \times \sqrt{3}$ hexagonal lattice in register with

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the basal planes of graphite that make up nearly all of the underlying surface. This agrees with our earlier results (Marlow *et al.* 1977, 1978) and with recent results of Vora *et al.* (1979) from methane on exfoliated graphite (Grafoil). Even at the lowest coverage, it is clear from the position and intensity of the peak that the molecules cluster into two-dimensional aggregates with the $\sqrt{3} \times \sqrt{3}$ structure rather than spreading uniformly over the surface to form a lattice gas. This shows that lateral attractive interactions between the methane molecules are relatively important in determining the overall structure. The best way to describe the contribution of these forces (as octupole–octupole or atom–atom interactions, for example) is still in doubt, despite recent theoretical calculations (O'Shea & Klein 1979; Maki & Nose 1979). We shall return to this question in the discussion below.

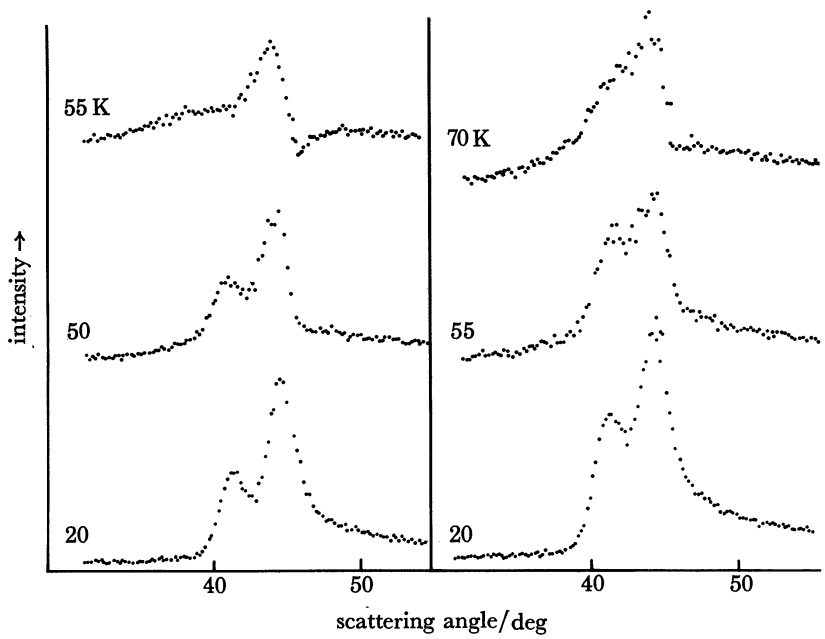

FIGURE 2. Diffraction patterns from methane-d_4 at two different coverages (left-hand side, $\theta = 0.7$; right-hand side, $\theta = 0.9$) and various temperatures on Vulcan III. The background patterns have been subtracted. The incident neutron wavelength was 2.4 Å.

When the coverage is increased above $\theta = 0.9$, the lattice parameter of the adsorbate decreases continuously, showing that the methane layer contracts out of register with the surface of the graphite. This behaviour is to be expected for two reasons. First, the van der Waals diameter of methane is 3.82 Å, markedly less than the methane–methane distance of 4.26 Å in the $\sqrt{3} \times \sqrt{3}$ structure. Thus at higher coverages the geometrical packing factor would be unreasonably low. Secondly, the interaction potential of graphite with an absorbed molecule does not vary much between different positions on the surface, so that little of the molecule–surface interaction energy is lost on going to a more compressed phase. There is a similar balance between these two opposing factors for nitrogen on graphite; this has been discussed by Steele (1977). At very high coverages (greater than two monolayers), the methane diffraction peak shifts until it is underneath the graphite (002) peak.

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(*b*) *The phase diagram of the adsorbate*

The phase diagram for methane physisorbed on graphite can be constructed by following the temperature and coverage dependence of the diffraction peak associated with the two-dimensional lattice. Figure 2 shows the diffraction from CD_4 (background subtracted) between 20 and 70 K for two coverages.

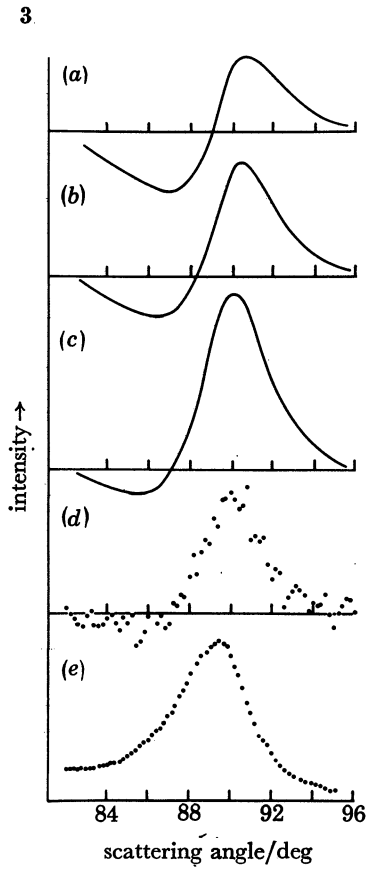
At a coverage of 0.7, the main effect of an increase in temperature between 20 and 55 K is to broaden the diffraction peak. The considerable broadening between 50 and 55 K is associated with melting of the two-dimensional layer. Some melting has already occurred at 50 K and the range over which melting takes place is about 10 K, significantly greater than the range observed for methane on exfoliated graphite (Vora *et al.* 1979). A similar phenomenon has been observed for benzene on the two forms of graphite (Bomchil *et al.* 1979*b*). In the two-dimensional fluid phase at 55 K there is still plenty of intensity in the very broad diffraction peak, and its centre of gravity has shifted to lower angles, indicating an expansion of the layer. At a coverage of one monolayer, only a small fraction of the layer has melted at 55 K, and at 70 K the centre of gravity has not appreciably shifted from its low temperature position. In contrast, at $\theta = 0.4$, the melting point is lowered from about 55 K to about 50 K. We associate this behaviour with the effects of a smaller two-dimensional particle size, similar to the effects of particle size on the melting point of three-dimensional solids (Peppiatt & Sambles 1975). The two-dimensional particle size can be determined from a detailed analysis of the shape of the methane diffraction peak and we are currently attempting to use this information to obtain a quantitative interpretation of the melting point behaviour.

(*c*) *The configuration of adsorbate molecules on the surface*

The effect of an adsorbed layer on the diffraction pattern of the adsorbent may be to enhance or reduce the intensity of a given diffraction peak or even to change its shape to an extent that it appears to have shifted to a slightly different angle. The effect depends mainly upon the phase and amplitude of the scattering from the adsorbed layer relative to that from the series of crystal planes of which the surface is one. To a lesser extent it also depends on the size and shape of the adsorbent particles and the distribution and nature of defects in the appropriate set of crystal planes. The relative phase and amplitude of the scattering from the adsorbate depend on its configuration with respect to the surface, and a quantitative analysis of the interference can therefore yield valuable structural information. The sensitivity of the shape of the interference, or difference, peak to the methane–graphite distance is illustrated in figure 3 for the (004) reflexion from Vulcan III. The solid lines were calculated by using the simple model of Marlow *et al.* (1978) in which the shape of the difference peak is given by the product of the structure factor of the methane layer, taken as part of the one-dimensional lattice of the graphite basal planes, and the profile of the (004) reflexion in the absence of methane. The structure factor changes with angle in such a way that the difference peak is shifted by nearly 1° from the peak from the adsorbent alone. A similar effect has been observed by Larher *et al.* (1979) for adsorption on lead iodide.

The size of the cross interference effect seems to vary in the range $\pm 10\%$, depending on both adsorbate and adsorbent. For methane on Vulcan III at 20 K and at a coverage of 0.7, the intensity of the (002) reflexion is enhanced by about 3%. To make accurate estimates of molecule–surface distances it is therefore essential to avoid any physical disturbance of the

sample during adsorption so that the background subtraction may be as precise as possible. Careful corrections for both self shielding and multiple scattering must be made; ideally, a model should be fitted to the shape of both the difference peak and the reflexion from the adsorbent alone. An upper limit may be put on the experimental correction necessary for Vulcan by using the diffraction patterns measured for ammonia-d_3 on Vulcan (Gamlen *et al.* 1979). At low temperatures most of the ammonia is desorbed from the basal planes of graphite and there should therefore be negligible cross interference between the adsorbate and the graphite (00*l*) planes. Indeed, only small intensity changes are observed, less than 0.5%.



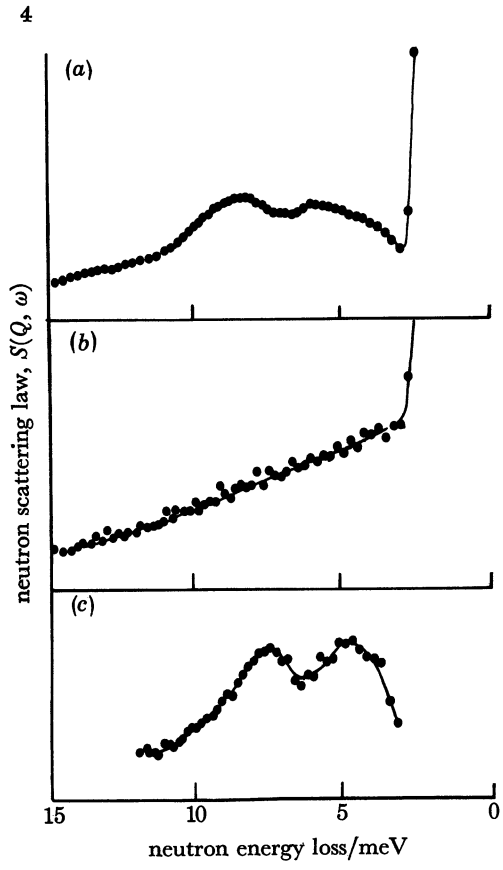


FIGURE 3. The interference effect of adsorbed CD_4 on the shape of the (004) reflexion of Vulcan III. (*a*), (*b*), (*c*) Profiles calculated for surface–molecule (carbon to carbon) distances of 3.25, 3.27 and 3.29 Å respectively; (*d*) the difference pattern observed at a coverage of one monolayer; (*e*) the profile observed for Vulcan III alone.

FIGURE 4. Vibrational spectra (neutron energy loss) of methane adsorbed on Vulcan III. (*a*) CH_4 at 10 K, coverage = 0.7; (*b*) CH_4 at 40 K, coverage = 0.7; (*c*) CD_4 at 10 K, coverage = 0.7. Incident neutron energy, 25 meV.

We have recently devised a quantitative model for describing the profiles of cross interference effects from layers adsorbed on carbon blacks. The model includes all of the factors mentioned above, as well as making allowance for thermal motion of the adsorbate. It will be described in full elsewhere. For methane at 20 K and at a coverage of 0.7 the molecule–surface distance

(carbon to carbon) is found to be 3.3 ± 0.05 Å, as much as 10% shorter than predicted by many models of the molecule–surface potential (Steele 1974) though only slightly shorter than predicted by atom–atom potential calculations (see table 1). At higher temperatures and coverages, changes in the shape of the (002) difference peak occur which result from quite small changes in the molecule–surface distance. Thus the change in the (002) profile when the temperature changes from 50 to 55 K at a coverage of 0.4 (figure 2) is caused by a 10% increase in the molecule–surface distance when the two-dimensional layer melts.

The dynamics of adsorbed methane

The dynamics of the adsorbed layer can be studied by incoherent inelastic neutron scattering. Incoherent scattering is predominantly from motions involving displacement of hydrogen atoms and therefore the contribution from the adsorbate is much stronger than that from the carbon substrate. Also, there is no cross interference effect in incoherent scattering so that, provided that any coherent scattering can be eliminated, the spectrum resulting from motion of the absorbed layer can be obtained by straight subtraction of the spectrum of the adsorbent from that of adsorbent plus adsorbate. Another feature of incoherent scattering is that spectra may be measured at very high resolution (less than 1 μeV (0.008 cm^{-1})) down to low energy transfers, making it possible to measure accurately any very low energy transitions associated with rotational motion.

(a) *Vibrational spectra*

The partial differential cross section for incoherent one phonon scattering from a cubic lattice containing only one kind of atom is

$$\frac{\partial^2\sigma_{\text{incoh}}}{\partial\Omega\,\partial E'} = \frac{k'}{k}\frac{N\sigma_{\text{incoh}}}{4\pi}\frac{Q^2\langle u^2\rangle}{2M}(n_s+\tfrac{1}{2}\pm\tfrac{1}{2})\exp(-2W)\frac{Z(\omega)}{\omega},$$

where $Z(\omega)$ is the density of vibrational states, $\exp(-2W)$ the Debye–Waller factor, $\langle u^2\rangle$ the mean square amplitude of vibration, M the mass of the vibrating atom, n_s the quantum number of mode s, $\boldsymbol{k}$ and $\boldsymbol{k}'$ the wavevectors (magnitudes k and k') of the ingoing and outgoing neutrons, $\boldsymbol{Q}$, the momentum transfer, and σ_{incoh} the incoherent scattering cross section. The important features of the formula are twofold.

(i) If the incoherent scattering cross section of the atom is large, the spectrum is intense.

(ii) The intensity increases with both Q^2 and $\langle u^2\rangle$ over the normally accessible range of Q. At higher values of Q the Debye–Waller factor will start to decrease rapidly and so reduce the intensity again. For anisotropic motion and an orientated sample, the formula becomes more complicated but the only important change is that the factor $Q^2\langle u^2\rangle$ is replaced by a term proportional to $\langle(\boldsymbol{Q}\cdot\boldsymbol{u})^2\rangle$. The intensity of a band then depends on the relative orientation of $\boldsymbol{Q}$ and $\boldsymbol{u}$. This is an important factor when studying the spectra of adsorbates on orientated adsorbents such as Papyex. With large amplitude motions such as might be expected from physisorbed species, overtones and combinations (multiphonon processes) of fundamental vibrations may appear in the spectrum. Their intensities relative to the fundamentals will vary approximately as $(Q^2)^n$ where n is the number of quanta involved.

An adsorbed methane molecule has six degrees of freedom, two translations along axes parallel to the surface, $\nu_T(\|)$, one translation perpendicular to the surface, $\nu_T(\perp)$, one rotation about the perpendicular axis, $\nu_R(\perp)$, and two rotations about the parallel axes, $\nu_R(\|)$. In the

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limit of large barriers to both transition and rotation, these motions will become six vibrational modes which may be distinguished in several ways.

Deuteration will shift the translational modes by a relatively smaller amount than the rotational modes because the carbon atom moves in the former but not the latter. The modes will also be differently polarized. If $\boldsymbol{Q}$ is perpendicular to the surface, only $\nu_{\mathrm{T}}(\perp)$ and $\nu_{\mathrm{R}}(\parallel)$ will be observed. If $\boldsymbol{Q}$ is parallel to the surface, the spectrum will be dominated by $\nu_{\mathrm{T}}(\parallel)$ and $\nu_{\mathrm{R}}(\perp)$, while $\nu_{\mathrm{R}}(\parallel)$ may also appear weakly. Finally some of the modes should be strongly dispersed. This will lead to a rather broad density of states giving a more diffuse spectrum whose maximum may also depend slightly on Q. Strongly dispersed modes will be those where the force field on a given methane molecule mainly originates from its interactions with neighbouring molecules. Since all theoretical calculations show that, for an isolated methane molecule on graphite, the barriers to translation across the surface or to rotation about an axis perpendicular to the surface are very small, we can expect either that the frequencies of $\nu_{\mathrm{T}}(\parallel)$ and $\nu_{\mathrm{R}}(\perp)$ will be near zero or that they will occur in the range up to about 100 cm^{-1} and show substantial dispersion. Taub *et al.* (1975) have measured the phonon spectrum of $^{36}\mathrm{Ar}$ on graphite and shown that the strongly dispersed $\nu_{\mathrm{T}}(\parallel)$ modes can be explained without invoking any surface molecule interaction.

Vibrational spectra of CH_4 on Vulcan were recorded over a range of coverage from 0.2 to 2 monolayers at temperatures from 10 to 70 K. Spectra of CD_4 on Vulcan and of CH_4 on Papyex were also measured. The spectra were recorded in neutron energy loss over a range 0–15 meV (0–120 cm^{-1}). Coherent scattering effects were eliminated by working at different wavelengths. The vibrational spectra of the adsorbate were obtained by subtraction of the background and, since there was only slight variation of the peak positions with Q, spectra recorded at different angles were added together to improve the statistics.

Figure 4*a*, *b* shows spectra from 0.7 monolayers of CH_4 on Vulcan at two different temperatures, 10 and 40 K. There are two pronounced peaks in the density of states at 10 K which completely disappear at 40 K even though the two-dimensional layer is still well below its melting point. The disappearance of the peaks implies that all the vibrations are strongly coupled to a diffusive motion at the higher temperature. Inelastic and quasielastic spectra at lower energy transfers (see below) show that, at 40 K, methane is undergoing rotational diffusion and it is therefore probable that all the vibrational modes are coupled to the rotation. In any case, it is clearly essential to measure the spectra of physisorbed species at as low a temperature as possible.

There are two strong peaks in the density of states at about 8.5 meV (70 cm^{-1}) and 6.2 meV (50 cm^{-1}) with a weaker peak at about 12.5 meV (100 cm^{-1}). Figure 4*c* shows the effects of deuteration (CD_4), again at a coverage of 0.7. The two peaks previously at 8.5 and 6.2 meV are now shifted to 7.6 (60 cm^{-1}) and 4.6 meV (38 cm^{-1}) giving isotope ratios of 1.15 and 1.35 respectively. The simplest interpretation would be that the higher energy peak is associated predominantly with translational modes while the lower energy peak is associated predominantly with rotation. The isotope shifts may, however, be misleading because of translation–rotation coupling and the overlap of widely dispersed modes.

Spectra from CH_4 on Papyex at a coverage of 0.7 are shown in figure 5. The general similarity of the spectra with $\boldsymbol{Q}$ perpendicular and $\boldsymbol{Q}$ parallel to the surface might suggest that the adsorbent is not very well orientated. The mosaic spread of the surface planes of Papyex is about 30°, and the material contains a proportion of randomly orientated crystallites. The

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contribution of vibrations with displacements in the direction of $\boldsymbol{Q}$ relative to those with displacements perpendicular to $\boldsymbol{Q}$ is

$$u^2 \cos^2\theta / u^2 \sin^2\theta,$$

so that even with $\boldsymbol{Q}$ misaligned by 30° the polarization is still strong. In measurements of the tunnelling transitions to be described below, the extent of polarization is observed to be almost complete so that it is reasonable to assume that it is also complete in the vibrational spectra. Since the spectra were obtained on a time of flight spectrometer there is also some variation in the direction of $\boldsymbol{Q}$ with energy. However, over the range of angles used for the spectra in figure 5 the direction of $\boldsymbol{Q}$ is within 10° of the specified direction up to energy transfers of about 12 meV.

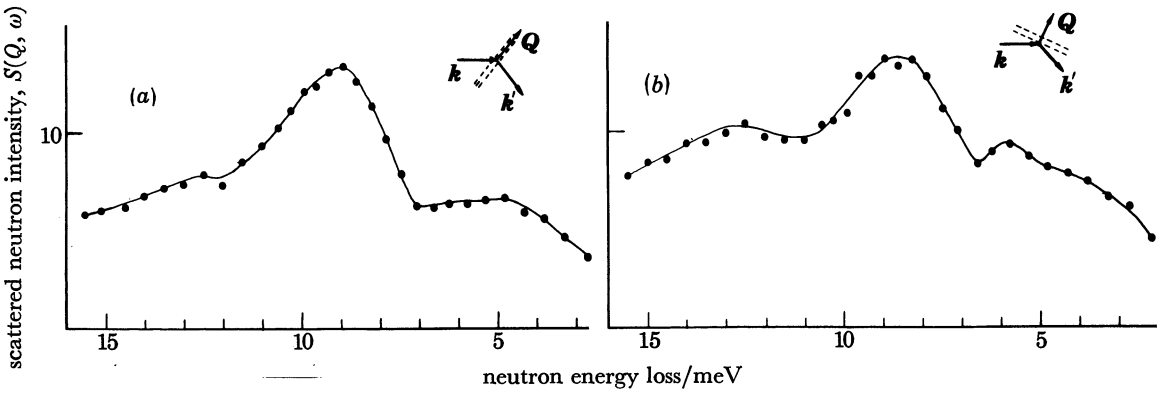

FIGURE 5. Vibrational spectra of methane adsorbed on exfoliated graphite (Papyex) at a coverage of 0.7 monolayers and a temperature of 10 K. (*a*) $\boldsymbol{Q}$ parallel to the surface; (*b*) $\boldsymbol{Q}$ perpendicular to the surface.

The main difference between the two spectra is in the relative intensity of the bands, the band at 12.5 meV being markedly stronger when $\boldsymbol{Q}$ is perpendicular to the surface. There are also small differences in energy. For example, the central peak is at 8.5 meV when $\boldsymbol{Q}$ is perpendicular but at 9 meV when $\boldsymbol{Q}$ is parallel. When $\boldsymbol{Q}$ is perpendicular, we expect to observe only the translational motion perpendicular to the surface ($\nu_T(\perp)$) and the two rotations about axes parallel to the surface ($\nu_R(\parallel)$). On the basis of intensity and polarization we assign the peak at 8.5 meV to $\nu_R(\parallel)$ and the peak at about 13 meV to $\nu_T(\perp)$. When $\boldsymbol{Q}$ is parallel to the surface, we expect to see two translational modes ($\nu_T(\parallel)$) and one rotational mode ($\nu_R(\perp)$) both strongly dispersed. Again, rotational modes are expected to be the most intense and we therefore assign the peak at 9 meV to $\nu_R(\perp)$. Taub *et al.* (1975) have calculated the dispersion curves for $\nu_T(\parallel)$ for two-dimensional argon on a triangular lattice by using a Lennard–Jones interaction potential. There are two main peaks in the density of states at 6 and 3.5 meV. Methane has the same lattice symmetry and its Lennard–Jones parameters are sufficiently similar to those of argon that the only difference between the two will be their different masses. On this basis the peaks in the translational density of states of methane would be at 9 and 5.3 meV. Thus the peak at 9 meV in figure 5*a* may also be partly due to translational motion parallel to the surface, which would be more consistent with the isotope effect. The peak at about 5 meV may then be the second maximum in the translational density of states. An analysis of the tunnelling spectrum presented below requires $\nu_R(\perp)$ to be close in frequency to $\nu_R(\parallel)$ consistent with the assignment given.

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The final assignments of the vibrations of adsorbed methane are given in table 1, and $\nu_T(\perp)$ is compared with calculated frequencies in table 3. The similarity of the energies of the three rotational modes indicates that an adsorbed methane molecule is in a fairly isotropic potential field. This is discussed further below.

TABLE 1. WAVENUMBERS OF MAXIMA IN THE DENSITY OF STATES OF METHANE ADSORBED ON GRAPHITE (PAPYEX)

wavenumber/cm^{-1}	assignment	description
35–50	$\nu_T(\parallel)$	translational motion on plane of surface, some contribution from rotation
47 ± 2	$\nu_R(\parallel)$	torsion about axes parallel to surface
69 ± 3	$\nu_R(\parallel)$	rotation of molecule about axes parallel to surface
73 ± 3	$\nu_R(\perp)$	rotational motion in plane of surface
100–110	$\nu_T(\perp)$	displacement of whole molecule in direction perpendicular to surface

(*b*) *Rotational motion*

For a free methane molecule the $J = 0 \rightarrow 1$ rotational transition requires an energy of 1.25 meV (10 cm^{-1}). For coverages less than one monolayer, no free rotational transition was observed in the incoherent scattering spectrum. This is as expected because the surface potential must be quite strong to give rise to the energies of torsional oscillations given in table 1. However, for a bilayer of methane on Vulcan a distinct excitation was observed at 720 μeV, indicating a slightly hindered rotation of methane molecules in the second layer (Newbery *et al.* 1978). The energy of the transition is close to that observed for methane molecules isolated in rare gas matrices (Kataoka *et al.* 1978).

(*c*) *Rotational tunnelling*

For coverages of methane less than about a monolayer, sharp transitions between 0 and 200 μeV (1.6 cm^{-1}) are observed in the high-resolution spectrum of methane adsorbed on Vulcan. These have been attributed to rotational tunnelling of the methane molecule in the surface potential field (Newbery *et al.* 1978). Figure 6 shows the spectra for CH_4 on Vulcan at a coverage of 0.7 and at a number of temperatures. They are similar in appearance to the tunnelling spectra of solid methane (Press & Kollmar 1975) but with transition energies lower by about 25%. This similarity suggests an unexpected isotropy of the crystal potential around an adsorbed methane molecule.

To resolve any finer structure in the rotational tunnelling spectrum, measurements were made with Papyex as adsorbent and with the momentum transfer, $\boldsymbol{Q}$, parallel and perpendicular to the surface planes. The two spectra and their assignments are shown in figure 7. Each of the transitions previously observed (figure 6) is now split into two and most of them are strongly polarized. With $\boldsymbol{Q}$ parallel to the surface the central elastic peak is also broadened, suggesting that there is a further low-energy transition, not observed owing to lack of resolution at the IN5 spectrometer. This transition has now been observed directly at 17 μeV (0.14 cm^{-1}) by using the 1 μeV resolution of IN10 and is shown in figure 8*b*. Its observation allows the complete energy level diagram to be drawn, summarizing the five nuclear spin allowed transitions. This is shown in figure 8*a* and the energies of the transitions are given in table 2.

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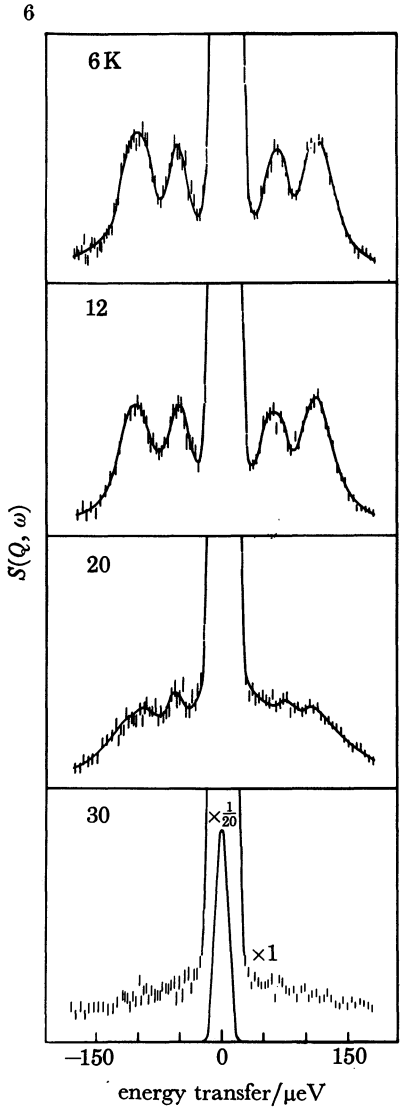

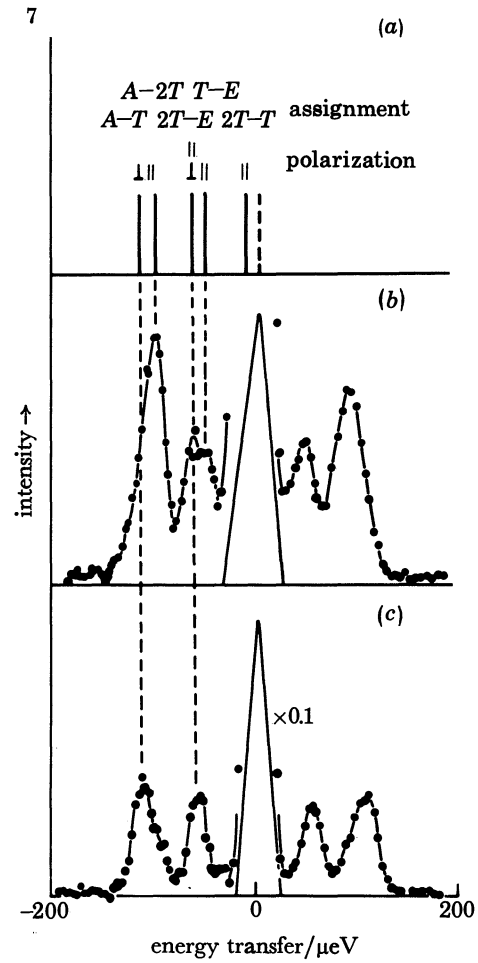

FIGURE 6. Rotational tunnelling spectra of methane adsorbed on Vulcan III at various temperatures. Coverage, 0.7 monolayers.

FIGURE 7. Rotational tunnelling spectra of methane adsorbed on exfoliated graphite (Papyex). (*a*) Assignment and polarization of transitions; (*b*) **Q** parallel to the surface; (*c*) **Q** perpendicular to the surface. Coverage, 0.7; temperature, 4 K.

TABLE 2. ENERGIES OF ROTATIONAL TUNNELLING TRANSITIONS OF ADSORBED METHANE

energy/μeV	assignment
17 ± 1	$2T \rightarrow T$
39 ± 2	$T \rightarrow E$
56 ± 2	$2T \rightarrow E$
94 ± 2	$A \rightarrow 2T$
112 ± 2	$A \rightarrow T$

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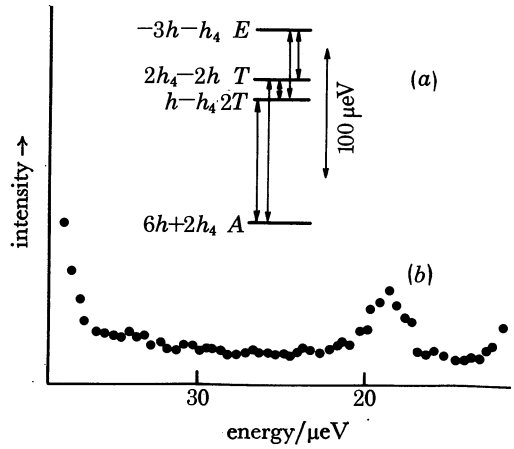

FIGURE 8. High-resolution spectrum of the rotational tunnelling spectrum of methane on exfoliated graphite (Papyex). Coverage, 0.7 layers; temperature, 4 K; Q parallel to the surface. The energy levels are given in (*a*) in terms of the two parameters h and h_4 (see text).

The energy level pattern shown in figure 8*a* is characteristic of a tetrahedral molecule tunnelling in a potential field with trigonal symmetry but which is not far from tetrahedral. In a tetrahedral field the two central levels coalesce and the energy of the $A \rightarrow T$ transition should then be approximately twice that of the $T \rightarrow E$ transition, as has been observed for phase II of solid CH_4 (Press & Kollmar 1975) and as is observed here for the centre of gravity of the two transitions for adsorbed methane. The earlier conclusion of Newbery *et al.* (1978), that the adsorbed methane on Vulcan was undergoing rotational diffusion about an axis perpendicular to the surface, was based on the presence of an envelope of scattering underneath the tunnelling peaks which resembled quasielastic scattering. This envelope is not present in the Papyex spectra, suggesting that it has its origin in methane molecules adsorbed at heterogeneities on the Vulcan or at defects in the two-dimensional layer.

The general procedure for calculating the rotational tunnelling levels has been described by Hüller & Kroll (1975). The potential energy is expanded as a series of cubic rotator functions whose allowed coefficients are determined by molecule and site symmetry. As in rotational tunnelling about one axis, the series rapidly converges and it is necessary to include only the lowest terms in the expansion. If the barrier to rotation is not too low, 'pocket state' wavefunctions form an adequate basis set. These have the properties that they are large in the region of a potential minimum but small elsewhere, they have an adjustable parameter so that a variational treatment may be used to minimize the final energies of the tunnelling levels, and they are readily adapted to the symmetry of the problem. The pocket states are not exact wavefunctions because of the finite probability of tunnelling between potential minima, and so the Hamiltonian is not diagonal. By using the pocket state wavefunctions as a basis, the matrix elements may be evaluated and the eigenvalues minimized with respect to the variational parameter. Because they are small, these off-diagonal elements in the Hamiltonian determine the tunnelling splitting directly. The energy levels may therefore be expressed in terms of these elements without explicitly evaluating them.

Hüller (1977) has derived a Hamiltonian for CH_4 in a tetrahedral field which may easily be adapted to the present problem. There are three matrix elements that might be important, H, h and h_4, which are respectively the matrix elements for 180° rotation about twofold axes

in CH_4, 120° rotation about one of the threefold axes pointing towards the surface, and 120° rotation about the threefold axis perpendicular to the surface. H is likely to be much smaller than h or h_4 because the overlap between pocket states 180° apart will be much less than between those that are 120° apart. Also, the ratio of the energies of the $A \rightarrow T$ and $T \rightarrow E$ transitions becomes exactly two, as observed, only when H is insignificant compared with h and h_4. Neglecting H, the relative spacing of the levels in terms of h and h_4 is given in figure 8*a*.

The splitting of the T levels is proportional to the difference between h and h_4, but it is not possible to determine the sign of the splitting from the energies of the tunnelling transitions alone. However, the ratio of the intensities of the A–T transitions with $\boldsymbol{Q}$ parallel and perpendicular to the surface is about two, suggesting on a simple argument of degeneracy that the former is the $A \rightarrow 2T$ transition. This completes the assignment of the transitions given in table 2, from which h and h_4 are found to be -14 and -8 μeV (0.11 and 0.06 cm^{-1}) respectively.

Since $|h_4|$ is smaller than $|h|$, the overlap between the pocket state wavefunctions must be smaller for rotation about an axis perpendicular to the surface than about the three equivalent C–H bonds pointing towards the surface. The barrier to rotation about the perpendicular axis must therefore be the greater one. We are currently making a full quantitative analysis of h and h_4 to obtain accurate values of the two barriers. At present, we can only give an approximate estimate of 150–200 cm^{-1} for both barrier heights with one about 25% greater than the other. The similarity of the two barrier heights means that the two torsional frequencies, $\nu_R(\perp)$ and $\nu_R(\parallel)$, must be similar in frequency.

Discussion

Table 3 summarizes the experimental parameters for methane on graphite as determined by neutron scattering. This is the first time that such a complete set of data has been assembled for a physisorbed molecule. Also included for comparison are the corresponding quantities calculated by using atom–atom potentials with different sets of empirical parameters. The calculation is based on a potential of the form

$$V = \tfrac{1}{2} \sum_i V(r_i) = -A/r_i^6 + B \exp(-Cr_i),$$

where A, B and C are constants appropriate to pairs of atoms (Williams 1967). Interactions with atoms in the first layer of the surface out to a distance of 18 Å from the methane molecule have been included. Terms arising from molecule–surface and molecule–molecule interactions are given separately and values are given for the methane molecule in two possible positions on the surface. The first and second differentials of the potential were used to obtain the equilibrium surface–molecule distance and the vibrational force constant respectively.

Some of the empirical parameter sets account quite well for the isosteric heat of adsorption and the distance of methane from the surface but they all grossly overestimate the changes in potential energy for any kind of displacement from the equilibrium position. The calculated values of the vibrational frequencies and barriers to rotation are therefore all too high. Despite the obvious deficiencies of the atom–atom calculations, they do allow some rationalization of the structural information derived from the diffraction data.

The methane–methane interaction energy calculated for the tripod configuration is a large fraction of the isosteric heat of adsorption. This interaction also provides the cohesion necessary for the formation of aggregates of methane molecules as observed at coverages down to 0.4

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TABLE 3. COMPARISON OF ATOM–ATOM POTENTIAL CALCULATIONS AND EXPERIMENTAL MEASUREMENTS FOR THE $\sqrt{3} \times \sqrt{3}$ PHASE OF METHANE ADSORBED ON GRAPHITE

source of empirical parameters	binding energy of isolated molecule / kJ mol^{-1}	methane–methane interaction energy / kJ mol^{-1} [cm^{-1}]	isosteric heat of adsorption at 130 K and zero coverage / kJ mol^{-1} [cm^{-1}]	distance from surface (C–C) / nm	vibration frequency perpendicular to surface E / cm^{-1}	barrier to rotation about perpendicular axis/cm^{-1}: methane–surface contribution	barrier to rotation about perpendicular axis/cm^{-1}: methane–methane contribution	barrier to rotation about perpendicular axis/cm^{-1}: total	barrier to rotation about C–H bond/cm^{-1}
Kitaigorodskii†	17.6 (17.3)	6.6 [505]	14.9 [1140]	0.325 (0.327)	102	57 (2)	582	639 (580)	614 (367)
Taddei (A)‡	17.5 (17.4)	5.2 [400]	14.8 [1130]	0.333 (0.333)	98	40 (2)	359	399 (357)	447 (288)
Taddei (B)‡	15.7 (15.8)	3.5 [270]	13.0 [990]	0.335 (0.335)	93	26 (1)	143	169 (142)	291 (196)
Williams no. 4§	16.6 (16.8)	3.8 [290]	13.9 [1060]	0.332 (0.331)	86	20 (1)	261	281 (260)	207 (173)
Williams‖	14.9 (15.0)	3.5 [270]	12.2 [930]	0.333 (0.332)	93	19 (1)	207	226 (206)	208 (173)
experiment	—	—	12.3¶	0.330 ± 0.005	100 ± 5	—	—	150–200	150–200

References: †, Kitaigorodskii (1973); ‡, Taddei *et al.* (1977); §, Williams (1967); ‖, Williams (1970); ¶, Kiselev & Poshkus (1976).

The barrier to rotation about C–H bond refers to one of the three equivalent C–H bonds pointing towards the surface. Values in parentheses are calculated for methane over the centre of a carbon hexagon, the others are for methane directly over a carbon atom. The isosteric heat is obtained from the binding energy by adding $\frac{5}{2}RT$ (three rotational, two translational, and one vibrational degree of freedom, $q_{st} = -\Delta U_0^0 - \frac{5}{2}RT$). The calculated vibration frequencies are those appropriate to a Morse potential.

monolayers. The tunnelling spectrum observed at 0.2 monolayers is similar to that observed at higher coverages showing that the aggregates persist to even lower coverages.

At a coverage of 0.9 monolayers the $\sqrt{3} \times \sqrt{3}$ structure of adsorbed methane changes to a more compressed phase. The lattice parameter decreases continuously over a range of coverage. Our results with Vulcan III as adsorbent agree here both with the results of Vora *et al.* (1979) for exfoliated graphite and with the theoretical predictions of Bak *et al.* (1979) for such a phase change in a two-dimensional lattice. A major factor allowing this phase change is the small variation of the surface–molecule interaction energy across the surface (column 1 of table 3). Indeed, the surface is so smooth that it is not possible to predict whether the equilibrium position of the methane in its low coverage phase is above the centre of a carbon hexagon or directly above one of the carbon atoms on the surface. Further studies of the intensity changes of the graphite (10) reflexion on adsorption are needed to resolve this point. Carlos & Cole (1979) have suggested that anisotropic pair potentials give a better description of the atom–graphite interaction and, since this potential enhances the difference in energy between the two sites, application of such anisotropy to the atom–atom calculations might distinguish more clearly between the two possible configurations. Pursuit of this potential is at present the most obvious single improvement that could be made to available potentials.

The temperature dependence of the tunnelling splitting presents new features compared with the behaviour of molecular crystals, where a distinct shift in energy as well as broadening often occurs. At present there is no known mechanism for the behaviour observed.

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Discussion

A. D. Buckingham, F.R.S. (*University Chemical Laboratory, Cambridge, U.K.*). Could Dr White clarify the nature of the torsional vibrations of the adsorbed methane molecules? What is the source of the potential barrier?

Secondly, would Dr White relate the potential energy deduced to other experimental results, for example the enthalpy of adsorption? Is there evidence for non-additive potentials?

J. W. White. Table 3 in the paper provides a number of the answers to Professor Buckingham's questions. The results are calculations for the $\sqrt{3} \times \sqrt{3}$ registered phase at low temperatures.

From the first two columns one can see that both graphite–methane and methane–methane interactions contribute to the hindering potential for molecular motion. Assuming a tripod configuration for the adsorbed molecule, the torsional vibrations occur about a C3 axis perpendicular to the surface and about another pair of axes, which may be chosen parallel to the surface.

Since there is coupling between neighbouring molecules, the torsional modes are almost certainly dispersed in the two-dimensional Brillouin zone. What we observe are the density of states maxima. The tunnelling results give a precise method of testing models for the potential barrier to rotation.

It can be seen that for either set of axes all of the commonly used 6-exp, atom–atom potential parameter sets give barriers to rotation that are too high. The calculated enthalpies of adsorption are also somewhat high.

I presume that by non-additive potentials Professor Buckingham means non-additivity of the molecule–surface and molecule–molecule parts to give, for example, isosteric heat of adsorption. The calculated values certainly do not add up to those found experimentally. As commented on in the paper, we are not sure whether to attribute this to anisotropic polarisation effects in the potential for adsorption on graphite or to real non-additive effects (Axelrod–Teller effects, etc.).

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