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Application of empirical interatomic potentials to the calculation of the structure and dynamics of paraffin molecules adsorbed on graphite

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The adsorption of a single molecule of ethane, propane, and butane on a basal-plane surface of graphite is investigated using empirically derived carbon-hydrogen and carbon-carbon potentials. The principal motivation for this study is the calculation of a number of structural and dynamical properties which can be compared with neutron scattering experiments on monolayer paraffin films adsorbed on graphite. For each molecule the equilibrium orientation and position with respect to the surface and contours of minimum potential energy have been calculated. We find that these molecules prefer to align themselves with their carbon skeleton parallel to the graphite basal plane with the hydrogen atoms closest to the surface occupying the center of the graphite carbon hexagons. We have also found that each of the molecules tends to distort upon adsorption by small antisymmetric rotation of the CH_3 groups about the terminal C–C bonds. Two different force-constant models have been used to calculate the frequencies of the surface vibratory modes of the adsorbed molecules. The calculated frequencies and, with few exceptions, the force constants are in reasonable agreement with values inferred previously from inelastic-neutron-scattering spectra of monolayer butane films. Finally, the anharmonicity of the molecule-substrate potential has been briefly studied by examining the temperature dependence of the height of a butane molecule above the graphite basal plane and of the frequency of the molecular vibration normal to the surface.

I. INTRODUCTION

A fundamental problem in surface physics and chemistry is the determination of the forces bonding a molecule to a substrate. If the substrate is sufficiently homogeneous, the vibrational states of the adsorbed molecule can provide a means of probing the interaction potential with the substrate. We have recently used inelastic neutron scattering to study the vibrational states of paraffin molecules adsorbed on a graphitized carbon powder.[1,2] In these experiments the substrate potential manifests itself by introducing new surface vibratory modes associated with hindered rotation and translation of the adsorbed molecule. In addition, the low-frequency intramolecular torsional modes of the end methyl (CH_3) and methylene (CH_2) groups are perturbed.

The paraffin-on-graphite systems offer several advantages for studying the dynamics of adsorbed molecules by inelastic neutron scattering. Graphitized carbon powers combine large surface area (~80 m^2/g) with exceptional homogeneity. The paraffin molecules contain mostly hydrogen which has an extremely large incoherent cross section (~80 barns) for thermal neutrons and whose small mass results in the large-amplitude torsional modes of vibration. Therefore, neutron excitation of these vibrational states can be detected even at submonolayer coverages.

Besides these experimental advantages, the paraffin-graphite systems also offer the possibility of calculating the interaction of the adsorbed molecule with the substrate from empirically derived atom-atom potentials. A considerable effort has been made in the last ten years in developing empirical potentials of the Van der Waals or nonbonding type to describe the interaction between molecules in crystalline hydrocarbons.[3] The purpose of this paper is to investigate the extent to which these empirical potentials can be used to interpret the excitation spectra of monolayer paraffin films adsorbed on graphite. Among the questions with which we shall be concerned are: (i) the equilibrium orientation and position of the adsorbed molecule, (ii) the internal distortions of the molecule which result from adsorption, (iii) the magnitude of the force constants which characterize the interaction between atoms in the adsorbed molecule and the substrate, and (iv) the frequencies of the surface vibratory modes and the perturbation of the intramolecular torsional frequencies resulting from adsorption. The calculations will be carried out for ethane, propane, and butane. We shall find certain structural and dynamical features common to all three paraffin molecules adsorbed on graphite.

As discussed in Ref. 1, the principal features of the butane monolayer excitation spectrum could be explained while neglecting the interaction between adsorbed molecules. We adopt a similar approach here, considering only a single molecule adsorbed on a basal plane surface of graphite. We note, though, that elastic neutron scattering experiments can be performed to determine the structure of paraffin films on graphite. These experiments which are now in progress[4] require deuterated molecules in order to enhance the coherent neutron cross section of the film. We intend to extend the calculations described here to include the intermolecular interaction once the film structures have been determined.

II. DESCRIPTION OF CALCULATIONS

A. Potential energy function

We consider interatomic potentials of the Van der Waals or nonbonded type having the form (exp −6):

$$E = Ar^{-6} + B\exp(-Cr)\ , \tag{1}$$

where r is the nonbonded interatomic distance and A, B, and C are parameters characteristic of each atomic pair. The total energy of a system is assumed to be the sum of these pairwise interactions. The attractive r^{-6} term in the potential function represents the usual dipole-dipole polarization energy. Higher-order contributions from dipole-quadrupole interactions are neglected, but they may may be partly absorbed into A and B. The repulsive part of the potential is represented by the exponential term which quantum-mechanical calculations[3] have shown to be superior to a r^{-n} form. We note that the spatial derivative of E,

$$\frac{dE}{dr} = -6Ar^{-7} - BC\exp(-Cr)\ , \tag{2}$$

vanishes at two r values. At small r the energy curve has a maximum and at larger r a minimum. The minimum corresponds to the equilibrium separation of the atomic pair whereas the maximum is clearly unphysical. It is important to be aware of this imperfection in the potential so that in calculations one never approaches a distance close to that of the maximum.

In this work, we are concerned with effective potentials for the C-C and C-H interactions between a carbon atom in the substrate and either a carbon or hydrogen atom in the adsorbed molecule. For the potential parameters A, B, and C we have used the parameter set IV given by Williams.[3] The potential-energy functions in kcal/mole are then given by the expressions

$$E_{\text{C-C}} = -535r^{-6} + 74\,460\exp(-3.60r)\ , \tag{3}$$

$$E_{\text{C-H}} = -139r^{-6} + 9411\exp(-3.67r)\ , \tag{4}$$

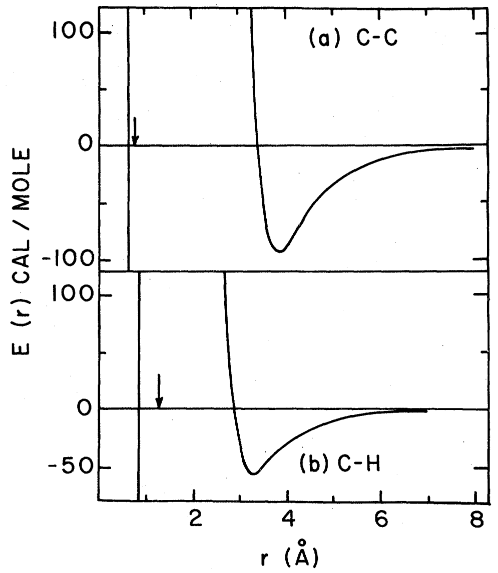

FIG. 1. Interatomic potentials used in this paper. The arrows indicate the position of the maximum in the energy function; (a) the C-C interaction of Eq. (3). (b) the C-H interaction of Eq. (4).

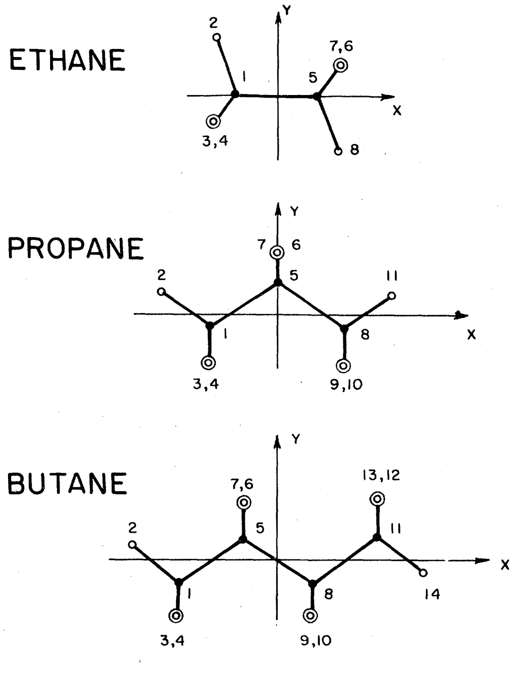

FIG. 2. Definition of the X, Y, Z coordinate systems for each molecule. The origin is taken at the molecular center of mass. Atom numbers refer to Table I where the atomic coordinates are listed. Open circles correspond to hydrogen atoms and solid circles to carbon atoms. The concentric circles indicate that a plane of even- and odd-numbered hydrogen atoms lie above and below the plane of the carbon skeleton, respectively.

TABLE I. Intramolecular atomic coordinates of ethane, propane, and butane. The atomic number in the first column identifies the atoms in Fig. 2. The atomic positions are given in angstroms with respect to the molecular coordinate system (X, Y, Z) defined in Fig. 2. Coordinates are listed for both the undistorted (free) molecule and the distorted molecule adsorbed at the equilibrium position indicated in Table II.

Ethane		Undistorted molecule			Distorted molecule		
Atom	Atom type	X	Y	Z	X	Y	Z
1	C	−0.771	0.0	0.0	−0.771	0.0	0.0
2	H	−1.137	1.037	0.0	−1.137	1.036	−0.0362
3	H	−1.137	−0.518	−0.898	−1.137	−0.549	−0.879
4	H	−1.137	−0.518	0.898	−1.137	−0.487	0.916
5	C	0.771	0.0	0.0	0.771	0.0	0.0
6	H	1.137	0.518	0.898	1.137	0.487	0.916
7	H	1.137	0.518	−0.898	1.137	0.549	−0.879
8	H	1.137	−1.037	0.0	1.137	−1.036	−0.0362
Propane		Undistorted molecule			Distorted molecule		
Atom	Atom type	X	Y	Z	X	Y	Z
1	C	−1.257	−0.283	0.0	−1.257	−0.383	0.0
2	H	−2.155	0.352	0.0	−2.554	0.351	−0.0543
3	H	−1.257	−0.918	−0.898	−1.23	−0.956	−0.87
4	H	−1.257	−0.918	0.898	−1.285	−0.879	0.924
5	C	0.0	0.606	0.0	0.0	0.606	0.0
6	H	0.0	1.241	0.898	0.0	1.241	0.898
7	H	0.0	1.241	−0.898	0.0	1.241	−0.898
8	C	1.257	−0.283	0.0	1.257	−0.283	0.0
9	H	1.257	−0.918	−0.898	1.23	−0.956	−0.87
10	H	1.257	−0.918	0.898	1.285	−0.879	0.924
11	H	2.155	0.352	0.0	2.154	0.351	−0.0543
Butane		Undistorted molecule			Distorted molecule		
Atom	Atom type	X	Y	Z	X	Y	Z
1	C	−1.885	−0.445	0.0	−1.885	−0.445	0.0
2	H	−2.783	0.191	0.0	−2.783	0.189	0.0543
3	H	−1.885	−1.080	−0.898	−1.859	−1.117	−0.870
4	H	−1.885	−1.080	0.898	−1.913	−1.041	0.924
5	C	−0.628	0.445	0.0	−0.628	0.445	0.0
6	H	−0.628	1.080	0.898	−0.628	1.08	0.898
7	H	−0.628	1.080	−0.898	−0.628	1.08	−0.898
8	C	0.628	−0.445	0.0	0.628	−0.445	0.0
9	H	0.628	−1.080	−0.898	0.628	−1.08	−0.898
10	H	0.628	−1.080	0.898	0.628	−1.08	0.898
11	C	1.885	0.445	0.0	1.886	0.445	0.0
12	H	1.885	1.080	0.898	1.913	1.041	0.924
13	H	1.885	1.080	−0.898	1.859	1.117	−0.87
14	H	2.784	−0.191	0.0	2.783	−0.189	−0.0543

which are plotted in Fig. 1. The coefficients A and B were fitted by weighted least squares to equations involving the geometrical crystal structures, elastic constants, and sublimation energies of nine aromatic hydrocarbons. For the C-H interaction, the geometrical mean combining law was used to obtain the attractive coefficient $A_{\text{C-H}} = (A_{\text{CC}} A_{\text{CH}})^{1/2}$. The magnitude of the C-C exponent was taken to be 3.60 Å^{-1} from a calculation of the interplanar spacing and compressibility of graphite, while the H-H exponent was calculated quantum mechanically to be 3.74 Å^{-1}. The geometrical mean of these two values was used for the C-H exponent.

The particular parameter set in Eqs. (3) and (4) was selected somewhat arbitrarily from others given by Williams[3] because it gave the best agreement with the observed structures of various aromatic hydrocarbon crystals. Williams[5] later obtained potential parameters based on data for nonaromatic hydrocarbons, but these agreed reasonably well with his previous results. He concluded[5] that the potential parameters were not particularly sensitive to the presence of π-electron systems in the hydrocarbons. With this in mind, our objective has not been to determine an optimal set of parameters for describing the paraffin-graphite interaction, but rather to calculate a variety of structural and dynamical properties for comparison with experiment using a single-parameter set. While small quantitative differences could result from employing different parameters, we do not believe any of our results would be qualitatively altered or significantly improved by an alternative parameter selection. It is our view that a deeper understanding of the applicability of these potentials to the adsorption of hydrocarbons on graphite will come instead from quantum-mechanical calculations on a paraffin-graphite system. For this reason we have initiated[6] calculations of the electronic structure of a paraffin-graphite cluster using a semiempirical MINDO/3 scheme.[7]

B. Representation of molecular positions and orientations

For the calculations described here, we assume that the equilibrium structure of the free paraffin molecules ethane, propane, and normal butane is the *trans* conformation. The atomic positions within each molecule are specified with respect to a Cartesian coordinate system (X, Y, Z) shown in Fig. 2 having its origin at the molecular center of mass. The atomic coordinates of the free molecule (undistorted) are listed in Table I. An arbitrary position and orientation of the molecule with respect to the graphite surface is specified by the three coordinates of the center of mass (x_s, y_s, z_s) and by the three angles of θ_X, θ_Y, and θ_Z about the orthogonal axes (X, Y, Z) (see Fig. 3).

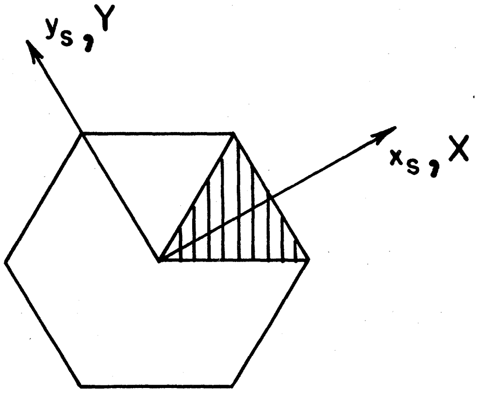

FIG. 3. Relative orientation of the X, Y, Z coordinate systems with respect to the graphite basal plane. The x_s-y_s plane coincides with the graphite basal plane and the direction of Z and z_s is normal to and out of the surface. The shaded area is the irreducible basis triangle of a carbon hexagon in the graphite basal plane.

It is also necessary to be able to describe distortions of the molecule caused by the surface interaction. We have allowed for the possibility of rotational distortions about the intramolecular C-C bonds but have neglected bending and stretching distortions. The calculation is set up so that an arbitrary number of internal rotation axes may be defined for any pair of atoms in the molecule and a specified group of atoms rotated about each axis. For example, in butane the rotation axes of the methyl groups are defined by two pairs of carbon atoms (1, 5) and (8, 11) (See Fig. 2) while the rotation axis of the CH_2 groups is defined by the carbon pair (5, 8).

III. RESULTS

A. Molecular position and orientation with respect to the surface

The objective of the first series of computations was to find the equilibrium position and orientation of a single paraffin molecule adsorbed on a graphite basal plane. A calculation scheme was designed to minimize the total potential energy of the molecule using the coordinates and rotation axes described in the previous section. Once the molecular position and configuration were defined the potential energy of the molecule with respect to the surface was calculated from the potentials in Eqs. (3) and (4) by summing over all interaction pairs consisting of a hydrogen or carbon atom in the adsorbed molecule and a carbon atom in the graphite basal plane. In practice, to limit the number of terms in the summation a cut-off length was imposed beyond which the interatomic potential was neglected. The cut-off lengths were the same as those used by Williams,[3] namely, 6.0 Å for the C-C interaction and 5.5 Å for the C-H interaction. The computer code included a test to insure that no matter which orientation of the molecule was considered, all substrate atoms within the cut-off length were included. It was found to be unnecessary to include carbon atoms in graphite layers below the surface basal plane since, in all cases, these atoms were beyond the cut-off length.

A potential-energy contour map was generated for each molecule by moving the molecular center of mass through a grid of points within a basis triangle of the graphite basal plane (the hatched area in Fig. 3). The contour maps of minimum energy for ethane, propane, and butane molecules having the undistorted structure of Table I are presented in Figs. 4–6. Since at each point in the basis triangle the potential energy is minimized with respect to the three rotational angles θ_X, θ_Y, and θ_Z and the distance z_s above the surface, the

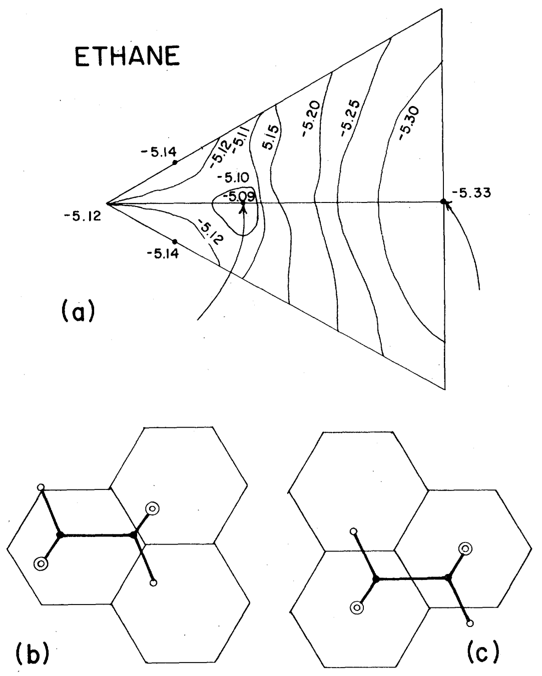

FIG. 4. (a) Minimum potential-energy contours in kcal/mole for ethane adsorbed on a graphite basal plane. At all points in the basis triangle the potential energy is minimized with the C-C bond parallel to the surface. The arrows mark points for which the molecular configuration is shown: (b) the least favorable configuration having the C-C bond parallel to the surface, $E = -5.09$ kcal/mole; (c) the equilibrium configuration, $E_{eq} = -5.33$ kcal/mole.

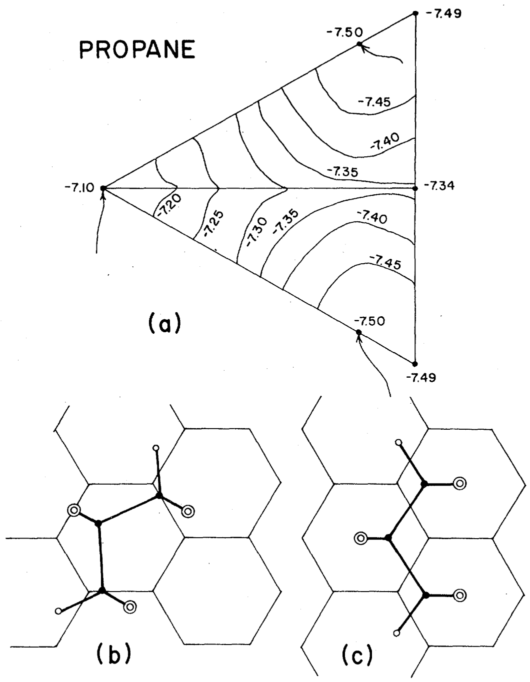

FIG. 5. (a) Minimum potential-energy contours in kcal/mole for propane on a graphite basal plane. At all points in the basis triangle the potential energy is minimized with the propane carbon skeleton parallel to the surface. The arrows mark points for which the molecular configuration is shown: (b) the least favorable configuration having the carbon skeleton parallel to the surface, $E = -7.1$ kcal/mole; (c) the equilibrium configuration, $E_{eq} = -7.5$ kcal/mole.

orientation and height of the molecules vary from point to point in the map. However, the range in heights is small. For all three molecules the height of the molecules above the surface varies by less than 0.1 Å throughout the map.

From the contour maps it can be seen that each molecule has a preferred configuration of lowest energy when adsorbed. The equilibrium configuration of each molecule with respect to the graphite basal plane is shown in Figs. 4(c)–6(c) and the corresponding position and orientational coordinates are listed in Table II. In the case of ethane, the equilibrium position occurs with the center of mass located midway between adjacent atoms in the graphite basal plane and at a height of 3.56 Å. Less favorable positions seem to occur with the ethane center of mass near the center of the graphite carbon hexagons [Fig. 4(b)]. Similarly, the equilibrium position of butane also occurs with the center of mass midway between adjacent carbon atoms in the graphite, while for propane the center of mass prefers a location very close to a graphite carbon atom.

The contour maps reveal several common features of the structure of paraffin molecules adsorbed on basal plane surfaces of graphite. It is easy to see that the equilibrium configurations are characterized by a tendency to keep all C atoms in the molecule at the same elevation above the surface. Thus in the case of propane and butane the plane of the carbon skeleton is aligned parallel to the surface at a height of 3.57 Å. For butane, the cost in energy to rotate 90° about the chain axis ($\theta_X = 90°$) so that the plane of the carbon skeleton is perpendicular to the surface is typically 20% of the binding energy at any point on the graphite plane. The equilibrium configurations also seem to be characterized by a preference of the H atoms nearest the surface to lie at the center of the graphite carbon hexagons. Configurations which place H atoms above or near graphite C atoms seem generally less favorable [compare Figs. 4(b)–6(b)]. We would anticipate that these general features of the surface bonding would also apply to longer paraffin chains adsorbed on graphite.

The effects of finite temperature and the intermolecular interaction have been neglected in these calculations of the equilibrium configuration of the

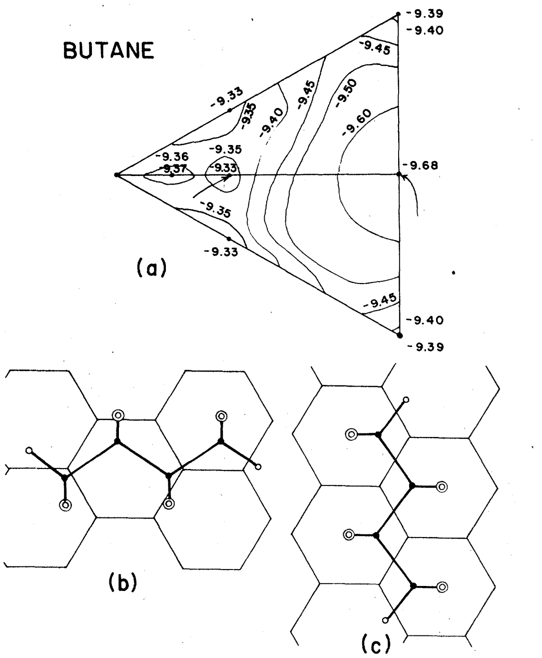

FIG. 6. (a) Minimum potential-energy contours in kcal/mole for butane on a graphite basal plane. At all points in the basis triangle the potential energy is minimized with the butane carbon skeleton parallel to the surface. The arrows mark points for which the molecular configuration is shown: (b) the least favorable configuration having the carbon skeleton parallel to the surface, $E = -9.33$ kcal/mole; (c) the equilibrium configuration, $E_{eq} = -9.68$ kcal/mole.

molecules. The temperature effects include tunneling of the molecules between symmetry equivalent sites and thermal expansion. We find a rather high probability of tunneling to occur at a temperature of 80 K, where the neutron scattering experiments were performed.[1] For example, for ethane the potential-energy barrier between symmetry-equivalent equilibrium sites is 230 cal (=165 K). Similarly, for propane and butane the translational tunneling barriers are in the range 200–300 cal. The thermal expansion of the films normal to the surface is treated in Sec. III D below.

It is straightforward to extend the present calculations to include the interaction between adsorbed molecules. However, it was felt that it would be difficult to predict the two-dimensional crystal structure of the paraffin films in this way. Instead, we decided to await the results of neutron-diffraction experiments[4] and then use the experimentally determined film structure to examine the effect of intermolecular coupling on height and orientation obtained in the single-molecule approximation.

B. Intramolecular distortions

In general, the structure of the paraffin molecules will be distorted upon adsorption due to the forces exerted by the substrate. Atomic positions within the molecule will be altered until the net force on each atom vanishes. Since the valence forces within the molecule are much stronger than the Van der Waals forces between the molecule and the substrate, we will assume the adjustments in bond lengths and angles to be negligible. Instead, we have investigated rotational distortions involving motion of hydrogen atoms in both CH_3 and CH_2 groups about a C-C bond. These rotational distortions involve the same atomic displacements as the torsional modes of vibration observed by inelastic neutron scattering.[1]

To determine the magnitude of these rotational distortions in ethane, propane, and butane, the molecular center of mass was placed at the point (x_s, y_s) corresponding to the equilibrium configurations in Figs. 4(c)–6(c). The angle of distortion about the C-C bond, the orientational parameters $(\theta_X, \theta_Y, \theta_Z)$, and the height above the surface were then varied until a minimum in the total potential energy was found. The total potential energy included the cost in energy associated with the internal rotational barrier of the molecule. The rotational barriers used were taken from the quan-

TABLE II. Calculated equilibrium configurations and energies of the undistorted ethane, propane, and butane molecules adsorbed on a graphite basal plane. The position of the molecular center of mass is given in the surface coordinate system (x_s, y_s, z_s) defined in Fig. 3. The molecular orientation is specified by the rotation angles θ_X, θ_Y, θ_Z about the (X, Y, Z) axes shown in Fig. 2.

	Center-of-mass coordinates in Å (x_s, y_s, z_s)	$\theta_X, \theta_Y, \theta_Z$	E_{eq} (kcal/mole)
Ethane	(1.23, 0.0, 3.56)	(0, 0, 150°)	−5.33
Propane	(0.985, −0.568, 3.57)	(0, 0, 60°)	−7.50
Butane	(1.23, 0.0, 3.57)	(0, 0, 60°)	−9.68

tum-mechanical calculations of Radom and Pople[8] and are given in the Appendix. They are plotted as the solid curves in Fig. 7.

The calculations showed that each molecule suffered a rotational distortion of the methyl groups about the terminal C-C bond. By symmetry it is clear that when the paraffin molecules are adsorbed at their equilibrium sites the rotation of the methyl groups should be coupled so that each group distorts in the opposite direction by the same angle. For the case of ethane, the sum of the internal methyl rotation barrier and the interaction potential with the substrate is plotted as the dashed curve in Fig. 7(b). It can be seen that the total potential energy is lowered by ~35 cal/mole when the relative angle of rotation α between the methyl groups is ~3.5°. Approximately the same values of α and the energy of the methyl distortion were obtained for propane and butane. The atomic coordinates of the distorted molecules are listed in Table I.

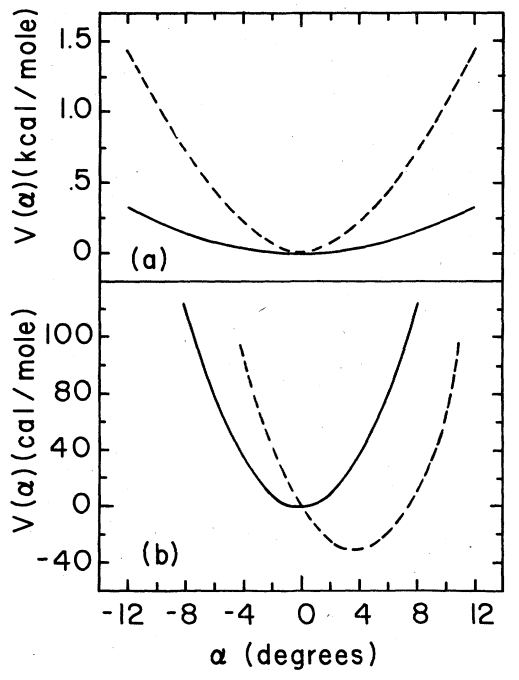

FIG. 7. (a) Potential energy of a CH_2 group in butane as a function of the relative rotation angle about the internal C-C bond. The solid curve shows the energy barrier for a free butane molecule, Eq. (A4). The dashed curve is the perturbed potential with the molecule adsorbed on graphite at the equilibrium site of Fig. 6(c). (b) Potential energy of a CH_3 group in ethane as a function of the relative rotation angle about the C-C bond. The solid curve shows the energy barrier for a free ethane molecule, Eq. (A1). The dashed curve is the perturbed potential obtained with the molecule adsorbed on graphite at the equilibrium site of Fig. 4(c).

No rotational distortion of the CH_2 groups about the internal C-C bond was found for butane. As shown by the dashed curve in Fig. 7(a), the perturbing potential of the substrate increases the energy of distortion for all angles α.

The numerical results for the energies and angles of these distortions are quite sensitive to the potentials assumed for the internal rotation barriers. Although the distortions calculated are small, they are large enough to be beyond the numerical uncertainties. A more detailed study of molecular distortions is planned for the semiempirical MINDO/3 calculations.[6]

C. Dynamics of the adsorbed molecule

1. Surface vibratory modes

When a molecule is adsorbed on a surface, the hindering of its three translational and three rotational degrees of freedom will, in general, result in the appearance of six new surface vibratory modes which do not appear in the spectra of the free molecule. If the surface potential is sufficiently strong, the new modes occur at high enough energy transfers to be resolved experimentally. Under these conditions one might also expect to observe perturbations of the low-frequency intramolecular excitations of the adsorbed molecule. Indeed, both of these effects have been observed in the inelastic neutron spectra of monolayer butane films adsorbed on graphite.[1]

The approximation used here of a single adsorbed molecule cannot give a complete dynamical description of the adsorbed film since coupling between molecules will give rise to propagating excitations or phonons.[9] For example, we would expect the translational vibratory modes of the molecule parallel to the surface and the rotational mode about an axis normal to the surface to be strongly affected by nearest-neighbor interactions. On the other hand, the observed excitation spectrum of adsorbed butane suggests that the rocking modes of the molecule about the X, Y axes parallel to the surface and the vibratory motion of the molecule in the z direction normal to the surface are determined primarily by the interaction of the molecule with the substrate. For this reason we believe it worthwhile to investigate the dynamics of the adsorbed paraffin molecules in the single-molecule approximation.

Two different force-constant models were used to calculate the frequencies of the surface vibratory modes of ethane, propane, and butane. The rigid-molecule model is based on the results of our previous normal-mode calculation[1,2] in which the eigenvectors of the surface vibratory modes were found to be rotational displacements about the principal symmetry axes of the molecule and a translation normal to the surface. In this model the term in the potential-energy function corresponding to each of these modes was obtained by computing the energy change as the rigid molecule was rotated or translated about its equilibrium position. Force constants were calculated numerically from the second derivative of the change in potential energy with respect to the appropriate angular or spatial coordinate. These force constants are listed in Table III(b). Using the moments of inertia of the undistorted molecule[10] in Table III(a), the frequencies of the normal modes could then be calculated and are given in Table III(c).

In the case of butane, the frequencies of the θ_X, θ_Y rotations and the T_z translation lie in the same range, 50–125 cm^{-1}, as the peaks assigned to these modes in the observed monolayer spectrum (Ref. 1). The rocking mode about the x axis was identified as an intense band at 112 cm^{-1} which is within the experimental uncertainty of the value of 123 cm^{-1} calculated here. It was suggested in Ref. 1 that a broad band observed at ~50 cm^{-1} contained both the T_z and θ_Y modes. The frequencies calculated here for these modes lie about 30 cm^{-1} above this band. The T_x and T_y modes are calculated to have frequencies well below 50 cm^{-1}, indicating very weak restoring forces parallel to the surface when the intermolecular interaction is neglected. The T_x and T_y modes will be spread into phonon bands when intermolecular forces are included. The frequencies of the T_x and T_y modes calculated in the single-molecule approximation will be lower bounds to the zone-boundary frequencies of these bands. We have not as yet identified any peaks in the butane inelastic spectra which can be associated with acoustic phonons propagating parallel to the surface. However, these modes may lie in the low-energy tail of the broad band observed at 50 cm^{-1}. It is interesting to note in Table III(c) that the T_z and θ_Y surface vibratory modes have nearly the same frequency for the three paraffin molecules while a small systematic increase of the θ_X frequency occurs upon going from ethane to butane. The small spread in the surface mode frequencies of the different molecules reflects the similarity in their orientation and position with respect to the graphite basal plane as described in Sec. III A.

A valence force-constant model was also used to calculate the frequencies of the surface vibratory modes. The purpose of this model was to enable a comparison between the force field of the empirical potentials in Eqs. (3) and (4) and that of the simple valence force model previously used to fit the monolayer excitation spectrum of butane.[1,2] The valence force model consisted of assuming an orientation of the molecule with respect to the surface and then introducing force constants directed along the surface normal between atoms in the molecule and an infinitely massive substrate. The various molecular orientations and bond schemes investigated are described in Ref. 2. The model which provided the best fit to the observed butane

TABLE III. Results of the rigid-molecule model for the surface vibratory modes of ethane, propane, and butane. The molecule is treated as a rigid body with three translational (T_x, T_y, T_z) and three rotational ($\theta_X, \theta_Y, \theta_Z$) degrees of freedom. (a) Moments of inertia of the molecules, (b) effective force constants for each surface vibratory mode, and (c) calculated frequencies of the surface modes.

			Moment of inertia (amu – Å^2)				
(a)		Mass (amu)	I_X	I_Y		I_Z	
	Ethane	30	6.38	25.24		25.24	
	Propane	44	17.86	58.36		66.55	
	Butane	58	25.35	132.4		144.9	
(b)	Force constant	T_x[a]	T_y[a]	T_z[a]	θ_X[b]	θ_Y[b]	θ_Z[b]
	Ethane	0.0065	0.0024	0.15	0.019	0.157	0.0029
	Propane	0.018	0.0055	0.21	0.132	0.20	0.018
	Butane	0.016	0.010	0.28	0.23	0.48	0.026
(c)	Normal mode (cm^{-1})	T_x	T_y	T_z	θ_X	θ_Y	θ_Z
	Ethane	19	12	92	103	72	14
	Propane	26	15	90	112	76	21
	Butane	22	17	90	123	78	18

[a] Units are mdyn/A.

[b] Units are mdyn cm/rad^2.

spectrum assumed the same molecular orientation as we have found from energy considerations in Sec. III A, i.e., the plane of the carbon skeleton aligned parallel to the graphite layers. Two different force constants were introduced between the substrate and the adjacent plane of hydrogen atoms in the molecule. One was used for each of the bonds between the CH_2 hydrogen atoms and the substrate and the other for the CH_3 hydrogen-surface bonds.

In order to calculate the force constants in this model using the potentials considered here, we computed the contribution to the molecular binding energy of the individual carbon and the hydrogen atoms as a function of their height z_s above the surface. The appropriate force constant is then obtained from the second derivative of this quantity with respect to z_s in the neighborhood of the potential minimum. Table IV(a) contains the force constants for the carbon atoms and the hydrogen atoms nearest the surface for each of the three paraffin molecules.[11] To within the uncertainty in the calculation, there is no variation in the magnitude of the force constants for the hydrogen-surface and carbon-surface bonds. Again, this reflects the similarity of the equilibrium configurations of the molecules adsorbed on the graphite basal plane and for each molecule the near equivalence of the hydrogen and carbon sites, respectively [see Figs. 4(c)–6(c)]. The force constants obtained previously by fitting to the observed excitation spectrum of monolayer butane have the same order of magnitude as those calculated here. Typically, they are a few per cent of the value used to represent the intramolecular C-H stretch. In the case of the CH_3 hydrogen-surface bond the empirically fit force constant and the value calculated here are virtually identical, but the calculation does not support the larger value of the CH_2 hydrogen-surface bond found necessary to fit the observed spectrum.[1,2] The calculation also predicts force constants for the carbon-surface bond which are a factor of 2 larger than for the hydrogen-surface bonds, while the fit to the observed spectrum was found to worsen if carbon-surface bonds were included. Nevertheless, the calculated carbon-surface force constants are not so large as to interchange the order of the T_z, θ_X, and θ_Y eigenfrequencies as was found in Ref. 2 when only the butane carbon atoms were bound to the surface.

In comparing the results of the rigid molecule and the valence force-constant models [Tables III(c) and IV(b)], we find that the frequencies obtained for the T_z and θ_Y modes agree reasonably well. The frequency of the θ_X mode is somewhat smaller in the valence force-constant model and does not show the systematic decrease found in the rigid-molecule model. We conclude that the essential features of the calculated surface vibratory spectra are independent of the particular force-constant model used.

2. Perturbation of the intramolecular torsional modes

In addition to the surface vibratory modes, the observed monolayer excitation spectrum of butane

TABLE IV. Results of the valence force-constant model. (a) Calculated force constants between individual carbon and hydrogen atoms in the molecule and the graphite basal plane. Atom numbers in parentheses are used for identification as in Table I and Fig. 2. The fitted values for butane are those inferred in Refs. 1 and 2 from the observed inelastic neutron spectra; (b) calculated frequencies of the surface vibratory modes. In the case of butane, the observed values are from the inelastic neutron spectra in Refs. 1 and 2.

(a)	Force constant (mdyn/Å)	C(1)	C(5)	C(8)	C(11)	H(3)	H(7)	H(9)	H(13)
	Ethane	0.038	0.038	···	···	0.021	0.021	···	···
	Propane	0.037	0.041	0.038	···	0.021	0.021	0.021	···
	Butane	0.037	0.039	0.039	0.037	0.020	0.021	0.021	0.023
	fitted	0.0	0.0	0.0	0.0	0.02	0.065	0.065	0.02

(b)	Normal mode (cm^{-1})	T_z	θ_X	θ_Y
	Ethane	81.2	92.8	33.7[a]
	Propane	81.3	92.7	70.9
	Butane	82.5	92.0	72.5
	obs.	~50[b]	112	~50[b]

[a] Ethane does not have a pure θ_Y mode for the simplified bonding scheme considered here.

[b] The observed T_z and θ_Y modes of adsorbed butane appear to be unresolved in a broad band centered at 50 cm^{-1}.

contained the intramolecular torsional modes of the CH_3 and CH_2 groups. The CH_2-CH_2 torsion occurred at a frequency of 157 cm^{-1} or about 25 cm^{-1} higher than in the bulk liquid spectrum.[12] Since the liquid spectrum best approximates that of the free molecule, this frequency shift was attributed to the perturbation of the substrate potential. No detectable shift was observed in the CH_3 torsional frequencies.

To investigate the effect of the surface potential on the intramolecular torsional modes of the paraffins, we have calculated the perturbation of the CH_2-CH_2 torsion frequency of butane and the CH_3 torsion frequency of ethane adsorbed on a graphite basal plane. The relevant potential-energy functions are the same ones used in the calculation of the intramolecular distortions of the adsorbed molecules in Sec. III B. Recall that the potentials are obtained by summing the internal rotation barrier energy and the molecule-substrate interaction as the molecule is distorted about its equilibrium configuration. Figure 7(a) contains the potential-energy function for the CH_2-CH_2 torsion in both free and adsorbed butane versus the relative angle of rotation of the CH_2 groups, α. The force constant obtained from the curvature of the potential at its minimum is 15.8 cal^2/deg^2 for the adsorbed molecule compared with 10.8 cal^2/deg^2 for the free molecule. Since the torsional frequency varies as the square root of the force constant, we estimate a ~25% increase in the CH_2-CH_2 torsional frequency of adsorbed butane. This is in reasonable agreement with the increase from 130 cm^{-1} to 157 cm^{-1} observed between the bulk liquid and monolayer spectra.

Figure 7(b) contains the similarly calculated potential-energy functions for the methyl torsion in free and adsorbed ethane. The force constant obtained for the adsorbed molecule is 4.8 cal^2/deg^2 compared with 4.6 cal^2/deg^2 for the unperturbed methyl rotation barrier. This results in a 2%–3% increase for the methyl torsion frequency in adsorbed ethane, which is too small to be detected by inelastic neutron scattering. Shifts of the same magnitude were calculated for the methyl torsional modes in adsorbed propane and butane.

D. Effects of anharmonicity in the potential energy functions

In the discussion of the dynamical properties of the adsorbed molecules in the previous section, we have only used the harmonic part of the potential-energy functions. To assess the importance of anharmonic contributions to the atom-atom potentials in Eqs. (3) and (4), we have calculated the temperature dependence of the height of a butane molecule above the graphite basal plane and of the frequency of the T_z vibration normal to the surface. These calculations are based on the potential energy $V(z_s)$ of a butane molecule with center of mass located at the equilibrium position (x_s, y_s) as a function of the height z_s above the graphite surface. This potential is obtained by summing over all interacting pairs of atoms as described in Sec. III and is plotted in Fig. 8. We should note that in the single-molecule approximation we are neglecting the thermal expansion of the film parallel to the surface. The in-film expansion can also affect the molecule-surface distance since the height of the molecule varies slightly from point to point in the graphite basal plane.

To determine the thermal expansion and the renormalization of the T_z frequency, we have used a first-order perturbation expansion of the Helmholtz free energy F and a minimum principle. The Hamiltonian for the molecular motion in the z direction is

$$H = p^2/2m + V(z) \ , \qquad (5)$$

where p is the momentum of the molecule and m its mass (for convenience we have dropped the subscript on z). A perturbation series of F may be written to first order as

$$F = F_0 + \langle H - H_0 \rangle_0 + \cdots \ , \qquad (6)$$

where $\langle \cdots \rangle_0$ denotes a thermal average for a system characterized by a Hamiltonian H_0. For H_0 we take

$$H_0 = p^2/2m + (m\omega^2/2)[(z - z_0) - a]^2 \ , \qquad (7)$$

which describes a harmonic oscillator of frequency ω with its center displaced from z_0 by a distance a. The minimum principle states that

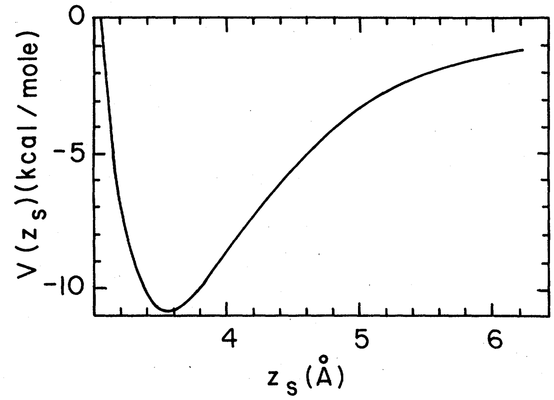

FIG. 8. Potential energy of butane as a function of its center-of-mass distance from the graphite basal plane. The molecule is in its most favorable position and orientation with respect to the surface as shown in Fig. 6(c).

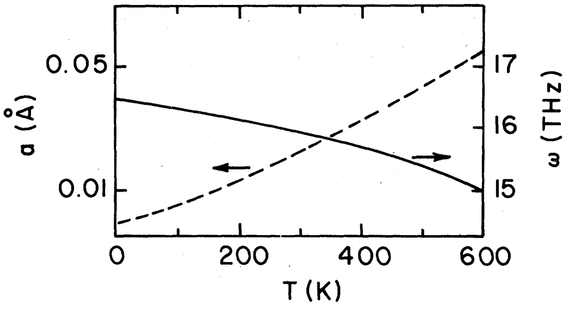

FIG. 9. Anharmonic effects. The change in height, a, of the butane molecule above the graphite basal plane and the frequency ω of the T_z mode normal to the surface as a function of temperature.

$$F \leq F_0 + \langle H - H_0 \rangle_0 \;, \tag{8}$$

from which the following equations for a and ω can be obtained[13]:

$$\left\langle \frac{dV}{dz}(z) \right\rangle_0 = 0 \;, \tag{9}$$

$$\left\langle z \frac{dV}{dz}(z) \right\rangle_0 = \frac{\langle p^2 \rangle_0}{m} \;. \tag{10}$$

Equations (9) and (10) were solved for the thermal expansion a and the frequency ω as a function of temperature. The results are plotted in Fig. 9. As the temperature increases from 0 to 300 K, the height of the molecule above the surface increases by less than 0.3 Å and ω shifts downward by only a few per cent. Thus neither of these effects is large enough to be observed experimentally. We expect similar results to be obtained for other paraffin molecules adsorbed on graphite.

IV. DISCUSSION AND CONCLUSIONS

In assessing the results presented here, it is helpful to begin by reviewing the underlying assumptions of the calculation. The initial assumption is that the perturbing potential of the surface is sufficiently weak that the electronic structure of the molecule is unchanged upon adsorption. That is, no change in the intramolecular potentials such as the torsion barriers occurs upon adsorption. In calculating the equilibrium position of the adsorbed paraffins, the molecules are assumed rigid except for rotational degrees of freedom about the C-C bonds. Also, no attempt has been made to take into account the electronic band structure of the graphite nor changes in it which result from the adsorption of a paraffin molecule. Finally, we have made the single-molecule approximation in which the interaction between adsorbed molecules is neglected.

Despite these simplifying assumptions the calculations reproduce both structural and dynamical properties of the paraffin films adsorbed on graphite as inferred from neutron scattering experiments. Two structural features which we have found to be common to all of the paraffin molecules adsorbed on a graphite basal plane are: (i) a tendency of the carbon skeleton of the molecules to align itself parallel to the surface, and (ii) a preference of the hydrogen atoms nearest the surface to lie at the center of the graphite carbon hexagons. For all three molecules, the height of the carbon skeleton above the graphite basal plane is computed to be in the range 3.55 to 3.60 Å. This distance is rather insensitive to the position of the molecule parallel to the surface so that we do not expect it to change appreciably when intermolecular forces are included.

In the case of butane, the equilibrium position of the molecule predicted here is consistent with a model which we previously developed to explain the monolayer excitation spectrum. The model assumed the carbon skeleton to be aligned parallel to the graphite basal plane with the H atoms nearest the surface at symmetry equivalent sites [compare Fig. 6(c) with Fig. 1(b) in Ref. 2]. Elastic neutron scattering experiments are now in progress to determine the long-range order in the films and the height and orientation of the molecules with respect to the surface.[4] The height of the molecule can be deduced from measurements of the modulation of the 002 Bragg reflection of the graphite by the hydrocarbon overlayer.[9] A preliminary experiment[4] on a hydrogenated butane film yielded a value of 3.9 ± 0.3 Å for the height of the carbon skeleton above the graphite basal plane surface which nearly overlaps with the value of 3.57 Å reported here.

The calculations described here suggest the type of intramolecular distortion which is energetically most favorable for a paraffin molecule adsorbed on a graphite basal plane. For each molecule we find small rotational displacements of the methyl groups about the terminal C-C bonds. Unfortunately, the predicted distortions are too small to be easily investigated experimentally. We intend to study the question of molecular distortions in greater detail in the quantum-mechanical calculations of the structure of paraffin molecules adsorbed on graphite.[6] Specifically, we shall try to determine whether there is a change in the methyl rotation barrier upon adsorption. Intramolecular distortions can also be induced by the interaction between the adsorbed molecules. This possibility can be investigated using the same interatomic potentials considered here once the two-dimensional crystal structure of the films has been determined.

The surface vibratory modes calculated for adsorbed butane are in reasonable agreement with the observed inelastic neutron spectra. The calculated modes lie in the observed frequency range, 50–125 cm^{-1}, and occur in the same order as deduced from their relative intensities in the monolayer spectrum. That is, the rocking mode about the chain axis occurs at the highest frequency followed by the uniform oscillatory mode normal to the surface and the rocking mode about the orthogonal symmetry axis. Although there is some variation depending on the force-constant model used the calculated frequencies are within 30 cm^{-1} of the experimental values.

In the valence force-constant model there are some qualitative differences between the force constants calculated from the empirical potentials and those deduced from the observed butane excitation spectrum. The calculation does not predict larger force constants between the CH_2 hydrogen atoms and the surface than for the CH_3 hydrogens. Nor does it suggest that the force constants between the butane carbon atoms and the surface can be neglected. An independent determination of the film structure by elastic neutron diffraction[4] will be helpful in resolving these discrepancies. In particular, it is important to confirm that the molecules are in registry with the graphite basal plane as predicted in the equilibrium configurations of Figs. 4(c)–6(c). A larger intramolecular distortion than calculated here could also contribute to the discrepancy between the calculated and fitted force constants.

In summary, we have found model calculations based on empirically derived C-C and C-H potentials to provide a useful first step in interpreting neutron scattering experiments on paraffin molecules adsorbed on graphite. The success of the single-molecule approximation in explaining some of the dynamical and structural features of monolayer butane films lends support to the contention that these properties are primarily determined by the molecule-substrate interaction. However, further work is necessary to assess the effect of intermolecular forces especially for the shorter, more weakly bound molecules, ethane and propane. Finally, calculations of the electronic structure of paraffin molecules adsorbed on graphite are necessary to provide a deeper understanding of the applicability of empirical potentials to these systems.

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APPENDIX

The potential-energy barriers for the different internal rotations of the paraffin molecules were taken from the self-consistent INDO calculations of Radom and Pople.[8] For the methyl rotation barrier in ethane they obtained (in units of kcal)

$$V(\alpha)=1.666(1-\cos 3\alpha)-0.007(1-\cos 6\alpha)\ , \tag{A1}$$

where α is the relative rotation angle of the two methyl groups about the C-C bond. As mentioned in the text, by symmetry it is necessary to couple the rotation of the methyl groups for the adsorbed molecule so that each group rotates in the opposite direction by an angle $\frac{1}{2}\alpha$. The potential-energy function Eq. (A1) is plotted in Fig. 7(b) as the solid curve.

The methyl rotation barrier for propane is given by

$$\begin{aligned}V(\alpha_1,\alpha_2)=&1.726(1-\cos 3\alpha_1)+1.726(1-\cos 3\alpha_2)\\&-0.002(1-\cos 6\alpha_1)-0.002(1-\cos 6\alpha_2)\\&-0.143(1-\cos 3\alpha_1)(1-\cos 3\alpha_2)\\&-0.152\sin 3\alpha_1\sin 3\alpha_2\ ,\end{aligned} \tag{A2}$$

where α_1, α_2 denote rotations of the two methyl groups. Again, symmetry dictates that $\alpha_1=\alpha_2$.

For butane, the potential energy for rotation of either methyl group is given by

$$V(\alpha)=1.70(1-\cos 3\alpha)\ , \tag{A3}$$

while the potential-energy function for a dihedral rotation about the internal C-C bond is

$$\begin{aligned}V(\alpha)=&1.500(1-\cos\alpha)-0.6705(1-\cos 2\alpha)\\&+1.882(1-\cos 3\alpha)+0.0495(1-\cos 4\alpha)\\&+0.0305(1-\cos 5\alpha)-0.065(1-\cos 6\alpha)\ .\end{aligned} \tag{A4}$$

The angle α represents the relative angle of rotation between a CH_2 and a CH_3 group in Eq. (A3) and between the two CH_2 groups in Eq. (A4).

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[10] The difference in the moments of inertia between the distorted and undistorted molecules is negligible in calculating the frequencies of the normal modes of vibration.

[11] Note that the individual atoms in the molecule may not have their minimum potential energy with respect to the surface when the total potential energy of the molecule is minimized. However, the procedure described for obtaining the atom-substrate force constants is still valid if the anharmonicity of the potential is small.

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[13] See, for example, R. P. Feynman, *Statistical Mechanics A Set of Lectures* (Benjamin, Reading, 1972), Chap. 2, p. 55.