Phonon Spectrum and Density of States for the $\sqrt{3}\times\sqrt{3}R30°$ Phase of D_2 and H_2 on Graphite

Anthony D. Novaco
Department of Physics, Lafayette College, Easton, Pennsylvania 18042

(Received 15 January 1988)

A self-consistent phonon calculation was used to calculate the phonon spectrum and density of states of D_2 and H_2 adsorbed on graphite. The adsorbed molecules are assumed to be in a free-rotor state and the molecular solid is taken to be the $\sqrt{3}\times\sqrt{3}R30°$ commensurate phase. The theoretical results are compared to recent neutron-scattering results for the phonon modes of D_2 and with older data for H_2. The effect of the use of coordinates both parallel to and perpendicular to the surface in the functional form for the wave function was found to be significant. Thus these are not purely two-dimensional systems.

PACS numbers: 63.20.Dj, 67.70.+n, 67.80.Cx, 68.35.Ja

The recent experimental interest[1-7] in the structure and dynamics of the adsorbed hydrogens (H_2, D_2, and HD) was the motivating force for this calculation of the phonon spectrum and density of states for these molecular solids adsorbed on graphite. The adsorbed hydrogens provide a wealth of different solid phases and corresponding phase transitions. These include the $\sqrt{3}\times\sqrt{3}R30°$ commensurate phase, at least two hexagonal incommensurate phases, and a uniaxial incommensurate phase.[1-3,5,6] Although interest in these systems goes back many years,[8,9] experimental techniques have now reached the point where a detailed comparison of the inelastic scattering with theoretical predictions is a realistic possibility.[4,7] The calculation presented here assumes that the molecules are spherically symmetric, that is, that they are in the $J=0$ free-rotor rotational state, and that the molecular solid is the $\sqrt{3}\times\sqrt{3}R30°$ commensurate phase. The interaction of each molecule with the graphite surface is assumed to be the same as that of a single isolated molecule with the surface. The intermolecular interaction is assumed to be the same as that of a pair of isolated molecules in three dimensions. The self-consistent phonon (SCP) calculation includes only the even terms of the standard theory. Only the in-plane modes will be discussed here, the out-of-plane modes being at a much higher energy.

The first step in the theory for the adsorbed hydrogens was to build a realistic model for the interaction of the hydrogen molecule with the graphite surface. Although many models do exist for this adsorption potential,[10-15] some of these models are not generally suitable for the purposes of this calculation. It was decided to modify a model used by Crowell[11,13] for this interaction and combine this with the expansion developed by Steele for adsorption potentials.[14] The model potential can then be used to calculate realistic Fourier coefficients for the periodic variation of the adsorption potential.

The original Crowell model uses a sum of spherically symmetric molecule-carbon interactions to build the total adsorption potential with the molecule-carbon pair potential being a Lennard-Jones LJ(12,6) interaction. Following Steele, the adsorption potential is expressed in terms of Fourier coefficients that depend on the surface-normal position. Theoretical bound-state energies for a molecule in the laterally (in-plane) averaged adsorption potential were obtained by numerical integration of the Schrödinger equation. The numerical uncertainties in the theoretical results are less than 0.1%. The LJ(12,6) depth parameter ϵ_0 and hard-core radius σ were adjusted so that the the theoretical values for these bound-state energies matched the experimental values as determined by selective adsorption measurements.[15] The values of ϵ_0 and σ determined by this calculation differ by about 5% from those determined previously in other work because of minor differences in the fitting criteria.[15] No attempt was made to include the anisotropic terms used in later versions of the Crowell model.[12,13] The LJ(12,6) potential parameters for the molecule-carbon interaction determined by this calculation are $\epsilon_0=47.7$ K and $\sigma=2.85$ Å. These values reproduce, within 5%, all the experimentally determined bound-state energies for both H_2 and D_2.

The numerical solutions for the bound-state wave functions show that the adsorption potential confines the hydrogen molecules to a narrow region near the surface of the graphite. These theoretical results show that the distance between the adsorbed molecules and the graphite surface is about 3.0 Å for H_2 and about 2.9 Å for D_2. The rms deviation from this plane is about 0.2 Å for both H_2 and D_2. These deviations are small enough, relative to the commensurate-phase intermolecular separation of 4.26 Å, that it is reasonable to use a wave function that is a product of single-particle Gaussians for the surface-normal part and a product of correlation Gaussians (the standard SCP ground state) for the in-plane part. The theory presented here is an extension of earlier SCP calculations for the dynamics of adsorbed solids which are strictly two-dimensional calculations.[16,17] It is important to note that the effects of the third dimension were found to be important, and that they cannot be ignored if realistic comparisons to data are to be made.

The ground-state energy for this system can be written as

$$E = E_z + E_{xyz} + E_{xy}, \tag{1}$$

where each term on the right-hand side corresponds to one of three different classes of contributions. To obtain specific expressions for these terms, let $\psi_j = \psi(z_j)$ represent the surface-normal Gaussian associated with the jth molecule, and $\phi_{ij} = \phi(x_{ij}, y_{ij})$ represent the in-plane Gaussian associated with the ith and jth molecules.

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 molecules each with mass m, this energy can be written as

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

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_{ij} factors. However, this energy depends on the ϕ_{ij} 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 molecule from its lattice site.[16] It is possible to write E_{xyz} as

$$E_{xyz} = \sum_{j=1}^{N} \sum_{\mathbf{G}} \langle \psi_j | U_{\mathbf{G}}(z_j) | \psi_j \rangle \exp(-\tfrac{1}{2} G^\alpha G^\beta \langle u_j^\alpha u_j^\beta \rangle. \tag{3}$$

$U_{\mathbf{G}}(z)$ is the z-dependent Fourier coefficient for the reciprocal lattice vector $\mathbf{G}$ of the graphite basal plane.[15]

The E_{xy} term is the kinetic energy associated with the in-plane coordinates plus the intermolecular interaction energy. If Φ represents the standard SCP product wave function constructed from the ϕ_{ij} factors, then E_{xy} can be written as

$$E_{xy} = \frac{-\hbar^2}{2m} \sum_{j=1}^{N} \langle \Phi | \frac{\partial^2}{\partial x_j^2} + \frac{\partial^2}{\partial y_j^2} | \Phi \rangle + \frac{1}{2} \sum_{i,j=1}^{N} \langle \Phi | V_{\text{eff}}(r_{ij}) | \Phi \rangle, \tag{4}$$

where the double sum includes 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 molecules, and it is defined by the equation

$$V_{\text{eff}}(r_{ij}) = \langle \psi_j | V(\eta_{ij}) | \psi_j \rangle. \tag{5}$$

The function $V(\eta)$ describes the interaction of two molecules separated by a distance $\eta = (x^2 + y^2 + z^2)^{1/2}$. The choice for this interaction was that used by Silvera and Goldman to describe the interaction between hydrogen molecules in the bulk solid phase, but with the C_9 many-body term set to zero.[18] If the effect of averaging of the intermolecular potential over the ψ_j part of the wave function can be ignored, then E_{xy} depends only on the ϕ_{ij}. Comparison of the functions $V_{\text{eff}}(r)$ and $V(r)$ showed that, to a good approximation, the $V_{\text{eff}}(r)$ term could be replaced by the "bare" $V(r)$ interaction. This was done and, 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_{ij} factors of the wave function. Minimization with respect to the ψ_j involves the z position of the center of the Gaussian and its width. This minimization process involves the E_z and E_{xyz} terms. Minimization of the energy with respect to the parameters in the ϕ_{ij} factors involves the E_{xyz} and E_{xy} terms. The equations that result from this latter minimization are those of a two-dimensional SCP theory with "two-dimensional" adsorption potential Fourier coefficients $\tilde{U}_{\mathbf{G}}$ given by

$$\tilde{U}_{\mathbf{G}} = \langle \psi_j | U_{\mathbf{G}}(z_j) | \psi \rangle. \tag{6}$$

These SCP equations generate the phonon frequencies and polarization vectors for the in-plane modes in the usual manner.[16,17] 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

TABLE I. Ground-state energy contributions for the $\sqrt{3} \times \sqrt{3}R30°$ commensurate phases of H_2 and D_2 on graphite. The energy terms are defined in the text by Eqs. (1)-(4), and all values are in kelvins.

	H_2		D_2	
	Initial[a]	Final[b]	Initial[a]	Final[b]
E_z	−478.4	−474.9	−515.3	−510.6
E_{xyz}	−16.0	−21.2	−18.9	−26.7
E_{xy}	−15.4	−14.7	−31.0	−30.0
E	−509.8	−510.8	−565.2	−567.3

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

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

step in this procedure is to generate a set of $\tilde{U}_G$ from the ψ_j that minimizes E_z only. Then these $\tilde{U}_G$ values are used to start the iteration procedure that minimizes the total energy E. Table I summarizes the results for the energy terms given in Eqs. (1)-(4).

Use of a self-consistent ψ_j instead of zeroth-order ψ_j does not have a large effect on the total energy, although there is significant shifting of the individual contributions to the total. However, there is a significant increase in the effective Fourier coefficients $\tilde{U}_G$, and a corresponding effect on ω_Γ, the phonon gap at the Γ or center point in the Brillouin zone, and on the width of the phonon density of states $\Delta\omega$. The corresponding phonon energies are listed in Table II, along with $\tilde{U}_{G_1}$, the effective Fourier coefficients corresponding to the nearest-neighbor reciprocal-lattice vector for the substrate potential. The effect on D_2 is much larger than on H_2, as might be expected from the mass difference. The increase in the effective Fourier coefficient and the corresponding narrowing of the width of the density of states is about a 25% effect for D_2. In both the H_2 and D_2 systems, there is a movement of the adsorbed molecules in towards the surface as these molecules are localized over adsorption sites. For ψ_j, this means that the initial functions are associated with a position slightly farther away from the surface than the final, fully self-consistent solutions. It is this "dropping down" of the molecules into the surface pockets formed by the absorption sites that is responsible for the energy gain of the fully self-consistent solutions.

The ground-state energies for both the H_2 and D_2 $\sqrt{3}\times\sqrt{3}R30°$ commensurate phases were compared to the corresponding energies of both the rotated and nonrotated incommensurate phases.[19] The commensurate phases are lower in energy than the incommensurate phases in both cases. For H_2 the energy difference is about 17 K, 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.[20]

TABLE II. Parameters characterizing the density of states for the in-plane modes of the $\sqrt{3}\times\sqrt{3}R30°$ commensurate phases of H_2 and D_2 on graphite. 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.

	H_2		D_2	
	Initial[a]	Final[b]	Initial[a]	Final[b]
$\tilde{U}_{G_1}$	−6.0	−7.7	−6.0	−8.1
$\hbar\omega_\Gamma$	40.5	46.6	31.1	36.9
$\Delta\hbar\omega$	48.0	42.1	19.6	14.8
$\hbar\tilde{\omega}_T$	61.7	64.9	40.4	44.2
$\hbar\tilde{\omega}_L$	83.1	83.8	48.7	50.3

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

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

The phonon spectrum for D_2 calculated with the fully self-consistent solutions for ψ_j is characterized by a phonon gap $\tilde{\omega}_\Gamma = 36.9$ K, a maximum in the phonon spectrum of the transverse model $\tilde{\omega}_T = 44.2$ K, and a local maximum of $\tilde{\omega}_L = 50.3$ K in the longitudinal mode. The density of states calculated for this spectrum was found to have peaks at both $\tilde{\omega}_T$ and $\tilde{\omega}_L$. Table II 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 neutron-scattering experiment for monolayer systems, the inelastic-scattering data that do exist are weighted averages of the phonon spectrum over the Brillouin zone. A model calculation based on two fitted coupling constants was used recently to infer the phonon spectrum and density of states from the neutron-scattering data for the D_2 system.[7] The empirically derived values for the D_2 spectrum parameters agree, within about several percent, with the theoretical values of the fully self-consistent calculation listed in Table II. In particular, the theoretical phonon gap is about 7% smaller than that deduced from experiment and the theoretical maximum phonon energy is about 3% too high. The theoretical width of the density of states is about 14.8 K, while the experimentally deduced width is about 10 K.

The theoretical results for the phonon spectrum of H_2 on graphite are also listed in Table II. The differences between D_2 and H_2 are striking, but easily understandable in terms of the mass difference. The H_2 density of states is much wider than the D_2 density of states because its zero-point motion is much larger, causing the molecules to be affected more by their nearest neighbors. The only inelastic-scattering data for the spectrum of the commensurate phase of H_2 on graphite are those of Nielsen, McTague, and Ellenson.[8] These data do not have the detail of the more recent data for D_2, and there is no convenient empirical model to compare with the theory. Nevertheless, it is possible to make preliminary comparisons between the H_2 data and the theory. The experimental results clearly show that the density of states for H_2 is much wider than that for D_2 as seen in the theoretical results. The experimental results also show a strong peak at $\hbar\omega \approx 57$ K and a weak peak at $\hbar\omega \approx 81$ K. Table II shows that these values are in reasonable agreement with the theoretical values for $\hbar\omega_T = 64.9$ K and $\hbar\tilde{\omega}_L = 83.8$ K, found for the fully self-consistent solutions.

Clearly there is good but not perfect agreement between theory and experiment for the phonon spectrum of both D_2 and H_2. The general agreement between theory and experiment shows that the interaction between the hydrogen molecules and the graphite surface, as well as the interaction between the hydrogen molecules themselves, can be described by the models that have been used here. This is not to say that substrate modification of the molecule-molecule interaction, many-body effects, and anisotropic effects of the molecule-substrate interaction can be entirely ignored.[21] It might well be that much of the discrepancy between theory and experiment is because of such effects. However, these effects would appear to be perturbations on the interactions used for this model calculation.

Finally, to describe properly the dynamics of the hydrogen monolayers, it is necessary to deal with the three-dimensional nature of the substrate interaction and the monolayer wave function. 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 one expects to compare a theoretical calculation of the phonon dynamics to the experimental results for these systems, the effects of the third dimension must be examined. Future theoretical calculations of the dynamics of commensurate quantum solids should include these effects.

It would be most useful at this point to have an experimental density of states of both H_2 and D_2. The published data for H_2,[8] while certainly a milestone in their time, are not detailed enough to warrant theoretical calculations beyond the present one. While the differences between the recent D_2 experimental results and these theoretical results do warrant further investigation, a proper experimental density of states would make the comparison between theory and experiment easier. I would strongly urge the experimentalists to consider such experiments.

I would like to thank L. W. Bruch, S. C. Fain, Jr., H. R. Glyde, H. J. Lauter, and L. Passell for useful discussions. Special thanks go to S. C. Fain, Jr., and H. J. Lauter for sharing experimental results before publication. This work was supported by the National Science Foundation under Grant No. DMR-8706219.

---

[1] H. P. Schildberg, H. J. Lauter, H. Freimuth, H. Wiechert, and R. Haensel, Jpn. J. Appl. Phys. Pt. 1 **26**, 345 (1987).

[2] H. Freimuth, H. Wiechert, and H. J. Lauter, Surf. Sci. **189-190**, 548 (1987).

[3] H. Wiechert, H. Freimuth, H. P. Schildberg, and H. J. Lauter, Jpn. J. Appl. Phys. Pt. 1 **26**, 351 (1987).

[4] V. L. P. Frank, H. J. Lauter, and P. Leiderer, Jpn. J. Appl. Phys. Pt. 1 **26**, 347 (1987).

[5] J. Cui, S. C. Fain, Jr., J. Vac. Sci. Technol. A **5**, 710 (1987).

[6] J. Cui, S. C. Fain, Jr., H. Freimuth, H. Wiechert, H. P. Schildberg, and H. J. Lauter, Phys. Rev. Lett. **60**, 1848 (1988).

[7] V. L. P. Frank, H. J. Lauter, and P. Leiderer, to be published.

[8] M. Nielsen, J. P. McTague, and W. Ellenson, J. Phys. (Paris) Colloq. **38**, C4-10 (1977).

[9] M. Nielsen, J. P. McTague, and L. Passell, in *Phase Transitions In Surface Films,* edited by J. G. Dash and J. Ruvalds (Plenum, New Yor, 1980), p. 127.

[10] A. D. Crowell, J. Chem. Phys. **29**, 446 (1958).

[11] A. D. Crowell and R. B. Steele, J. Chem. Phys. **34**, 1347 (1961).

[12] A. D. Crowell, Surf. Sci. **111**, L667–L670 (1981).

[13] A. D. Crowell and J. S. Brown, Surf. Sci. **123**, 296 (1982).

[14] William W. Steele, Surf. Sci. **36**, 317 (1973).

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

[16] A. D. Novaco, Phys. Rev. B **19**, 6493 (1979).

[17] L. K. Moleko, B. Joos, T. M. Hakim, H. R. Glyde, and S. T. Chui, Phys. Rev. B **34**, 2815 (1986).

[18] I. F. Silvera and V. V. Goldman, J. Chem. Phys. **69**, 4209 (1978).

[19] A. D. Novaco, unpublished. See Ref. 16 for a description of the theory of the rotated and nonrotated incommensurate solids.

[20] X. Z. Ni and L. W. Bruch, Phys. Rev. B **33**, 4584 (1986).

[21] L. W. Bruch, Surf. Sci. **125**, 194 (1983), and private communication.