Neutron-scattering Spectra from the Hindered Rotation of Methane in Methane + Krypton Mixtures Adsorbed on Graphite

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Incoherent neutron-scattering spectra associated with the hindered rotation of CH_4 in $CH_4 + Kr$ mixtures adsorbed on graphite are described. The spectra, taken over a composition range from 0.3 to 0.9 mole fraction of Kr, indicate partial phase separation into domains of pure CH_4 and krypton-rich domains.

Using the energies, intensities and polarization of the transitions the spectra of CH_4 in the krypton-rich domains have been assigned and found to be consistent with a potential field of trigonal symmetry.

Quantitative calculations of the barriers to rotation have been made using a procedure which uses symmetrized free-rotor functions as a basis set. In the limit when CH_4 is nearly completely surrounded by Kr atoms the barrier heights for threefold rotation about the unique C—H axis normal to the surface and about each of the three equivalent C—H bonds are 31 ± 5 and $79 \pm 10 \, cm^{-1}$, respectively. As the Kr/CH_4 ratio is reduced the unique barrier height increases from 31 (10:1), through 39 (6:1) and 47 (2:1) to 55 cm^{-1} for a 1:1 mixture. The other barrier height does not change over the same concentration range.

Atom–atom potential calculations on an ordered $CH_4 + Kr_2$ mixture with each CH_4 surrounded by six Kr atoms are able to account for the barrier about the equivalent C—H bonds but not for that about the unique axis.

Although restricted to species with small moments of inertia, incoherent neutron scattering from hindered rotational motion in condensed phases gives valuable information about intermolecular forces.[1] This is particularly the case for molecules on a surface where there is a shortage of detailed information on the interactions, and it is also often easier to interpret the spectra because the structure is simpler than in bulk solids. For example, in layers commensurate with the surface the molecules are held at a fixed distance from one another and this distance may have the same value for a variety of different adsorbed species.

In a previous paper we interpreted in detail the neutron spectra associated with the rotational tunnelling of a CH_4 molecule in its commensurate $(\sqrt{3} \times \sqrt{3}R30°)$ phase on graphite, obtaining values of the two different barriers to rotation.[2] As a result of comparable contributions of molecule–molecule and molecule–surface interactions to both barriers the trigonal potential field that governs the rotation of the CH_4 molecule on graphite is not far from being tetrahedral. It would be useful to be able to make an experimental distinction between these two contributions to the potential. In principle this could be done by studying the rotation of CH_4 in mixtures with other molecules on the surface of graphite. With complete mixing and low concentrations of CH_4 the spectrum should become that of CH_4 on graphite,

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but with a molecule–molecule potential determined by the interaction of CH_4 with six surrounding molecules of a species other than CH_4 itself. Furthermore, if the second species were also to form the commensurate $\sqrt{3} \times \sqrt{3}$ structure the separation of the molecules would be defined by the graphite and there should be none of the geometrical factors that complicate the interpretation of comparable experiments on the hindered rotation of impurities in solids or of matrix-isolated species. However, in contrast to the latter experiment there is the practical limitation that the adsorption experiments are done under equilibrium conditions and are therefore limited by the extent to which CH_4 will mix with a second component.

    The most promising mixture for studying on graphite is $CH_4 + Kr$. CH_4 and Kr have similar Lennard-Jones parameters, suggesting that they ought to mix completely in all phases. Indeed, they are known to mix completely in the bulk solid to form a continuous series of solid solution.[3] Their adsorptions on graphite are almost identical, both forming commensurate $\sqrt{3} \times \sqrt{3}$ phases up to a coverage close to a monolayer, when they then form incommensurate phases of similar lattice parameter.[4] This paper presents incoherent neutron-scattering spectra for a range of $Kr + CH_4$ mixtures adsorbed on graphite at coverages where the commensurate phase is expected to be stable.

EXPERIMENTAL

    The absorbent used was the recompressed, exfoliated graphite, Papyex, the same material as used in earlier experiments on CH_4 on graphite.[2] The sample cans and outgassing and dosing procedures were the same as in ref. (2). In order to compensate for the smaller amounts of CH_4 present in the mixtures, the amount of Papyex in the beam was increased from the earlier experiments and varied from 30 to 120 g. With a specific surface area of ca. $20 \, m^2 \, g^{-1}$ and a CH_4/Kr ratio of 0.1 this meant that with a 120 g sample of Papyex there was a maximum of ca. 0.04 g of CH_4 in the beam. This is close to the limit of sensitivity. In all cases the coverage was chosen to be 0.7–0.8 monolayers. Although there is some uncertainty in the absolute determination of the coverage, it was shown to be below the coverage for the commensurate–incommensurate phase change for CH_4 simply by recording the spectrum of pure CH_4 on graphite.

    All experiments were done on the multichopper time-of-flight spectrometer IN5 at the Institute Laue–Langevin, Grenoble.[5] The wavelength of the incident neutrons was 6 Å with a resolution of 45 μeV, 8 Å with a resolution of 30 μeV or 10 Å with a resolutiom of 20 μeV. Scattering was measured at the highest possible angles to give an average momentum transfer (Q) of ca. 1.7, 1.2 and 1 Å^{-1}, respectively. The majority of experiments were done with the Papyex sheets stacked so that Q was parallel to the surface of the graphite.

RESULTS

    Two surprising features in the spectra of $CH_4 + Kr$ mixtures on graphite have been discussed previously.[4] The first is that the pure-CH_4 tunnelling spectrum persists with reasonable intensity in spectra of mixtures up to Kr concentrations of ca. 1/3 (mole fraction). This indicates that mixing is far from complete. The tunnelling spectrum is very sensitive to changes in both barrier height and symmetry of the potential. For example, calculations show that a reduction of 5% in either of the barriers to rotation in the pure CH_4 layer leads to a reduction of ca. 30% in one of the higher energy ($A \leftrightarrow T$) transitions. Each CH_4 molecule in the layer is surrounded by six nearest neighbours. If mixing is uniform an average of one of the nearest neighbours will be replaced by Kr when the Kr concentration is 1/6.

As well as lowering the symmetry of the potential this would be expected to change the barriers to rotation significantly and hence to change the tunnelling spectrum by an easily measurable amount. In solutions of Kr in bulk solid CH_4 the structure of the tunnelling spectrum of CH_4 is indeed lost when the mole fraction of Kr reaches 0.08.[1] That this does not happen in the adsorbed mixtures shows that even when the Kr concentration is 1/3 there are domains of pure CH_4. Mixing is not complete.

The second surprising feature is that lines appear in the spectrum at energies $> ca.$ 500 μeV at Kr concentrations of 1/3 upwards. Although they sharpen and shift towards higher energies as the concentration of Kr is increased up to 0.9, these additional changes correspond to relatively small changes in the barriers to rotation. To give the reasonably simple and sharp spectra observed the rotational potential would have to be of fairly high symmetry and reasonably well defined. This will only occur if mixing is incomplete and/or there is a certain amount of ordering in the mixture. For example, if the nearest neighbours are three each of CH_4 and Kr and we ignore the effect of the surface, there are three possible potentials, only one of high symmetry. For two nearest neighbours of one kind and four of another there are again three potentials, none of high symmetry. Complete mixing would therefore give a set of complicated overlapping spectra and it would probably be impossible to resolve any one feature. The maximum value of the first transition for free rotation of CH_4 would be at 1300 μeV, and lines at energies $> ca.$ 500 μeV will be associated with CH_4 molecules rotating in a field with quite low potential barriers. This suggests that the molecules giving rise to these spectra have more Kr atoms as nearest neighbours than CH_4 molecules. That the spectrum changes only by a small amount as the Kr concentration increases from 0.3 to 0.9 also indicates that these lines are associated with CH_4 molecules almost completely surrounded by Kr atoms.

There is therefore strong evidence for a separation into pure-CH_4 domains and Kr-rich domains. An earlier interpretation of these results suggested that there was phase separation between a pure-CH_4 phase and a phase of composition CH_4Kr_2.[4] If this second phase is also structurally ordered it could have a structure in which each CH_4 is surrounded by six Kr atoms. This would largely account for the observations above, but further measurements described below indicate that it is an oversimplified picture. We shall not consider any further the question of phase separation but concentrate on interpreting the spectrum of the CH_4 molecule in the Kr-rich domains.

Fig. 1 shows spectra of a series of $CH_4 + Kr$ mixtures in the region 500–1000 μeV. The coverage is 0.8 and Q is parallel to the surface. There are at least two lines, one at *ca.* 650 μeV and the other at *ca.* 800 μeV. Values of the energies of all the lines observed are given in table 1. The effects of increasing the concentration of Kr are to sharpen the lines and to increase their separation, although the centre of gravity of the pair of lines changes little. At a Kr/CH_4 ratio of 10 the spectrum should be dominated by the hindered rotation of CH_4 molecules completely surrounded by Kr atoms. The qualitative behaviour of the spectra in fig. 1 is therefore consistent with the discussion in the previous paragraph. However, the spectra at lower Kr concentrations are broadened and this can be attributed to disorder in the Kr-rich domain. At these high energies the energy levels are much less sensitive to small changes in barrier height than in the lower-energy range appropriate to the pure-CH_4 layer. The broadening effects could even result just from variations in the distribution of next nearest neighbours of CH_4 molecules that already have six Kr atoms as nearest neighbours.
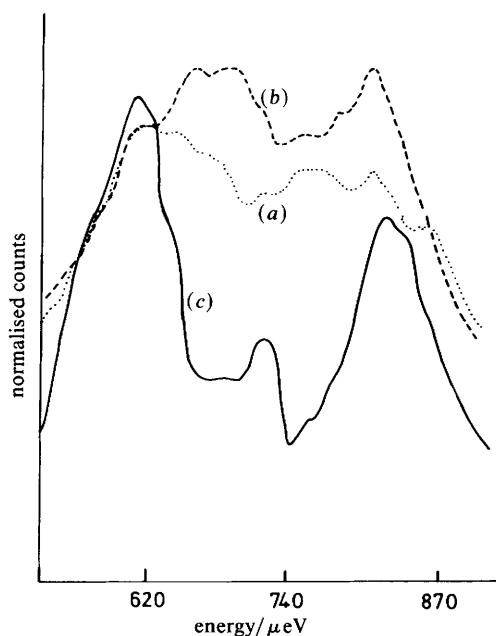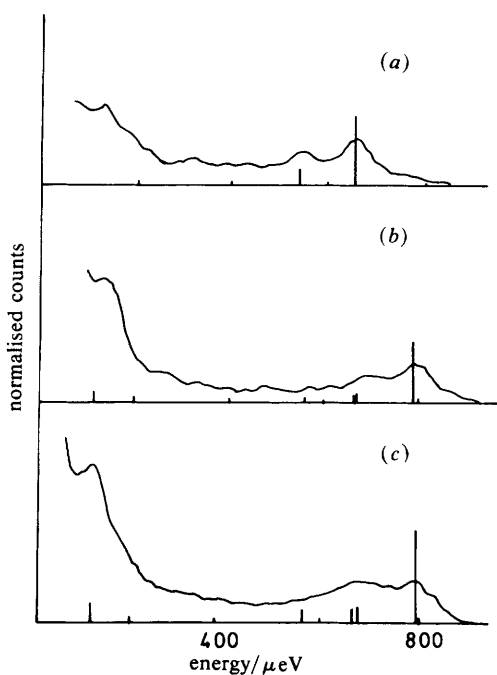
Fig. 1. Neutron energy-gain spectra of $Kr+CH_4$ mixtures in the energy range 0.5–1 meV: (a) 1:1, (b) 2:1 and (c) 6:1. $T = 7.5$ K and Q is parallel to the surface.

Table 1. Positions of lines in CH_4 tunnelling spectra from fig. 1–3

Kr/CH_4 ratio	line positions/μeV	direction of Q
1:1	660, 530?, 120?	⊥
1:1	780, 650, 120?	∥
2:1	810, 640	∥
6:1	840, 620, 720?	∥
10:1	910, 620, 260	∥
	720?, 1800, 200	

Fig. 2 shows spectra of 1:1 mixtures with Q perpendicular ($Q_\perp$) and parallel to the surface. The most intense line in the Q-parallel ($Q_\parallel$) spectrum is at *ca.* 780 μeV. Comparison of the two spectra shows that this line is polarised parallel to the surface. Similarly, in the $Q_\perp$ spectrum there is a line at *ca.* 660 μeV predominantly polarised perpendicular to the surface. A line also occurs at *ca.* 120 μeV in all spectra. This is probably the tunnelling from domains of pure CH_4, but at this rather low resolution it is not possible to identify it with any certainty. Fig. 2 also shows the effect of increasing the temperature on the $Q_\parallel$ spectrum. The transition at 650 μeV becomes more intense relative to that at 780 μeV. In all the spectra of fig. 2 there is a large amount of background scattering and possibly some other features. This shows that there is a significant proportion of CH_4 molecules in environments different from the two extremes so far described.

Fig. 2. Neutron energy-gain spectra of $1:1$ $Kr+CH_4$ mixtures: (a) momentum transfer Q perpendicular to the surface and (b) and (c) Q parallel to the surface; (a) and (b) are at 5 K and (c) is at 7.5 K. Positions and intensities of lines for the assignment given in the text and fig. 4 are also shown.

Fig. 3 shows the spectrum of a $10:1$ $Kr+CH_4$ mixture at temperatures of 5 and 10 K. At 5 K three lines are observed below 1 meV, the two already shown in fig. 1 and a line at 260 μeV. Further broad lines are also observed at *ca.* 2 meV, which disappear on warming to 10 K. The line at 910 μeV also broadens on increasing the temperature.

ASSIGNMENT OF THE SPECTRA

The tunnelling spectrum of pure CH_4 on graphite has been interpreted using the pocket-state treatment of Hüller.[6] The energies and intensities of the five allowed transitions for a tetrahedron in a field of trigonal symmetry are accounted for by just two overlap matrix elements. One, h_4, depends on the barrier height to rotation about the unique C—H bond perpendicular to the surface and the other, h, on the barrier to rotation about one of the three equivalent C—H bonds pointing towards the surface. The pocket-state treatment uses a basis set of wavefunctions that are essentially vibrational wavefunctions. It is appropriate to use it when the barriers to rotation are high, but when the hindered rotation is closer to the free rotational limit it becomes less easy to calculate the energy levels accurately. For CH_4 in Kr the energies of the transitions are closer to the free-rotor limit ($2B \approx 1300$ μeV). However, the pocket-state approach is easier to use for an initial qualitative interpretation of the spectrum.
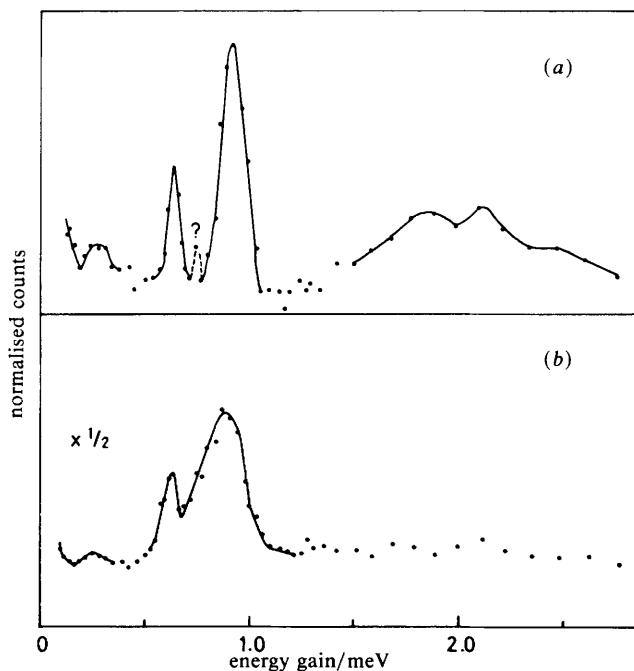
Fig. 3. Neutron energy-gain spectra of a $10:1$ $Kr + CH_4$ mixture with $\boldsymbol{Q}$ parallel to the surface: (a) $T = 5$ K and (b) $T = 10$ K.

The energy levels and transitions of CH_4 in a trigonal field are given in terms of the two parameters h and h_4 in table 2. Also given are the predicted intensities of the transitions at the value of $\boldsymbol{Q}$ appropriate to the spectra of fig. 2. These intensities do not include a Boltzmann factor. If we assume that the spectra of fig. 2 and 3 are those of CH_4 in a trigonal field we can use table 1 to predict the spectrum for a variety of potentials.

The two main situations likely to occur are (a) the barrier to rotation about the unique C—H bond is low but the other barrier is high with a value similar to that for pure CH_4 on graphite and (b) both barriers are low. In case (a) $-h_4$ will be large and $-h$ will be small and in case (b) both will be large. If case (a) is appropriate it is immediately clear from table 2 that there will be no lines in the $\boldsymbol{Q}_\perp$ spectrum above ca. 150 μeV. The spectrum of fig. 2(a) therefore shows that the barrier about the three equivalent C—H bonds must be low.

We first assign the lines in the spectra of the $1:1$ mixture shown in fig. 2. Only two lines are predicted to appear in the $\boldsymbol{Q}_\perp$ spectrum, the $T \to A$ and $E \to 2T$ transitions with intrinsic intensities of 1.1 and 0.9, respectively. For case (b) above the E level will be well above the single T level and therefore the $E \to 2T$ transition will be reduced by a Boltzmann factor because the spectra are in neutron-energy gain. For a temperature of 5 ± 1 K this reduction will be between one-third and one-sixth. The line at 660 μeV must therefore be the $T \to A$ transition and the weak line at 530 μeV may tentatively be assigned to the $E \to 2T$ transition. The pocket-state treatment predicts that the transition energies should be in the ratio $2:1$ $(T \to A : E \to 2T)$. This is a deficiency of the simple pocket-state treatment when the barriers are low, because in the free-rotor limit the ratio must be reversed to

Table 2.[a] Energies and intensities of rotational tunnelling of the CH_4 ion a trigonal field[2]

energy levels	transitions	intensity $(Q_\parallel)$	intensity $(Q_\perp)$
$E, -3h - h_4$	$A \rightarrow T, -8h$	0.1	1.1
$T, -2h + 2h_4$	$2T \rightarrow E, -4h$	0.5	0.9
$2T, h - h_4$	$A \rightarrow 2T, -5h - 3h_4$	1.0	—
$A, 6h + 2h_4$	$T \rightarrow E, -h - 3h_4$	0.4	—
	$T \rightarrow 2T, -3h + 3h_4$	0.2	—

[a] For CH_4 on graphite, $h = -14\ \mu eV$ and $h_4 = -8\ \mu eV$.
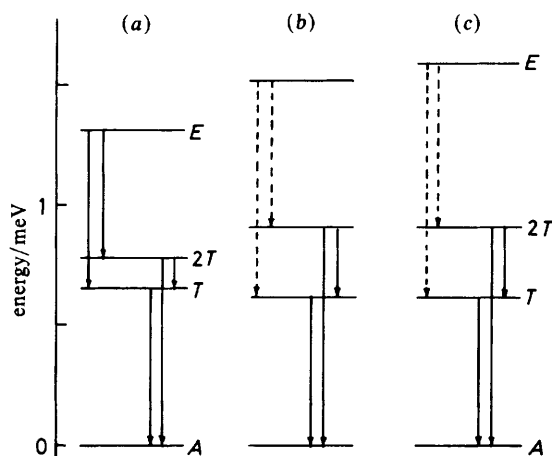
Fig. 4. Assignment of levels and transitions for CH_4 in krypton-rich domains of (*a*) a 1:1Kr+CH_4 mixture and (*b*) a 10:1 Kr+CH_3 mixture; (*c*) is an alternative assignment for the 10:1 mixture.

1:2 since A, T and E levels correlate respectively with the free rotor levels of 0, 2B and 6B. The observed ratio of 1.2 indicates that the system is not far from the free-rotor limit.

In the $Q_\parallel$ spectrum the most intense line is the $2T \rightarrow A$ transition. The $E \rightarrow 2T$ and $E \rightarrow T$ transitions are both allowed but will again be reduced by Boltzmann factors. The $T \rightarrow A$ transition will also appear weakly. We therefore assign the line at 780 μeV to the $2T \rightarrow A$ transition. This is sufficient with the $T \rightarrow A$ and $E \rightarrow 2T$ lines from the $Q_\perp$ spectrum to complete the assignment. The levels are shown in fig. 4. The intensities and energies of the lines are superimposed on all the spectra in fig. 2. Within the considerable uncertainties of the experiment the agreement is quite good.

The clearer spectra associated with the 6:1 and 10:1 Kr+CH_4 mixtures are less easy to assign, partly because we only have the $Q_\parallel$ spectra, although all the lines should appear. Fig. 2 shows that the broad peak is better resolved as the Kr concentration increases, with the two peaks moving further apart. This suggests that the most intense peak in fig. 3, at 910 μeV, is the $2T \rightarrow A$ transition. In fig. 3 the line at 260 μeV is probably the $2T \rightarrow T$ transition, which then suggests that the

line at 620 μeV is the $T \rightarrow A$ transition. A difficulty with this assignment is that the $2T \rightarrow T$ and $T \rightarrow A$ transitions should be of comparable intensity. It also leaves the position of the E level uncertain. A possible solution is shown in fig. 4(b). In this assignment the $T \rightarrow A$ and $E \rightarrow 2T$ transitions exactly coincide and the $E \rightarrow T$ transition almost coincides with the $2T \rightarrow A$ transition. This could account for the extra intensity of the line at 620 μeV and would contribute to a broadening of the line at 910 μeV. However, an alternative assignment is shown in fig. 4(c). In both the 6:1 and 10:1 spectra there is a suggestion of a weak line at $ca.$ 720 μeV. If this were assigned to the $E \rightarrow 2T$ transition the $E \rightarrow T$ transition would occur at 980 μeV. This is just about plausible. It will be shown in the calculations that the differences in these assignments have little effect on the calculated barrier heights.

A final possibility is that the $E \rightarrow T$ transitions are the broad lines at 1800 and 2000 μeV. The maximum value of these transitions in the free-rotor limit is 2600 μeV [fig. 4(b)]. However, we believe this assignment to be unlikely. The ratio $\Delta E(E \rightarrow T)/\Delta E(T \rightarrow A)$, taking the mean of the $3T$ levels, would be $ca.$ 2.5. The maximum value of this ratio is 2 at the free-rotor limit. As the barrier increases from zero $\Delta E(E \rightarrow T)$ drops much more rapidly than $\Delta E(T \rightarrow A)$, and so the ratio is well below 2 even at quite small barrier heights. Calculations below indicate that these high-energy transitions may be transitions from the next manifold of rotational states. The possibility, however, of a more complex potential cannot be entirely eliminated.

CALCULATION OF THE BARRIERS TO ROTATION

The limitations of the pocket-state treatment when the barriers to rotation are low have already been mentioned. We have therefore used the method of King and Hornig,[7] extended by Smith,[8] to calculate the energy levels of the system. This uses symmetry-adapted rotational wavefunctions as a basis set. The overall procedure has been described by Smith.[8]

The Hamiltonian that describes the motion of a tetrahedron in a trigonal potential field is invariant under the product group $\bar{T} \times C_3$ where $\bar{T}$ is the tetrahedral group of rotations about body-fixed axes and C_3 the group of rotations about space-fixed axes. The wavefunctions take the form

$$\phi = \sum_{M\bar{M}} C(\bar{r}, J, \bar{n}, \bar{M}) C(r, J, n, M) | JM\bar{M} \rangle$$

where $| JM\bar{M} \rangle$ are the spherical-top wavefunctions and C are the coefficients of spherical harmonics in expansions of surface harmonics, which are themselves basis functions for irreducible representations of $\bar{T}$ or C_3. Tables of the C coefficients for the problem have been published.[9]

The potential function must span the totally symmetric representation of $\bar{T} \times C_3$ and is therefore of symmetry $\bar{A} \times A$:

$$V(\omega) = (8\pi^2)^{1/2} \sum_j \beta_j | \bar{A} \times A, J \rangle.$$

If only the lowest terms in the expansion are taken the angle-dependent potential can be reduced in terms of Euler angles to

$$V(\omega) = \frac{\sqrt{7}}{2}\beta B \left(\frac{\sqrt{30}}{2} a_0^3 \sin^2 \theta \cos \theta \sin 2\phi + \frac{\sqrt{6}}{2} a_3^3 [(1 + \cos^2 \theta) \sin \theta \sin 2\phi \cos 3\psi \right.$$

$$\left. + \sin 2\theta \sin 3\psi \cos 2\phi] \right)$$

where β is a field-strength parameter, B is the inertial constant and α_0^3 and α_3^3 are parameters determining the deviation of the field from tetrahedral symmetry. They are related to one another by

$$(\alpha_0^3)^2 + 2(\alpha_3^3)^2 = 1$$

The field is tetrahedral when $\alpha_0^3 = \dfrac{\sqrt{5}}{3}$. Reducing the potential to these terms only is equivalent to assuming that rotation about either the unique C—H bond or one of the three equivalent C—H bonds is of the $\cos 3\theta$ form with no contribution from higher terms, *e.g.* $\cos 6\theta$. This is the same as the assumption made previously in analysing the spectrum of the pure CH_4 layer[2] and the assumption usually made in analysing one-dimensional hindered rotation. Substitution of the appropriate coordinates θ, ψ, ϕ into the expression for the potential can be made to obtain the two barriers to rotation already described.

The matrix elements of the Hamiltonian have been given by Smith. The use of symmetry factorizes the Hamiltonian matrix so that it may be diagonalized separately to obtain each subgroup of levels. The important levels for CH_4 in Kr are the $\bar{A} \times A$, $\bar{T} \times A(T)$, $\bar{T} \times E(2T)$ and $\bar{E} \times E$. A program was written to do the calculations, which was tested by comparison with levels previously calculated by Smith for both trigonal and tetrahedral fields. The accuracy of the ground-state splittings was determined by testing the convergence as the size of the matrix was increased. For our fairly weak potential field it was sufficient to include values of J up to 12. The largest matrix was then 244×244 for the $\bar{T} \times A$ levels. For a higher field, as in the pure CH_4 layer, the calculations would become impractically large.

An approximate value of the dimensionless field-strength parameter, β, was first determined by assuming the field to be tetrahedral. Final calculations were then done for values of β close to the approximate value and for different values of α_3^3. A selection of results is given in table 3.

The values given in table 3 are rather a coarse grid in terms of the two field parameters. However, it is possible to obtain quite a good agreement with the observed spectra in table 1 and fig. 4. Thus for the 1:1 mixture we have calculated (observed) lines for $\beta = 6.0$ and $\alpha = 0.35$ of 502 (530?), 611 (660), 109 (120?), 778 (780) and 669 (650) μeV. Some lines can be matched slightly better with $\beta = 6.0$ and $\alpha = 0.3$ or with $\beta = 5.5$ and $\alpha = 0.35$. This indicates that the field parameters are accurate to *ca.* 10–15%. What is interesting is the change in the parameters as the concentration increases. For the 2:1 mixture the combination $\beta = 6.0$ and $\alpha = 0.3$ is now definitely better than $\beta = 6.0$ and $\alpha = 0.35$. At 6:1 the increase in the splitting of the $2T \rightarrow T$ levels suggests that α should now be *ca.* 0.25, and finally at 10:1 a good fit is obtained to fig. 4(b) with $\beta = 6$ and $\alpha = 0.2$. The trend in these changes corresponds to little change in the barrier about the three equivalent C—H bonds but a decrease in the barrier to rotation about an axis normal to the surface from 55 cm^{-1} (1:1), through 47 (2:1) and 39 (6:1), to 31 cm^{-1} for the 10:1 mixture. The other barrier height does not change over this concentration range and is 79 cm^{-1}. Thus as the CH_4 becomes more and more dilute the unique barrier height approximately halves. The value of 55 cm^{-1} for the 1:1 mixture compares with 202 cm^{-1} for the pure CH_4 layer.[2] It suggests that the CH_4 molecule is already largely surrounded by Kr atoms in the 1:1 mixture.

The good agreement of calculated and observed spectra largely confirms the assignments of fig. 4(a) and (b). The assignment of fig. 4(b) assumes that the lines observed at *ca.* 2 meV were transitions from the next manifold of rotational states.

METHANE + KRYPTON ON GRAPHITE

Table 3. Calculated rotational transitions (in μeV) of CH_4 in a trigonal field[a]

transition	$\alpha_3^3 = 0.2$				$\alpha_3^3 = 0.3$				$\alpha_3^3 = 0.35$				$\alpha_3^3 = 0.4$			
$\beta =$	4.5	5.0	5.5	6.0	4.5	5.0	5.5	6.0	4.5	5.0	5.5	6.0	4.5	5.0	5.5	6.0
$E \rightarrow 2T$	859	752	656	578	795	689	597	519	775	669	580	502	765	661	571	495
$E \rightarrow T$	1054	969	885	909	928	832	747	673	870	772	687	611	823	722	634	559
$2T \rightarrow T$	195	217	229	247	133	143	150	155	95	103	107	109	58	61	63	64
$2T \rightarrow A$	1044	999	947	903	996	936	876	817	969	906	942	778	947	880	813	747
$T \rightarrow A$	849	782	718	656	863	793	726	662	847	803	735	669	889	819	750	683

[a] B for CH_4 has been taken to be 649.7 μeV.

We have calculated the approximate positions of these transitions. For $\beta = 6.0$ and $\alpha = 0.35$ the first of these lines would be at *ca.* 3 meV, rather higher than observed. However, the discrepancy may be a result of neglecting higher-order terms in the potential. In the limit where CH_4 is completely surrounded by Kr atoms the potential for rotation abut the unique axis would be expected to have a $\cos 6\theta$ contribution, although it has been argued that the 'polaron' effect will make the $\cos 3\theta$ term dominant.[1] The energy levels that would most be affected by the introduction of a $\cos 6\theta$ term would be the levels in the first excited manifold of states. Their energy would be drastically lowered, and this may be the cause of the discrepancy between calculated and observed transition energies.

DISCUSSION

On changing the nearest neighbours of CH_4 from CH_4 to Kr the barrier about the unique axis to rotation is reduced from 202 to $31 \pm 5\ cm^{-1}$. This is much as would be expected, since this barrier is largely created by the molecule–molecule interactions. However, the reduction of the other barrier from 172 to $80\ cm^{-1}$ is more surprising, since it would be expected that this barrier is largely the result of molecule–surface forces. To examine what is happening more closely we have calculated the barriers using the atom–atom model.

The calculations were done for an ordered CH_4Kr_2 layer, each CH_4 molecule being surrounded by six Kr atoms. The potential parameters for C–C, C–H and H–H interactions were those of potential VII of Williams.[9] The Kr–Kr potential was taken from Hirshfelder *et al.*,[10] the Kr–H potential from Das *et al.*[11] and the C–Kr potential was derived by combining the potential parameters σ and ε from the Kr–Kr and C–C potentials as described by Yasuda.[12] Interactions with graphite atoms were included out to a distance of 13 Å (3 layers) and with adsorbate atoms out to 9 Å (nearest and next-nearest neighbours). Calculations were done for a central CH_4 molecule placed on sites over the graphite hexagons (S site), over a carbon atom (A site) or over a C—C bond (SP site). The layer was taken to be commensurate (3×3) and both the methane-surface and krypton-surface distances were allowed to vary in order to find the most stable configuration. The barriers to rotation were then calculated. Calculations were done for CH_4 in tripod-down and tripod-up configurations.

In decreasing order of stability the alternative configurations of a CH_4 molecule were found to be tripod-down on an S site, tripod-up on an S site, tripod-down on an SP site, tripod-up on an A site, tripod-down on an A site and tripod-up on an SP site. The minimum energy for the first three configurations was -10.36, -9.67 and $-8.87\ kJ\ mol^{-1}$, indicating that the tripod-down S site is significantly the most favourable. In this configuration the equilibrium surface–Kr distance is 3.40 Å and the surface–CH_4 carbon atom distance is 3.325 Å. The latter is similar to the experimentally determined value for a pure CD_4 layer.

The barriers to rotation are both found to have threefold symmetry. For the unique axis this is because the CH_4Kr_2 structure has threefold symmetry in its next-nearest neighbours, although sixfold in its nearest neighbours. The unique barrier height is found to be negligible, *ca.* $4\ cm^{-1}$, and the barrier about the three equivalent C—H bonds is found to be $72\ cm^{-1}$, close to the experimental value. The drop from the value of $172\ cm^{-1}$ in the pure CH_4 layer to $79\ cm^{-1}$ can therefore be attributed to a large contribution of CH_4–CH_4 interactions to the barrier in the former case. The difference between experimental and calculated values of the

unique barrier height is not easily explained. It may arise from a 'polaron' effect[1] or, less likely, from an interaction with the surface.

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