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Rotational states of H_2, HD, and D_2 on graphite

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The rotational states of H_2, HD, and D_2 adsorbed on graphite in the $\sqrt{3}\times\sqrt{3}\,R30°$ commensurate phase, were calculated using a product wave function consisting of a rotational part, itself a product of single-molecule rotational wave functions, multiplied by a spatial part which describes the motion of the molecular center of mass. The single-molecule rotational term is written as an expansion in free-rotor basis functions. The spatial part is given by a self-consistent-phonon wave function determined in a previous calculation. The rotational ground state for each species is found to be a nearly pure $J=0$ state, and the lowest group of excited states, which are essentially $J=1$ states, are split with an energy separation of about 2.5–2.7 meV. These excited states are separated from the ground state by an average energy which is given approximately by $BJ(J+1)$, where B is the rotational constant of the molecule. Thus the rotational states of hydrogen molecules adsorbed on graphite are, to a good approximation, slightly hindered three-dimensional rotor states.

I. INTRODUCTION

There has been much recent interest in the phases of the various isotopic species of molecular hydrogen adsorbed on graphite.[1–16] In both the theoretical and experimental investigations, these molecules have been assumed to exist in a $J=0$ rotational state, there being some experimental justification for this assumption.[17–21] Since each molecule experiences a nonspherical potential, due both to the interaction of the molecule with the substrate and the anisotropic intermolecular interaction,[22–29] this assumption needs some examination. Classical calculations for homonuclear diatomic molecules adsorbed on a surface show that they tend to lie down with their molecular axis parallel to the surface.[30] Because hydrogen molecules have such a small mass, it is reasonable to expect that this is not the case for these molecules, and to expect that they should behave more like hindered rotors.[17–21,31] Nevertheless, without explicit calculations it is difficult to know just how much tendency there is for these molecules to lie parallel to the surface, or conversely, to what extent they exist as essentially free rotors. This paper describes the results of a calculation of those effects on the rotational states of molecular hydrogen which are the result of the interactions of these molecules with the substrate. The effects due to the anisotropic interaction between the molecules on the surface are discussed briefly.

Interest in the hindered rotations of molecular hydrogen adsorbed on surfaces goes back many years.[31] The approach used in this work is similar to these earlier calculations in that free rotor eigenstates, which are spherical harmonics, are used as a basis set for the expansion of the true rotational eigenstates. The earlier calculations, however, used a parametrized cosine function to describe the interaction of the molecule with the substrate, and considered only the case of a fixed center of mass for the molecule. In this work, the interaction with the substrate is built from a site-site model with parameters chosen to match a previously determined isotropic molecule-carbon potential. This isotropic potential had its parameters chosen to fit the values of the bound-state energies as determined by selective adsorption experiments,[32,33] and was used in a recent calculation of the lattice dynamics of the commensurate phase of H_2 and D_2 adsorbed on graphite.[3] The calculations presented here for the rotational states also include the effects upon these states due to the zero-point motion of the molecular center of mass. The ground-state wave function of the above lattice-dynamics calculation provides the form and the numerical values for the parameters of the spatial part of the wave function used in this calculation of the rotational states. This lattice-dynamics calculation, which assumed that the molecules were all in a $J=0$ state, was a self-consistent-phonon calculation of the phonon modes of the $\sqrt{3}\times\sqrt{3}\ R\ 30°$ phase at zero degrees Kelvin.

II. INTERACTION MODEL

The model used for the interaction of each molecule with the graphite lattice is a sum of site-site interactions between the two sites on a given molecule and each carbon atom in the graphite.[30,34] The molecular intersite distance is given by the same value d for all isotopic species, and the individual site-carbon interaction chosen is Lennard-Jones (LJ) in functional form with well depth and hard-core separation parameters ε_o and σ_o. The value of d was determined in such a way that the "shape" of the model molecule is essentially the same as that of the real molecule. The values of ε_o and σ_o were chosen so that the resulting well depth and hard-core separation of the isotropic part of the anisotropic molecule-carbon interaction matched that of the previously determined isotropic molecule-carbon potential mentioned above.

The electronic charge-density profiles of molecular hydrogen, at distances corresponding to the hard-core separation of the interaction with other molecules, form elliptical-like contours.[22] The aspect ratio, or ratio of the long axis to the short axis, is 1.07 as estimated from drawings of these contours.[35] The distance chosen for the separation of the charge centers of the molecule was constrained by the condition that the profile of the zero potential energy contour for the interaction of the molecule with a carbon atom has the same aspect ratio as the electron density contours of the molecule. The small differences between these contours for the various isotopes were ignored.

The model molecule has charge centers located at $\boldsymbol{\delta}_1$ and $\boldsymbol{\delta}_2$ relative to the molecular center of mass located at $\mathbf{R}$ as shown in Fig.1. The vector $\boldsymbol{\delta}_2-\boldsymbol{\delta}_1$ has magnitude d, and its orientation relative to the surface is determined by the polar angle θ and azimuthal angle ϕ, with the z axis taken to be perpendicular to the surface. The interaction between this molecule and a carbon atom located at a position $\mathbf{r}$ is given by

$$\Phi(\mathbf{R}-\mathbf{r},\theta,\phi)=v(\mathbf{R}+\boldsymbol{\delta}_1-\mathbf{r})+v(\mathbf{R}+\boldsymbol{\delta}_2-\mathbf{r}). \tag{1}$$

where v depends only upon the magnitude of its argument and has the standard LJ(12,6) form

$$v(\mathbf{r})=v(|\mathbf{r}|)=v(r)=4\varepsilon_o\left[\left[\frac{\sigma_o}{r}\right]^{12}-\left[\frac{\sigma_o}{r}\right]^{6}\right]. \tag{2}$$

The contour defined by $\Phi=0$ has a shape that is independent of ε_o, and depends only upon the ratio of d to σ_o. The value of d/σ_o which produces a 1.07 ratio of the long and short axes of this contour was found numerically to be 0.189.

The isotropic molecule-carbon interaction used in Ref. 3 has a hard core separation of 2.85 Å and a well depth of 4.13 meV. The isotropic part of the model site-site interaction is given by the average of Φ over all angles, which is simply the diagonal matrix element of Φ for the $J=0$ state. A value of 2.24 meV for ε_o was found numerically to produce the proper well depth for the isotropic part of the site-site molecule-carbon interaction. A numerical search then determined that a value of $\sigma_o=2.78$ Å produces a hard-core separation which matches that of the isotropic interaction used in Ref. 3. The resultant value of d is 0.525 Å. This is significantly less than the bond length of 0.741 Å, this reduction being a reflection of the fact that the electron cloud in molecular hydrogen is concentrated between the protons instead of having each electron charge centered about its own proton.[36] As a check on how reasonable this value of d is, a classical calculation of the quadrupole moment was carried out,[22,29,37] separating the protons by the bond length of 0.741 Å and placing the electrons symmetrically on the molecular axis separated by d. The value of the quadrupole moment of the model molecule which results from this calculation differs from the accepted value for H_2 by about 1%.[37] This is evidence that the model molecule has a reasonable relation to the real molecule.

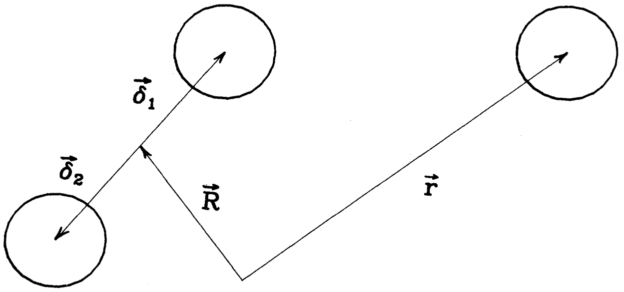

FIG. 1. Diagram of the coordinates used to specify the relative location of a hydrogen molecule and a carbon atom. The symbols shown in the diagram are defined in Sec. II of the text.

Figure 2 shows the isotropic part of the molecule-carbon interaction used in this work along with the isotropic interaction used in Ref. 3. The match is quite good in that region of the potential which extends from the hard-core separation to a point well beyond the potential minimum. At larger separations there is some discrepancy, but this is to be expected since the asymptotic values of the two functions do differ by about 7%. However, the range of separations which are important in the determination of the mixing of the rotational states due to the anisotropic part of the interaction, is just that range where the two isotropic functions match well. The effect of the mismatch of the potentials at large separations means that the sum over all carbon atoms of the molecule-carbon terms, using the rotationally averaged site-site interaction, will differ from that determined from the isotropic interaction of Ref. 3. However, the lowering of the ground-state energy due to rotational mixing and the energy separation between the rotational levels should not be affected. Since we are interested only in the relative shifts produced by the mixing of rotational states, all energies of the rotational eigenstates will be given relative to the interaction energy of the $J=0$ state.

The interaction between each molecule and the graphite substrate is a simple sum of LJ(12,6) interactions between each molecular site and each carbon atom, so it is possible to use Steele's formalism to represent this energy.[30,38] The interaction energy is a function of the position $\mathbf{R}$ of the center of mass of the molecule and the angles θ and ϕ which give the orientation of the molecular axis. If V_1 represents the interaction of a single molecule with a single graphite plane located at $R^z=0$, then using the Steele formalism for each site within the molecule,

$$V_1(\mathbf{R},\theta,\phi)=\sum_{\mathbf{G}}\sum_{i}U_{\mathbf{G}}(R^z+\delta_i^z)\exp[i\mathbf{G}\cdot(\mathbf{R}+\boldsymbol{\delta}_1)], \tag{3}$$

where $\mathbf{G}$ is a reciprocal lattice vector of the graphite sur-

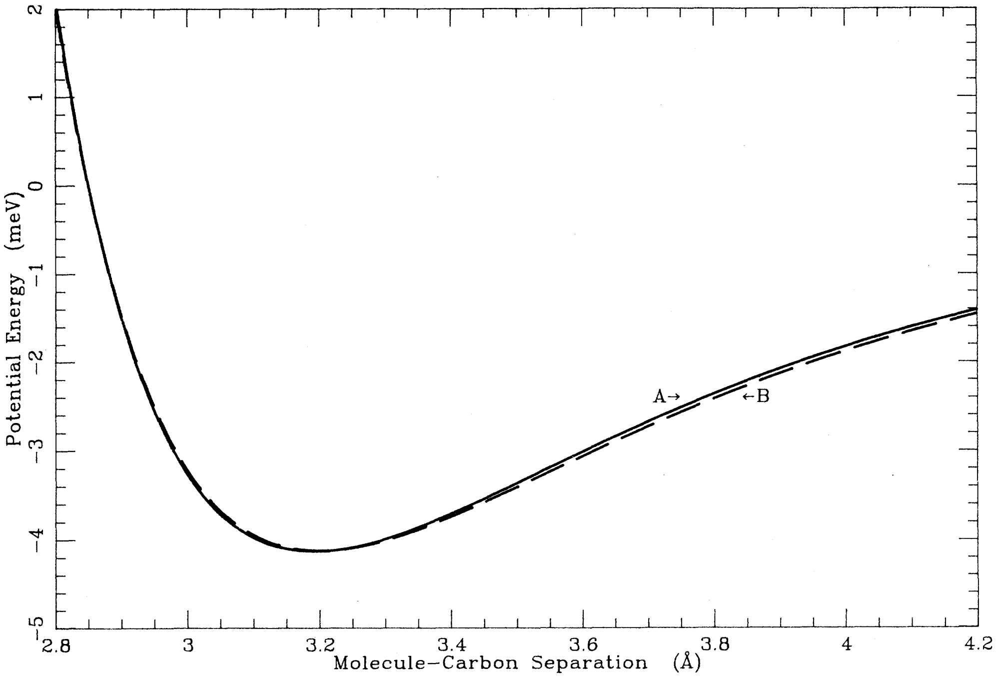

FIG. 2. The interaction between a single hydrogen molecule and a single carbon atom. Curve A shows the isotropic part of the interaction used in this work, and curve B shows the isotropic interaction of Ref. 3.

face lattice and $U_{\mathbf{G}}$ is the corresponding z-dependent Fourier amplitude. Since $\mathbf{G}$ is parallel to the surface, the argument of the exponential depends only on the x and y components of the vectors $\mathbf{R}$ and $\boldsymbol{\delta}$. The prescription for calculating $U_{\mathbf{G}}$ is given in Ref. 38. The expression given in Eq. (3) can be simplified by using the invariance of $U_{\mathbf{G}}$ to the transformation $(\mathbf{G}\rightarrow -\mathbf{G})$ and factoring. The result is

$$V_1(\mathbf{R},\theta,\phi)=\sum_{\mathbf{G}}\sum_{i}U_{\mathbf{G}}(R^z+\delta_1^z)\cos[\mathbf{G}\cdot(\mathbf{R}+\boldsymbol{\delta}_i)]. \tag{4}$$

In principle, it is necessary to add contributions from each plane of carbon atoms in the graphite, each contribution having the form of Eq. (4). However, as shown in Ref. 38, the contributions from all planes below the surface plane can be approximated, to a high degree of accuracy, by a simple analytic function of the z-component of the nucleus. It is possible to include the contributions of all planes below the top plane by using a correction term given by

$$V_{\text{corr}}=-\sum_{i=1}^{2}\frac{8\pi\varepsilon_0\sigma_0^6}{3\sqrt{3}b^2d}(R^z+\delta_i^z+0.61d)^{-3}\ . \tag{5}$$

In all calculations, Eq. (4) was used for the surface plane only, and Eq. (5) was used to represent the contributions from the rest of the graphite substrate.

In what follows, it is convenient to separate out the isotropic and anisotropic parts of the total interaction potential, $V(\mathbf{R},\theta,\phi)=V_1+V_{\text{corr}}$. V^I, which depends only upon the position molecular center of mass, is the isotropic part of the interaction between the molecules and the substrate, and V^A, which depends upon both the molecule's position and orientation, is the anisotropic part of this interaction.

III. MOLECULAR ROTATIONAL LEVELS

The total Hamiltonian for this system consists of the translational and rotational kinetic energies, the interaction energy between the molecules and the substrate, and the intermolecular interaction energy. The molecules are being treated as rigid rotors, so there is no intramolecular vibration term, and the intermolecular interaction used in this calculation is just the isotropic part of the full hydrogen intermolecular interaction.[3,22,39] Thus the only anisotropic terms considered are those due to the substrate. Given these assumptions, the Hamiltonian can be written as

$$\hat{H}=\hat{H}_T+\hat{H}_R\,, \tag{6a}$$

$$\hat{H}_T=\frac{\hbar^2}{2M}\sum_j\nabla_j^2+\tfrac{1}{2}\sum_{ij}v(R_{ij})+\sum_j V^I(\mathbf{R}_j)\ , \tag{6b}$$

$$\hat{H}_R=\frac{\hbar^2}{2I}\sum_j\hat{L}_j^2+\sum_j V^A(\mathbf{R}_j,\theta_j,\phi_j)\ , \tag{6c}$$

where the sums are over molecules located at positions $\mathbf{R}_j$ and $\mathbf{R}_i$; M is the mass of a molecule; I is its moment of inertia; $\hat{L}$ is the angular momentum operator; v is the isotropic intermolecular interaction which depends only on the magnitude of $\mathbf{R}_{ij}$, the relative displacement of each molecular center of mass.

Since the anisotropic part of the molecule-substrate interaction does depend upon **R**, the translational and rotational parts of the Hamiltonian do not decouple exactly. However, we will approximate the true wave function by a product of spatial and rotational parts and thus ignore any correlations between rotational and translational modes. That is, we are treating the interaction of translational and rotational modes in a mean-field manner. Furthermore, since the rotational Hamiltonian is a sum of single-molecule terms, the rotational wave function is itself a simple product of single-molecule terms. Let $\Upsilon(\mathbf{R}_1,\ldots,\mathbf{R}_N)$ represent the spatial part of the wave function, and $\Psi(\theta_1,\phi_1,\ldots,\theta_N,\phi_N)$ represent the rotational part of the wave function. Then the total wave function is approximated by $\Xi=\Upsilon\Psi$ where the translation part is determined by the eigenvalue equation:

$$\hat{H}_T\Upsilon = E_T\Upsilon, \tag{7}$$

and the rotational part is determined by

$$\hat{H}_{R_{\text{eff}}}\Psi = E_R\Psi, \tag{8}$$

with $H_{R_{\text{eff}}}$ being an effective rotational Hamiltonian.

The translational part of the problem is that of a $\sqrt{3}\times\sqrt{3}$ R 30° lattice of isotropic objects, subjected to a single-particle potential due to the substrate and to two-body interactions due to its neighbors. This problem has been worked out for H_2 and D_2, and we refer the reader to Ref. 3 for the details. The calculations for HD were done in a similar fashion.[40]

The effective rotational Hamiltonian $\hat{H}_{R_{\text{eff}}}$ is given by

$$\hat{H}_{R_{\text{eff}}} = \frac{\hbar^2}{2I}\sum_j \hat{L}_j^2 + \sum_j \tilde{V}^A(\theta_j,\phi_j), \tag{9}$$

and the effective anisotropic interaction $\tilde{V}^A$, which now depends only on the average position of the molecular center of mass, is given by

$$\tilde{V}^A(\theta,\phi) = \langle\Upsilon|V^A(\mathbf{R},\theta,\phi)|\Upsilon\rangle. \tag{10}$$

The calculation of the effective anisotropic interaction is a matter of averaging the original anisotropic interaction over the motion of the molecular center of mass. Although the evaluation of Eq. (10) appears formidable, the use of a correlated Gaussian wave function for the spatial part, as is the case in a self-consistent-phonon calculation,[41,42] makes this task quite straightforward. Because V^A depends only upon the coordinates of a single molecule, the integration over the center-of-mass coordinates can be done in closed form. The details of such a calculation are given in Ref. 42, and only the results are presented here.

The end result of the integration over the spatial coordinates is to replace the displacement **R** in Eq. (4) by the average or lattice position, and to replace the U_{G} in that same equation with an effective Fourier coefficient $\tilde{U}_{\text{G}}$ where

$$\tilde{U}_{\text{G}} = \langle U_{\text{G}}(z,\theta,\phi)\rangle_z \exp(-\tfrac{1}{4}G^2\delta u_{\text{rms}}^2). \tag{11}$$

Here z is the z-displacement of the molecular center of mass of a given molecule, δu_{rms} is the rms deviation of the xy motion from its average position, and the term $\langle\cdots\rangle_z$ refers to an average over the z-wise motion of the molecule. The calculation of this z-wise average is discussed in Ref. 3. The result depends only on the average position of the molecular center of mass $\bar{z}$ and the rms deviation of the z-position δz_{rms}. We refer the reader to Refs. 3 and 42 for the details.

The effective rotational Hamiltonian $\hat{H}_{R_{\text{eff}}}$ is a sum of single-molecule terms, so that the eigenvalue E_R is a sum of single-molecule eigenvalues ε_R, where this energy is determined by the eigenvalue equation for the single-molecule rotational wave function $\psi(\theta,\phi)$, namely

$$\frac{\hbar^2}{2I}\hat{L}^2\psi(\theta,\phi)+\tilde{V}^A(\theta,\phi)\psi(\theta,\phi)=\varepsilon_R\psi(\theta,\phi). \tag{12}$$

To solve this equation, the rotational wave function is expanded in the basis set of the free rotor. Let $|JM_J\rangle$ represent a state with a total angular momentum quantum number J and a quantum number M_J for the z component. These functions are, of course, just the spherical harmonics $Y_{JM_J}(\theta,\phi)$. Then if

$$|\psi\rangle = \sum_{J,M_J} C_{J,M_J}|J,M_J\rangle, \tag{13}$$

Eq. (12) can be transformed in the standard way into a matrix equation for the expansion coefficients C_{JM_J}. Using the Einstein summation convention, the result is

$$\frac{\hbar^2 J(J+1)}{2I}C_{JM_J} + \langle JM_J|\tilde{V}^A|J'M'_J\rangle C_{J'M'_J} = \varepsilon_R C_{JM_J}, \tag{14}$$

where the matrix elements of $\tilde{V}^A$ are given by

$$\begin{aligned}\langle JM_J|\tilde{V}^A|J'M'_J\rangle = \int_0^{\pi} d\theta\sin\theta \\ \times\int_0^{2\pi} d\phi\, Y^*_{JM_J}(\theta,\phi) \\ \times Y_{J'M'_J}(\theta,\phi)\tilde{V}^A(\theta,\phi)\ .\end{aligned} \tag{15}$$

It should be noted that the use of the spatial wave functions from Ref. 3 does presume that the rotational ground state is essentially a $J=0$ state. Should that not be the case, it would be necessary to recompute this spatial term. However, as will be seen in the next section, the $J=0$ assumption is a very good one.

IV. RESULTS

The shape of the potential profiles showing the interaction energy of the hydrogen molecule with the graphite surface is similar to that found for N_2 using a similar site-site model.[30] Figure 3 shows potential curves for three locations on the graphite surface, one over an adsorption site (center of the hexagon rings formed by the carbon atoms), one directly over a carbon atom, and one midway between two carbon atoms. The absolute depth of these wells should be looked at with caution because of

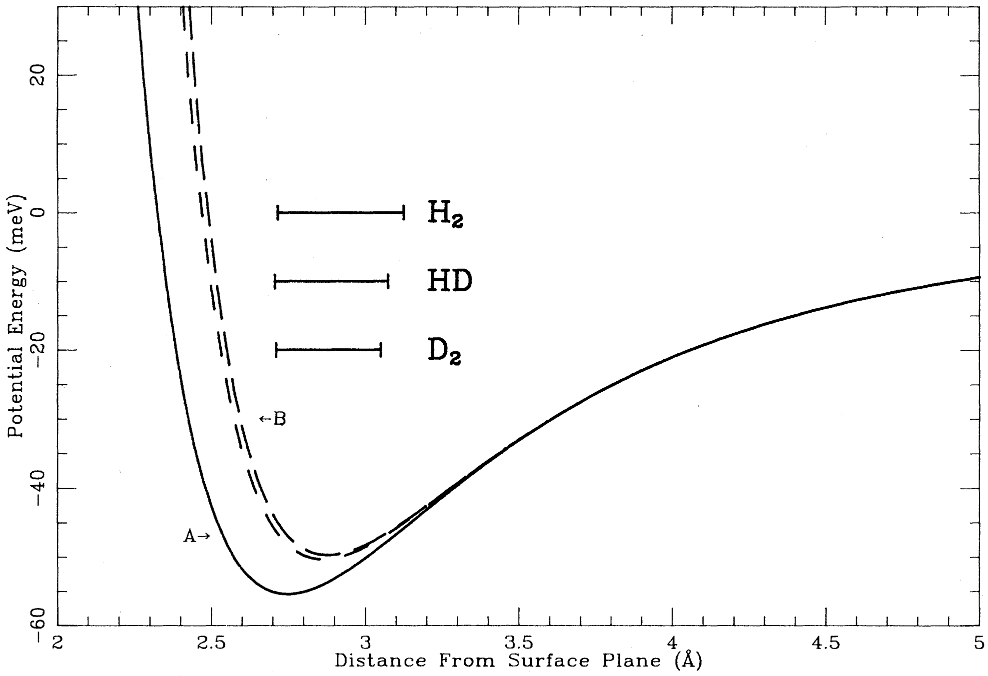

FIG. 3. The isotropic part of the interaction of a hydrogen molecule with a graphite surface as a function of the distance from that surface. Curve *A* shows the energy along a line passing through an adsorption site, and curve *B* shows the energy along a line passing through a carbon atom. The curve showing the energy along a line passing midway between two carbon atoms is just below curve *B*. The lines with bars show the values of z included in the range from $\bar{z}-\delta z_{\rm rms}$ to $\bar{z}+\delta z_{\rm rms}$ for each molecular species.

the asymptotic dependence of the model potential is not quite correct. The total substrate potential used in Ref. 3 is a few percent deeper than that used here, but the shapes of the profiles are very similar. It should also be noted that use of an anisotropic site-carbon interaction would also change this potential well by a slightly larger amount, increasing the Fourier coefficients by 5% to 10%.[43] Nevertheless, these modifications are small enough not to have any important effect upon the main conclusions of this work.

The mixing of the rotational states is strongly dependent on the variation of the potential with the orientation of the molecule. Figure 4 shows how the potential energy of an H_2 molecule varies with orientation when its molecular center of mass is placed at its average spatial position. Note that the important variable is the angle θ between the molecular axis and the axis normal to the surface. The variation seems to be adequately described by a $\cos^2\theta$ function with an amplitude of about 1.05 meV. The variation with the azimuthal angle ϕ is very small, and at this distance can be ignored. The amplitude of this variation does depend upon the z position of the molecule however, and the zero-point motion of the molecule, especially in the case of H_2, carries it into regions where this amplitude can change by an order of magnitude from the value shown in Fig. 4. In fact, in the case of H_2, the curve of Φ versus θ is actually inverted at the outer reaches of this motion.

Table I gives the values of the rotational constants ($\hbar^2/2I$) used in this calculation, and the parameters for the spatial part of the wave function that affect the effective rotational Hamiltonian. The range of z values given by $\bar{z}\pm\delta z_{\rm rms}$ is shown in Fig. 3 for each isotope. These ranges are quite large for all the isotopes, but especially for H_2. The zero-point motion in the plane is also large as can be seen from the values of $\delta u_{\rm rms}$ given in Table I.

Table II shows the results of solving Eq. (12) for each molecular isotope. In all cases, the rotational matrix was expanded to include all J up to $J=3$ and all the corresponding M_J states. Notice that in each case, the ground-state energy is only a small fraction of an meV below the pure $J=0$ state. An examination of the expansion coefficients shows that the $J=0$ component in the ground-state wave function ranges from 0.999 in the case of H_2 to 0.997 in the case of D_2. The important coupling was found to be between states with the same M_J values and J values that differed by 2. This is a consequence of the rotational variation of the interaction of the molecule with the graphite having the $\cos^2\theta$ dependence shown in Fig. 4. The nature of the mixing for the ground-state rotational wave function was not very sensitive to the values of z associated with the zero-point motion, and in all cases this state is dominated by the $J=0$ component. The energy of the rotational ground state calculated at z values within the range $\bar{z}\pm\delta z_{\rm rms}$ is not very different from that obtained from the spatially averaged matrix elements that comprise the effective rotational Hamiltonian $H_{R_{\rm eff}}$. This is not the case with the excited rotational states.

The two excited states just above the ground state consist of a singlet dominated by the $M_J=0$ state and a dou-

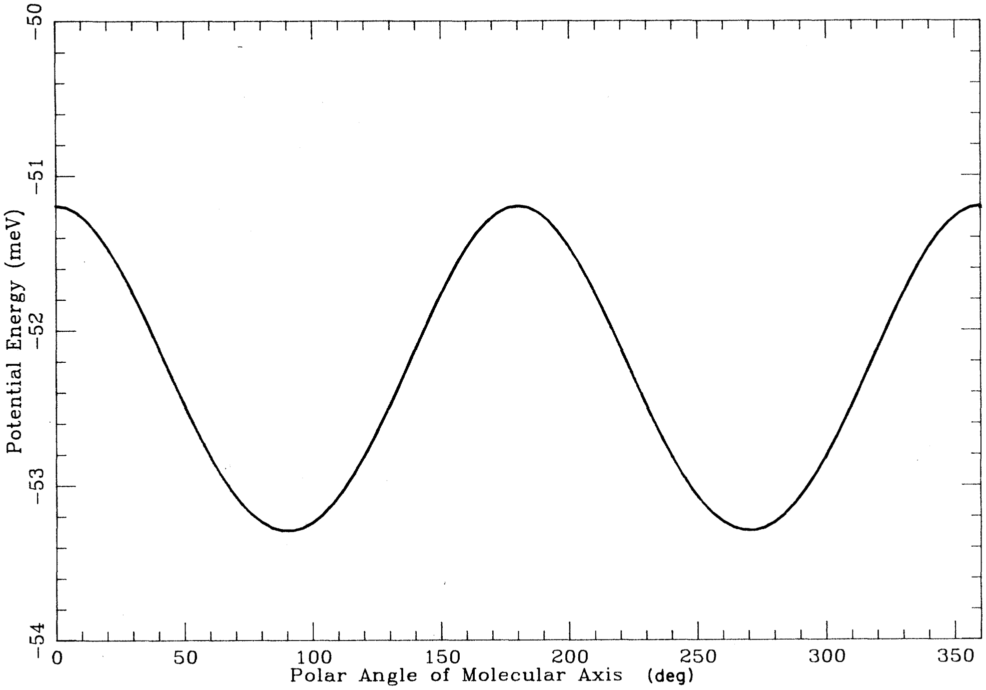

FIG. 4. The potential energy of an H_2 molecule as a function of its orientation. The molecule is located at a distance of $\bar{z}=2.92$ Å from the surface. The curve shown is for $\phi=0$. The curve for $\phi=90°$ is indistinguishable from the one shown.

blet dominated by states with $M_J=\pm 1$. This particular nature of the rotationally excited states is not very sensitive to z within the range of $\bar{z}\pm\delta z_{\mathrm{rms}}$, but the magnitude of the splitting of these states is sensitive to z. In fact, for $z=\bar{z}+\delta z_{\mathrm{rms}}$, the order of the states in the case of H_2 is switched, with the singlet being the lower in energy. Since the splitting between the vibrationally excited states associated with the motion in the z direction is not that different than the splitting between the various rotationally excited states, one can expect mixing of rotational and translational states for excited states. Thus the product wave function used in this work needs to be modified to properly describe these excited levels.

There has been much interest in the possibility of molecular ordering of ortho-H_2 and para-D_2 ($J=1$ rotational states) adsorbed on graphite.[18,19,44,45] The crystal field effect on the rotational states of molecular hydrogen in a $J=1$ state can be estimated from Fig. 4. As has been assumed in previous work, both experimental and theoretical, the crystal field is mainly an out-of-plane effect and is adequately represented by a $\cos^2\theta$ variation. However, the amplitude of this variation as deduced from recent NMR experiments is an order of magnitude smaller than the 1–2 meV amplitude obtained from this work.[18] Even averaging this effect over the zero-point motion of the molecules does not change things that much. The most likely answer to this discrepancy lies in the proper treatment of the rotational-translational coupling in the excited states.

Preliminary work on this rotational-translational coupling indicates that a proper treatment will require a great deal of care. The rotational matrix elements are sensitive enough to the parameters of the spatial part of the wave function, that care must be taken to have the mean position, rms variation, and perhaps even the precise functional form correct. To complicate the matter,

TABLE I. Values of the rotational constants and the parameters for the spatial part of the wave functions for H_2, HD, and D_2. The details of the spatial part of each wave function is given in Refs. 3 and 42. Distances are given in Å, and the rotational constants are in meV.

	H_2	HD	D_2
$\frac{\hbar^2}{2I}$ (Rotational constant)[a]	7.356	5.538	3.709
$\bar{z}$ (Mean distance from surface)[b]	2.92	2.89	2.88
δz_{rms} (rms displacement ⊥ to surface)[b]	0.205	0.184	0.170
δu_{rms} (rms displacement ∥ to surface)[b]	0.594	0.549	0.518

[a] See Ref. 37.

[b] See Ref. 3.

TABLE II. Rotational energy levels for H_2, HD, and D_2 in the $\sqrt{3}\times\sqrt{3}$ R 30° phase on graphite. The total angular momentum quantum number J and its z-component quantum number M_J are those values associated with the dominant term(s) in the expansion of rotational part of the wave function. Energy levels are given in meV, and are relative to the energy of the pure $J=0$ state.

Rotational quantum numbers J	M_J	H_2	Rotational energy levels HD	D_2
0	0	−0.09	−0.12	−0.15
1	±1	13.80	10.15	6.51
1	0	16.43	12.81	9.05
2	±2	42.88	31.96	21.04
2	±1	44.73	33.83	22.83
2	0	45.54	34.68	23.68
3	±3	86.82	64.98	43.09
3	±2	88.22	66.41	44.46
3	±1	89.19	67.39	45.41
3	0	89.52	67.74	45.75

the z dependence of the molecule-substrate interaction is sensitive to the rotational state. For example, the minimum in this potential for a $J=0$ state is -55.7 meV and is located at a distance of 2.75 Å from the surface. However, in a $(J=1, M_J=1)$ state, this minimum is -56.3 meV and located at 2.72 Å from the surface while it is -53.8 meV and located at 2.79 Å for the $(J=1, M_J=0)$ state. This nonseparability between the translational and rotational coordinates will complicate the determination of the appropriate basis set for the spatial part of the wave function.

V. CONCLUSIONS

The rotational ground state of adsorbed molecular hydrogen in the $\sqrt{3}\times\sqrt{3}$ R 30° phase on graphite is a nearly pure $J=0$ state. Furthermore, the ground-state wave function for all the isotopic species of molecular hydrogen can be adequately represented as a product of rotational and spatial terms. Thus the assumption, used in the recent lattice-dynamics calculation for H_2 and D_2 on graphite, that the molecules could be assumed to be in a pure $J=0$ rotational state is justified. Although we have not considered the effects of the anisotropic intermolecular interaction, there is good reason to believe that this interaction will not alter the conclusions of this study. A simple perturbation theory calculation of the effects of this anisotropic potential for the bulk solid shows that these effects lead to a mixing of rotational states which is the same order of magnitude as that found here due to substrate effects alone.[22] Since the adsorbed solid has half the number of nearest neighbors as does the bulk solid, the effects should be even smaller in the adsorbed solid case.

The situation for the rotationally excited states of all isotopic species, but especially for H_2, is not as simple as that for the ground state. Numerical studies of the variation of the rotational matrix elements with distance from the surface strongly indicate that the rotationally excited states are coupled in a significant way to those vibrationally excited states corresponding to motion perpendicular to the surface. This coupling produces a motion in which the molecule tends to line up perpendicular to the surface at the outer reaches of its zero-point motion and parallel to the surface at the inner reaches of this motion. In classical language, the molecule is rocking to and fro as it moves back and forth. In quantum language, this will produce a mixing of the $M_J=0$ and $M_J=\pm1$ states of the $J=1$ manifold. While other rotational states will mix with these, given the small spacing between these levels without this mixing, these levels should exhibit the dominant effects. It is probably this mixing which is the explanation for the very small crystal field effects found in the NMR experiments compared to what is found in this work.[18]

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