Elementary excitations of solid ortho-hydrogen diluted with para-hydrogen

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The elementary librational excitations of solid molecular hydrogen are calculated using the recursion method of Haydock. This method permits a correct treatment of the problem of dilution with para-hydrogen. Agreement is obtained with previous calculations of the excitations of pure ortho-hydrogen. It is found that the gap in the single-excitation density of states decreases much faster than the ortho concentration. The specific heat and the NMR line shapes and relaxation times are calculated and compared with experimental data. For ortho concentration less than 0.5, the data suggest the existence of excitations with energies several times smaller than those of the collective librations we consider.

I. INTRODUCTION

At low temperatures, solid hydrogen exhibits a phase transition in which the molecular axes become aligned along directions related to the crystal axes. Because of the small moment of inertia of the hydrogen molecule, the molecular angular momentum J is a good quantum number in the solid. This means that para-hydrogen molecules are all in the isotropic state $J = 0$, and cannot participate in the orientational ordering. Ortho-hydrogen molecules are in states with $J = 1$, and interact primarily through the electric quadrupole-quadrupole (EQQ) interaction.[1] Ortho-para conversion is sufficiently slow to allow the system to be studied as a function of the fraction X of ortho molecules. The problem is thus to study the properties of a randomly diluted lattice of molecules with unit effective spin and with quadrupolar interactions.

For pure ortho-hydrogen $(X = 1)$, there is a transition at 2.8 K to the four-sublattice $Pa3$ structure, in which the molecules are aligned along the body diagonals of a face-centered-cubic (fcc) lattice.[2] [This orientational transition actually drives a crystallographic transition into the fcc lattice structure; hydrogen crystallizes in the hexagonal-close-packed (hcp) lattice structure. The fcc structure however is apparently stable or metastable at low temperatures,[3] allowing the orientational transition with which we are concerned to be observed independently.]

The orientational phase transition in pure ortho-hydrogen has been studied theoretically using mean field theory,[4] a restricted-trace method,[5] and diagrammatic techniques.[6] Elementary excitations in the ordered phase (librons) have been computed by several authors,[7-10] using closely related approximations based on Green's-function or operator equation-of-motion formalisms. Berlinsky and Coll[11] used an approximation developed by Coll and Harris[12] to compute the effects of anharmonicity on the libron density of states. The correction to the libron energy averages about -20%, although the high-energy edge of the libron band is shifted downward considerably more than this. As a result, the total width of the band is reduced by almost 50%.

These corrections brought the theory of pure ortho-hydrogen at zero temperature into good agreement with experiment.[13] On the other hand, understanding the effects of para-hydrogen dilution has remained an outstanding problem. As X is reduced from one, the temperature of the transition falls toward zero at $X \approx 0.5$. For $X < 0.5$, there is evidence of orientational freezing at very low temperatures $(T < 0.3$ K), from NMR studies.[14] Sullivan et al. have hypothesized that the system is similar to a spin-glass,[15] but some controversy remains about the sharpness of the transition into the orientationally frozen state.[16-18]

For $X > 0.5$, the orientational state is apparently closely related to the $Pa3$ phase of pure ortho-hydrogen. Nevertheless, Harris[19] found that a simple scaling of libron energies with X failed to reproduce the rapid variation of NMR relaxation times with X. Similarly, Harris, Berlinsky, and Meyer[20] introduced a phenomenological X dependence of the average libron energy to fit the observed X dependence of the orientational specific

heat. The low-temperature properties of hydrogen are largely determined by the gap in the libron density of states, and this gap apparently shrinks very rapidly with decreasing ortho concentration. Scaling theories based on the $X = 1$ density of states are unable to reproduce this rapid X dependence.

Diehl and Biem have used a coherent-potential approximation (CPA) to compute the libron density of states for $0.8 < X < 1$.[21] Their computations suggest that dilution with para-hydrogen has a drastic effect on the shape of the libron band and on the size of the gap. It is therefore desirable to find a computational method which is valid for arbitrary ortho concentrations and which does not involve an effective-medium approximation. The dilution problem is difficult because the introduction of random para-hydrogen substitutions breaks the crystal and sublattice symmetries. The problem may no longer be simplified by taking Fourier transforms. Even when the usual linearizing or decoupling approximations are made, one is left with the problem of diagonalizing a Hamiltonian of dimensionality on the order of N (the number of ortho molecules); the matrix elements of the Hamiltonian will depend upon the random occupation of the lattice with ortho molecules.

The recursion method of Haydock[22] has proved very useful for problems of this type. In the recursion method, a new basis is found in which the Hamiltonian assumes the form of a Hamiltonian for a one-dimensional system. The physical properties of the system are then extracted from this "chain" Hamiltonian. We refer the reader to Ref. 22 for a complete description of the recursion method.

In this paper we calculate the elementary excitations of solid hydrogen for $X < 1$, using the recursion method. Of necessity, we work within the harmonic approximation. Thus, the substantial anharmonic effects computed by Berlinsky and Coll[11] are not included in our calculation. These effects could be introduced in a crude way by reducing the EQQ coupling constant by 20%. We prefer to use the best estimate of the actual EQQ coupling constant, bearing in mind that anharmonic corrections apply.

II. MODEL AND CALCULATIONAL PROCEDURES

Let $\alpha, \beta, \ldots$ label ortho-hydrogen molecules, and let $\Omega_\alpha = (\theta_\alpha, \phi_\alpha)$ describe the orientation of molecule α with respect to a fixed laboratory coordinate system. Then the Hamiltonian we wish to consider is a function of the orientations of all of the molecules:

$$\mathcal{H}(\Omega_\alpha, \Omega_\beta, \ldots) = \sum_{\langle \alpha, \beta \rangle} q_{ij}(\Omega_\alpha) F_{ijkl}^{\alpha\beta} q_{kl}(\Omega_\beta) .$$

(1)

Here $q_{ij}(\Omega_\alpha)$ is the quadrupole moment tensor for molecule α, defined in terms of the molecular charge density $\rho(r)$ as

$$q_{ij} = \int \rho(r)(r_i r_j / 2) d^3 r .$$

$F_{ijkl}^{\alpha\beta}$ is the EQQ interaction tensor between molecules α and β, and $\langle \alpha, \beta \rangle$ signifies that the summation is over nearest-neighbor pairs of molecules (with each pair counted only once). Throughout this paper, indices $i, j, \ldots$ may take on the values (x, y, z) for the three basis directions of the laboratory coordinate system. Summation over repeated indices is implied. We restrict the Hamiltonian to nearest-neighbor interactions for simplicity; this is a good approximation because the interaction energy varies as r^{-5}, where r is the distance between molecules. The interaction tensor is given by

$$F_{ijkl}^{\alpha\beta} = R_0^{-5}(3\delta_{ij}\delta_{kl} + 3\delta_{il}\delta_{jk} + 3\delta_{ik}\delta_{jl}$$
$$- 15\delta_{ij}n_k n_l - 15\delta_{il}n_j n_k - 15\delta_{ik}n_j n_l$$
$$- 15\delta_{kl}n_i n_j - 15\delta_{jk}n_i n_l - 15\delta_{jl}n_i n_k$$
$$+ 105 n_i n_j n_k n_l) ,$$

(2)

where R_0 is the distance between nearest neighbors and n_i is a unit vector along the direction of the intermolecular separation. Because the interaction tensor is traceless, $\delta_{ij}F_{ijkl}^{\alpha\beta} = 0$, we do not need to subtract the trace from the quadrupole moment tensor. In particular, if $e_i(\Omega_\alpha)$ is a unit vector oriented along the direction Ω_α of the internuclear axis of molecule α, we may take

$$q_{ij}(\Omega_\alpha) = (\tfrac{1}{2}eQ)e_i(\Omega_\alpha)e_j(\Omega_\alpha) .$$

(3)

Here, eQ is the conventionally defined[23] quadrupole moment of a hydrogen molecule. This form of the EQQ interaction is much easier to use in numerical calculations than the more usual form involving spherical harmonics.[4] Following convention, we will generally express our results in units of $\Gamma = \tfrac{6}{25}(eQ)^2/R_0^5$. Experimental values for Γ in the solid range from $0.82 - 0.85$ K.[24-26]

Our calculation proceeds in four stages, which are described in detail below. First, we generate a

cluster of molecules corresponding to a randomly occupied lattice with the desired ortho concentration X. [In what follows, "molecule" will always mean "ortho molecule," since the para molecules do not enter into the Hamiltonian (1) in any way.] Second, a mean-field "ground-state" configuration is found by iterative relaxation of the orientations of the molecules in the cluster. Third, a truncated EQQ Hamiltonian is transformed into two chain Hamiltonians (tridiagonal matrices) for each of a number of the molecules in the cluster. Finally, these chain Hamiltonians are used to calculate single-excitation densities of states and physical properties such as NMR relaxation times and line shapes, and specific heats.

Generation of the cluster. A small segment of an fcc or hcp lattice is given periodic boundary conditions and randomly populated with ortho molecules. A typical cluster contains 64 lattice sites, but clusters containing up to 512 lattice sites have been studied to determine the effects of cluster size. The recursion method works well with these small clusters because it is sensitive mainly to the local environments of the molecules used to start the chain calculations (see below). Periodic boundary conditions allowed us to calculate chains for all of the molecules in the cluster. This is desirable because the next stage of the calculation, determination of a ground state, is time consuming.

Determination of a mean-field ground state. The full orientational wave function is an unknown function of all the molecular orientations. In a mean-field (Hartree) approximation, we assume that the wave function may be approximated by a product of single-molecule wave functions,

$$\Psi(\Omega_\alpha, \Omega_\beta, \ldots) = \psi^\alpha(\Omega_\alpha)\psi^\beta(\Omega_\beta) \cdots . \tag{4}$$

The approximation to the ground state is found by varying the molecular wave functions so as to minimize the expectation of the Hamiltonian (1). In the fully occupied ($X = 1$) case, all of the molecular wave functions are the same within each sublattice. The problem is thus reduced to a small number of variables and may be solved analytically. For $X < 1$, we must determine each of the molecular wave functions individually.

Because the Hamiltonian (1) is a real function of the set of molecular orientations, we may choose all of our wave functions to be real. Any real molecular wave function within the space $J = 1$ may be written in the form

$$\psi^\alpha(\Omega_\alpha) = \sqrt{3}\zeta_i^\alpha e_i(\Omega_\alpha) , \tag{5}$$

where ζ_i^α is a unit vector describing the orientation of the molecular wave function and e_i is a unit vector pointing in the direction Ω_α. This wave function is normalized so that $\int (\partial\Omega/4\pi)\psi^2 = 1$. The expectation value of the quadrupole moment tensor for this wave function is

$$\langle q_{ij}(\Omega_\alpha)\rangle = \int (\partial\Omega_\alpha/4\pi)[\psi^\alpha(\Omega_\alpha)]^2 q_{ij}(\Omega_\alpha)$$

$$= \tfrac{1}{5}eQ(\zeta_i^\alpha\zeta_j^\alpha + \tfrac{1}{2}\delta_{ij}) . \tag{6}$$

As pointed out above, the term in δ_{ij} may be ignored. The expectation value above is then seen to be just $\tfrac{2}{5}$ times the quadrupole tensor for a molecule oriented along the direction ζ_i^α.

To find the mean-field ground state, we must find the set of vectors $\zeta_i^\alpha, \zeta_i^\beta, \ldots$ which minimizes the expectation value of the Hamiltonian. It is not possible in general to find the absolute minimum of a function of so many variables. Rather, we find a local minimum by choosing the vectors $\zeta_i^\alpha, \zeta_i^\beta, \ldots$ so as to minimize the expectation value of the Hamiltonian with respect to small variations of each vector's orientation. The condition for such a local minimum is that each vector ζ_i^α be the eigenvector with lowest eigenvalue, of the local field tensor

$$\mathcal{F}_{ij}^\alpha = \sum_\beta F_{ijkl}^{\alpha\beta}\langle q_{kl}(\Omega_\beta)\rangle$$

$$= \tfrac{1}{5}eQ\sum_\beta F_{ijkl}^{\alpha\beta}\zeta_k^\beta\zeta_l^\beta , \tag{7}$$

where the sum runs over nearest neighbors of molecule α. Our procedure for generating the mean-field ground state is as follows. Initial orientations of the vectors ζ_i^α are chosen either randomly, or according to the $Pa3$ structure (that is, along the appropriate body diagonals of the fcc lattice). We then step through the lattice, executing the following procedure for each molecule α:

(a) The local field tensor $\mathcal{F}_{ij}^\alpha$ is constructed, using the vectors ζ_i^β of neighboring molecules.

(b) Its three eigenvalues A_ξ^α, A_η^α, A_ζ^α and the corresponding eigenvectors $\xi_i^\alpha, \eta_i^\alpha, \zeta_i^\alpha$ are found and stored. We choose $A_\xi^\alpha > A_\eta^\alpha > A_\zeta^\alpha$ and we choose the eigenvectors to be orthonormal.

This whole procedure is repeated until the vectors ζ_i^α remain constant (within rounding error). This generally requires several hundred passes through the lattice, unless $X \gtrsim 0.9$ and the starting configuration was $Pa3$ (i.e., the ground state for $X = 1$). This part of our calculation is mathematically

equivalent to iteratively relaxing a lattice of classical quadrupoles by rotating them one by one to the orientations of lowest energy in the fields produced by their neighbors. We note that Klenin and Pate[27] have performed Monte Carlo studies of arrays of classical quadrupoles.

Transformation to chain Hamiltonians. Now that we have found an approximation to the ground state of the system, we wish to calculate the elementary excitations. Within the mean-field approximation, the excitations consist simply of raising an individual molecule α from its lowest state in the local field (corresponding to the eigenvector ζ_i^α of the local field tensor) to one of the two higher states (corresponding to the eigenvectors ξ_i^α, η_i^α). The energies of these two excitations of molecule α are

$$E_\xi^\alpha = \tfrac{1}{5}eQ(A_\xi^\alpha - A_\zeta^\alpha) ,$$
$$E_\eta^\alpha = \tfrac{1}{5}eQ(A_\eta^\alpha - A_\zeta^\alpha) . \tag{8}$$

As our more detailed calculation will show, these are good approximations to the elementary excitations for low ortho concentration X. This is apparently because the high degree of disorder introduced into the Hamiltonian by diluting the occupation of the lattice, results in highly localized eigenstates. In the case $X = 1$, however, the crystal symmetry ensures that the true excitations are infinitely extended (librons). Indeed, the mean-field approximation gives the energies of all excitations as 19Γ, while Green's-function and equation-of-motion treatments of the $X = 1$ problem[7-10] generally predict a band of excitations about 15Γ wide, centered on 19Γ.

At this stage, we could introduce two annihilation and creation operators for each molecule, which would take the molecule from its lowest state in the mean field, to its two upper states. The operators would obey approximately bosonlike commutation relations. The equations of motion for the operators would be complicated, but could be simplified by replacing some operators by their expectation values in the ground state. This is a standard linearizing-type approximation (see Raich and Etters[9] for an example of this procedure for the case $X = 1$). Within one such approximation, the equation of motion of a creation operator would contain only the creation operator itself, and creation operators for other molecules. Creation operators for the elementary excitations would be found by taking appropriate linear combinations of the creation operators of the individual molecular

states.

An entirely equivalent procedure, which avoids the introduction of much notation, is to restrict the Hamiltonian to the subspace of product states of the form (4), in which one molecule is in one of its two mean-field excited states, and all other molecules are in their mean-field lowest states. There are $2N$ such states, where N is the number of ortho molecules. The restricted Hamiltonian is diagonalized within this $2N$-dimensional space to find the elementary excitations. These excitations are then assumed to be approximately superposable (that is, they are assumed to be approximately bosonlike), just as in the operator equation-of-motion formalism outlined above.

The eigenstates and eigenvalues of the $2N$-dimensional restricted Hamiltonian are found with the aid of the recursion method. We will label the $2N$ states defined above with indices like $(i),(j),\ldots$ where $(i)=(\alpha,X)$ with α labeling one of the N molecules and X labeling one of the two states (ξ or η) for each molecule. The diagonal elements of the restricted Hamiltonian are simply given by

$$\mathscr{H}_{(\alpha,X)(\alpha,X)} = E_X^\alpha \tag{9}$$

while the off-diagonal elements are given by

$$\mathscr{H}_{(\alpha,\xi)(\beta,\eta)} = (eQ/10)^2(\xi_i^\alpha\zeta_j^\alpha + \zeta_i^\alpha\xi_j^\alpha)$$
$$\times F_{ijkl}^{\alpha\beta}(\eta_k^\beta\zeta_l^\beta + \zeta_k^\beta\eta_l^\beta) . \tag{10}$$

Let the normalized eigenstates of the Hamiltonian be given by $V_{(i)}^\mu$, satisfying

$$\sum_{(i)} V_{(i)}^\mu V_{(i)}^\nu = \delta^{\mu\nu} ,$$
$$\sum_{(j)} \mathscr{H}_{(i)(j)} V_{(j)}^\mu = \mathscr{E}^\mu V_{(i)}^\mu . \tag{11}$$

The recursion method allows us to evaluate expressions of the form

$$\int_{-\infty}^{\infty} n(E)f(E)dE , \tag{12}$$

where $f(E)$ is an arbitrary function and the "local density of states" is defined by

$$n(E) = \sum_\mu \delta(E - \mathscr{E}^\mu) \left[\sum_{(i)} V_{(i)}^\mu U_{(i)}\right]^2 . \tag{13}$$

Here, $U_{(i)}$ is the "starting vector" for the chain calculation. By choosing appropriate starting vectors, the integral (12) may be related to the various physical quantities we wish to calculate. Nex[28] and Haydock[22] provide details of the method, as well as a procedure for generating the approximate local density of states, itself.

We choose our starting vectors localized on one excited state of one molecule,

$$U_{(i)} = \begin{cases} 1 & \text{if } (i)=(\alpha,\chi) \\ 0 & \text{otherwise .} \end{cases} \tag{14}$$

There are $2N$ different such starting vectors, corresponding to the $2N$ possible choices for (α,χ) in the equation above. In practice, we choose a subset of the N molecules (typically 30 molecules), and calculate two chain-Hamiltonian matrices for each molecule in the subset. For each starting vector

(14), we obtain a local density of states $n_{(\alpha,\chi)}(E)$.

Let $A(\Omega_\alpha)$ be an operator depending only on the orientation of molecule α. Within the subspace of states with $J=1$, $A(\Omega_\alpha)$ has matrix elements

$$A_{\xi\eta} = \int \frac{\partial\Omega_\alpha}{4\pi} [\sqrt{3}\xi_i^\alpha e_i(\Omega_\alpha)] A(\Omega_\alpha) [\sqrt{3}\eta_j^\alpha e_j(\Omega_\alpha)] . \tag{15}$$

Let $|\mu\rangle$ and $|\nu\rangle$ be two single-excitation states of the system. The matrix element of the operator $A(\Omega_\alpha)$ between these two states is then

$$\langle\mu|A(\Omega_\alpha)|\nu\rangle = \sum_{(i),(j)} V_{(i)}^\mu \langle (i)|A(\Omega_\alpha)|(j)\rangle V_{(j)}^\nu$$

$$= P_{\xi\xi}A_{\xi\xi} + P_{\eta\eta}A_{\eta\eta} + P_{\xi\eta}A_{\xi\eta} + P_{\eta\xi}A_{\eta\xi} + (\delta^{\mu\nu} - P_{\xi\xi} - P_{\eta\eta})A_{\zeta\zeta} , \tag{16}$$

where

$$P_{\xi\xi} = V_{(\alpha,\xi)}^\mu V_{(\alpha,\xi)}^\nu ,$$
$$P_{\eta\eta} = V_{(\alpha,\eta)}^\mu V_{(\alpha,\eta)}^\nu ,$$
$$P_{\xi\eta} = V_{(\alpha,\xi)}^\mu V_{(\alpha,\eta)}^\nu ,$$
$$P_{\eta\xi} = V_{(\alpha,\eta)}^\mu V_{(\alpha,\xi)}^\nu . \tag{17}$$

Calculation of physical quantities. The total density of states for one excitation may be obtained by averaging all of the local densities of states:

$$N(E) = \frac{1}{2M} \sum_{\alpha=1}^{M} \sum_{\chi=\xi,\eta} n_{(\alpha,\chi)}(E) , \tag{18}$$

where M is the number of molecules for which chains have been calculated. While this density of states is not itself a physically measurable quantity, it provides important information about the excitations. For example, the gap in the density of states (the energy below which the density is zero) gives a good indication of the temperature below which the specific heat will fall off rapidly, the NMR spin-lattice relaxation time will rise rapidly, and the NMR line shape will assume its zero-temperature form. The total density of states calculated for $X=1$ may be compared directly with the calculation of the same quantity by Green's-function or equation-of-motion techniques, thereby providing an important test of both the numerical and theoretical aspects of the calculation. In addition, the specific heat is directly related to the total density of states:

$$c_v = RX \int dE\, N(E) e^{\beta E} \left[\frac{\beta E}{e^{\beta E}-1} \right]^2 . \tag{19}$$

Here c_v is the molar specific heat, R is the gas constant, and $\beta=1/kT$. The results of this calculation may be compared with experimental measurements of the derivative of pressure with respect to temperature through the relation[25]

$$\left[\frac{dP}{dT} \right]_v = \frac{1}{v} \frac{5}{3} c_v , \tag{20}$$

where v is the molar volume. This relation depends upon the (excellent) approximation that the translational degrees of freedom (phonons) are frozen out at the temperatures of interest, and upon the assumption that the anisotropic interaction energy varies as $v^{-5/3}$.

The nuclear spin Hamiltonian for a hydrogen molecule may be written

$$\mathcal{H}_N = -haB_0(I_z^{(1)}+I_z^{(2)}) - hc(I_i^{(1)}+I_i^{(2)})J_i$$
$$+ 5hdI_i^{(1)}(\delta_{ij}-3n_i n_j)I_j^{(2)} . \tag{21}$$

Here $I_i^{(1)}$ and $I_i^{(2)}$ are spin operators for the two protons, n_i is a unit vector oriented along the internuclear axis, J_i is the molecular angular momentum, and B_0 is the applied magnetic field (which we assume is along the z direction). For the free hydrogen molecule, Ramsey[29] has measured $a=4.25776$ kHz/G, $c=113.8$ kHz, and $d=57.67$ kHz. The expectation value of J_i is zero for any real orientational wave function (the orbital angular momentum is quenched). This means that the term in c has no effect upon the NMR line shape. However, since J_i can have nonvanishing matrix elements between two different real wave functions, this term can contribute to the NMR spin-lattice relaxation rate.

The NMR absorption lines contributed by molecule α are located at the frequencies[30]

$$v_{\pm} = B_0 a \pm \frac{15d}{2} \left\langle\left\langle \frac{3n_z^2 - 1}{2} \right\rangle\right\rangle .$$ (22)

The double brackets signify a thermal average of the expectation value of the enclosed operator. We may compute this thermal average using Eqs. (16) and (17):

$$5\left\langle\left\langle \frac{3n_z^2 - 1}{2} \right\rangle\right\rangle = p_{\xi}^{\alpha}[3(\xi_z^{\alpha})^2 - 1] + p_{\eta}^{\alpha}[3(\eta_z^{\alpha})^2 - 1] + p_{\xi\eta}^{\alpha}(3\xi_z^{\alpha}\eta_z^{\alpha}) + (1 - p_{\xi}^{\alpha} - p_{\eta}^{\alpha})[3(\zeta_z^{\alpha})^2 - 1] ,$$ (23)

where

$$p_{\xi}^{\alpha} = \int dE \, n_{(\alpha,\xi)}(E)(e^{\beta E} - 1)^{-1} ,$$

$$p_{\eta}^{\alpha} = \int dE \, n_{(\alpha,\eta)}(E)(e^{\beta E} - 1)^{-1} ,$$ (24)

$$p_{\xi\eta}^{\alpha} = \int dE \, n_{(\alpha,\xi\eta)}(E)(e^{\beta E} - 1)^{-1} .$$

The three densities of states appearing in these formulas are defined in terms of the eigenvectors and eigenvalues of the restricted Hamiltonian by

$$n_{(\alpha,\xi)}(E) = \sum_{\xi} \delta(E - \mathscr{E}^{\mu})(V_{(\alpha,\xi)}^{\mu})^2 ,$$

$$n_{(\alpha,\eta)}(E) = \sum_{\mu} \delta(E - \mathscr{E}^{\mu})(V_{(\alpha,\eta)}^{\mu})^2 ,$$ (25)

$$n_{(\alpha,\xi\eta)}(E) = \sum_{\mu} \delta(E - \mathscr{E}^{\mu})V_{(\alpha,\xi)}^{\mu}V_{(\alpha,\eta)}^{\mu} .$$

The first two of these are simply local densities of states as defined in Eq. (13) above. The third function involves the product of the projections of eigenvectors onto two different starting vectors which are not connected by the restricted Hamiltonian. Unlike the first two functions, we do not have a convenient means of evaluating it and we make the approximation of setting it equal to zero. This is reasonable because, unlike the local densities of states, this quantity is not positive definite and thus tends to cancel in averages. Moreover, when the eigenvectors become highly localized (for $X < 1$) the lack of a matrix element connecting the two starting vectors makes this term inherently small. In the case $X = 1$, the starting vectors may be chosen to make this term identically zero by symmetry.

For comparison with experiments on polycrystalline samples, we must average the NMR line shape over all possible orientations of the applied magnetic field. In order to perform this "powder average," we construct a list of several hundred directions distributed randomly over the unit sphere. These are taken to be the relative orientation of the magnetic field with respect to the local vectors ξ_i^{α},

η_i^{α}, and ζ_i^{α}. The several thousand line frequencies calculated in this manner [via Eqs. (22)−(25)] are accumulated in a histogram. This histogram gives the powder-averaged NMR absorption line shape. When the temperature is much smaller than the gap in the density of states, the quantities p_{ξ}^{α} and p_{η}^{α} calculated from Eq. (24) are essentially zero. The powder-averaging procedure then yields the familiar Pake-doublet[30] line shape.

Homma[31] has calculated that the major contribution to the NMR relaxation rate T_1^{-1} comes from the Raman process, in which a change of nuclear Zeeman quantum number is accompanied by the annihilation of one elementary excitation and the creation of another. The term in d in the Hamiltonian (21) causes transitions with $\Delta m = 1$ or 2, where m is the nuclear Zeeman quantum number, while the term in c causes transitions with $\Delta m = 1$ only. The relaxation rate is

$$T_1^{-1} = w_{\Delta m = 1} + 2w_{\Delta m = 2} ,$$ (26)

where the transition rates for the individual processes may be calculated using the golden rule:

$$w = \frac{2\pi}{\hbar} \sum_i p(i) |\langle f | \mathscr{H} | i \rangle|^2 \rho(E_f = E_i) .$$ (27)

Here $p(i)$ is the thermal probability for the given initial state, and $\rho(E)$ is the total density of states (not the local density of states). The matrix elements of the Hamiltonian (21) within the subspace $(J = 1, I = 1)$ may be found using Eqs. (16) and (17). When these matrix elements are squared, we find positive-definite terms which may be computed from the local densities of states, along with interference terms which are difficult to evaluate. As in our computation of the NMR line shape, we make the approximation of neglecting the interference terms. The reasons for the validity of this approximation are the same in both cases. Equation (27) then gives

$$w = \frac{2\pi}{\hbar} \int dE (e^{\beta E} - 1)^{-1} \{ [n_{(a,\xi)}(E)]^2 | \mathcal{H}_{\xi\xi} - \mathcal{H}_{\zeta\zeta} |^2 + [n_{(a,\eta)}(E)]^2 | \mathcal{H}_{\eta\eta} - \mathcal{H}_{\zeta\zeta} |^2$$

$$+ [n_{(a,\xi)}(E) n_{(a,\eta)}(E)] (| \mathcal{H}_{\xi\eta} |^2 + | \mathcal{H}_{\eta\xi} |^2) \} . \tag{28}$$

When evaluating this formula, we have averaged the squared matrix elements of each term over all possible orientations of the applied magnetic field. Our final result is

$$T_1^{-1} = \pi^3 h \int dE (e^{\beta E} - 1)^{-1} (\{ [n_{(a,\xi)}(E)]^2 + [n_{(a,\eta)}(E)]^2 \} 96 d^2 + [n_{(a,\xi)}(E) n_{(a,\eta)}(E)] (\tfrac{196}{5} d^2 + \tfrac{64}{15} c^2)) . \tag{29}$$

Similar formulas for the case $X = 1$ have been obtained by Homma[31] and Harris.[19] The integral approximations developed by Nex[28] only allow the evaluation of integrals over the local density of states, not its square. To evaluate formula (29), we therefore numerically integrate the square of the smoothed local density of states as calculated by the procedure given in Ref. 28.

30 molecules, or over all of the occupied sites, whichever was smaller. All of the results presented here were calculated using fcc lattice structure and the $Pa3$ starting configuration. Several calculations carried out with hcp lattice structure and/or random initial configurations showed that these factors have a small numerical effect upon the quantities we calculate, but that the qualitative differences between theory and experiment are not affected.

III. RESULTS

Averaged density of states. Figure 1(a) shows the total density of states calculated for $X = 1$, with the $Pa3$ structure. Note that all densities of states calculated in this paper (both local and total) are for a single excitation, and should not be confused with the density of states for the solid as a whole. This calculation was performed both with a cluster containing 512 molecules and a chain of length 9, and with a cluster containing 64 molecules and a chain of length 5. For comparison, Figs. 1(b) and 1(c) show the densities of states calculated by Mertens *et al.* using an equation-of-motion technique,[10] and by Ueyama and Matsubara using a Green's-function technique.[8] The chain calculation accurately reproduces the size of the gap and the width of the one-excitation band, as well as the overall asymmetry of the density of states. The density of states calculated with the 64-molecule cluster is not as smooth as that calculated with the 512-molecule cluster, but otherwise the agreement with the earlier calculations is not degraded. Calculations for $X < 1$ require much longer computations, because the ground-state configuration must be found and because we must average over many molecules to obtain physical quantities. Therefore, the remainder of the calculations were performed on clusters containing 64 lattice sites, and with chains of length 5. For quantities which depended on averages over molecules, we averaged either over
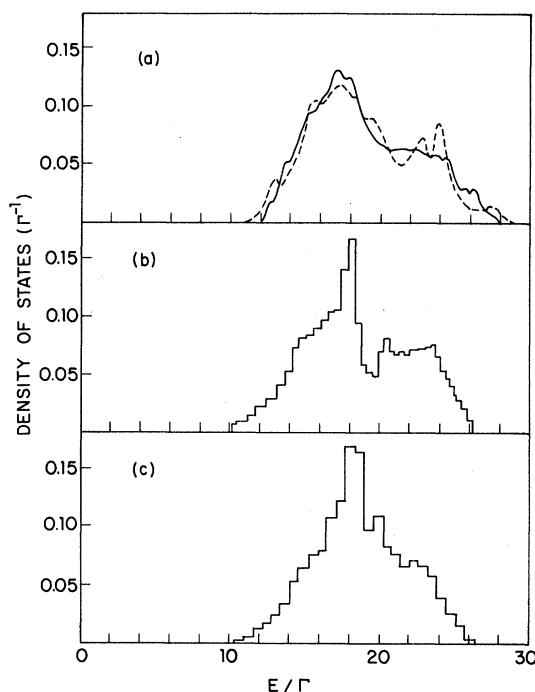

FIG. 1. Single-excitation densities of states for solid ortho-hydrogen, calculated by various methods. (a) Recursion method (present paper), using the 512-molecule cluster (solid line) and using the 64-molecule cluster (dashed line). (b) Operator equation-of-motion method (Ref. 10). (c) Green's-function method (Ref. 8). $\Gamma = 0.83$ K is the quadrupole-quadrupole coupling constant.

Figure 2 shows the variation of the average density of states with ortho concentration X. The band shape changes considerably with X, and the gap decreases in size much more rapidly than X.

Local density of states. In the $Pa3$ structure at $X = 1$, all molecules are in equivalent sites. Thus the total density of states [Fig. 1(a)] for $X = 1$ is also the local density of states for any molecule. It is interesting to compare this with typical local densities of states for low X. In Fig. 3, we show the two local densities of states associated with a molecule in a cluster with $X = 0.34$. The arrows in Fig. 3 indicate the mean-field approximations to the excitation energies, from Eq. (8). The local densities of states are approximately δ functions (in the sense that the full width at half maximum is a small fraction of the peak location), located near the mean-field estimates for the excitation energies. [By contrast, the mean-field estimates for $X = 1$, Fig. 1(a), are both at energy 19 Γ.] This indicates that the excitations have become essentially localized on single molecules. One consequence is that increasing the cluster size or chain length would not have much effect upon the results presented here.

Specific heat. The specific heat was calculated for the same sequence of ortho concentrations using formula (19). In Fig. 4 we show these results, along with some experimental results from Jarvis *et al.*[25] and from Haase and Saleh.[32] Our results have been expressed in terms of $(dP/dT)_v$, using formula (20). A value of 22.9 cm^3 was used for the molar volume.[33] Here and throughout, we used $\Gamma = 0.83$ K. The agreement is good for X
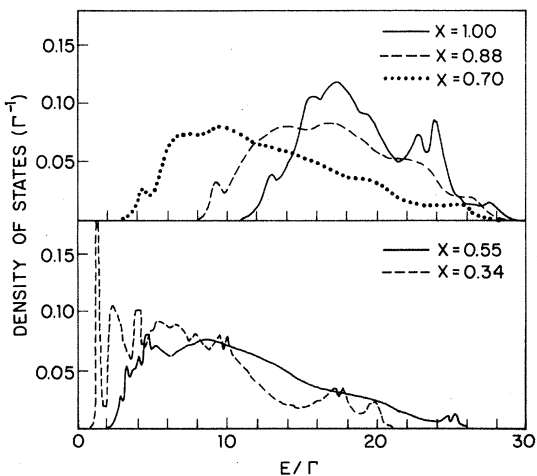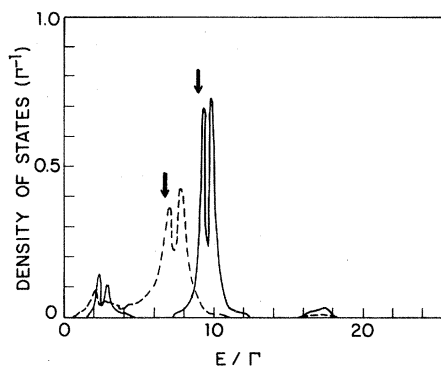

FIG. 3. Typical local densities of states for a molecule in a cluster with ortho concentration 0.34. The two curves give the local densities of states associated with the two excited substates of this molecule. Arrows indicate the mean-field-theory estimates of the excitation energies. Note the large change in vertical scale from Fig. 2.

near 0.7, a direct result of the drastic reduction in the gap in the density of states, brought about by a relatively mild dilution of the system with rotationally inert paramolecules (see Fig. 2). For $X \lesssim 0.5$, the agreement with experiment is poor. The experimental $(dP/dT)_v$ curves lie consistently above the theoretical ones, suggesting that the cal-

FIG. 2. Average single-excitation density of states as a function of the ortho concentration X.
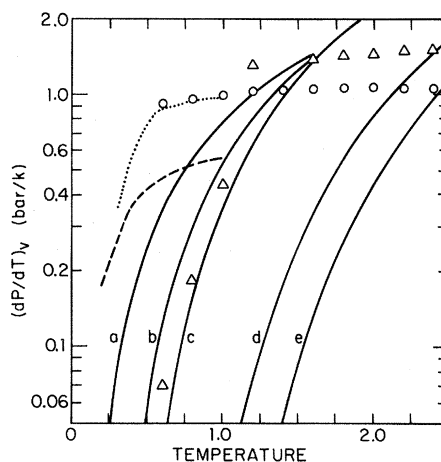

FIG. 4. Derivative of pressure with respect to temperature at constant volume, as a function of temperature. The solid curves show our calculations for various ortho concentrations X: a, $X = 0.34$. b, $X = 0.55$. c, $X = 0.70$. d, $X = 0.88$. e, $X = 1.00$. Circles ($X = 0.47$) and triangles ($X = 0.71$) indicate the experimental data of Jarvis *et al.* (Ref. 25). The dashed line ($X = 0.32$) and the dotted line ($X = 0.45$) indicate experimental data of Haase and Saleh (Ref. 32).

culation overestimates the size of the gap in the density of states by a factor of about 3.

NMR relaxation times. Figure 5 shows our calculations of T_1, using Eq. (29). Also shown in Fig. 5 are some representative experimental data from Washburn *et al.*[17] at a Larmor frequency of 10 MHz, from Sullivan and Pound[34] at 310 MHz, and from Ishimoto *et al.*[35] at 22 MHz. Other recent T_1 measurements are consistent in order of magnitude with this data.[36,37] We note that within our model, T_1 is frequency independent and a strictly decreasing function of temperature. The data for $X \approx 0.7$ appear consistent with a frequency independent T_1, at least in the low-temperature limit. However, the experimental relaxation times are 2 orders of magnitude smaller than those predicted from Eq. (29). The specific heat is very directly related to the density of states, so the agreement between theory and experiment for this quantity suggests that the calculated densities of states are approximately correct. This tells us that the simple Raman process calculated above is not
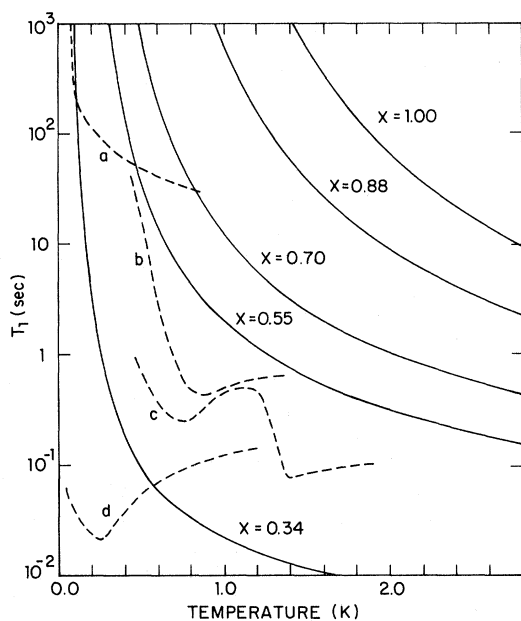
the dominant contribution to spin-lattice relaxation for $X < 1$. It would be desirable to have more data for very low temperatures and ortho concentrations close to one.

NMR line shapes. Figure 6 shows the NMR line shapes we have calculated for $X = 0.55$. The sequence of shapes is similar to that observed experimentally, but the temperatures at which the line shapes are observed are about 5 times smaller than the temperatures we calculate (see Ref. 18 and references therein). This discrepancy in temperatures for $X \le 0.55$ is comparable to that noted for the specific heat, above. While the Pake-doublet shape which we calculate for very low temperatures is not seen experimentally at these low ortho concentrations, it has been shown that ortho-para conversion heating places a practical limit on the temperature to which hydrogen may be cooled, on the order of 100 mK.[38]

IV. DISCUSSION

In this paper we have described a calculation of the excitations in solid hydrogen which treats the problem of dilution in a fundamentally correct manner. In the limit $X \to 1$ our calculation agrees with previous calculations which relied on the crystal symmetry of the $X = 1$ case. Also, as the dilution becomes large, the density of states we calculate clearly shows signs of strong localization, as would be expected for this highly disordered sys-

FIG. 5. Nuclear spin-lattice relaxation time T_1 as a function of temperature and ortho concentration X. Solid lines show our calculations. Dotted lines are experimental data taken at various Larmor frequencies. Curve a ($X = 0.67$): Sullivan and Pound (Ref. 34) at 310 MHz. Curve b ($X = 0.71$): Ishimoto *et al.* (Ref. 35) at 22 MHz. Curve c ($X = 0.67$) and curve d ($X = 0.32$): Washburn *et al.* (Ref. 17) at 10 MHz. Experimental data have been drawn as curves rather than points for clarity.
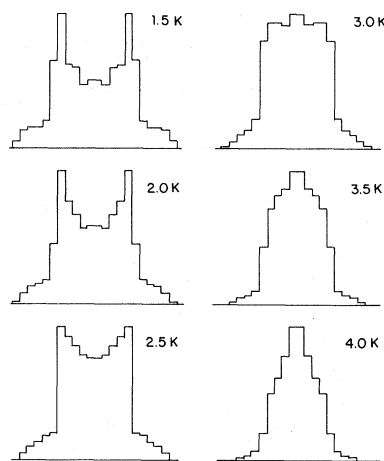

FIG. 6. NMR absorption line shapes calculated for ortho concentration 0.55, as a function of temperature. The horizontal width of each graph is $6d = 346$ kHz. The vertical scale is arbitrary.

tem. The calculation therefore interpolates successfully between two different regimes.

Some qualitative features of experimental results are reproduced, in particular, the rapid decrease in the size of the gap in the density of states with ortho concentration, as manifested in the specific heat. The agreement becomes increasingly poor as X decreases toward 0.5. The calculation fails completely to reproduce experimental NMR relaxation times, NMR line shapes, and specific heats for $X < 0.5$. The experimental data suggest the existence of excitations with energies several times lower than the lowest excitations found by our method. In an earlier paper,[18] we introduced a phenomenological model of "effective-spin — one-quadrupole" excitations, to explain experimental NMR line shapes and specific heats. Consistent with the discussion above, agreement with experiment required a significant density of states with energies below 1 K.

This suggests that a model involving small collective oscillations about a fixed mean-field ground-state configuration does not apply for solid hydrogen with ortho concentrations less than 0.5. The phase diagram strongly suggests that the rotational freezing which occurs at very low temperatures for $X < 0.5$ is of a fundamentally different character than the long-range ordering which occurs for $X > 0.5$. This is supported by x-ray measurements by Gates et al.,[39] which indicate that the crystal structure remains hcp at all temperatures for $X < 0.5$, thus precluding the possibility of remnant $Pa3$ structure. It seems possible that the lack of long-range order for $X < 0.5$ results in instability for any mean-field ground-state configuration.

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