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Phonon spectrum and density of states for commensurate monolayer phases of H_2, HD, and D_2 on graphite

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A self-consistent-phonon approximation was used to calculate the ground-state properties and phonon density of states for the $\sqrt{3}\times\sqrt{3}$ R 30° commensurate phase of monolayer H_2, HD, and D_2 adsorbed on graphite. The adsorbed molecules were assumed to be in a pure $J=0$ rotational state, and the wave function for the solid included coordinates both parallel and perpendicular to the surface. The proper inclusion of the surface-normal terms in the wave function was found to have a significant effect on both the phonon spectrum and the ground-state properties. The calculations for the ground-state energy and the phonon spectrum of these solids were done both with and without the inclusion of short-range correlations, these short-range correlations being treated within a version of the T-matrix approximation. The possible effects of various substrate-mediated interactions, anisotropic admolecule-carbon interactions, and finite temperatures were also investigated. The current theoretical results are compared to those of recent inelastic-neutron-scattering experiments and to previous theoretical results for these systems.

I. INTRODUCTION

The recent experimental interest[1-8] in the structure and dynamics of the adsorbed molecular hydrogen isotopic species (H_2, HD, and D_2) was the motivation for this and earlier calculations[9,10] of the phonon spectrum and density of states for these monolayer molecular solids. The work presented here is both an elaboration and an extension of our earlier calculations for the H_2 and D_2 systems.[9] The goal of the current study was to do a careful assessment of the importance of various effects not studied in the earlier work, to understand how each of these effects alters the phonon dynamics, and to extend these calculations to HD.

The three molecular hydrogen isotopic species adsorbed on the basal plane surface of graphite provide a wealth of different solid phases and corresponding solid-solid phase transitions. These phases include the $\sqrt{3}\times\sqrt{3}$ R 30° commensurate phase, at least two hexagonal-incommensurate phases, and a uniaxial-incommensurate phase.[1-3,5,6,8,11,12] Although interest in these systems goes back many years,[13,14] experimental techniques have now reached the point where a detailed comparison of the inelastic-neutron-scattering (INS) data with corresponding theoretical predictions is a realistic possibility.[4,7,9,11] The calculations presented here for the $\sqrt{3}\times\sqrt{3}$ R 30° commensurate phase assume that the admolecules are spherically symmetric, that is, they are in the $J = 0$ free-rotor rotational state.[15] The interaction of each admolecule with the graphite substrate is assumed to be the same as that of a single isolated H_2 molecule with a rigid surface. The dominant contribution to the intermolecular interaction is assumed to be essentially the same as a pair of isolated H_2 molecules. However, in an attempt to understand the possible sources of the discrepancies between earlier theoretical results and the INS results, the effects of substrate-mediated interactions, two-particle short-range correlations, and anisotropic hydrogen-carbon interactions were all investigated, even in those cases where conventional wisdom would say that the given effect was not of practical importance.[16] Finally, the effects of finite temperatures on the phonon spectrum were calculated and the results compared to recent experimental results.

A survey was made of possible substrate mediated effects, and the sizes of these effects were estimated for H_2 on graphite. For those effects which could result in more than a few percent shift in the effective longitudinal and transverse coupling constants of the lattice dynamics,[17] the actual shift in the phonon spectrum was calculated. The anharmonic lattice dynamics was carried out in either the standard self-consistent-phonon (SCP) manner,[9] or using a SCP calculation with an effective interaction generated by a T-matrix approximation. The pure SCP calculation includes only the even terms of the standard theory. The T-matrix theory used in this calculation is a modification of that used by Glyde and Khanna,[18] and includes ladder diagrams in the usual manner. The modification, introduced in the work presented here, incorporates certain elements of the approach used by Horner[19]

Only the in-plane phonon modes of the monolayer will be discussed here in detail. The surface-normal phonons have much higher energies than the in-plane phonons, and so these two sets of modes are essentially decoupled. These surface-normal modes, which exhibit a nearly flat dispersion curve possessing a zone-center gap,[10,20] have widths that are much less than the minimum mode energy. Thus the surface-normal vibrations are approximated very well by those of uncoupled Einstein oscillators. For the sake of completeness, estimates are given here for the Einstein frequencies associated with these surface-normal modes, these values corresponding to the zone-center mode in a more complete treatment.

II. ADMOLECULE-GRAPHITE INTERACTION

Various models for the interaction of a hydrogen molecule with a graphite surface have been proposed over the years,[9,15,21–25] but many of these models are not convenient for the purposes of the calculation presented here. The earliest models assume that the interaction energy of a single admolecule with the graphite surface can be written as a sum of two-body terms, using an isotropic function for the interaction of an admolecule with a single carbon atom, and then summing these terms over all carbon atoms in the graphite substrate.[21,22] Later this approach was extended to the case where the two-body term had an anisotropic dependence of a special form, namely one which was axially symmetric about an axis perpendicular to the surface.[23] More recent attempts to model this type of interaction have focused on use of embedded-atom models to treat the repulsive part of the interaction, while using a phenomenological attractive term for the London dispersion part.[24,25] While the more recent approaches do have a better theoretical basis, all these models have some uncertainty in their justification.

The simplest two-dimensional models, which have been used widely in calculations of monolayer phonon modes, do not allow for any effects generated by the zero-point motion of the adsorbed species in the direction perpendicular to the surface.[26–28] If it is desired to include the effects of such motion, and these effects are relevant to both the energetics and dynamics of the commensurate monolayer solids, these simple two-dimensional models are inadequate.[9] The most sophisticated models for the admolecule-substrate interaction use the embedded-atom approach, which, while quite realistic, still requires experimental input to determine one or more parameters.[24] In addition, these sophisticated models are more complicated to implement then was desired for this calculation. Thus the first task in this investigation was to construct a realistic, but relatively simple model for the interaction of a single hydrogen molecule with the graphite surface.

Given the uncertainties associated with all these models, it was decided to use the simplest approach that would give a realistic treatment of the interaction of a H_2 molecule with a graphite surface.[9] For this purpose, the model that was chosen is a modification of one of the earliest models used, namely that of Crowell.[21] The original Crowell model approximates the total adsorption potential by a sum of spherically symmetric admolecule-carbon interactions, with the admolecule-carbon pair interaction being Lennard-Jones LJ(12,6). The parameters for the LJ(12,6) interaction were originally determined through the use of combination rules. The modification of the Crowell model used in the current work involves simply adjusting the LJ(12,6) parameters to fit the experimental bound-state energies. With the assumption of a pure $J=0$ rotational state for the hydrogen molecules, there would be no dependence on molecular orientation for this interaction, but there is no guarantee that there is not some relatively small anisotropy due to the anisotropic electronic orbitals of the carbon atoms in the graphite. However, anisotropic terms in this interaction, when modeled with the axially symmetric form, do not contribute to the bound-state energies of the laterally averaged potential,[29,30] but only to the band-structure splittings. With only the bound-state energies known experimentally, there would be no way of independently determining the contribution of the anisotropic terms. Since recent estimates of the effects of such anisotropies are relatively small, in the range of 10–15%,[24] it was decided to ignore such terms in the actual calculation of this interaction, and simply test the sensitivity of the final results of the lattice dynamics to variations of this magnitude in the corrugation of the empirically determined hydrogen-graphite interaction. In this manner, the importance of the effects of the anisotropic hydrogen-carbon interactions could be investigated without a detailed calculation of the actual anisotropic potential. Given the current state of our knowledge of the hydrogen-graphite interaction, there seems little justification for a calculation of the anisotropic effects on the phonon spectrum beyond what is done here.

The energy levels for the bound states of both H_2 and D_2 molecules in the laterally averaged admolecule-graphite potential well have been obtained experimentally through the analysis of selective adsorption measurements.[31] These bound-state values have been used to obtain model parameters by a number of authors,[9,22,23] the model parameters being the LJ(12,6) well depth, given by ϵ_0, and the hard-core separation, given by σ. The values so obtained for these parameters do depend slightly on the particular criteria used to fit the data, but relative variations in these values are of the order of only a few percent.

The Steele formulation for the LJ(12,6) adsorption potentials gives explicit closed forms for the calculation of the Fourier coefficients of $U(\mathbf{r},z)$, the potential energy of a single admolecule located at a position $\mathbf{r}$ parallel to the surface, and at a displacement of z in the direction perpendicular to the surface. These Fourier coefficients have values that depend upon the position of the adsorbed molecule in the direction perpendicular to the surface.[32] If these coefficients are denoted by $U_{\mathbf{G}}(z)$, then one has:

$$U(\mathbf{r},z)=\sum_{\mathbf{G}} U_{\mathbf{G}}(z)e^{i\mathbf{G}\cdot\mathbf{r}}, \tag{2.1}$$

where $\mathbf{G}$ is a reciprocal lattice vector for the graphite basal plane lattice. The calculations of the $U_{\mathbf{G}}(z)$ for the LJ(12,6) interaction involve summations over the carbon atoms that can be reduced to a closed form involving Bessel functions of the second kind. The details of this calculation are given in Ref. 32.

It is well known that the summation over carbon atoms in those basal planes below the surface plane make an insignificant contribution to the periodic variation of the interaction potential. Furthermore, the only significant contributions from these lower planes are the attractive ones, and the summation of these attractive terms can be replaced by an integral (with appropriately chosen limits) without any significant loss of accuracy.[33] Thus it is a good approximation to write the $\mathbf{G}=0$ Fourier amplitude, which is the laterally averaged substrate potential term, as

$$U_0(z)=\frac{8\pi\epsilon_0\sigma^2}{\sqrt{3}b^2}\left[\frac{2}{5}\left[\frac{\sigma}{z}\right]^{10}-\left[\frac{\sigma}{z}\right]^{4}-\frac{\sigma^4}{3d}(z+0.61d)^{-3}\right], \qquad (2.2)$$

where d = 3.4 Å is the graphite interplanar separation and b = 2.46 Å is the basal plane lattice parameter.

To obtain the values of the LJ(12,6) parameters used here, the one-dimensional Schrödinger equation for a particle with the mass of the H_2 molecule, subjected to the potential well given by U_0, was solved numerically.[34] By means of a manual search, the interaction parameters were adjusted to obtain a close fit to the lowest and highest experimentally determined energy levels. The parameters for the admolecule-carbon interaction, as determined by this procedure, are $\epsilon_0=47.7$ K and $\sigma=2.85$ Å. The parameters thus chosen for the H_2 interaction with the carbon atoms were then used to calculate the interaction of both the D_2 and the HD molecules with the graphite; and the corresponding values for the bound-state energy levels of these admolecules were then calculated. Table I gives the theoretical and experimental values for the energy levels of H_2 and D_2 along with the theoretical values for HD. These parameters reproduce, within 5%, all the experimentally determined bound-state energies for both H_2 and D_2; and they differ by only a few percent from previously determined values. It is possible to obtain a much better fit to the bound-state energies (about 1% error) by using a different functional form to describe the isotropic hydrogen-carbon interaction.[35] However, given the other uncertainties in the various interactions associated with this problem, it was decided not to use this improved (but more complicated) functional form for this series of calculations.

The numerical solutions for the bound-state wave functions show that the U_0 adsorption potential energy confines all three molecular species to a narrow region near the surface of the graphite. Table II gives the average position and corresponding rms deviations for the three isotopic species. They all show the same general behavior, being roughly 3.0 Å from the surface and having an rms deviation of about 0.2 Å. These rms deviations are small enough, relative to the commensurate-phase intermolecular separation of 4.26 Å, that it is reasonable to use a product of in-plane and surface-normal factors in the wave function used to describe the solid phase. Such a product wave function effectively decouples the in-plane and surface-normal modes. A product of single-particle (Einstein-oscillator) terms, both Gaussian and non-Gaussian, were used for the surface-normal part of the wave function. This assumption precludes any study of the dispersion in the surface-normal phonon modes. However, recent theoretical calculations have shown that the width of these surface-normal modes is very small compared to the zone-center frequency.[10] This is consistent with the INS experiments.[20] Thus ignoring this dispersion should not have any significant effect on the calculation of the in-plane modes. Either a product of correlated Gaussians (the standard SCP ground state), or a more complicated function of the in-plane coordinates (the T-matrix ground state) was used for the in-plane part. By implication, the rotational part of the wave function is taken to be a pure $J=0$ state. Both theoretical and experimental results are consistent with this last assumption. See Ref. 15 and references listed therein.

TABLE I. A comparison of theoretical[a] and experimental[b] results for bound-state energies of the laterally averaged substrate potential. All energies are in kelvins.

Level	H_2		HD	D_2	
v	Theory	Expt.	Theory	Theory	Expt.
0	-484.1	-482.9	-505.3	-518.2	
1	-296.4	-306.4	-341.5	-370.8	
2	-170.0	-177.9	-221.5	-257.5	-268.2
3	-89.9	-92.4	-136.8	-172.8	-178.7
4	-42.9	-41.9	-79.8	-111.4	-116.1
5	-18.0	-16.9	-43.3	-68.5	-73.9
6	-6.3		-21.6	-39.9	-43.9
7	-1.7		-9.6	-21.7	-22.4

[a] As described in Sec. II.

[b] L. Mattera, F. Rosatelli, C. Salvo, F. Tommasini, U. Valbusa, and G. Vidali, Surf. Sci. 93, 515 (1980).

TABLE II. Properties of the single-particle wave functions for the hydrogen molecular isotopes in the laterally averaged graphite substrate potential. The distances are in Å and the energies are in kelvins. The distance from the surface graphite plane is given by z, and $\tilde{U}_{G_1}$ is the effective Fourier coefficient for the (10) reciprocal lattice vector of the graphite basal plane. The averages given by $\langle \cdots \rangle$ are calculated using the ground-state solutions for the corresponding single-particle Schrödinger equation.

Adsorbate	$\bar{z}=\langle z\rangle$	$\delta z_{rms}=\langle(z-\bar{z})^2\rangle^{1/2}$	$\tilde{U}_{G_1}=\langle U_{G_1}\rangle$
H_2	2.99	0.24	-5.91
HD	2.96	0.21	-5.96
D_2	2.94	0.20	-5.98

III. THE INTERMOLECULAR INTERACTIONS

The interaction between two adsorbed molecules is a combination of the direct interaction associated with these two molecules in vacuum and the indirect interactions caused by the presence of the substrate.[16] These substrate-mediated interactions typically cause a shift in the attractive portion of the intermolecular interaction on the order of 10–15 % relative to the interaction in the absence of the substrate. Rather than add together all the possible substrate effects and only present the final results, it was decided to do a series of calculations to examine the effect of each indirect interaction when separately added to the direct interaction, and then present representative results for those cases where there is a major contribution to the total intermolecular interaction. In this way, the importance and the uncertainties associated with these effects are more easily understood. As will be demonstrated, some contributions were estimated to be so small that it was not worth the effort to calculate the phonon spectrum with these terms included.

The assumption that the adsorbed molecules are in a pure $J=0$ rotational state means that the direct interaction between two such molecules is described by an isotropic function of the intermolecular distance. The validity of this assumption has been discussed in the previous section, and this has been confirmed by recent calculations using an anisotropic molecule-molecule interaction.[10] For the majority of the calculations described here, this isotropic interaction was based upon the one used by Silvera and Goldman in their study of the phonon modes of H_2 bulk solid.[36,37] Although there is another empirical interaction which might be slightly better for general condensed phases[38] the differences between these two interactions, especially at the interatomic separations relevant here, are very small compared to all the other uncertainties. Furthermore, the Silvera-Goldman (SG) interaction was optimized for the description of the bulk solid phases of hydrogen, which makes it somewhat preferable for a treatment of the hydrogen monolayer solids. However, the SG interaction does contain a many-body term which models many-body effects in the bulk system. Since the system under consideration here is quasi-two-dimensional and exhibits larger interatomic separations than the bulk system, the strength of this term (which is given by their C_9 coefficient) was set equal to zero. There was no attempt, as was done in a recent calculation by Gottlieb and Bruch,[39] to estimate the size of this many-body term for the case of a two-dimensional solid nor include this term in the lattice-dynamics calculations reported here. However, some exploratory calculations were done to estimate the effects of this term using the Gottlieb-Bruch value of the C_9 coefficient, and the effects were found to be very small.

The most important modifications of the interaction between two nonpolar admolecules, which results from the presence of a graphite substrate, are due to the substrate's dielectric properties and its deformability. The dielectric properties of the substrate alter the long-range attraction of the London dispersion term.[40] This modification is the source of the McLachlan interaction, an additive term which modifies the original two-body interaction.[41] Although this contribution to the two-body interaction can be approximated reasonably well by a reduction in the C_6 coefficient of the London dispersion term of the original interaction,[39] the actual McLachlan interaction has a complicated functional dependence on both the in-plane and surface-normal coordinates. The most common form of the McLachlan interaction, one that places the two admolecules in the same plane parallel to the surface,[16] was examined for its importance in the calculations of the phonon modes. With the constraint that the admolecules are at the same distance L from the image plane of the substrate, the McLachlan interaction depends upon two dispersion coefficients, C_{S1} and C_{S2}, besides the dependence on L and on the intermolecular separation parallel to the surface. The form of this interaction, as used in the current calculations, is given by Eq. 3.4 in Ref. 16 and the values of the two dispersion coefficients were taken from Table I of this same reference. The value of L was chosen to be 1.4 Å as suggested by Bruch.[16,42] Results with and without the McLachlan term were compared to assess the importance of this interaction for both the ground-state energy and the phonon spectrum.

The effects of the deformability of the substrate have been treated by a number of authors, with various results depending upon the details of the assumptions used.[43-47] The theory of Schick and Campbell was motivated by the indirect interaction between two electrons in a bulk solid caused by the exchange of virtual phonons.[43] Using a similar calculational approach, Schick and Campbell found a static, essentially attractive, long-range interaction which oscillated with intermolecular separation, but which at large separations decreased as the inverse $3/2$ power of the separation distance.

Employing an isotropic continuum model of the substrate, Lau and Kohn[44] found that the effective interaction between two identical static admolecules was repulsive, and monotonically decreasing with the inverse third power of the intermolecular separation. Later, Lau[45] and separately Kappus[46] investigated the effects of the anisotropy of the crystalline surface. They found that the interaction could be either attractive or repulsive, depending upon the orientation of the intermolecular displacement vector relative to the symmetry axis of the crystalline surface, and could even oscillate, but otherwise the results were consistent with those of Lau and Kohn. These predictions are somewhat at odds with the Schick and Campbell predictions, and the source of the discrepancy is not easy to understand.[44] In a recent paper, Tiersten, Reinecke, and Ying have reexamined this effect for admolecules on a crystalline substrate.[47] Although they also find a long-range behavior similar to that of Kappus, the short-range oscillations are reminiscent of the behavior found by Schick and Campbell. These differences might be due to the approximations made in the Schick-Campbell calculation for the wave-vector dependence of the lattice response functions.

Rather than critically assess any of these various theories and how they apply to the case of hydrogen on graphite, two rough estimates were made of the importance of this class of indirect interactions. A simple estimate using the Schick-Campbell theory was made, and then an alternate estimate of these effects was carried out in the spirit of the variational calculations of Wagner and Horner for the elastic distortion energy associated with hydrogen-in-metal systems.[48]

The original Schick-Campbell theory was applied to the case of He adsorbed on argon-plated copper. The theory requires knowledge of the LJ(12,6) parameters for the admolecule-substrate interaction, the shape of the wave function that describes the probability of locating the admolecule at some position above the surface, and the sound velocity for the substrate bulk mode with propagation vector parallel to the surface and polarization perpendicular to the surface. In addition, the number density of the substrate atoms and the mass of the admolecule are required. Estimates for the appropriate sound velocity for graphite were made using the experimental phonon modes.[49] The wave function was obtained by solving the one-dimensional Schrödinger equation as discussed in the previous section. The numerical evaluation of the Schick-Campbell term showed that it might increase the binding energy by 1–2 K, but would have virtually no effect (less than about 1%) on the lattice dynamics.

An independent check for the order of magnitude of this effect was made by using a simple mass and spring model for the substrate surface atomic plane, and to examine the response of this system to an admolecule which has an inverse cube attraction to a semi-infinite bulk. The style of this calculation was similar to the Wagner-Horner calculation for defect energies.[48] The model consists of a two-dimensional hexagonal lattice of masses and nearest-neighbor springs attached to the surface of a rigid semi-infinite solid, each mass being connected to this surface with a single spring. The lattice spacing of the two-dimensional system was set at 2.46 Å, and the associated mass value was chosen to produce the proper surface-mass density for the graphite basal plane. The static distortion of this system, when subjected to the forces of two hydrogen molecules, was studied as a function of the intermolecular displacement of these admolecules. These admolecules were attracted to the rigid semi-infinite solid by an inverse-cube attractive interaction with a strength appropriate to the hydrogen-graphite system. The admolecules were attached to a surface lattice site by a spring adjusted to give the appropriate vibrational frequency for a hydrogen molecule on graphite. The induced interaction was determined by a calculation of the difference between the total energy at a fixed value of admolecule separation and the same energy for "infinite" separation. This induced interaction between the admolecules was found to be anisotropic and oscillatory, consistent with the results of Tiersten, Reinecke, and Ying.[47] Nevertheless, the corresponding estimates for the increase in the binding energy of these admolecules and the effects on the lattice dynamics were of the same order of magnitude as those obtained from the Schick-Campbell theory. In the final analysis, the distortion-induced interaction seems to have an effect which is smaller than any of the other effects investigated.

In summary, all the estimates made of the effects of the deformability of the substrate confirmed the conventional wisdom that these effects are smaller by about an order of magnitude than the McLachlan interaction term.[16] Since all these phonon-mediated interaction corrections are so small, none of these terms were included in the calculation of the phonon dynamics of the monolayer discussed here.

IV. SCP LATTICE DYNAMICS

The wave function for the ground state of the monolayer solid is written as

$$\Psi_0 = \Phi_0 \prod_j \psi_j , \tag{4.1}$$

where $\psi_j = \psi(z_j)$ is a function of the surface-normal displacement (z position) of the jth admolecule, and Φ_0 is the standard SCP ground-state wave function.[15] The Φ_0 function is a product of correlated-Gaussian factors that depend upon $\{r_i^\alpha - r_j^\alpha\}$, the set of α components of the in-plane displacements between the ith and the jth admolecules. However, it is more common to express this dependence in terms of the set of $\{u_j^\alpha = r_j^\alpha - R_j^\alpha\}$, where u_j^α represents the α component of the in-plane displacement of the jth admolecule from R_j^α, its ideal lattice site. It is convenient to think of the system's energy as consisting of five major contributions: the kinetic energy associated with the in-plane motions; the kinetic energy associated with the surface-normal motions; the intermolecular interaction (which, strictly speaking, depends upon both in-plane and the surface-normal displacements); the laterally-averaged interaction of the admolecules with the graphite (which depends only upon the surface-normal positions of the admolecules); and the remainder of the admolecule-graphite interaction (which depends upon both the in-plane and surface-normal positions of the admolecules). The ground-state energy E_T for this system can then be written conveniently as

$$E_T = E_z + E_{xyz} + E_{xy} , \tag{4.2}$$

where each term on the right corresponds to one of three different groupings of the five contributions discussed above.

The E_z term is the kinetic energy associated with the z motion plus the potential energy associated with the laterally averaged substrate potential $U_0(z_j)$. E_z depends only on the ψ_j factors in the wave function and, for a system of N admolecules each with mass m, this energy can be written as

$$E_z = \frac{-\hbar^2}{2m} \sum_{j=1}^{N} \left\langle \psi_j \left| \frac{\partial^2}{\partial z_j^2} \right| \psi_j \right\rangle + \sum_{j=1}^{N} \left\langle \psi_j \left| U_0(z_j) \right| \psi_j \right\rangle . \tag{4.3}$$

The E_{xyz} term is the potential energy term associated with the periodic variation of the adsorption potential, and it depends on both the ψ_j and the Φ_0 factors. However, this energy depends on the Φ_0 only through $\langle u_j^\alpha u_j^\beta \rangle$, the tensor for the average second moment of the in-plane displacements of the jth admolecule from its lattice site. For in-plane, correlated-Gaussian wave functions, it is possible to write E_{xyz} as[50]

$$E_{xyz} = \sum_{j=1}^{N} \sum_{\mathbf{G}\neq 0} \langle \psi_j | U_{\mathbf{G}}(z_j) | \psi_j \rangle \exp(-\tfrac{1}{2} G^\alpha G^\beta \langle u_j^\alpha u_j^\beta \rangle) , \tag{4.4}$$

where the Einstein summation convention is assumed for the summations over the α and β indices. Here $U_{\mathbf{G}}(z)$ is the z-dependent Fourier coefficient associated with the graphite basal plane reciprocal lattice vector $\mathbf{G}$.

The E_{xy} term is the kinetic energy associated with the in-plane coordinates plus the intermolecular interaction energy. This term can be written

$$E_{xy} = \frac{-\hbar^2}{2m}\sum_{j=1}^{N}\left\langle \Phi \left| \frac{\partial^2}{\partial x_j^2} + \frac{\partial^2}{\partial y_j^2} \right| \Phi \right\rangle + \frac{1}{2}\sum_{i,j=1}^{N} \langle \Phi | V_{\text{eff}}(r_{ij}) | \Phi \rangle , \tag{4.5}$$

where the double sum excludes the $i = j$ contributions. The effective two-dimensional interaction V_{eff} is a function of r_{ij}, the in-plane separation between the ith and jth admolecules, and it is defined by the equation

$$V_{\text{eff}}(r_{ij}) = \langle \psi_j | V(\eta_{ij}) | \psi_j \rangle . \tag{4.6}$$

The function $V(\eta)$ describes the interaction of two admolecules separated by a distance $\eta = (x^2+y^2+z^2)^{1/2}$. If the effect of averaging the intermolecular potential over the ψ_j factors in the wave function can be ignored, then E_{xy} depends only on the Φ_0. Numerical comparison of the functions $V_{\text{eff}}(r)$ and $V(r)$ showed that the "bare" $V(r)$ interaction is an excellent approximation (about 1% error) to the $V_{\text{eff}}(r)$ term for the relevant range of r values. The replacement of $V_{\text{eff}}(r)$ by the "bare" $V(r)$ was used for all calculations presented here. Under these circumstances, the E_{xy} term becomes independent of the ψ_j functions.

The optimum wave function is determined by minimization of the total energy as a function of the parameters in the ψ_j and Φ_0 factors of the wave function. Minimization with respect to the ψ_j involves both the E_z and the E_{xyz} terms. This is the quasi-one-dimensional problem of finding the minimum energy of a single particle with a mass m in a quasi-one-dimensional potential well given by

$$U_0(z) + \sum_{\mathbf{G}\neq 0} U_{\mathbf{G}}(z)\exp(-\tfrac{1}{2}G^{\alpha}G^{\beta}\langle u_j^{\alpha}u_j^{\beta}\rangle) . \tag{4.7}$$

If the trial ψ_j is a simple Einstein oscillator Gaussian, then the problem is a straightforward variational calculation for finding both the z position of the center of the Gaussian and its width. However, it is also possible to find the "exact" ψ_j by solving the quasi-one-dimensional Schrödinger equation for the potential given by Eq. (4.7) just as was done in Sec. II for the U_0 term alone. Both these procedures were used, and the results compared to each other.

Minimization of the energy with respect to the parameters in the Φ_0 factors involves both the E_{xyz} and the E_{xy} terms. The equations that result from this second minimization are those of a two-dimensional SCP theory with effective "two-dimensional" Fourier coefficients $\tilde{U}_{\mathbf{G}}$ given by

$$\tilde{U}_{\mathbf{G}} = \langle \psi_j | U_{\mathbf{G}}(z_j) | \psi_j \rangle . \tag{4.8}$$

These SCP equations generate the phonon frequencies and polarization vectors for the in-plane modes in the usual manner.[26,50] Clearly, the minimization procedures for the ψ_j and the Φ_0 are not independent. The trial ψ_j determines the values of the $\tilde{U}_{\mathbf{G}}$, which determine the phonon spectrum, which determines the values of the $\langle u_j^{\alpha}u_j^{\beta}\rangle$, which determine ψ_j. Several iterations between the equations for the optimum wave-function parameters of the ψ_j and of the SCP parameters are necessary to produce a fully self-consistent solution set for the energies, phonon modes, and corresponding wave functions. The first step in this procedure is to generate a set of $\tilde{U}_{\mathbf{G}}$ from the zeroth order ψ_j, that is, the ψ_j that minimizes the E_z term only. Then these $\tilde{U}_{\mathbf{G}}$ values are used to start the iteration procedure that minimizes the total energy E.

V. *T*-MATRIX LATTICE DYNAMICS

The study of the effects of short-range correlations on the phonon dynamics of highly quantum bulk solids has a long history.[19,51–54] The initial work focused on the use of Jastrow factors in the wave function,[55] while later efforts used variations of the *T*-matrix approach.[18,56,57] The problems associated with combining short-range correlations with a SCP wave function in either of these approaches are well documented,[54] and are associated with the difficulty of untangling the long-range two-body correlations built into the SCP Gaussian wave function from the short-range two-body correlations associated with either the Jastrow wave function or the *T*-matrix equations. Previous investigations of the effects of short-range correlations in the two-dimensional quantum solids have focused on the ground-state properties and Jastrow approaches.[39,58–61] The effects of short-range correlations on the ground-state properties of the commensurate molecular hydrogen solids, it turns out, can be as large or larger than the effects associated with the more important of the substrate-mediated interactions. Given this, a treatment of the effects of short-range correlations on the phonon dynamics of these quantum solids is warranted.

A very detailed (but intrinsically complicated) theory for the inclusion of short-range correlations in the phonon dynamics of quantum solids was developed by Horner some years ago.[19] Horner's approach includes short-range correlations while maintaining self-consistency between two-particle moment functions calculated by means of appropriate real-space integrations of the pair-distribution function and the same quantities calculated by using momentum-space integrations of the appropriate phonon correlation functions. However, the full implementation of Horner's method is extremely difficult, and the typical approach is to use an ansatz for the functional form of the pair distribution function and apply some of the conditions of the theory to determine the unknown parameters. A more straightforward approach is that of Glyde and Khanna,[18,56] who used a variation of the Bruckner *T*-matrix theory to determine the ground-state properties and phonon modes. In this approach, a two-particle Schrödinger equation is solved for a two-particle function that defines the *T*-matrix effective interaction. Then this effective interaction is used in place of the bare interaction (in an otherwise typical SCP calculation) to calculate the phonon dynamics and ground-state properties. The Glyde-Khanna theory, however, produces small but bothersome inconsistencies between the real-space and momentum-space integrations discussed above. Given the uncertainties and difficulties involved in both these and other methods for dealing with the short-range correlations in phonon dynamics,[52] it was decided to try an approach which takes the best parts of the first two methods described above. Although this modified approach is an ansatz, and cannot be rigorously derived from first principles, it seems to have about the same justification as the actual implementations of other approaches.[62]

The Glyde-Khanna approach constructs an effective interaction $T(r)$ from the bare interaction $V(r)$ by multiplying this bare interaction by a two-particle function $g(r)$, and normalizing. The function $g(r)$ satisfies a two-particle Schrödinger equation which involves both the bare interaction and the parameters of the SCP Gaussian ground state. In the Glyde-Khanna papers, this approach was justified by means of the summation of ladder diagrams for a T-matrix theory which involve the SCP Gaussian wave function instead of the usual plane-wave states. In the approach used for this calculation, a two-particle function is also used to define an effective interaction and this effective interaction is used exactly as that in the Glyde-Khanna approach. The calculation here differs from the Glyde-Khanna theory in that the $g(r)$ function is constrained to satisfy the two-particle Schrödinger equation only for small separations of the two particles. For very large separations, the g factor is functionally constrained to go to unity, while for intermediate distances, it is allowed some freedom to oscillate through the use of free parameters. Then, following Horner's arguments, the free parameters in this pair function are determined by demanding that the momentum-space and real-space evaluations of the two-particle moment functions are consistent with each other. This ansatz for the treatment of the short-range correlations works very well in practice, and it easier to both understand and implement than the full Horner method. It uses the Glyde-Khanna approach in that region of space where it is most reliably implemented, and modifies this method in that region where it is most suspect. While not as satisfactory as a rigorous theory, it suffers from uncertainties that are no worse than common implementations of the other theories.

The first step in the current approach is to construct the T-matrix given by the equation

$$T(r)=g(r)\frac{V(r)}{\langle g(r)\rangle_S}, \tag{5.1}$$

where $\langle \cdots \rangle_S$ is the appropriate average over the SCP ground-state wave function $\langle \Phi_0| \cdots |\Phi_0\rangle$. For values of r deep inside the repulsive core of the bare interaction $V(r)$, the pair-function $g(r)$ satisfies the two-particle radial Schrödinger equation:

$$-\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{\partial}{\partial r}r\frac{\partial}{\partial r}g(r)+V(r)g(r)=0, \tag{5.2}$$

where μ is the reduced mass of the pair of admolecules, and the strongly repulsive nature of $V(r)$ at small values of r has been used to justify dropping the other terms from the corresponding equation in the Glyde-Khanna theory. This equation is solved approximately by looking for solutions of the form

$$g(r)=e^{-u(r)}, \tag{5.3}$$

where the function $u(r)$ is expected to go to zero rapidly at large values of r, and to become very large as r goes to zero (the WKB approximation). For example, the SG interaction is of the form

$$V(r)=e^{\alpha-\beta r} \tag{5.4}$$

for small values of r. It is straightforward to demonstrate that for this repulsive interaction the appropriate form for $u(r)$ is given by

$$u(r)=\frac{2}{\lambda\beta}e^{(\alpha-\beta r)/2}, \quad \lambda^2\equiv\frac{\hbar^2}{m}, \tag{5.5}$$

and m is the mass of a single admolecule. Now, using the ideas of Horner, the functional form of $g(r)$ is generalized at intermediate values of r so that consistency conditions for the first- and second-moment functions can be applied. This was done by modifying the g function so that it has the form

$$g(r)=e^{u(r)f(r)}, \tag{5.6}$$

where the function f is a polynomial in the separation distance r. It was sufficient in this calculation to use the quadratic function

$$f(r)=1+ar+\tfrac{1}{2}br^2, \tag{5.7}$$

where a and b are free parameters. The fact that it is possible to satisfy the consistency equations using a function of the scalar variable r is a consequence of the hexagonal lattice symmetry. For lattices of less symmetry, the more general form

$$f(\mathbf{r})=1+\mathbf{a}\cdot\mathbf{r}+\tfrac{1}{2}\mathbf{r}\cdot\overleftrightarrow{b}\cdot\mathbf{r} \tag{5.8}$$

would be needed because the consistency equations involve tensor objects. The consistency equations which need to be satisfied involve the first and second moments of $\hat{u}_{ij}^{\alpha}=\hat{u}_i^{\alpha}-\hat{u}_j^{\alpha}$, the relative displacements of the molecular pair ij. Since the first moments of $\hat{u}_{ij}^{\alpha}$ are identically zero within the phonon description, these conditions translate into the equations

$$\langle g^2\hat{u}_{ij}^{\alpha}\rangle_S=0 \tag{5.9}$$

and

$$\frac{\langle g^2\hat{u}_{ij}^{\alpha}\hat{u}_{ij}^{\beta}\rangle_S}{\langle g^2\rangle_S}=\Gamma_{ij}^{\alpha\beta}, \tag{5.10}$$

where $\Gamma_{ij}^{\alpha\beta}$ is the corresponding second moment of $\hat{u}_{ij}^{\alpha}\hat{u}_{ij}^{\beta}$ calculated using phonon coordinates; and it is given by Eq. (8) in Ref. 50. It is clear that $g(r)$ depends upon both the bare interaction and upon the parameters of the SCP wave function, but in a way that differs somewhat from both the Horner and the Glyde-Khanna theories. To find the free parameters in g, the T-matrix is used in place of the bare interaction in the otherwise standard SCP equations for the commensurate solid[27,50] starting with a and b values set to zero. Once the preliminary phonon dynamics has been determined, it is a matter of iterating the consistency equations, the T-matrix equations, and the SCP equations until a consistent set of parameter values has been found. This generally takes about half a dozen cycles through the entire set of equations.

The use of the T matrix alters the calculation of the ground-state energy so that it is no longer given by the standard SCP form. This alteration is due to the combination of additional kinetic energy due to the increased curvature of the wave function produced by the g pair function and the decreased potential energy produced by the decreased probability of finding two admolecules close together.[18] It is convenient to rewrite the Glyde-Khanna form for the energy in terms of the SCP equations with the bare potential and an additional correlation energy ϵ_{ij} which results from the g pair function. Then the ground-state energy takes the form

$$E=\left\langle \frac{\hat{p}_j^{\alpha}\hat{p}_j^{\alpha}}{2m}\right\rangle_S+\sum_{i<j}\langle V(r_{ij})\rangle_S+\sum_{i<j}\epsilon_{ij}, \tag{5.11}$$

where the correlation energy ϵ^{ij} is given by

$$\epsilon_{ij}=\frac{\langle [g(r_{ij})-\langle g\rangle_S]\times[V(r_{ij})-V(R_{ij})+\frac{1}{2}\hat{u}_i^{\alpha}\Phi_{ij}^{\alpha\beta}\hat{u}_j^{\beta}]\rangle_S}{\langle g\rangle_S}, \tag{5.12}$$

and the $\Phi_{ij}^{\alpha\beta}$ are the renormalized force constants of the SCP theory. The $\Phi_{ij}^{\alpha\beta}$ matrix is given by Eq. (30a) in Ref. 50 with the bare interaction replaced by the effective interaction $T(r)$.

VI. ZERO-TEMPERATURE RESULTS

A series of initial calculations were carried out for the purpose of comparing the current calculations to previous theoretical work on this problem. For comparison with the previous results of Ni and Bruch,[60] some trial calculations were done with a Lennard-Jones LJ(12,6) potential and a fixed effective $\tilde{U}_{G_1} = 6.4$ K. The parameters for the LJ(12,6) interaction were taken from the work by Michels, deGraaff, and Ten Seldam[63] but any differences between the various isotopes were ignored, as was done by Ni and Bruch.[60] The SCP calculation showed that the long-range correlations in the SCP wave function reduced the ground-state energy for H_2 by only 1 K relative to the Hartee calculation of Ni and Bruch. For D_2 it was only a fraction of a kelvin. The amplitude of the in-plane zero-point motion was virtually the same.

Additional calculations for H_2 and D_2, again using a fixed effective $\tilde{U}_{G_1} = 6.4$ K, were carried out using the SG interaction and the T-matrix approximation for the purposes of comparison to the Jastrow calculations of Gottlieb and Bruch.[39,61] This comparison showed that the Jastrow variational calculation and the T-matrix approximation differed by less that 0.5 K in the estimates for the ground-state energy of the two commensurate phases. There were, however, differences of about 1–2 K in the individual terms like E_{xyz}. So although these calculations differ in some respects, they essentially agree on the results for the basic parameters of the ground state. Since the Jastrow calculation, as a variational technique, provides an upper bound to the ground-state energy, while the T-matrix approximation does not satisfy such a constraint, the close agreement of these two calculations does indeed indicate that the ground state of either system is very close to an Einstein oscillator.

Comparison to the calculation of Janssen, Van den Berg, and van der Avoird[10] is more complex because of the nature of that calculation. However, that work includes a comparison to the earlier version of this calculation[9] and this comparison demonstrates good agreement between the two approaches.

The ground-state energies for both the H_2 and D_2 $\sqrt{3}\times\sqrt{3}$ R 30° commensurate phases were compared to the corresponding energies of both the rotated and nonrotated incommensurate phases. using both the LJ(12,6) and the SG interactions.[50,64] The commensurate phases are lower in energy than the incommensurate phases in all cases. Using the LJ(12,6) interaction, the energy difference for H_2 is about 17 K per admolecule, while for D_2 this difference is about 16 K. These results are reasonably consistent with calculations based on the Hartree approximation for the ground-state wave function and the LJ(12,6) interaction.[60] Similar calculations with the SG interactions lead to similar conclusions.[39] It can be said that both the earlier Einstein oscillator models and the current lattice-dynamics models all lead to the conclusion that the $\sqrt{3}\times\sqrt{3}$ R 30° commensurate phase is the stable ground state for these admolecules. Furthermore, the additional decrease in the ground-state energy due to the long-range correlations associated with the phonons is about a few kelvins at most for these states.

A. SCP calculations

Table III lists the various energy terms given by Eqs. (4.2)–(4.5) for the case of a Gaussian $\psi(z)$ and the SG intermolecular interaction without the many-body term. The calculation of the matrix elements of the dynamical matrix used a sum over three nearest-neighbor shells (18 neighbors). The potential-energy calculations used the SCP real-space integrals summed over these same neighbors, but included a correction for the contributions to the potential energy from other molecules beyond this limit. This correction, which approximates the missing contributions by using a corresponding lattice sum over fixed lattice sites, works quite well.

Although a SCP calculation using the self-consistent ψ_j rather than the zeroth-order ψ_j does not have a large effect on the total energy, there is a significant shifting among the individual energy contributions to the total as a result of using this self-consistent criterion. The alteration of these various energy terms is a direct result of the contraction of the SCP Gaussians in the surface plane as the solutions go from the zeroth-order case to the fully self-consistent case. Furthermore, this in-plane contraction drives a shift of the ψ function toward the surface with a corresponding contraction of its width. These changes are a direct reflection of the nonadditivity of the substrate interaction in its dependence on the in-plane and surface-normal coordinates of the admolecules, and they demonstrate the importance of a proper treatment of the wave function's z dependence. The clearest

TABLE III. Ground-state energy contributions, calculated within the standard SCP approximation, for the $\sqrt{3}\times\sqrt{3}$ R 30° commensurate phases of H_2, HD, and D_2 on graphite. These calculations were carried out using a Gaussian trial wave function for $\psi(z)$ and the SG interaction ($C_9 = 0$) for the intermolecular interaction. The energy terms are defined in the text by Eqs. (4.2)–(4.5), and all values are in kelvins.

	H_2		HD		D_2	
	Initial[a]	Final[b]	Initial[a]	Final[b]	Initial[a]	Final[b]
E_z	-478.4	-474.9	-501.4	-497.3	-515.3	-510.6
E_{xyz}	-16.0	-21.2	-17.8	-24.4	-18.9	-26.7
E_{xy}	-15.4	-14.7	-25.6	-24.7	-31.0	-30.0
E_T	-509.8	-510.8	-544.8	-546.4	-565.2	-567.3

[a] Solutions which are based upon the zeroth-order Gaussian ψ_j that minimizes only the E_z term.

[b] Solutions which are based upon the fully self-consistent Gaussian ψ_j that minimizes the total energy.

demonstration of this is the dependence of the self-consistent effective Fourier coefficients on the mass of the admolecule. As the equations are iterated towards the self-consistent solutions, there is a significant increase in these effective Fourier coefficients $\tilde{U}_G$, and corresponding effects on ω_Γ, the phonon gap at the Γ or center point in the Brillouin zone, and $\Delta\omega$, the width of the DOS (phonon density of states). The magnitude of these changes depends upon admolecule mass. The corresponding phonon energies for the cases shown in Table III are listed in Table IV, along with $\tilde{U}_{G_1}$, the effective Fourier coefficients corresponding to the nearest-neighbor reciprocal lattice vector for the substrate potential. The overall effect for D_2 is much larger than that for H_2, as might be expected from the mass difference, with the HD case being between the two extremes. The increase in the effective Fourier coefficients and the corresponding narrowing of the width of the DOS is about a 25% effect for D_2. In all cases (H_2, HD, and D_2), there is a movement of the adsorbed molecules in towards the surface by about 2% as these admolecules are localized over adsorption sites. It is this "dropping down" of the admolecules into the surface pockets formed by the adsorption sites that is responsible for the decrease in the ground-state energy and the alteration in the DOS associated with the fully self-consistent solutions. For clarity, it should be noted that if the starting point for these calculations (zeroth-order solutions) had been the classical position of the admolecule in the full substrate potential, there would have been a "lifting out" of the admolecule away from the surface, and a corresponding decrease in the effective Fourier coefficients. In this case, the greatest shift would be associated with H_2 and the smallest shift with D_2. The important point being made here is that the effective substrate interaction for quantum solids depends upon admolecule mass, with the more massive admolecule sitting closer to the substrate surface and experiencing a larger effective lateral variation in the substrate interaction and the least massive being further away, which reduces the size of the effective lateral variation.

Figure 1 shows the DOS (obtained by a finite sampling of the phonon dispersion curves in the irreducible part of the Brillouin zone) for the three species of admolecules calculated within the fully self-consistent approximation

TABLE IV. Parameters, calculated within the SCP approximation, characterizing the phonon density of states for the $\sqrt{3}\times\sqrt{3}$ R 30° commensurate phases of H_2, HD, and D_2 on graphite. These values correspond to the ground states described in Table III. All values are in kelvins. $\tilde{U}_{G_1}$ is the effective Fourier coefficient corresponding to the nearest-neighbor reciprocal lattice vector. $\hbar\omega_\Gamma$ is the phonon energy gap at the zone center, and $\Delta\hbar\omega$ is the width of the density of states. $\hbar\tilde{\omega}_T$ and $\hbar\tilde{\omega}_L$ are phonon energies corresponding to peaks in the density of states. All the above modes correspond to modes polarized in the direction parallel to the surface plane. The $\hbar\omega_\perp$ term corresponds to the mode polarized in the direction perpendicular to the surface; it is an Einstein-oscillator mode in this model, and thus independent of wave vector.

	H_2		HD		D_2	
	Initial[a]	Final[b]	Initial[a]	Final[b]	Initial[a]	Final[b]
$\tilde{U}_{G_1}$	-6.0	-7.7	-6.0	-7.9	-6.0	-8.1
$\hbar\omega_\Gamma$	40.5	46.6	34.9	40.7	31.1	36.9
$\Delta\hbar\omega$	48.0	42.1	24.1	23.8	19.6	14.8
$\hbar\tilde{\omega}_T$	61.7	64.9	48.1	51.6	40.4	44.2
$\hbar\tilde{\omega}_L$	83.1	83.8	60.7	62.0	48.7	50.3
$\hbar\omega\perp$	250.2	285.4	206.5	238.3	180.0	209.5

[a] Solutions which are based upon the zeroth-order Gaussian ψ_j that minimizes only the E_z term.

[b] Solutions which are based upon the fully self-consistent Gaussian ψ_j that minimizes the total energy.

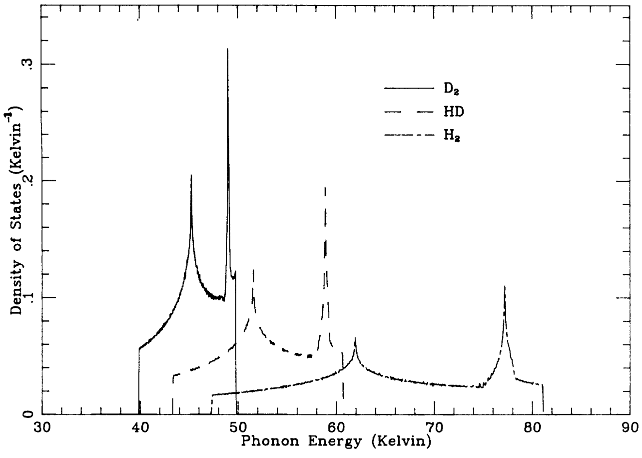

FIG. 1. Phonon density of states for the in-plane modes of the $\sqrt{3}\times\sqrt{3}$ R 30° phase of H_2, HD, and D_2 on graphite. These calculations used the SCP approximation, the SG interaction ($C_9 = 0$), and the Gaussian ψ functions.

discussed above. The comparison between D_2 and H_2 is striking, with the HD case again being between the two extremes. The narrow DOS for D_2 compared with that of H_2 is easily understandable in terms of the smaller mass of H_2. The H_2 DOS is much wider than the D_2 DOS because the zero-point motion of H_2 is much larger, causing these molecules to be affected more by their nearest neighbors. The D_2 molecule is more classical in nature, and thus it is more localized by its interaction with the substrate. Correspondingly, it is much less affected by interactions with its nearest neighbors and has a DOS that is significantly narrower than that for H_2. In fact, the D_2 behavior approaches that of an in-plane Einstein oscillator.

The phonon spectrum for D_2, calculated with the fully self-consistent solutions for ψ_j, is characterized by a phonon gap $\omega_\Gamma = 36.9$ K, a maximum in the phonon spectrum of the transverse modes at $\tilde{\omega}_T = 44.2$ K, and a local maximum at $\tilde{\omega}_L = 50.3$ K in the longitudinal modes. The DOS calculated for this spectrum was found to have peaks at both $\tilde{\omega}_T$ and $\tilde{\omega}_L$. Table IV lists these values as well as the corresponding values for the zeroth-order ψ_j functions. Since it is not yet possible to do a single-crystal INS experiment for monolayer systems, the INS data that do exist are either weighted averages of the phonon spectrum over the Brillouin zone (for D_2), or a direct measure of the DOS (for H_2 and HD). An empirical model, based on fitted coupling constants, was used to infer the phonon spectrum and DOS from the INS data for the H_2, HD, and D_2 systems.[7,11,65] The empirically derived values for the zone-center gap in the phonon spectrum of the various admolecules agree, within a few percent, with the theoretical values of the fully self-consistent calculation listed in Table IV. However, the results for the width of the DOS are clearly not as good as those for the zone-center gap.

Examining the D_2 case first, the theoretical phonon gap is about 7% smaller than that deduced from experiment and the theoretical maxima in the DOS have phonon energies that are about 2–5% too high. However, the theoretical width of the DOS is about 14.8 K while the experimentally deduced width is about 9.5 K. For H_2, the agreement is about as good as that for D_2. While the theoretical zone-center gap of 46.6 K is only about 1.5% too low, the theoretical width of the DOS is 42.1 K, which is about 50% larger than the experimentally derived value. The theoretical positions of the transverse and longitudinal peaks are also too high. The disagreement for HD is, as might be guessed, about the same as that for the D_2 and the H_2 systems. The theoretical zone-center gap for HD of 40.7 K is about 6% too low and the theoretical width of the DOS has a value of 23.8 K, which is about 60% too large.

Given an admolecule's large zero-point motion in the surface-normal direction, it would be reasonable to question the validity of using a Gaussian for the $\psi(z)$ trial functions. Since the effective Fourier coefficients do depend upon the averaging of the "bare" Fourier coefficients over these functions, and the effective Fourier coefficients do have a rather dramatic effect upon the DOS, an obvious point to examine is the validity of the Gaussian approximation. The proper minimization of the ground-state energy with respect to the functional form of $\psi(z)$ involves only the pseudo-one-dimensional potential energy term given by Eq. (4.7) and the kinetic energy associated with $\psi(z)$. The exact solution of this problem is given by the ground-state solution to the pseudo-one-dimensional Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial^2 z}\psi(z) + \left[U_0(z) + \sum_{G\neq 0} U_G(z)\exp(-\tfrac{1}{2}G^\alpha G^\beta\langle u_j^\alpha u_j^\beta\rangle) \right]\psi(z) = E_{1D}\,\psi(z), \tag{6.1}$$

where E_{1D} is just the sum of E_z and E_{xyz}. Since the pseudo-one-dimensional potential depends on the solutions to the SCP equations through the $\langle u_j^\alpha u_j^\beta\rangle$ tensor, the solutions to Eq. (6.1) must be iterated with the SCP equations until a self-consistent solution set is found. This generally takes about a half-dozen iterations as per the Gaussian case. Although the phonon modes polarized in the surface-normal-direction are not explicitly incorporated into the SCP treatment, the use of an Einstein-oscillator function for the z dependence of the wave function implies that the "theoretical" mode frequency is independent of wave vector and its value is given by the excitation energy of the first excited state of this oscillator. For the Gaussian trial function, this means that $\hbar\omega_\perp$ is just four times the kinetic energy associated with the Gaussian. For the exact $\psi(z)$, $\hbar\omega_\perp$ is determined by the energy difference between the ground-state and first-excited-state solutions of Eq. (6.1). This value differs slightly from that for the single molecule as found in Sec. II.

The results using the exact ψ are compared to those using the Gaussian trial function in Table V. The effects upon E_z (which then affects E_T), and upon $\hbar\omega_\perp$ are significant, especially the effect upon the latter. However, except for these two particular effects, there appears to be little difference between using a Gaussian $\psi(z)$ rather than using the exact $\psi(z)$. The E_z values calculated using the exact $\psi(z)$ are consistent, of course, with the single-particle solutions shown in Table I, while there is naturally some error introduced by calculating E_z using a trial Gaussian wave function. In general, the purely in-plane quantities are not much affected by use of a Gaussian rather than the exact $\psi(z)$, but those quantities which are sensitive to the z dependence of the wave function are altered substantially.

Measurements of the total kinetic energy have been made using deep INS.[66] The kinetic energy associated with the Gaussian trial function (52.4 K for D_2) is generally about 25% larger than the kinetic energy associated with the exact $\psi(z)$ (42.4 K for D_2). Similar results are found for the other isotopic species, indicating that using the exact wave functions clearly makes a significant difference here. The experimental value for the kinetic energy of H_2 in the $\sqrt{3}\times\sqrt{3}$ R 30° phase at a temperature of about 10 K is 115±32 K, while the kinetic energy for H_2 using the SCP calculation and the exact $\psi(z)$ functions is 92 K (35 K for the in-plane motion and 57 K for the surface-normal motion). The experimental and theoretical values are consistent, but the error bar on the experimental value is large enough to justify some caution in comparing these values. The changes in the theoretical values due to finite temperature and other effects discussed below are rather small, being on the order of 2–5 K.

The trend in these calculations is quite clear. The SCP calculation using an intermolecular interaction that ignores the influence of the substrate does a very good job of deducing the values of the zone-center gap in the phonon spectrum, but a rather poor job of estimating the width of the DOS. It also does a respectable (but not very good) job of estimating the positions of the peaks in the DOS. In an attempt to understand these discrepancies, an investigation of some of the effects ignored in the above calculations was carried out. In particular, the effects of short-range correlations, the modification of the intermolecular interaction due to the substrate, and the effects of anisotropic terms in the hydrogen-carbon interaction were examined.

B. *T*-matrix calculations

T-matrix calculations were carried out using the SG interaction ($C_9 = 0$) and the exact $\psi(z)$. The consistency conditions on the moments of u_{ij}^{α} (as well as the correlation energy and the two-body potential energy) require the calculation of real-space integrals of two-body functions. These were carried out in the standard fashion using the *T*-matrix pair distribution function.[18] The solutions to Eqs. (5.9)–(5.10) were obtained using the standard multivariate Newton-Raphson method.[67] Table VI summarizes the results and compares these *T*-matrix results to those of the corresponding SCP calculations.

The effects of two-body correlations are strongest for H_2 and least for D_2, as would be the obvious guess, since the more massive admolecules have smaller zero-point amplitudes and thus less direct contact with their neighbors. Two-body correlations lower the total energy of the system (relative to the SCP ground state) with the maximum effect being about 3 K and the minimum about 1 K. These effects are smaller for the commensurate adsorbed phase than they would be for the incommensurate adsorbed phase or the bulk phase. This is a result of the

TABLE V. Comparison of the Gaussian ψ function results vs those for the exact ψ functions. The parameters listed, calculated within the SCP approximation, characterize the ground-state wave function and the phonon density of states for the $\sqrt{3}\times\sqrt{3}$ R 30° commensurate phases of H_2, HD, and D_2 on graphite. All values are in kelvins. The first four energies are the same quantities as those in Table III, while the other quantities are defined in Table IV.

	H_2		HD		D_2	
	Gaussian[a]	Exact[b]	Gaussian[a]	Exact[b]	Gaussian[a]	Exact[b]
E_z	-474.9	-481.6	-497.3	-502.2	-510.6	-514.5
E_{xyz}	-21.2	-20.8	-24.4	-24.0	-26.7	-26.4
E_{xy}	-14.7	-14.7	-24.7	-24.7	-30.0	-30.0
E_T	-510.8	-517.1	-546.4	-550.9	-567.3	-570.9
$\tilde{U}_{G_1}$	-7.7	-7.5	-7.9	-7.8	-8.1	-8.0
$\hbar\omega_\Gamma$	46.6	46.1	40.7	40.4	36.9	36.7
$\Delta\hbar\omega$	42.1	42.7	23.8	24.0	14.8	15.0
$\hbar\tilde{\omega}_T$	64.9	64.8	51.6	51.3	44.2	44.0
$\hbar\tilde{\omega}_L$	83.8	84.0	62.0	62.0	50.3	50.2
$\hbar\omega\perp$	285.4	190.8	238.3	166.3	209.5	149.5

[a] Solutions which are based upon the fully self-consistent Gaussian ψ_j that minimizes the total energy.

[b] Solutions which are based upon the fully self-consistent exact ψ_j that solves Eq. (6.1).

TABLE VI. Comparison of the T-matrix approximation to the SCP approximation. These parameters, calculated using the Silvera-Goldman interaction ($C_9 = 0$) and the exact ψ functions, characterize the ground-state wave function and the phonon density of states of the $\sqrt{3}\times\sqrt{3}$ R 30° commensurate phases of H_2, HD, and D_2 on graphite. All values are in kelvins. The first energy is the correlation energy defined by Eq. (5.12), and is identically zero for the SCP approximation. The next three energies are defined by Eqs. (4.3)–(4.5), using the T-matrix effective interaction where appropriate. The total energy E_T is just the sum of the first four energy terms. The others quantities are defined in Table IV.

	H_2		HD		D_2	
	T matrix[a]	SCP[b]	T matrix[a]	SCP[b]	T matrix[a]	SCP[b]
ϵ_{corr}	-3.6		-1.9		-1.2	
E_z	-482.0	-481.6	-502.3	-502.2	-514.8	-514.5
E_{xyz}	-19.2	-20.8	-22.9	-24.0	-25.5	-26.4
E_{xy}	-15.4	-14.7	-25.4	-24.7	-30.6	-30.0
E_T	-520.2	-517.1	-552.5	-550.9	-572.1	-570.9
$\tilde{U}_{G_1}$	-7.4	-7.5	-7.7	-7.8	-7.9	-8.0
$\hbar\omega_\Gamma$	44.5	46.1	39.5	40.4	36.1	36.7
$\Delta\hbar\omega$	36.1	42.7	20.1	24.0	12.3	15.0
$\hbar\tilde{\omega}_T$	60.2	64.8	48.9	51.3	42.4	44.0
$\hbar\tilde{\omega}_L$	76.4	84.0	57.5	62.0	46.3	50.2
$\hbar\omega\perp$	190.4	190.8	166.1	166.3	149.5	149.5

[a] Solutions which are based upon the fully self-consistent T-matrix approximation.

[b] Solutions which are based upon the fully self-consistent SCP approximation.

substrate causing an in-plane localization of the admolecules, which restricts the direct contact of these admolecules with their neighbors.

The most important effect of the two-body correlations is to decrease the width of the DOS. This effect causes about a 15% shift for H_2 and a 18% shift for D_2. There are corresponding shifts in the other DOS parameters. This is typical of such calculations, since the inclusion of two-body correlations softens the effective interaction and lowers the energy of the zone-boundary phonons.[54] The surface-normal mode is virtually unaffected. These shifts in the DOS are in the right direction (closer to the experimental values), but the discrepancies between theory and experiment are still larger than the estimated uncertainties of these experiments. Nevertheless, it is clear that two-body effects are important for accurate calculations of the phonon dispersion curves and they have a significant effect on the DOS of these admolecules.

C. Effects of the McLachlan interaction

The McLachlan interaction is essentially repulsive in nature, and as such it can be expected to stiffen the phonon dynamics, thus increasing the width of the DOS. It can be a significant enough effect, that a study of the phonon dynamics needs to examine the importance of this term. The usual form used for this interaction requires an estimate of the effective distance of the admolecule from a mathematical image surface plane, and this differs from the plane of the surface carbon atoms.[16] The uncertainty in the value of this parameter is not easy to estimate without a first-principles calculation. Furthermore, the theoretical functional form for this interaction is the result of a perturbation theory calculation which is only valid at large intermolecular separations. This perturbation calculation predicts an inverse-cube functional dependence for small separations where the theory is not valid. As such, the effect of this term on the zone-boundary modes, which are dominated by the short-range interaction between nearest-neighbor admolecules, is suspect. The effect of this term on the total energy of the system is on a much better theoretical foundation, and these results are more reliable.

Table VII shows the results of including the McLachlan interaction. The only significant effect on the various energies is on the in-plane energy E_{xyz}, and this is due primarily to the effect of the McLachlan term on the interadmolecule potential energy. The effects on the DOS are very small except for an increase in the width of the DOS. This increase is in the 10–20% range. However, it is not clear how reliable these increases might be for the reasons stated above. It is most likely that these increases must be considered as upper limits to the actual effect.

The most likely overall effect of the McLachlan interaction is to raise the ground-state energy of the commensurate solid (decrease the binding energy), and to introduce some small increase in the DOS, although not as large an increase as typically shown in Table VII. Nevertheless, this term does have some influence on the behavior of the solid, and whether it is included or not, this influence produces some uncertainty in the predicted behavior of the system.

D. Effects of an anisotropic hydrogen-carbon interaction

The use of isotropic atom-carbon interactions has been criticized for some time as predicting Fourier coefficients for the admolecule-graphite interaction that are too small.[30] In some cases, the error has been estimated to be as large as 40–50%. Recent calculations, using the embedded-atom method to calculate the hydrogen-

TABLE VII. Comparison of calculations using the SG interaction ($C_9 = 0$) with and without the additional McLachlan interaction. All calculations used the T-matrix approximation and the exact ψ functions. The parameters in this table are the same as those in Table VI.

	H_2		HD		D_2	
	Without[a]	With[b]	Without[a]	With[b]	Without[a]	With[b]
ϵ_{corr}	-3.6	-3.2	-1.9	-1.9	-1.2	-1.0
E_z	-482.0	-481.9	-502.3	-502.3	-514.8	-514.6
E_{xyz}	-19.2	-19.6	-22.9	-23.3	-25.5	-26.0
E_{xy}	-15.4	-5.3	-25.4	-15.4	-30.6	-20.6
E_T	-520.2	-510.0	-552.5	-542.9	-572.1	-562.2
$\tilde{U}_{G_1}$	-7.4	-7.5	-7.7	-7.7	-7.9	-8.0
$\hbar\omega_\Gamma$	44.5	44.9	39.5	39.9	36.1	36.4
$\Delta\hbar\omega$	36.1	38.2	20.1	22.0	12.3	14.1
$\hbar\tilde{\omega}_T$	60.2	60.9	48.9	49.5	42.4	43.1
$\hbar\tilde{\omega}_L$	76.4	78.6	57.5	59.4	46.3	49.6
$\hbar\omega\perp$	190.4	190.7	166.1	166.2	149.5	149.5

[a] Results of the fully self-consistent solutions without the McLachlan interaction.

[b] Results of the fully self-consistent solutions with the McLachlan interaction.

graphite interaction, estimated that isotropic interactions would lead to Fourier coefficients that are too small only by about 15%.[24] Since the isotropic model used here results in effective Fourier coefficients in the range 7.5–8.0 K, this would imply that a more sophisticated anisotropic model would lead to effective Fourier coefficients in the range 8.8–9.4 K. These are significant changes because both the zone-center gap and the width of the DOS are very sensitive to relatively small alterations in the Fourier coefficients in the above range of values. While it would be possible to reconstruct the entire admolecule-graphite interaction using an anisotropic model as developed in Ref. 30, it seemed more profitable at this time to adjust the effective Fourier coefficients to obtain a better fit between the theoretical DOS parameters and the experimental ones. Since an *ad hoc* adjustment of the effective Fourier coefficients is inconsistent with self-consistent solutions involving surface-normal terms, the calculation was carried out as a purely two-dimensional one.

An increase in the effective Fourier coefficients would cause an increase in the phonon gap and a decrease in the width of the DOS. This would bring the theoretical values more in line with the experimental ones. No attempt was made to obtain the "best" fit in any sense. Rather, the value of $\tilde{U}_{G_1}$ was increased until a reasonable fit between the theoretical and experimental value for the zone-center phonon gap was obtained. The goal was simply to see if the required adjustment of this coefficient was reasonable in light of the results of Ref. 24, and if the other parameters characterizing the DOS were close to the experimental values. Table VIII shows the results of these calculations and the corresponding experimental values.[11] Figure 2 shows the theoretical DOS curves for the three isotopic species. The agreement between the theoretical values and the experimental results is quite good.

It is clear that the required increases in the effective Fourier coefficients are quite modest and within the 15% shift discussed above. Furthermore, there is a significant decrease in the width of the DOS and a corresponding shift downward of the $\tilde{\omega}_T$ and $\tilde{\omega}_L$ values. The agreement between the theoretical results and experimental results for D_2 is very good. In fact, numerical results showed

TABLE VIII. Comparison of the two-dimensional model calculation with the experimental results. These parameters characterize the phonon density of states of the $\sqrt{3}\times\sqrt{3}$ R 30° commensurate phases of H_2, HD, and D_2 on graphite. All values are in kelvins and the quantities listed are defined in Table IV. The theoretical parameters were calculated using the Silvera-Goldman interaction ($C_9 = 0$) and the T-matrix approximation.

	H_2		HD		D_2	
	Theory	Expt.[a]	Theory	Expt.[a]	Theory	Expt.[a]
$\tilde{U}_{G_1}$	-8.0		-8.7		-9.0	
$\hbar\omega_\Gamma$	47.3	47.3	43.3	43.2	39.9	40.0
$\Delta\hbar\omega$	33.8	27.5	17.4	14.7	9.9	9.5
$\hbar\tilde{\omega}_T$	62.0	57.9	51.6	48.8	45.3	43.3
$\hbar\tilde{\omega}_L$	77.3	71.4	59.0	55.8	49.0	48.1

[a] H.J. Lauter, in *Phonons 89*, edited by S. Hunklinger, W. Ludwig, and G. Weiss (World Scientific, Hong Kong, 1990), p. 871.

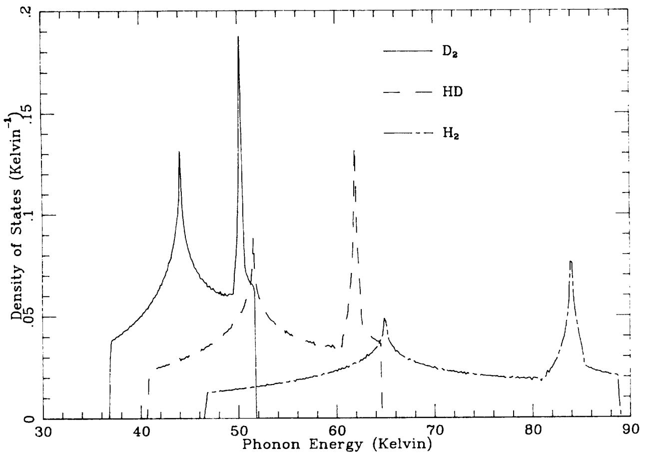

FIG. 2. Phonon density of states for the in-plane modes of the $\sqrt{3}\times\sqrt{3}$ R 30° phase of H_2, HD, and D_2 on graphite. These calculations used the T-matrix approximation, the SG interaction ($C_9 = 0$), and the model $\tilde{U}_{G_1}$.

that any adjustment of the Fourier coefficients as large as 40–50 %, as has been suggested for some other adsorbed systems, would lead to a DOS that is incompatible with the INS experiments. Although the agreement between theory and experiment for the other admolecules is not as good, it is still quite reasonable. Note that the required effective Fourier coefficients do depend upon the admolecule mass, as would be expected from the results of the other calculations, and they exhibit the appropriate trends as a function of this mass. Further adjustment of the $\tilde{U}_{G_1}$ could have been carried out to improve the overall fit to the DOS, but in the absence of detailed knowledge of the sensitivity of DOS parameters to errors in the experiment or subtleties in the analysis, such adjustments makes little sense. It is obvious that a very reasonable increase in the effective Fourier coefficients due to anisotropies in the admolecule-carbon interaction could account for much of the remaining discrepancy between the theoretical and experimental parameters for the DOS.

VII. TEMPERATURE DEPENDENCE OF THE DENSITY OF STATES

A series of calculations were carried out to determine the temperature dependence of both the DOS gap and its width. Since the temperature dependence of the DOS has been measured experimentally for each isotopic species,[12] these calculations serve as a further check on the general validity of the lattice-dynamics calculations. The finite-temperature SCP calculations are essentially the same as the zero-temperature calculations and only require the insertion of the Bose-Einstein distribution function into the appropriate functions. This occurs mainly in the calculation of the $\Gamma_{ij}^{\alpha\beta}$ and in the kinetic-energy expressions.[26,50] Both SCP calculations and T-matrix calculations were carried out at finite temperature. The T-matrix approximation was applied to the SCP theory just as in the zero-temperature case, even though it is not clear that this is completely justified. All these calculations showed the same general tendencies.

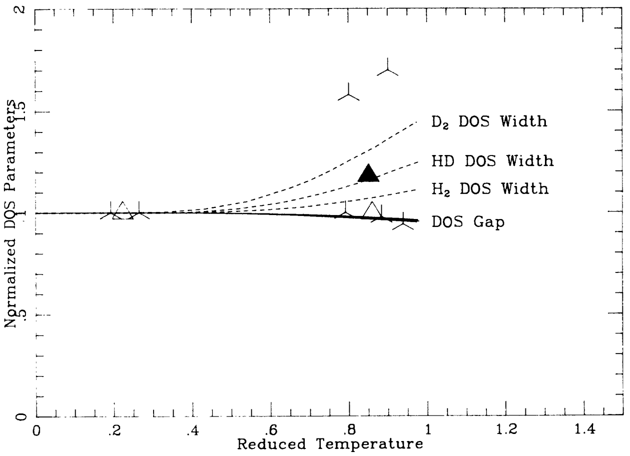

FIG. 3. Temperature dependence of the DOS (phonon density of states) parameters for the $\sqrt{3}\times\sqrt{3}$ R 30° phase of H_2, HD, and D_2 on graphite. The curves show the results of calculations using the T-matrix approximation, the SG interaction ($C_9 = 0$), and the model $\tilde{U}_{G_1}$. The experimental results are shown as open triangles for D_2, skeletal triangles for HD, and as solid triangles for H_2. The six experimental points for the DOS gap (Ref. 11) are very close to the theoretical results, but the three experimental points for the DOS width (Ref. 68) are significantly larger than the theoretical results.

Figure 3 shows the results of a two-dimensional calculation using the model $\tilde{U}_{G_1}$ values shown in Table VIII. Also shown are the experimental results for the DOS gap from Ref. 12. The lower three curves show the theoretical gap (normalized by the corresponding value at zero temperature) as a function of the reduced temperature (the absolute temperature divided by the experimental melting temperature).[12] The theoretical results shown used the T-matrix approximation, the SG interaction ($C_9 = 0$), and the model $\tilde{U}_{G_1}$. In all cases the theoretical gap energy varies very little with temperature, which is just the behavior found experimentally as can be seen from the six experimental points shown. Even at the experimental melting temperature, the gap is within about 5% of its zero-temperature value. Given that the melting temperatures are in the range of 18–20 K, and the gap energies are in the range of 40–47 K, perhaps this near independence of the gap energy on temperature is not very surprising.

It is interesting to note that when the normalized gap is plotted against the reduced temperature, all three curves are so close together that it almost suggests a universal curve. However, the DOS width does not show this behavior. The upper three curves in Fig. 3 are the theoretical widths (normalized by the corresponding value at zero temperature) of the three admolecules plotted as a function of the reduced temperature. All three curves show a significant increase in this width with temperature, and these relative changes are substantially different from admolecule to admolecule. There are three experimental points shown,[68] two for HD and one for H_2. While there is respectable qualitative agreement between the theoretical and experimental trends, all three experimental points show a much larger increase of the DOS width with temperature than is found theoretically. It appears that the theoretical values for the DOS width are too large at zero temperature, but show a smaller increase with temperature than is found experimentally. Whether this is due to some general inadequacy in the phonon dynamics, or is due to some simplifying assumption in the general interaction model, is not at all clear at this point in time.

VIII. DISCUSSION

These calculations demonstrate that to describe the dynamics of hydrogen monolayers properly, it is necessary to deal with the three-dimensional nature of both the substrate interaction and the monolayer wave function. In particular, the effective Fourier coefficients depend upon the mass of the admolecule due to the dependence of the zero-point motion on this mass. Any admolecule with substantial zero-point motion should show these effects. The coupling between the parameters for the surface-normal and the in-plane factors in the wave function has a significant effect on the dynamics of these systems and cannot be ignored. That is, commensurate quantum solids cannot be treated as simple two-dimensional systems if accurate phonon spectra are to be calculated.

Clearly there is good, but not perfect agreement between theory and experiment for the in-plane DOS of the $\sqrt{3}\times\sqrt{3}$ R 30° phase of H_2, HD, and D_2. The general agreement between theory and experiment shows that the interaction between hydrogen molecules and the graphite surface, as well as the interaction between the hydrogen molecules themselves, can be described reasonably well by the models that have been used here. However, it is clear that two-particle correlations, anisotropic effects of the admolecule-substrate interaction, and substrate modification of the admolecule-admolecule interaction cannot be entirely ignored. In particular, two-body correlations and anisotropic modifications of the admolecule-substrate interaction play significant roles in determining the in-plane DOS. Much of the discrepancy between the earlier SCP theory[9] and experimental results is a consequence of such effects.

The excitation energies of the surface-normal modes are in rough agreement with the experimental values provided that the exact ψ functions are used. The simple Einstein-oscillator treatment of the surface-normal modes yields a phonon energy for the Γ-point mode that is slightly higher than the excitation energy of the first excited state of the corresponding isolated admolecule. The small shift to higher energy is the result of the effective surface-normal potential well being dependent upon the in-plane part of the wave function. Table IX lists the theoretical values for each of the three isotopic species along with the experimental values, which are somewhat higher than the theoretical ones.[20]

TABLE IX. Comparison of theoretical and experimental results for $\hbar\omega_\perp$ corresponding to the phonon mode polarized in the direction perpendicular to the surface. These parameters characterize the $\sqrt{3}\times\sqrt{3}$ R 30° commensurate phases of H_2, HD, and D_2 on graphite. The theoretical values were calculated using the SCP approximation and the exact ψ functions. In this model, $\omega_\perp$ is an Einstein-oscillator mode and thus independent of wave vector. All values are in kelvins.

Adsorbate	Initial[a]	Final[b]	Expt.[c]
H_2	187.7	190.8	226
HD	163.8	166.3	172.8
D_2	147.4	149.5	

[a] Solutions which are based upon the zeroth-order exact ψ_j that minimizes only the E_z term.

[b] Solutions which are based upon the fully self-consistent exact ψ_j that minimizes the total energy.

[c] J.L. Armony, V.L.P. Frank, H.J. Lauter, and P. Leider, in *Phonons 89*, edited by S. Hunklinger, W. Ludwig, and G. Weiss (World Scientific, Singapore, 1990), p. 916.

A more sophisticated treatment of the surface-normal modes yields mode energies that are even lower than those found here, and predicts a width of about 35 K for these modes.[10] The differences between the two calculations are significant, and yet the simpler one seems closer to the experimental results. Reference 10 suggested an alternate assignment to the experimental modes as a way to explain the discrepancy between theory and experiment. This might be the case, although a simple physical argument indicates that the surface-normal mode at the Γ point would most likely have a higher, not a lower, excitation energy than the isolated molecule. In particular, the in-plane localization of the admolecule in the solid causes it to be closer to the surface than is the case for the isolated admolecule, thus it experiences that part of the substrate potential well that has more curvature, and hence it exhibits a higher energy for the surface-normal excitation. It may be that both the model presented here and the more sophisticated model of Ref. 10 both suffer from the same two difficulties. First, the excited surface-normal states are most likely more sensitive than the ground-state properties and in-plane modes to the precise shape of the effective surface-normal potential well, and this shape would be affected by any anisotropic nature of the admolecule-carbon interaction. Second, neither of these theoretical models treats the dynamical coupling between the substrate and the monolayer which affects surface-normal mode much more than it does the in-plane modes.[69] Perhaps a full understanding of the nature of these surface-normal modes must await the resolution of these two issues.

The intermolecular interaction is clearly dominated by the direct interaction of two admolecules, and the site-site model for the interaction of each admolecule with the graphite does produce the dominant part of the admolecule-graphite interaction. The role of the McLachlan interaction in the determination of the DOS is somewhat uncertain, although it does have a significant effect on the total binding energy of the solid. It may also play an important role in the stability of the commensurate phase, since it clearly favors lower-density phases. However, as far as the phonon modes are concerned, this interaction and the other smaller substrate-mediated effects would appear to be relatively minor perturbations on the direct interactions used for this model calculation.

The critical question about the interaction model, for the purposes of determining the DOS, is clearly the unknown role of the anisotropic admolecule-graphite interactions. These systems are borderline commensurate phases in that small changes in the substrate Fourier coefficients have qualitative effects upon the dynamics of these systems. For adsorbed He on graphite, the role of the anisotropic terms is known to be important.[29] However, the relevant band-structure matrix elements were measured by appropriate selective adsorption experiments,[70,71] and so there is independent experimental information that can be used to determine the size of the anisotropic terms. This additional experimental information is lacking for the molecular hydrogen isotopic species, which makes the calculation of these terms using an empirical model rather difficult. Lacking such experimental information, it might be possible to use the recent theoretical calculations based upon the embedded-atom model[24,25] as a constraint in building an appropriate model for use in phonon-dynamics calculations.

An important calculation to do in the future, for the purposes of comparing theory to experiment, would be a proper quantum treatment of the dynamic structure factor. The analysis of the experimental results used a classical approach to deduce the DOS from the INS measurements.[7,11] Because of the large zero-point motion of quantum solids, there is at least the need to consider the interference term between the single-phonon and two-phonon scattering.[72] This requires the calculation of a phonon response function that includes the cubic-anharmonic correction, a term which also contributes to phonon damping. Furthermore the effects of phonon damping on the DOS, which shifts and broadens the phonon energy, could be as important as the short-range correlation effects calculated here. The direct effects of phonon damping can be expected to lead to a further decrease in the zone-boundary phonon frequencies, and the concomitant reduction in the width of the DOS, and the interference effects would lead to an alteration of the shape of the dynamic structure factor. While the cubic-anharmonic damping term has been calculated for some monolayer solids,[27,28,73] the calculation of the interference term has yet to be done for any of the monolayer solids. This is certainly a fertile and important area of future theoretical research. Once these effects are known, it will be possible to make more critical comparisons between theory and experiment. This could make the determination of the effective $\tilde{U}_{G_1}$ from the experimental phonon-dynamics results a viable option. Such a comparison could help settle the question of just how important the anisotropic admolecule-substrate effects are. Clearly the DOS is a sensitive probe of the admolecule-substrate interaction for these systems.

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