5-15-1973

Effects of Librational Anharmonicity in the Solid Hydrogens

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Recommended Citation

Harris, A., Berlinsky, A., & Meyer, H. (1973). Effects of Librational Anharmonicity in the Solid Hydrogens. *Physical Review B, 7* (10), 4720-4733. http://dx.doi.org/10.1103/PhysRevB.7.4720

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Abstract

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Disciplines

Physics | Quantum Physics

Comments

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PHYSICAL REVIEW B VOLUME 7, NUMBER 10 15 MAY 1973

Effects of Librational Anharmonicity in the Solid Hydrogens*

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(Received 15 November 1972)

We compare the results of the recently published anharmonic theory of librons to the best available data on the libron Raman frequencies. This allows us to deduce a refined estimate of the effective value of the intermolecular quadrupolar coupling constant Γ_{eff} for solid H_2 and D_2. The effect on the librons of virtual transitions to the $(J = 3)$ rotational state is included with the result that Γ_{eff} is decreased. Our estimate from the optical data is then $\Gamma_{\text{eff}} = 0.72 \pm 0.04$ and 0.58 ± 0.03 cm^{-1} for $D_2(x = 1)$ and $H_2(x = 1)$, respectively, at zero pressure, where x denotes the mole fraction of $J = 1$ molecules. We also use the anharmonic density of states to analyze specific heat and $(\partial P/\partial T)_V$ data from which we obtain the average libron energy as a function of x. For $D_2(x = 1)$ the result is $\Gamma_{\text{eff}} = 0.70 \pm 0.04$ cm^{-1}. Measurements of the conversion-induced pressure change in H_2 give $\Gamma_{\text{eff}} = 0.56 \pm 0.03$ cm^{-1}. Both these determinations are in good agreement with the results from optical data for librons. Furthermore, it is found that there is no significant difference between $\Gamma_{\text{eff}}(x = 1)$ and Γ_{eff} determined from pair spectra in H_2 and D_2 with $x \ll 1$. The anharmonic density of states is also used to interpret the infrared absorption sideband spectrum for the creation of a vibron plus libron(s). The part of the spectrum which we attribute to one-libron processes has a width in agreement with this model and as expected there are two-libron processes resulting from cubic anharmonic libron-libron interactions. Incoherent-neutron-scattering data is also consistent with the anharmonic-libron spectrum.

I. INTRODUCTION

The purpose of this paper is to discuss the various manifestations of anharmonic interactions between librational waves (librons) in solid H_2 and D_2.[1,2] Here we consider the following four experimental quantities: (i) the Raman scattering due to librons,[3] (ii) the specific heat of librons[4] and the related quantity $(\partial P/\partial T)_V$,[5] (iii) the infrared absorption due to simultaneously exciting the stretching mode of a molecule (a vibron) and creating one or more librons,[6] and (iv) the cross section for inelastic neutron scattering due to librons.[7] As has been shown previously,[1] the Raman spectrum provided conclusive proof that even a qualitative understanding of the libron spectrum at zero wave vector requires a consideration of anharmonic effects. Here we show the effects at nonzero wave vector by studying the effects of anharmonic interactions of the libron specific heat and $(\partial P/\partial T)_V$. We also point out that the infrared and neutron experiments show evidence of the same effects.

Before discussing individual experiments, let us briefly review the physical effects of librational anharmonicity. In so doing, one should distinguish between cubic and quartic anharmonic interactions. In this connection it is useful to recall that the harmonic libron Hamiltonian is dominated by those terms which conserve the number of librational excitations. As a result, although, in principle, the transformation which diagonalizes the quadratic libron Hamiltonian mixes libron creation and destruction operators, the effect of the anharmonic interactions can be estimated neglecting this mixing. Then the predominant effect of the cubic interactions is to cause one libron to decay into two and vice versa, whereas the quartic interactions mainly cause two initial-state librons to scatter into two final-state librons. These processes are shown schematically in Fig. 1.

Note that the cubic anharmonic interactions connect the single-libron states with the two-libron states. The familiar "repulsion of energy levels" causes large downward shifts in the higher-energy single-libron states, thereby leading to the observed compression of the single-libron spectrum. Thus, whereas a harmonic calculation gives the single-libron energies at $k=0$ as 13.66Γ, 17.72Γ, and 29.04Γ, where Γ is the quadrupolar coupling constant, the anharmonic calculation yields the values 11.29Γ, 14.07Γ, and 19.55Γ.[1] Furthermore, the cubic anharmonicity leads to the appearance of two-libron bands in the Raman spectrum at the same time distorting the intensity in the single-libron part of the spectrum. It is clear that the quartic anharmonic interactions do not grossly affect the propagation of a single libron at zero temperature, since there are no thermal librons present to give rise to quartic scattering events. Hence the cubic interactions are the dominant perturbation for the single-libron spectrum. For the two-libron spectrum, however, quartic interactions are allowed and they have a marked effect on the shape of the spectrum, since

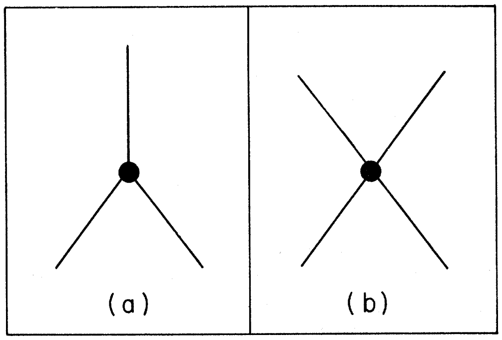


FIG. 1. (a) Cubic and (b) quartic interaction vertices.

the two-librons are created on adjacent lattice sites and therefore strongly sample the anharmonic interactions.[2]

Although the above effects have been calculated and shown to agree with the Raman spectrum at zero wave vector, similar behavior occurs throughout the Brillouin zone. For instance, (a) the single-libron density of states calculated anharmonically has only about half the bandwidth of the harmonic density of states[8] and (b) the two-libron states are expected to appear in the cross section for inelastic neutron scattering from librons.[7] Here we present evidence for the effects and thereby corroborate for the first time the anharmonic calculations of the libron spectrum for $k \neq 0$. Similar interpretations have been proposed by Hardy to explain the anomalous features of the $J=0 \rightarrow J=2$ and the $J=1 \rightarrow J=3$ excitons in nominally pure $(J=1)$ hydrogen in the orientationally ordered phase.[9] However, the detailed calculations of these effects are rather complicated inasmuch as they involve a discussion of libron-exciton interactions.

Briefly, this paper is organized as follows. In Sec. II we discuss the determination of the quadrupolar coupling constant Γ from the experimental data. In Sec. III we discuss the calculation of the libron specific heat including anharmonic effects. These calculations allow us to deduce the concentration dependence of the average libron energy from specific-heat and $(\partial P/\partial T)_V$ data. In Sec. IV we discuss the manifestation of the above-mentioned effects of anharmonicity in the infrared and neutron data. Our conclusions are summarized in Sec. V.

II. DETERMINATION OF $\Gamma_{\rm eff}$ FROM THE RAMAN SPECTRUM

As mentioned, the currently best-available experimental[3] and theoretical[1] treatments of the libron spectrum appeared at almost the same time, and hence their comparison has not yet been published. For completeness we give such an analysis here. The objective of this comparison is to determine an "effective" value of Γ, denoted $\Gamma_{\rm eff}$, which we define in the following way. The full Hamiltonian of the libron-phonon system is written in the form

$$\mathcal{H}=\mathcal{H}_P+\mathcal{H}_L+V_{\rm LP} \tag{2.1}$$

as the sum of terms due to phonons, librons, and libron-phonon interactions, respectively. We assume that the effects of the interaction term $V_{\rm LP}$ can be included by suitably renormalizing $\mathcal{H}_P$ and $\mathcal{H}_L$, so that we may write

$$\mathcal{H}=\mathcal{H}_P^{\rm ren}+\mathcal{H}_L^{\rm ren} , \tag{2.2}$$

where the superscript ren indicates a renormalized Hamiltonian. We further assume that only the electrostatic quadrupole-quadrupole (EQQ) interactions are important.[10] The most important renormalization of these interactions is to replace the bare EQQ coupling constants

$$\Gamma_0 \equiv 6e^2Q^2/25R_0^5 \tag{2.3}$$

by $\Gamma_{\rm eff}$. Thus, the difference between Γ_0 and $\Gamma_{\rm eff}$ is due to phonon renormalizations,[11] dielectric screening,[12] and other neglected interactions.[13] However, since the theoretical determination of $\Gamma_{\rm eff}$ from Γ_0 is slightly uncertain and subject to change, we will determine $\Gamma_{\rm eff}$ from the experimental data and leave it an open question to relate $\Gamma_{\rm eff}$ to Γ_0. In determining $\Gamma_{\rm eff}$ we wish to take full account of the EQQ interactions, including those due to EQQ interactions off-diagonal in J.

We will first compare the experimental libron energies with the corresponding values from a theory which includes anharmonic libron-libron interactions but which neglects virtual $(J=3)$ excitations. We will then discuss the effects of virtual $(J=3)$ processes on the determination of $\Gamma_{\rm eff}$ from the Raman spectrum. Accordingly, in Table I we list the single-libron frequencies which Hardy *et al.* have obtained by extrapolating their data for $x>0.95$ to $x=1.0$. Their results show that the procedure used previously[1] to extrapolate the Raman frequencies to $x=1.0$ introduced an error of order a few percent. The experimental values in Table I are accurate to within approximately 1%. The theoretical values for the lower two libron frequencies are estimated to have an error of less than ~5% and that of the highest libron frequency to be less than ~10%.

Thus, in the average value of $\Gamma_{\rm eff}$ deduced from the three libron lines, the value for the lowest frequency line, which is also the most intense, should be weighted most heavily. As we shall see in Sec. III, analysis of $(\partial P/\partial T)_V$ and specific-heat data yield the same value of $\Gamma_{\rm eff}$.

Now let us discuss corrections due to virtual processes involving the $(J=3)$ levels. This problem has been considered by Nakamura *et al.*,[14] but our results differ from theirs. Although the full details of our calculation are rather complicated, one can easily obtain an estimate of these effects as follows. We consider the truncated EQQ Hamiltonian

$$\mathcal{H}=\frac{1}{2}\sum_{ij}\zeta_{ij}^{00}\mathcal{O}_i^0\mathcal{O}_j^0\ , \tag{2.4}$$

where ζ_{ij}^{00}, defined in Ref. 1, is a coupling constant proportional to Γ_0 and

$$\mathcal{O}_i^0=-\tfrac{5}{2}(\cos^2\theta_i-\tfrac{1}{3})\ . \tag{2.5}$$

Within the manifold $(J=1)$ we have $\mathcal{O}_i^0=J_{zi}^2-\frac{2}{3}=-\frac{2}{3}+n_i$, where n_i is a libron occupation number. Thus, Eq. (2.4) is similar to an Ising model with an energy gap E_0 which we identify as the average harmonic energy

$$E_0=-\tfrac{2}{3}\sum_j\zeta_{ij}^{00}=21.20\Gamma_0\ . \tag{2.6}$$

To take account of virtual processes to the $(J=3)$ manifold we write

$$\mathcal{O}_i^0=-\tfrac{2}{3}+n_i+\gamma(q_i^\dagger+q_i)+(\delta-\gamma)n_i(q_i^\dagger+q_i)+\cdots\ , \tag{2.7}$$

where $q_i^\dagger$ creates an excitation with $J=3$ on the ith site and

$$\gamma=\langle 30|\mathcal{O}^0|10\rangle\ , \tag{2.8a}$$

$$\delta=\langle 31|\mathcal{O}^0|11\rangle\ . \tag{2.8b}$$

Also, we add to the Hamiltonian a term $10B\sum_i q_i^\dagger q_i$ for the kinetic energy of the $J=3$ excitons. Then the Hamiltonian may be written

$$\begin{aligned}\mathcal{H}=&\frac{1}{2}\sum_{ij}(-\tfrac{2}{3}+n_i)(-\tfrac{2}{3}+n_j)\zeta_{ij}^{00}\\&+10B\sum_j\left(q_j^\dagger+\frac{\gamma+(\delta-\gamma)n_j}{10B}\sum_i\zeta_{ij}^{00}(-\tfrac{2}{3}+n_i)\right)\\&\times\left(q_j+\frac{\gamma+(\delta-\gamma)n_j}{10B}\sum_k\zeta_{kj}^{00}(-\tfrac{2}{3}+n_k)\right)\\&-\frac{1}{10B}\sum_j[\gamma+(\delta-\gamma)n_j]^2\\&\times\sum_{ik}\zeta_{ij}^{00}\zeta_{kj}^{00}(-\tfrac{2}{3}+n_i)(-\tfrac{2}{3}+n_k)\ .\end{aligned} \tag{2.9}$$

The first term is the Ising Hamiltonian of Eq. (2.4) for the $(J=1)$ manifold. The second term is a displaced harmonic oscillator for the $J=3$ excitons and the final term is the effect on the $(J=1)$ manifold of the virtual processes. The associated shift in the average libron energy, denoted ΔE_0, is the value of this term when there is a single libron on the lattice relative to its value in the zero-libron state. This is found to be

$$\begin{aligned}\Delta E_0=&-\frac{\delta^2-\gamma^2}{10B}\sum_{i,k}\tfrac{4}{9}\zeta_{ij}^{00}\zeta_{ij}^{00}\\&-\frac{2}{10B}\sum_{j,i}\gamma^2\zeta_{ij}^{00}\zeta_{kj}^{00}(-\tfrac{2}{3})\ .\end{aligned} \tag{2.10}$$

In doing this calculation we neglected some contributions of the $i=k$ term. Using the evaluation of Eq. (2.6) and taking $\gamma^2=\frac{3}{7}$, $\delta^2=\frac{2}{7}$, we obtain

$$\Delta E_0=E_0^2/7B\approx 64\Gamma^2/B\ . \tag{2.11}$$

The more complete treatment given in Appendix A shows that virtual $(J=3)$ processes give rise to the effective interaction $\mathcal{H}_{\text{eff}}$:

$$\begin{aligned}\mathcal{H}_{\text{eff}}=-\Bigg(&E_G^{\text{eff}}+E_0^{\text{eff}}\sum_l n_l+\sum_{i,k}\sum_{m=\pm1}\sum_{n=\pm1}[\Omega_{ik}^{mn}\mathcal{O}_2^m(i)\mathcal{O}_2^n(k)\\&+\Lambda_{ik}^{mn}\mathcal{O}_1^m(i)\mathcal{O}_1^n(k)]\Bigg)\Big/10B\ .\end{aligned} \tag{2.12}$$

The terms in Ω and Λ primarily affect the band-

TABLE I. Determination of Γ_{eff} from the Raman data for high concentrations of $(J=1)$ molecules.

Mode	Experimental Raman frequencies[a] extrapolated to $x=1$, in cm^{-1}	Theoretical anharmonic libron frequencies,[b] neglecting virtual $(J=3)$ processes.	Γ_{eff} [without $(J=3)$ corrections], in cm^{-1}		Γ_{eff} [with $(J=3)$ corrections (see text)], in cm^{-1}.
		(A) Solid H_2			
E_g	6.75	$(11.29\pm0.56)\Gamma_{\text{eff}}$	0.598 ± 0.030	0.600 ± 0.030	0.580 ± 0.030
$T_g^{(1)}$	8.58	$(14.07\pm0.70)\Gamma_{\text{eff}}$	0.610 ± 0.030		
$T_g^{(2)}$	11.80	$(19.55\pm2.00)\Gamma_{\text{eff}}$	0.604 ± 0.060		
		(B) Solid D_2			
E_g	9.07	$(11.29\pm0.56)\Gamma_{\text{eff}}$	0.803 ± 0.040	0.802 ± 0.040	0.722 ± 0.040
$T_g^{(1)}$	11.28	$(14.07\pm0.70)\Gamma_{\text{eff}}$	0.802 ± 0.040		
$T_g^{(2)}$	15.43	$(19.55\pm2.00)\Gamma_{\text{eff}}$	0.789 ± 0.080		

[a] See Ref. 3.

[b] See Ref. 1.

width and, in any event, are estimated to be small. The second term gives the shift in E_0 and is found to be

$$\Delta E_0 = -E_0^{\text{eff}}/10B = 45.21\Gamma^2/B \quad . \tag{2.13}$$

Thus, our result shows an *increase* in the average libron energy. This contrasts with the results of Nakamura *et al.*[14] for the shifts in the $(k=0)$ energies which were of about the same magnitude but of opposite sign to that given in Eq. (2.13).

In passing we observe that E_G^{eff} leads to a significant change in the ground-state energy E_G. Using Nakamura and Miyagi's result for $E_G(B=\infty)$,[15] we write Eq. (A36) as

$$E_G/N = -7.37\Gamma - 32.02\Gamma^2/B \quad , \tag{2.14}$$

where N is the total number of molecules. Even larger effects are to be expected in the zero-temperature orientational pressure $p = -\partial E_G/\partial V$:

$$p = -N\frac{\partial\Gamma}{\partial V}\left(7.37 + \frac{64.04\Gamma}{B}\right) \quad . \tag{2.15}$$

Since Γ is proportional to $V^{-5/3}$, as verified experimentally,[16] we have $\partial\Gamma/\partial V = -\frac{5}{3}\Gamma/V$. The second term is of order 20% and 10% of the first one for solid D_2 and H_2, respectively.

We consider the situation for H_2, where data[16] for the orientational pressure P are available for the molar volume $V = 22.3$ cm^3. Using Eq. (2.15), we obtain from these data $\Gamma_{\text{eff}} = 0.56 \pm 0.03$ cm^{-1} for ortho-H_2.

Now let us include the effect of $(J=3)$ processes on the libron spectrum. For simplicity, we shall calculate the percentage shift in the average anharmonic libron energy E_L and use this to make the necessary adjustment to Γ due to $(J=3)$ processes. For this purpose, we use the approximation[1] that

$$E_L(B) = E_0(B) - |V_3|^2/E_L(B) , \tag{2.16}$$

where the $(J=3)$ processes are included by setting

$$E_0(B) = 21.2\Gamma + 45.21\Gamma^2/B \quad , \tag{2.17}$$

where $B = 30$ cm^{-1} for D_2 and $B = 60$ cm^{-1} for H_2.[17] The fractional shift in E_L due to $(J=3)$ processes is then

$$[E_L(B) - E_L(\infty)]/E_L(\infty) \equiv r \quad . \tag{2.18}$$

The factor r is found to be $r = 0.10$ for D_2 and 0.04 for H_2. A simple way to include these effects in Γ_{eff} is to set $\Gamma_{\text{eff}}(B) = r\Gamma_{\text{eff}}(B=\infty)$. The effect on the value of Γ_{eff} is seen in column 4 of Table I. We note the good agreement with the pressure data obtained above.

Finally, one can compare these results with the EQQ coupling constant obtained from the Raman studies of pairs of $(J=1)$ molecules in nearly pure $(J=0)$ solid hydrogen.[18] Again, to eliminate the uncertainties due to renormalization effects, we consider only EQQ interactions and therefore we tabulate Γ_{eff}. For this purpose, we use the Raman line which is both the best determined and also the most unambiguously compared to theory, namely, the transition of $h\nu = 10\Gamma_{\text{eff}}$. Here we have found the effect of $(J=3)$ processes to be negligible. Although we do not present the full calculation here, we may justify this assertion by noting that the effect of $(J=3)$ processes on either pair or libron energies is of the form

$$\Delta E = |V_{1\text{-}3}|^2/10B \quad , \tag{2.19}$$

where for librons $V_{1\text{-}3}$ is proportional to a single libron energy $V_{1\text{-}3} \propto E_0$; and for pair states $V_{1\text{-}3}$ is proportional to a typical pair-state energy $E_{\text{pair}} \approx 4\Gamma$. Thus, using Eqs. (2.6) and (2.19), we expect that the shift in the pair-state energies due to $(J=3)$ processes will be only a few percent of the corresponding shift in the libron energies. In fact, a more detailed calculation shows this to be about a 1% effect. For the results in Table II it is seen that Γ_{eff} is the same, within the experimental error, in both dilute and concentrated systems. Also note that these optical values fall within the error bounds of the previous thermodynamic data at low concentrations[5,16] and the NMR pair spectrum determination.[19]

TABLE II. Γ_{eff} determined from experiments using small concentrations of $(J=1)$ molecules.

	$h\nu$ (Raman)	$\Gamma_{\text{eff}}^{\text{pairs}}$ (Raman)	$\Gamma_{\text{eff}}^{(\partial P/\partial T)_V}$	$\Gamma_{\text{eff}}^{\text{NMR}}$ $(x<0.10)$
H_2	5.51 ± 0.1[a]	0.551 ± 0.010	0.56 ± 0.03[b]	0.57 ± 0.015[c]
D_2	6.85 ± 0.1	0.685 ± 0.010	0.74 ± 0.05[d]	

[a] Energies are in cm^{-1}.
[b] See Ref. 16.
[c] See Ref. 19.
[d] See Ref. 5.

It is of some interest to note that, at zero temperature and pressure, the lattice contracts by $\partial V/V \simeq 2\%$, when x increases from $x=0$ to $x=1$.[16] This should cause an increase of Γ_{eff} by $1/\Gamma \times (\partial\Gamma/\partial V)\delta V/V \simeq 3.5\%$. Such increase is not inconsistent with the experiment (see Tables I and II) within the admittedly still large uncertainty in the data analysis.

Most recently, Stein *et al.*[7] have made a new determination of Γ from the neutron scattering line caused by the $J=1$ to $J=0$ conversion. These authors claim that their value of $\Gamma(H_2) = 0.55_5 \pm 0.007$ cm^{-1} is much more accurately determined than from the other methods. However in their analysis, the authors have not considered the corrections that will modify their reported value of Γ, namely, (i) the virtual $J=1$ to $J=3$ corrections as described in the present paper, (ii) tipping corrections,[20] wherein the neighbors of the $J=0$ defect created by the conversion process relax to new equilibrium orientations, and (iii) changes in zero-point motions due to the presence of a $J=0$ defect in the final state. A calculation of these corrections is presently being carried out by two of us (A. J. B. and A. B. H.).

III. ANALYSIS OF $(\partial P/\partial T)_V$ AND SPECIFIC-HEAT DATA IN CUBIC D_2 USING ANHARMONIC THEORY

Our knowledge of the anharmonic density of states enables us to calculate the specific heat at constant volume C_V as a function of temperature. The specific heat is simply related to $(\partial P/\partial T)_V$ for which extensive experimental evidence is available.[5] This relation is

$$\left(\frac{\partial P}{\partial T}\right)_V=\frac{\gamma_{\mathrm{EQQ}}C_V^{\mathrm{EQQ}}}{V}+\frac{\gamma_{\mathrm{Latt}}C_V^{\mathrm{Latt}}}{V} , \qquad (3.1)$$

where γ_{EQQ} is the Grüneisen constant for electric quadrupolar forces which has the theoretical value of $\frac{5}{3}$ and C_V has been decomposed into EQQ and lattice contributions. We will work with data for solid D_2 from which the lattice contribution to $(\partial P/\partial T)_V$ has already been subtracted out. This subtraction was performed using the experimentally determined value $\gamma_{\mathrm{Latt}}=2$ and also $V=19.56$ cm^3/mole.

In Appendix B we have derived a formula [Eq. (B21b)] for the quadrupolar specific heat in terms of the anharmonic single-libron density of states. The coefficient of the integral in Eq. (B21b) has the value

$$E_L(2E_L+E_0)/3(E_L^2+|V_3|^2)=0.83 , \qquad (3.2)$$

where we have used $E_L=16.0\Gamma$, obtained from the anharmonic single-libron density of states,[8] $E_0=21.2\Gamma$ and $|V_3|^2=84.8\Gamma$.[1] From Eq. (3.2) and the arguments of Appendix B, we deduce that about 17% of the single-libron spectral weight has been shifted up into the two-libron band of the spectrum. We ignore contributions from the two-libron band to the specific heat since they are second order in the parameter $e^{-\beta E_L}$ and βE_L is greater than 8 for the temperature region of interest, $T<2$ K. Using Eq. (3.2) we write Eq. (B21b) as

$$\frac{C_V^{\mathrm{EQQ}}}{R}=0.83\int_0^\infty d\omega\,\hat{\rho}(\omega)\,C(\omega) , \qquad (3.3)$$

where $\hat{\rho}(\omega)$ is the anharmonic single-libron density of states (not including the effect of virtual $J=3$ states) which is normalized by

$$\int d\omega\,\hat{\rho}(\omega)=2.0 , \qquad (3.4)$$

and $C(\omega)$ is given by

$$C(\omega)\equiv\frac{(\beta\hbar\omega)^2e^{-\beta\hbar\omega}}{(1-e^{-\beta\hbar\omega})^2}\approx(\beta\hbar\omega)^2e^{-\beta\hbar\omega} . \qquad (3.5)$$

In the last step of Eq. (3.5) we have again dropped terms of order $e^{-2\beta E_L}$.

Because we do not have a reliable theory relating the libron energies to the concentration of $(J=0)$ impurities we will determine the average libron energy as a function of the concentration x of $(J=1)$ molecules from experimental data. We generalize Eq. (3.2) for $x\neq 1$ as

$$C_V/R=0.83x\int\rho_x(\omega)\,d\omega\,C(\omega) . \qquad (3.6)$$

The density of states per ortho molecule $\rho_x(\omega)$ for $x\neq 1$ will be approximated as follows. It is normalized by

$$\int\rho_x(\omega)\,d\omega=2 . \qquad (3.7)$$

We are now faced with the problem of parametrizing $\rho_x(\omega)$. Clearly, the simplest procedure is to use the calculations[8] for the pure system with a suitable scaling of the average libron energy, denoted by $E_L(x)$, and of the bandwidth W. As we shall see, $E_L(x)$ varies more rapidly with x than one would expect from a mean-field model. In fact, we find later that for $x\approx 1$, $E_L(x)$ is proportional to $[1-1.8(1-x)]$. Simple arguments[21] show that due to random alloy scattering the libron bandwidth decreases much more slowly than this and we shall assume it to be proportional to $x^{1/2}$, which for $x\approx 1$ is approximately $[1-\frac{1}{2}(1-x)]$. Thus, we set

$$\rho_x(\omega)=x^{-1/2}\hat{\rho}\left(E_L(1)+\frac{\omega-E_L(x)}{x^{1/2}}\right) . \qquad (3.8)$$

The exact assumption about the x dependence of the bandwidth is not crucial for our analysis.

Unfortunately, the published[8] calculations of $\hat{\rho}(\omega)$ are given in terms of ω/Γ rather than ω/E_L. To relate these variables we use the fact that for the anharmonic density of states $E_L=16.0\Gamma$ and thus we may express the results of Ref. 8 in the form $\hat{\rho}(\omega)=E_L^{-1}\Phi(\omega/E_L)$, where Φ is a dimensionless normalized function given graphically in Ref. 8. Then Eq. (3.8) reads

$$\rho_x(\omega)=E_L(1)^{-1}x^{-1/2}\phi\left(1+\frac{\omega-E_L(x)}{x^{1/2}E_L(1)}\right) . \qquad (3.9)$$

In order to use this form to determine $E_L(x)$ it is necessary first to determine $E_L(1)$. This we did by fitting the experimental $(\partial P/\partial T)_V$ measurements[5] for $T\lesssim 2K$ extrapolated to $x=1$ to calculations based on $\rho_x(\omega)$ for $x=1$. In this way we found

$$E_L(1)=12.4\pm 0.5\ \mathrm{cm}^{-1} , \qquad (3.10)$$

which corresponds to $\Gamma_{\mathrm{eff}}=0.77\pm 0.04$ cm^{-1}. Finally, using the results following Eq. (2.18), we may include the effect of $(J=3)$ processes. We then find that

$$\Gamma_{\mathrm{eff}}=0.70\pm 0.04\ \mathrm{cm}^{-1} , \qquad (3.11)$$

which is in good agreement with the optical data.

Equations (3.6)–(3.9) allow us to analyze both

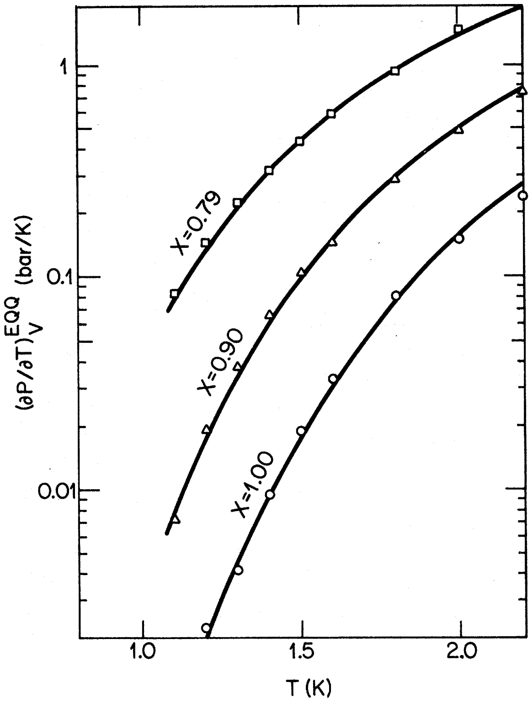


FIG. 2. Comparison of $(\partial P/\partial T)_V^{EQQ}$ data to anharmonic theory (solid curves) for $x = 0.79$, 0.90, and 1.00 (squares, triangles, and circles). Here the lattice contribution has been subtracted from the observed $(\partial P/\partial T)_V$ results (Ref. 5). The data for $x = 1.00$ were obtained by graphic extrapolation of measurements between $x = 0.66$ and $x = 0.90$. The theoretical fit to the data gives the respective average libron energies shown in Fig. 3.

$(\partial P/\partial T)_V$ and C_V data in terms of a single parameter $E_L(x)$. Of course as x decreases, the simple approximations of Eq. (3.8) begin to fail and we are not able to fit the data at all. Thus, we could not apply this theory for $x < 0.79$. Figure 2 shows the fit of $(\partial P/\partial T)_V$ data.

In Fig. 3 we plot the concentration dependence of the average libron energy, using both $(\partial P/\partial T)_V$ data[5] and also the specific-heat data of Grenier and White.[4] The libron energy appears to decrease linearly for $x \gtrsim 0.79$ and is described by

$$E_L(x)/E_L(1) = [1 - 1.8(1 - x)] \quad . \tag{3.12}$$

The factor 1.8 is of considerable theoretical interest since it represents the linear dependence of the libron energies on the concentration of $(J = 0)$ impurities. In the simplest approximation of nonpropagating noninteracting librons, this factor has the value of one. A more realistic theoretical value requires the calculation of the effect of multiple scattering of propagating librons off of an isolated impurity site. One of us (A. J. B.) is currently involved in an effort to calculate these effects and the results should be available soon.

IV. TWO-LIBRON EFFECTS AT NONZERO WAVE VECTOR

There are several ways to observe the single-libron density of states. Usually, the experiments are sensitive to the $\langle Y_2^m(\omega_i(t))Y_2^{m'}(\omega_j(0))\rangle_T$ correlation function, where $\omega_i(t)$ describes the orientation of the ith molecule at time t, Y_2^m is a spherical harmonic, and $\langle\ \rangle_T$ indicates a thermal average. The orientational spectral weight function associated with this correlation function may be thought of as consisting of a single-libron part, a two-libron part, etc. This simply reflects the fact that libron number is not conserved in the presence of cubic anharmonicity. The two experiments we shall discuss here are (i) the infrared absorption associated with the libron side bands of the intramolecular vibrational excitation and (ii) the incoherent scattering of neutrons by librons.

In Fig. 4 we show the infrared absorption spectrum near the intramolecular vibrational excitation as observed by Clouter *et al.*[6] These authors were not able to understand the libron side band in terms of the harmonic density of states. However, the ideas described in the introduction lead to a natural interpretation. From the Fig. 1 it is seen that the narrower anharmonic density of states[8] reproduces the lower-frequency peak rather well. Furthermore, the higher-frequency feature is very reminiscent of the two-libron feature observed in the Raman data. In fact, the energy of the former, 15.3 cm^{-1}, is very close to that of the peak in the two-libron Raman spectrum at 16.8 cm^{-1}.

It should be noted that this interpretation explicitly relies on the existence of anharmonic

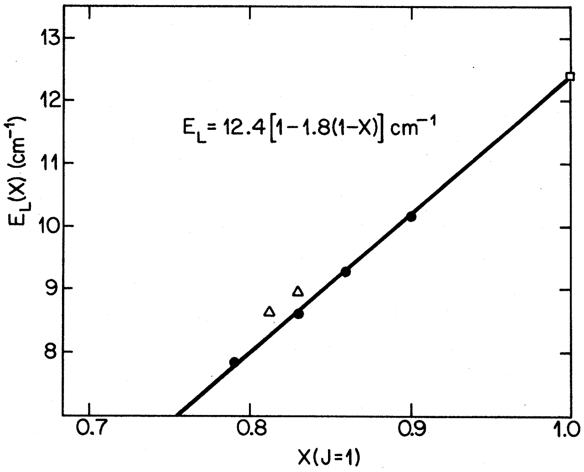


FIG. 3. Dependence of the average libron energy for D_2 on the molefraction x, as deduced from specific-heat (Ref. 4) and $(\partial P/\partial T)_V$ (Ref. 5) experiments (triangles and circles, respectively). The libron energy at $x = 1.00$, $E_L(1)$, was taken to be 12.4 cm^{-1} from the fit in Fig. 2, and is shown by the open square.

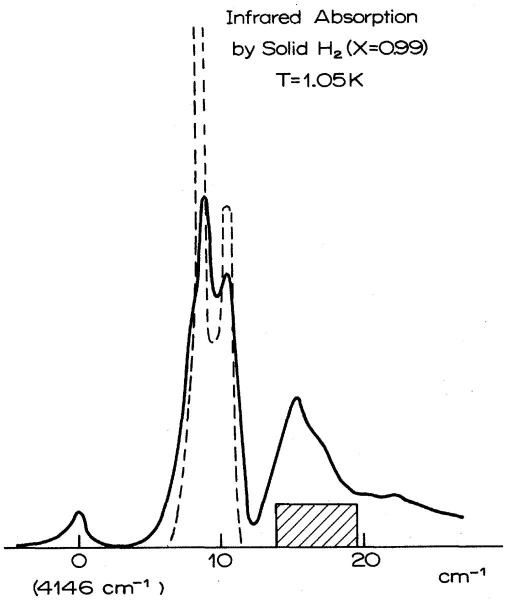


FIG. 4. Comparison of the infrared absorption vibron sideband spectrum in solid orthohydrogen, with $x = 0.99$ and $T = 1.05$ K, of Clouter *et al.* to the anharmonic single-libron density of states. The shaded block represents the expected two-libron absorption. The theoretical curve has been normalized to the experimental one so that the integrated intensities of the one-libron spectrum are roughly the same. Instrumental resolution and other effects contribute no doubt in the broadening of the observed line.

libron-libron interactions. Earlier, Homma *et al.*[22] made a similar identification based on an incorrect harmonic density of states. However, the correct harmonic density of states has so large a bandwidth that if one bases an interpretation on harmonic theory, one is forced to identify the entire spectrum as being due to single-libron processes.[23] In view of our present knowledge, our interpretation[24] based on anharmonic interactions seems to be the more plausible one.

Homma and Matsuda[23] have also given calculations of the intensity due to various processes. They have not yet included virtual processes involving anharmonic libron-libron interactions, however. One is tempted to estimate that the ratio of integrated intensity due to two-libron creation J_2 to that J_1 due to single-libron creation is the same as in the Raman experiments, viz., $J_2/J_1 \approx 0.2$. Experimentally, J_2/J_1 for the vibron sideband is much larger than this: $J_2/J_1 \approx 0.5$. Unfortunately, detailed calculations are much more complicated for the infrared spectrum than in the case of the Raman intensities due to the creation of an extra excitation, the vibron. The result of a crude calculation given in Appendix C is that $J_2/J_1 = 0.3$ for the vibron sideband. Possibly a more complete calculation will yield further improvement in the theoretical value of this ratio.[25]

Now we consider the cross section for the incoherent scattering of neutrons by librons in solid H_2. The data of Stein *et al.*,[7] taken at 1.1 K with 95% ($J = 1$) molecules, is shown in Fig. 5. According to Eq. (3.12) one expects E_L ($x = 0.95$) $= 0.91E_L$ ($x = 1.0$). Therefore, we also show on the same graph the anharmonic single-libron density of states in which the energies have been scaled by this factor 0.91. Note that the peak of the theoretical spectrum agrees with the experimental peak and that the bandwidths are in reasonable agreement if one takes into account the large experimental resolution width. The two-libron states are responsible for the high-energy tail in the libron cross section, but the data are not precise enough to yield quantitative information thereon. Because of the scatter in the data the harmonic density of states whose width is ~ $10\Gamma \approx 5.6$ cm^{-1} would also be compatible with the data, if one were somehow allowed to ignore two-libron processes.

V. CONCLUSION

The main results of this paper are as follows: The effective value of the quadrupole coupling constant for hydrogen molecules in the solid may be accurately determined by comparing the theoretical values of the ($k = 0$) anharmonic libron frequencies of Coll and Harris[1] to the Raman data of Hardy *et al.*[3] However, it is also necessary to include,

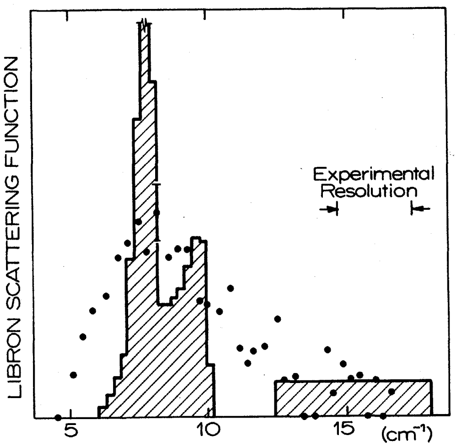


FIG. 5. Libron scattering functions $S_L(\omega)$ taken from incoherent neutron scattering by a powder sample of H_2 ($x = 0.95$) at $T = 1.1$ K. On the same scale we have plotted the anharmonic single-libron density of states. The shaded block on the right-hand side represents the expected two-libron scattering. The theoretical curve has been normalized to the experimental one so that the integrated intensities of the one-libron spectrum are roughly the same.

in the theoretical libron frequencies, the effect of virtual transitions of $(J=1)$ molecules to the $(J=3)$ rotational states. This effect reduces Γ_{eff} by 10% for D_2 and 4% for H_2. Our best estimate for Γ_{eff} from the optical data is then

$$\Gamma_{\text{eff}}(x=1)=0.72\pm 0.04\ \text{cm}^{-1}\ \text{for}\ D_2\ , \tag{5.1a}$$

$$\Gamma_{\text{eff}}(x=1)=0.58\pm 0.03\ \text{cm}^{-1}\ \text{for}\ H_2\ , \tag{5.1b}$$

the uncertainty in Γ_{eff} being mainly due to that in the anharmonic theory. In addition, we have developed an expression for an effective EQQ Hamiltion H_{eff}, which includes the effect of virtual transitions to $(J=3)$ states. The expression for H_{eff} could be used to compute the effect of the $(J=3)$ states on the shape of the libron density of states, although we expect that this effect will be small. Virtual $(J=3)$ excitations do have a significant effect on the EQQ ground-state energy and are expected to modify the orientational pressure by 10 and 20% for H_2 and D_2, respectively. For H_2, the pressure data lead to $\Gamma_{\text{eff}}=0.56\pm 0.03\ \text{cm}^{-1}$, in good agreement with the Raman data.

Using the anharmonic-libron density of states we have derived a theoretical expression for the specific heat and the related quantity $(\partial P/\partial T)_V$ in which the average libron energy is a free parameter. Fitting this expression to experimental data with $(J=1)$ concentration $0.79<x<0.90$, we obtain the average libron energy as a function of x. The result for D_2 is

$$E_L(x)=12.4[1-1.8(1-x)]\ \text{cm}^{-1}\ . \tag{5.2}$$

This differs from previously published results[5] which were obtained using a harmonic density of states. When account is taken of virtual processes with $(J=3)$, the result of Eq. (5.2) at $x=1$ corresponds to the value $\Gamma_{\text{eff}}=0.70\pm 0.04\ \text{cm}^{-1}$ for D_2, where the error again reflects the uncertainty in the theory. This result is consistent with Eq. (5.1a).

We have found that the effect of virtual transitions $(J=1)$ to $(J=3)$ is much smaller for the energy spectrum of isolated pairs of $(J=1)$ molecules. Hence the correction to the value of Γ deduced from the properties of $(J=1)$ pair configurations, is negligible. The values of Γ_{eff} from such experiments, both optical and thermodynamic, are consistent with one another and for convenience we summarize the best estimates. These are

$$\Gamma_{\text{eff}}(\text{pairs})=0.69\pm 0.01\ \text{cm}^{-1}\ \text{for}\ D_2\ , \tag{5.3a}$$

$$\Gamma_{\text{eff}}(\text{pairs})=0.56\pm 0.02\ \text{cm}^{-1}\ \text{for}\ H_2\ . \tag{5.3b}$$

Hence within the uncertainties associated with the experiments and the theory, the values of Γ_{eff} deduced from experiments measuring the properties of "librons" and of pairs coincide.

Finally, we have compared the anharmonic density of states to existing experimental data which includes the sideband spectrum for infrared absorption by vibrons and also the incoherent neutron scattering spectrum. In the former case there is very good agreement between experiment and the anharmonic theory. The neutron data, on the other hand, although consistent with anharmonic theory, is still somewhat ambiguous because of insufficient experimental resolution.

ACKNOWLEDGMENTS

We would like to thank Dr. W. N. Hardy, Dr. I. F. Silvera, and Dr. J. P. McTague for allowing us to quote their experimental results prior to publication.

APPENDIX A: EFFECTS OF VIRTUAL $(J=3)$ EXCITONS

In this Appendix we calculate the effects of order Γ^2/B due to virtual fluctuations to the $(J=3)$ manifold. We write

$$\mathcal{H}=\frac{1}{2}\sum_{ij}\sum_{mn}\zeta_{ij}^{mn}\mathcal{O}_2^m(i)\mathcal{O}_2^n(j)\ , \tag{A1}$$

where

$$\mathcal{O}_2^{\pm 2}(i)=-\tfrac{5}{4}\sin^2\theta_i e^{\pm 2i\varphi_i}\ , \tag{A2a}$$

$$\mathcal{O}_2^{\pm 1}(i)=\mp(5/2\sqrt{2})\sin\theta_i\cos\theta_i e^{\pm i\varphi_i}\ , \tag{A2b}$$

$$\mathcal{O}_2^{0}(i)=-\tfrac{5}{2}(\cos^2\theta_i-\tfrac{1}{3})\ , \tag{A2c}$$

where θ_i and φ_i are measured relative to the local equilibrium axes of the ith molecule. (For more details of the model and notation, see Ref. 1.) Using second-order perturbation theory, we evaluate the effective Hamiltonian due to $(J=3)$ processes as

$$\mathcal{H}_{\text{eff}}=-(10B)^{-1}\sum_i\mathcal{H}P_i\mathcal{H}-(20B)^{-1}\sum_{i<j}\mathcal{H}P_iP_j\mathcal{H} \tag{A3a}$$

$$\equiv-(10B)^{-1}\sum_i h_i-(40B)^{-1}\sum_{ij}h_{ij}\ . \tag{A3b}$$

Here P_i indicates a virtual state with $J_i=3$. Molecules for which no P factor appears have virtual states restricted to $J=1$. We shall drop anharmonic terms in $\mathcal{H}_{\text{eff}}$ which involve more than two librons. We decompose $h\equiv\sum h_i$ as

$$h=h^a+h^b+h^c+h^d\ , \tag{A4}$$

where

$$h^a=\sum_i\sum_{kl}\sum_{mm'}\zeta_{ik}^{m0}\zeta_{il}^{m'0}\mathcal{O}_2^0(k)\mathcal{O}_2^0(l)\{\mathcal{O}_2^m(i)P_i\mathcal{O}_2^{m'}(i)\}\ , \tag{A5a}$$

$$h^b=\sum_i\sum_{kl}\sum_{mm'}\sum_{n\neq 0}\zeta_{ik}^{mn}\zeta_{il}^{m'0}\mathcal{O}_2^n(k)\mathcal{O}_2^0(l)\{\mathcal{O}_2^m(i)P_i\mathcal{O}_2^{m'}(i)\}\ , \tag{A5b}$$

$$h^c=\sum_i\sum_{kl}\sum_{mm'}\sum_{n'\neq 0}\zeta_{ik}^{m0}\zeta_{il}^{m'n'}\mathcal{O}_2^0(k)\mathcal{O}_2^{n'}(l)\{\mathcal{O}_2^m(i)P_i\mathcal{O}_2^{m'}(i)\}\ , \tag{A5c}$$

$$h^d=\sum_i\sum_{kl}\sum_{mm'}\sum_{\substack{n\neq 0\\ n'\neq 0}}\zeta_{ik}^{mn}\zeta_{il}^{m'n'}\mathcal{O}_2^n(k)\mathcal{O}_2^{n'}(l)\{\mathcal{O}_2^m(i)P_i\mathcal{O}_2^{m'}(i)\}. \tag{A5d}$$

It is useful to define

$$\mathcal{O}_2^m(i)P_i\mathcal{O}_2^{m'}(i)+\mathcal{O}_2^{m'}(i)P_i\mathcal{O}_2^m(i)\equiv R_{mm'}^i\ , \tag{A6a}$$

$$\mathcal{O}_2^m(i)P_i\mathcal{O}_2^{m'}(i)-\mathcal{O}_2^{m'}(i)P_i\mathcal{O}_2^m(i)=S_{mm'}^i\ , \tag{A6b}$$

$$\{\mathcal{O}_2^m(i),\ \mathcal{O}_2^{m'}(i)\}_+=T_{mm'}^i\ , \tag{A6c}$$

$$[\mathcal{O}_2^m(i),\ \mathcal{O}_2^{m'}(i)]_-=U_{mm'}^i\ , \tag{A6d}$$

and for the situation of interest where both the initial and final states have $J=1$, we have the relations

$$R_{nm}=-3\left(\frac{1}{70\pi}\right)^{1/2}\frac{A_{m+n}}{A_mA_n}C(222;m,n)\mathcal{O}_2^{m+n}+\frac{3}{10\pi}\frac{(-)^m}{A_m^2}\delta_{m+n,0}\ , \tag{A7a}$$

$$S_{nm}=-\frac{3\sqrt{10}}{20\pi}\frac{1}{A_mA_n}C(221;m,n)\mathcal{O}_1^{m+n}\ , \tag{A7b}$$

$$T_{nm}=-\left(\frac{7}{10\pi}\right)^{1/2}\frac{A_{m+n}}{A_mA_n}C(222;m,n)\mathcal{O}_2^{m+n}+\frac{1}{5\pi}\frac{(-)^m}{A_m^2}\delta_{m+n,0}\ , \tag{A7c}$$

$$U_{nm}=-S_{nm}\ , \tag{A7d}$$

where

$$\mathcal{O}_1^{\pm 1}(i)=\mp(1/\sqrt{2}\,)J_i^{\pm}\ , \tag{A8a}$$

$$\mathcal{O}_1^0(i)=J_z\ , \tag{A8b}$$

$C(JKL;m,n)$ is the Clebsch–Gordan coefficient,[26] and

$$-\frac{1}{\sqrt{3}}A_0=-\frac{1}{\sqrt{2}}A_{\pm 2}=A_{\pm 1}=\frac{1}{10}\left(\frac{15}{\pi}\right)^{1/2}\ . \tag{A9}$$

In particular, we have the libron expansion

$$R_{m,-m}^i=(-)^m[r_m+\delta r_mn_i]\ , \tag{A10a}$$

$$T_{m,-m}^i=(-)^m[t_m+\delta t_mn_i]\ , \tag{A10b}$$

where the coefficients are

$$r_0=\tfrac{6}{7}\ ,\qquad r_{\pm 1}=+\tfrac{16}{7},\qquad r_{\pm 2}=\tfrac{5}{7}\ ; \tag{A11a}$$

$$\delta r_0=-\tfrac{2}{7},\quad \delta r_{\pm 1}=-\tfrac{3}{7},\quad \delta r_{\pm 2}=\tfrac{3}{7}\ ; \tag{A11b}$$

$$t_0=\tfrac{8}{9}\ ,\qquad t_{\pm 1}=2\ ,\qquad t_{\pm 2}=0\ ; \tag{A11c}$$

$$\delta t_0=-\tfrac{2}{3}\ ,\quad \delta t_{\pm 1}=-1\ ,\quad \delta t_{\pm 2}=1\ . \tag{A11d}$$

Also we shall use the lattice sums

$$\sum_k\zeta_{ik}^{m0}=-\tfrac{3}{2}E_O\delta_{m,0}\ , \tag{A12}$$

$$\Gamma^{-2}\sum_k|\zeta_{ik}^{\mu\nu}|^2=\mathcal{S}_{\mu\nu}\ . \tag{A13}$$

When the lattice sum in Eq. (A13) is restricted to nearest neighbors the result for $\mathcal{S}_{\mu\nu}$ is shown in Table III.

TABLE III. Numerical values for the lattice sum $\mathcal{S}_{\mu,\nu}$.

μ \ ν	2	1	0	−1	−2
2	32.891	35.245	68.771	8.134	4.002
1	35.245	4.398	20.708	7.509	8.134
$\mathcal{S}_{\mu\nu}$=0	68.771	20.708	67.6875	20.708	68.771
−1	8.134	7.509	20.708	4.398	35.245
−2	4.002	8.134	68.771	35.245	32.891.

For h^a, we write

$$h^a=\sum_i\sum_{kl}\sum_{mm'}\zeta_{ik}^{m0}\zeta_{il}^{m'0}\mathcal{O}_k^0\mathcal{O}_l^0\{\mathcal{O}_2^m(i)P_i\mathcal{O}_2^{m'}(i)\} \tag{A14a}$$

$$=\frac{1}{2}\sum_i\sum_{kl}\sum_{mm'}\zeta_{ik}^{m0}\zeta_{il}^{m'0}(-\tfrac{2}{3}+n_k)(-\tfrac{2}{3}+n_l)R_{m,m'}^i \tag{A14b}$$

$$=\frac{1}{2}\sum_i\sum_{kl}\sum_{mm'}\zeta_{ik}^{m0}\zeta_{il}^{m'0}(\tfrac{4}{9}-\tfrac{2}{3}n_l-\tfrac{2}{3}n_k+n_kn_l)R_{m,m'}^i. \tag{A14c}$$

The term involving $\frac{4}{9}$ is readily evaluated using Eq. (A12):

$$\frac{1}{2}\sum_i\sum_{kl}\sum_{mm'}\zeta_{ik}^{m0}\zeta_{il}^{m'0}(\tfrac{4}{9}).R_{m,m'}^i=\tfrac{1}{2}E_O^2\sum_iR_{00}^i=\sum_i(\tfrac{3}{7}-\tfrac{1}{7}n_i)E_O^2\ . \tag{A15}$$

For the other terms in Eq. (A14c) we set $R_{m,m'}^i$ equal to its value in the ground state, so that $m+m'=0$ and within the single-libron manifold we may write

$$\frac{1}{2}\sum_i\sum_{kl}\sum_{mm'}\zeta_{ik}^{m0}\zeta_{il}^{m'0}(-\tfrac{2}{3}n_k-\tfrac{2}{3}n_l+n_kn_l)R_{m,m'}^i=-\tfrac{9}{14}E_O^2\sum_kn_k-\tfrac{9}{14}E_O^2\sum_ln_l+\frac{1}{2}\sum_{ikm}|\zeta_{ik}^{m0}|^2r_mn_k\ . \tag{A16}$$

Thus,

$$h^a=\tfrac{3}{7}NE_O^2+\sum_kn_k[-\tfrac{10}{7}E_O^2+A]\ , \tag{A17}$$

where N is the number of molecules and

$$A=\frac{1}{2}\sum_mr_m\mathcal{S}_{0m}\ . \tag{A18}$$

In h^b and h^c we use, for $n\neq 0$,

$$\mathcal{O}_k^n\mathcal{O}_l{}^0=[-\tfrac{2}{3}\mathcal{O}_k^n(1-\delta_{lk})+\delta_{kl}\mathcal{O}_k^n\mathcal{O}_l^0]\ , \tag{A19}$$

which includes correctly all harmonic terms. Then we may write

$$h^b+h^c=\sum_i\sum_{kl}\sum_{mm'}\sum_{n\neq 0}\zeta_{il}^{m'0}\zeta_{ik}^{mn}(-\tfrac{2}{3}\mathcal{O}_k^n)R_{m,m'}^i+\sum_i\sum_k\sum_{mm'}\sum_{n\neq 0}\zeta_{ik}^{mn}\zeta_{ik}^{m'0}[\tfrac{2}{3}\mathcal{O}_k^0+\tfrac{1}{2}T_{0,n}^k]R_{m,m'}^i$$

$$+\sum_i \sum_k \sum_{mm'} \sum_{n\neq 0} \zeta_{ik}^{m'0}\zeta_{ik}^{mn}(\tfrac{1}{2}U^k_{n,0})S^i_{m,m'} , \quad \text{(A20)}$$

where R, S, T, and U were given in Eq. (A6). Consider the first term in this equation. Terms with two libron operators (i.e., harmonic terms) have either $n=\pm 1$ and $m+m'=\pm 1$ or $n=2$ and $m+m'=0$. The latter terms vanish because

$$\sum_{il} \zeta_{il}^{m'0}\zeta_{ik}^{mn}=0 , \quad n\neq 0 . \quad \text{(A21)}$$

Thus the harmonic contributions are correctly given by

$$-\frac{2}{3}\sum_i \sum_{kl} \sum_{mm'} \sum_{n\neq 0} \zeta_{il}^{m'0}\zeta_{ik}^{mn}\mathcal{O}_k^n R^i_{n,m'}$$

$$=-\tfrac{1}{7}E_O\sum_{ik} {\sum_{mm'}}' \zeta_{ik}^{mm'}\mathcal{O}_i^m\mathcal{O}_k^m , \quad \text{(A22)}$$

where the prime indicates m, $m'=\pm 1$ and we have used

$$R^i_{\pm 1,0}=-\tfrac{1}{7}\mathcal{O}_2^{\pm 1}(i) . \quad \text{(A23)}$$

The second and third terms in Eq. (A20), likewise, have harmonic contributions only for $n=\pm 1$ and $m+m'=\pm 1$. Thus, we have

$$h^b+h^c=-\tfrac{1}{7}E_O\sum_{ik} {\sum_{mm'}}' \zeta_{ik}^{mm'}\mathcal{O}_2^m(i)\mathcal{O}_2^{m'}(k)$$

$$+\sum_{ik} {\sum_{mm'}}' D_{ik}^{mm'}\mathcal{O}_2^m(i)\mathcal{O}_2^{m'}(k)$$

$$+\sum_{ik} {\sum_{mm'}}' E_{ik}^{mm'}\mathcal{O}_1^m(i)\mathcal{O}_1^{m'}(k) , \quad \text{(A24)}$$

where, for $n=\pm 1$, we have

$$D_{ik}^{1n}=\tfrac{1}{14}[3\zeta_{ik}^{-10}\zeta_{ik}^{2n}+3\zeta_{ik}^{20}\zeta_{ik}^{-1n}-\zeta_{ik}^{00}\zeta_{ik}^{1n}-\zeta_{ik}^{10}\zeta_{ik}^{0n}] , \quad \text{(A25a)}$$

$$D_{ik}^{1n}=(D_{ik}^{1-n})^* , \quad \text{(A25b)}$$

$$E_{ik}^{1n}=\tfrac{1}{2}n[\zeta_{ik}^{-10}\zeta_{ik}^{2n}-\zeta_{ik}^{20}\zeta_{ik}^{-1n}-\zeta_{ik}^{00}\zeta_{ik}^{1n}+\zeta_{ik}^{10}\zeta_{ik}^{0n}] , \quad \text{(A25c)}$$

$$E_{ik}^{-1n}=(E_{ik}^{1-n})^* . \quad \text{(A25d)}$$

Now we examine h^d:

$$h^d=\sum_i \sum_{kl} \sum_{mm'} \sum_{n,n'\neq 0} \zeta_{ik}^{mn}\zeta_{il}^{m'n'}\mathcal{O}_k^n\mathcal{O}_l^{n'}$$

$$\times(1-\delta_{kl})\delta_{m+m',0}(-1)^m\gamma_m$$

$$+\sum_{ik} \sum_{mm'} \sum_{n,n'\neq 0} \zeta_{ik}^{mn}\zeta_{ik}^{m'n'}\mathcal{O}_k^n\mathcal{O}_k^{n'}\{\mathcal{O}_2^m(i)P_i\mathcal{O}_1^{m'}(i)\} . \quad \text{(A26)}$$

Again we have dropped terms involving more than two librons. The first line gives a contribution

$$\sum_{kl} {\sum_{mm'}}' \hat{\zeta}_{kl}^{mm'}\mathcal{O}_2^m(k)\mathcal{O}_2^{m'}(l) , \quad \text{(A27)}$$

where

$$\hat{\zeta}_{kl}^{mm'}=(1-\delta_{kl})\sum_{in} \zeta_{ik}^{nm}\zeta_{il}^{-nm'}(-1)^n\gamma_m . \quad \text{(A28)}$$

To evaluate the second term in Eq. (A26) we write it as

$$\frac{1}{4}\sum_{ik} \sum_{mm'} \sum_{n,n'\neq 0} \zeta_{ik}^{mn}\zeta_{ik}^{m'n'}[T^k_{n,n'}R^i_{m,m'}+U^k_{n,n'}S^i_{m,m'}]\equiv h_2^d \quad \text{(A29)}$$

and set

$$R^i_{m,m'}=(-1)^m\gamma_m\delta_{m+m',0}+\delta R^i_{m,m'}$$

$$T^i_{m,m'}=(-1)^m t_m\delta_{m+m',0}+\delta T^i_{m,m'} . \quad \text{(A30)}$$

Here δR and δT involve at least one libron each. Also $U_{m,m'}$ and $S_{m,m'}$ vanish in the ground state and hence they each involve at least one libron. Thus,

$$h_2^d=\frac{1}{4}\sum_{ik} \sum_m \sum_{n\neq 0} |\zeta_{ik}^{mn}|^2 t_n\gamma_m$$

$$+\frac{1}{4}\sum_{ik} \sum_m \sum_{n\neq 0} |\zeta_{ik}^{mn}|^2 t_n(-1)^m\delta R^i_{m,-m}$$

$$+\frac{1}{4}\sum_{ik} \sum_m \sum_{n\neq 0} |\zeta_{ik}^{mn}|^2\gamma_m(-1)^n\delta T^k_{n,-n}$$

$$+\frac{1}{4}\sum_{ik} {\sum_{mm'}}' \sum_{n,n'\neq 0} \zeta_{ik}^{mn}\zeta_{ik}^{m'n'}$$

$$\times[\delta T^k_{n,n'}\delta R^i_{m,m'}+U^k_{n,n'}S^i_{m,m'}] . \quad \text{(A31)}$$

In the last line the only terms of interest are those for which $m+m'=\pm 1$ and $n+n'=\pm 1$. Since h_{ij} gives rise to similar terms, we consider it now:

$$\sum_{ij} \tfrac{1}{4}h_{ij}=\frac{1}{16}\sum_{ik} \sum_{mn} |\zeta_{ik}^{mn}|^2\gamma_\eta\gamma_m+\frac{1}{16}\sum_{ik} \sum_{mn} |\zeta_{ik}^{mn}|^2\gamma_n(-1)^m\delta R^i_{m,-m}$$

$$+\frac{1}{16}\sum_{ik} \sum_{mn} |\zeta_{ik}^{mn}|^2\gamma_m(-)^n\delta R^i_{n,-n}+\frac{1}{16}\sum_{ik} \sum_{mm'} \sum_{nn'} \zeta_{ik}^{mn}\zeta_{ik}^{m'n'}[\delta R^k_{n,n'}\delta R^i_{m,m'}+S^k_{n,n'}S^i_{m,m'}] . \quad \text{(A32)}$$

Collecting all these results, we have

$$-10B\mathcal{H}_{\text{eff}}=E_G^{\text{eff}}+E_O^{\text{eff}}\sum_l n_l+\sum_{ik} {\sum_{mn}}' \Omega_{ik}^{mn}\mathcal{O}_2^m(i)\mathcal{O}_2^n(k)+\sum_{ik} {\sum_{mn}}' \Lambda_{ik}^{mn}\mathcal{O}_1^m(i)\mathcal{O}_1^n(k) , \quad \text{(A33)}$$

where

$$N^{-1}E_G^{\text{eff}}=\tfrac{3}{7}E_Q^2+\frac{1}{4}\sum_m \sum_{n\neq 0} s_{mn}\gamma_m(t_n+\tfrac{1}{4}\gamma_n) , \quad \text{(A34a)}$$

$$E_O^{\mathrm{eff}} = -\tfrac{10}{7} E_O^2 + \frac{1}{2} \sum_m r_m s_{0m} + \frac{1}{4} \sum_m \sum_{n\neq 0} s_{mn} r_m \delta t_n + \frac{1}{4} \sum_{mn} s_{mn} \delta r_m [t_n(1-\delta_{n0}) + \tfrac{1}{2} r_n] \ , \tag{A34b}$$

$$\Omega_{ik}^{mn} = -\tfrac{1}{7} E_O \zeta_{ik}^{mn} + D_{ik}^{mn} + \hat{\zeta}_{ik}^{mn} + \frac{1}{4} \sum_{\mu\nu} \sum_{\mu'\nu'} \delta_{m,\mu+\mu'} \delta_{n,\nu+\nu'} \zeta_{ik}^{\mu\nu} \zeta_{ik}^{\mu'\nu'} \left(\frac{A_1}{A_\mu} \frac{A_1}{A_\nu} \frac{A_1}{A_{\mu'}} \frac{A_1}{A_{\nu'}} \right) \times C(222; \mu\mu') C(222; \nu\nu') [2(1-\delta_{\nu 0})(1-\delta_{\nu' 0}) + \tfrac{3}{14}] \ , \tag{A34c}$$

$$\Lambda_{ik}^{mn} = E_{ik}^{mn} + \frac{1}{4} \sum_{\mu\nu} \sum_{\mu'\nu'} \delta_{m,\mu+\mu'} \delta_{n,\nu+\nu'} \zeta_{ik}^{\mu\nu} \zeta_{ik}^{\mu'\nu'} \left(\frac{A_1}{A_\mu} \frac{A_1}{A_\nu} \frac{A_1}{A_{\mu'}} \frac{A_1}{A_{\nu'}} \right) \times C(221; \mu\mu') C(221; \nu\nu') [-10(1-\delta_{\nu 0})(1-\delta_{\nu' 0}) + \tfrac{5}{2}] \ . \tag{A34d}$$

Numerically, we find

$$N^{-1} E_G^{\mathrm{eff}} = 320.2 \Gamma^2 \ , \tag{A35a}$$

$$E_O^{\mathrm{eff}} = -452.1 \Gamma^2 \ . \tag{A35b}$$

The terms in Ω and Λ seem to be somewhat smaller and for D_2 they lead to energy shifts of order 1% or less. This is a consequence of the fact that terms in E_O^2 are of order z^2, where z is the number of nearest neighbors, whereas the other terms are of order z. Note that Eq. (A35a) gives a shift in the ground-state energy per molecule of

$$-32.02 \Gamma^2 / B \ , \tag{A36}$$

which is more than a 10% effect in the energy for D_2.

APPENDIX B: FORMULA FOR SPECIFIC HEAT OF SYSTEMS WITH CUBIC ANHARMONICITY

For the usual Hamiltonian with two-body interactions,

$$\mathcal{H}_1 = \sum_k \epsilon_k a_k^\dagger a_k + \sum_{k_1,k_2,k_3,k_4} V(k_1, k_2; k_3, k_4) a_{k_1}^\dagger a_{k_2}^\dagger a_{k_3} a_{k_4} \ , \tag{B1}$$

the internal energy is given by

$$U = \frac{1}{2} \sum_k \int \frac{d\omega}{2\pi} n(\omega) \rho(k;\omega)(\omega + \epsilon_k) \ , \tag{B2}$$

where ρ is the single-particle spectral weight function,

$$\rho(k;\omega) = i[\langle\langle a_k; a_k^\dagger \rangle\rangle_{\omega+i0^+} - \langle\langle a_k; a_k^\dagger \rangle\rangle_{\omega-i0^+}] \ , \tag{B3}$$

where $\langle\langle a; a_k^\dagger \rangle\rangle_\omega$ is the Green's function in Zubarev's notation.[27] We restrict our discussion to the case of boson operators a_k in which it is most convenient to use commutator Green's functions, so that $n(\omega) = (e^{\beta\omega} - 1)^{-1}$.

We wish to obtain an analogous formula for a Hamiltonian with cubic interactions, which is of the form

$$\mathcal{H} = \sum_k \epsilon_k a_k^\dagger a_k + \frac{1}{2} \sum_{k_1,k_2,k_3} [B(k_1, k_2, k_3) a_{k_1}^\dagger a_{k_2}^\dagger a_{k_3} + \mathrm{H.c.}] + \frac{1}{6} \sum_{k_1,k_2,k_3} [C(k_1, k_2, k_3) a_{k_1}^\dagger a_{k_2}^\dagger a_{k_3}^\dagger + \mathrm{H.c.}] \ , \tag{B4}$$

where H.c. denotes the Hermitian conjugate of the preceding term. The derivation will be based on the relations

$$\langle BA \rangle = \frac{1}{2\pi i} \int_{-\infty}^{+\infty} d\omega\, n(\omega) [\langle\langle A; B \rangle\rangle_{\omega-i0^+} - \langle\langle A; B \rangle\rangle_{\omega+i0^+}] \ , \tag{B5}$$

$$\omega \langle\langle A; B \rangle\rangle_\omega = \langle [A, B] \rangle + \langle\langle [A, \mathcal{H}]; B \rangle\rangle_\omega \ , \tag{B6a}$$

$$\omega \langle\langle A; B \rangle\rangle_\omega = \langle [A, B] \rangle + \langle\langle A; [H, B] \rangle\rangle_\omega \ . \tag{B6b}$$

For the Hamiltonian of Eq. (B4), Eq. (B6a) yields

$$\omega \langle\langle a_k; a_k^\dagger \rangle\rangle_\omega = 1 + \epsilon_k \langle\langle a_k; a_k^\dagger \rangle\rangle_\omega + \sum_{k_2,k_3} B(k, k_2, k_3) \langle\langle a_{k_2}^\dagger a_{k_3}; a_k^\dagger \rangle\rangle_\omega + \sum_{k_1,k_2} \tfrac{1}{2} B(k_1, k_2, k)^* \langle\langle a_{k_1} a_{k_2}; a_k^\dagger \rangle\rangle + \sum_{k_2,k_3} \tfrac{1}{2} C(k, k_2, k_3) \langle\langle a_{k_2}^\dagger a_{k_3}^\dagger; a_k^\dagger \rangle\rangle \ , \tag{B7}$$

where we assume without loss of generality that B and C have been symmetrized. Use of Eqs. (B3) and (B5) then gives

$$\sum_k \int_{-\infty}^{+\infty} \rho(k;\omega) \omega n(\omega) \frac{d\omega}{2\pi} = \sum_k \epsilon_k \langle a_k^\dagger a_k \rangle + \sum_{k,k_2,k_3} B(k, k_2, k_3) \langle a_k^\dagger a_{k_2}^\dagger a_{k_3} \rangle + \sum_{k,k_2,k_3} \tfrac{1}{2} B(k_2, k_3, k)^* \langle a_k^\dagger a_{k_2} a_{k_3} \rangle + \sum_{k,k_2,k_3} \tfrac{1}{2} C(k, k_2, k_3) \langle a_k^\dagger a_{k_2}^\dagger a_{k_3}^\dagger \rangle \ . \tag{B8}$$

Similar use of Eq. (B6b) leads to the result

$$\sum_k \int_{-\infty}^{+\infty} \rho(k;\omega)\omega n(\omega)\,\frac{d\omega}{2\pi} = \sum_k \epsilon_k\langle a_k^\dagger a_k\rangle + \sum_{k,k_2,k_3} \tfrac{1}{2} B(k,k_2,k_3)\langle a_k^\dagger a_{k_2}^\dagger a_{k_3}\rangle + \sum_{k,k_2,k_3} B(k_2,k_3,k)^*\langle a_k^\dagger a_{k_2} a_{k_3}\rangle + \sum_{k,k_2,k_3} \tfrac{1}{2} C(k,k_2,k_3)^*\langle a_{k_2} a_{k_3} a_k\rangle \ . \tag{B9}$$

Adding Eqs. (B8) and (B9) and dividing by 3 yields

$$\frac{2}{3}\sum_k \int_{-\infty}^{+\infty} \rho(k;\omega)\omega n(\omega)\,\frac{d\omega}{2\pi} = \langle H\rangle - \frac{1}{3}\sum_k \epsilon_k\langle a_k^\dagger a_k\rangle \ . \tag{B10}$$

Expressing the last term in Eq. (B10) in terms of the spectral weight function as in Eq. (B5), we obtain

$$U = \sum_k \int_{-\infty}^{-\infty} \rho(k;\omega) n(\omega)\left[\tfrac{2}{3}\omega + \tfrac{1}{3}\epsilon_k\right] \ , \tag{B11}$$

which is the desired analog of Eq. (B2).

If the harmonic normal modes are labeled by a mode index τ, then one has

$$U = \sum_{k,\tau} \int_{-\infty}^{+\infty} \rho(k,\tau;\omega) n(\omega)\left[\tfrac{2}{3}\omega + \tfrac{1}{3}\epsilon_{k,\tau}\right] \ , \tag{B12}$$

where $\epsilon_{k,\tau}$ is the harmonic energy of the τth normal mode created by $a_{k\tau}^\dagger$ and $\rho(k,\tau;\omega)$ is the spectral weight function for the Green's function $\langle\langle a_{k\tau}; a_{k\tau}^\dagger\rangle\rangle_\omega$.

We will now obtain an approximate evaluation of the specific heat based on Eq. (B12). We write

$$\frac{C}{R} = \frac{1}{R}\frac{dU}{dT} = \frac{1}{N}\sum_{k,\tau}\int_{-\infty}^{+\infty}\frac{d\omega}{2\pi}\left(\rho(k,\tau;\omega)\,\frac{dn(\omega)}{dk_BT} \times\left[\tfrac{2}{3}\hbar\omega + \tfrac{1}{3}\epsilon_{k,\tau}\right] + \frac{d\rho(k,\tau;\omega)}{dk_BT}\,n(\omega)\left[\tfrac{2}{3}\hbar\omega + \tfrac{1}{3}\epsilon_{k,\tau}\right]\right). \tag{B13}$$

The specific heat will have contributions of order $e^{-\beta E_L}$, which we will keep, and those of order $e^{-2\beta E_L}$ or smaller, which will be neglected. For instance, $d\rho/dk_BT \sim e^{-\beta E_L}$ and $n(\omega)$ is of order $e^{-\beta E_L}$; so we drop the last term in Eq. (B13). Also note that

$$\frac{dn(\omega)}{dk_BT} = \frac{\hbar\omega}{(k_BT)^2}\left(\frac{e^{-\beta\omega}}{1-e^{-\beta\omega}}\right)^2 \equiv \frac{1}{\hbar\omega}\,C(\omega) \ ,$$

so that

$$\frac{C}{R} = \frac{1}{N}\sum_{k,\tau}\int_{-\infty}^{+\infty}\frac{d\omega}{2\pi}\,\rho(k,\tau;\omega)C(\omega)\left[\frac{2}{3} + \frac{1}{3}\,\frac{\epsilon_{k,\tau}}{\hbar\omega}\right] \ . \tag{B14}$$

Since we are neglecting contributions of order $e^{-2\beta E_L}$, we only need to carry the integration over the single-libron band. Then we may replace ω by the average anharmonic libron energy E_L which is approximately $E_L = 16.0\Gamma$. By contrast, the harmonic-libron energy $\epsilon_{k,\tau}$ on the average is $E_0 = 21.2\Gamma$. Accordingly, we set

$$\epsilon_{k,\tau}/\hbar\omega = E_0/E_L \ . \tag{B15}$$

Now we consider the behavior of $\rho(k,\tau;\omega)$ in single-libron band. Including cubic anharmonicity, we have approximately

$$G(k,\tau;\omega) = \left(\omega - \epsilon_{k,\tau} - \frac{|V_3|^2}{\omega - 2E_L}\right)^{-1} \ . \tag{B16}$$

In writing this equation we used the fact that the C coefficients of Eq. (B4) are much smaller than the B coefficients, schematically represented here as V_3. For $\hbar\omega \approx \epsilon_{k,\tau}$, Eq. (B16) becomes

$$G(k,\tau;\omega) \approx \frac{1}{\omega - \tilde{\epsilon}_{k,\tau}}\left(1 + \frac{|V_3|^2}{(\tilde{\epsilon}_{k,\tau} - 2E_L)^2}\right)^{-1} \ , \tag{B17}$$

where $\tilde{\epsilon}_{k,\tau}$ is the anharmonic libron energy found by setting $G^{-1} = 0$. From Eq. (B17), we see that

$$(1/2\pi)\,\rho(k;\tau;\omega) \approx P_{k,\tau}\delta(\omega - \tilde{\epsilon}_{k,\tau}) \ , \tag{B18}$$

where

$$P_{k,\tau} = \left(1 + \frac{|V_3|^2}{(\tilde{\epsilon}_{k,\tau} - 2E_L)^2}\right)^{-1} \ . \tag{B19}$$

We now replace $P_{k,\tau}$ by its average value $\overline{P}$, which is estimated to be

$$\overline{P} = [1 + (V_3/E_L)^2]^{-1} \ . \tag{B20}$$

Thus, we write

$$\frac{C}{R} = \overline{P}\int d\omega\,\hat{\rho}(\omega)C(\omega)\left[\frac{2}{3} + \frac{1}{3}\,\frac{E_0}{E_L}\right] \tag{B21a}$$

$$= \frac{E_L^2}{E_L^2 + |V_3|^2}\,\frac{2E_L + E_0}{3E_L}\int d\omega\,\hat{\rho}(\omega)C(\omega) \ , \tag{B21b}$$

where $\hat{\rho}(\omega)$ is the anharmonic density of single-libron states:

$$\hat{\rho}(\omega) = N^{-1}\sum_{k,\tau}\delta(\omega - \tilde{\epsilon}_{k,\tau}) \tag{B22}$$

Since the number of k vectors is equal to the number of unit cells $\frac{1}{4}N$ and since τ ranges over the eight modes, we see that $\hat{\rho}(\omega)$ is normalized so that

$$\int_{-\infty}^{+\infty}\hat{\rho}(\omega)\,d\omega = 2 \ . \tag{B23}$$

APPENDIX C: INTENSITY OF THE LIBRON SIDEBAND IN THE INFRARED SPECTRUM

In this Appendix we estimate the relative intensities J_1 and J_2 of the infrared absorption processes

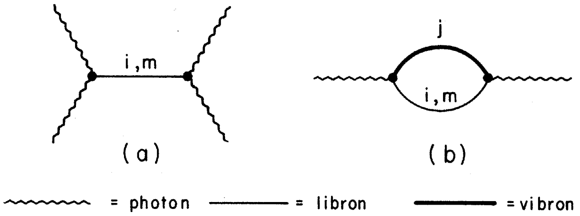


FIG. 6. Diagrammatic representation of (a) harmonic Raman and (b) infrared processes. Here the wavy lines represent photons, the thin lines represent librons (with site and magnetic quantum numbers as indices), and the heavy lines represent vibrons (with site indices).

in which a vibron and, respectively, one and two librons are created. We compare the ratio J_2/J_1 to I_2/I_1, where I_1 and I_2 are the intensities of the one- and two-libron Raman processes, respectively.

For simplicity, we initially disregard the effect of zero-point motion by dropping all terms in the Hamiltonian which do not vanish when applied to the state having no excitations. In other words, we assume that the harmonic librons and vibrons are described by Hamiltonians of the form

$$\mathcal{H}_L = E_0 \sum_{i,m} n_{i,m} + \sum_{i,j;m,m'} R_{i,j}^{m,m'} c_{i,m}^\dagger c_{j,m'} \tag{C1a}$$

and

$$\mathcal{H}_V = E_V \sum_{i} n_i + \sum_{i,j} R_{i,j} b_i^\dagger b_j \quad , \tag{C1b}$$

respectively, where $c_{i,m}^\dagger$ creates a librational excitation with $\Delta J_Z = m$ on the ith site, $b_i^\dagger$ creates a vibronic excitation on the ith site, $n_{i,m} = c_{i,m}^\dagger c_{i,m}$, and $n_i = b_i^\dagger b_i$. For the purposes of estimating intensities, it is well known that a localized calculation in which the "hopping" terms in Eqs. (C1) are neglected is a good approximation.

In the localized picture the interaction with photons is of the form

$$V_R = \sum_{i,m} A_{i,m}^R (c_{i,m}^\dagger - c_{i,-m}) + \text{H.c.} \quad , \tag{C2a}$$

$$V_I = \sum_{i,j,m} A_{i,j;m}^I (c_{i,m}^\dagger - c_{i,-m}) b_j^\dagger + \text{H.c.} \tag{C2b}$$

for the Raman[1,15] and infrared[23,28] processes, respectively. Here H.c. denotes the Hermitian conjugate of the preceding term, $A_{i,m}^R$ is a matrix element for photon scattering, and $A_{i,j;m}^I$ is a matrix element for photon absorption. Absorption is allowed because in the presence of a vibron the librons no longer have even symmetry. It is found[28] that $A_{i,j;m}^I \propto r_{ij}^{-4}$ and we shall neglect it when i and j are not nearest neighbors. The harmonic model predicts a one-libron Raman process and an absorption when a vibron and a libron are created on neighboring sites. These processes are represented schematically in Fig. 6.

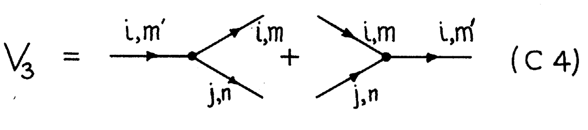


FIG. 7. Diagrammatic Eq. (C4).

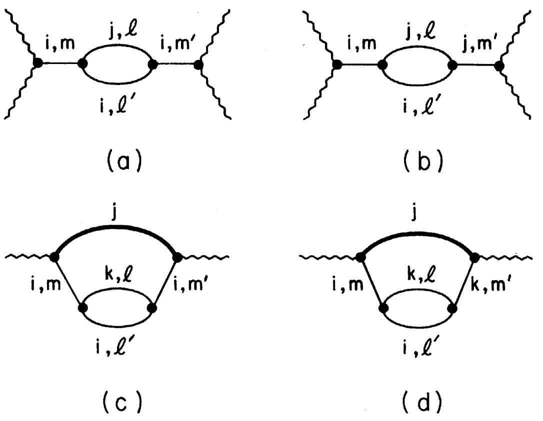


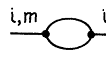
FIG. 8. Diagrammatic representation of (a) and (b) anharmonic Raman and (c) and (d) infrared processes. The conventions are the same as for Fig. 6.

The creation of two librons in such experiments has been shown[2] to arise from anharmonic processes in which a virtual libron decays into two librons under the cubic anharmonic libron-libron interaction V_3, where V_3 is

$$V_3 = \sum_{i,j} \sum_{m,m',n} \{ \zeta_{ij}^{m-m',n} c_{i,m}^\dagger c_{i,m'} c_{j,n}^\dagger + (\zeta_{ij}^{m-m',n})^* c_{i,m'}^\dagger c_{i,m} c_{j,n} \} \tag{C3}$$

and may be represented diagrammatically by Eq. (C4) as shown in Fig. 7 with matrix elements given in Eq. (C3). The Raman and infrared cross sections for two-libron processes are then given by the diagrams shown in Fig. 8.

Note that for the Raman spectrum there are "local" and "nonlocal" processes as shown in Figs. 8(a) and 8(b), respectively. For the infrared absorption, one need consider only the "local" processes shown in Fig. 8(c). The "nonlocal" process shown in Fig. 8(d) is negligible because it requires sites i and k both to be nearest neighbors of site j. In contrast, for the process of Fig. 8(b) there is no such restriction. One might argue that the vibron in Fig. 8(d) could propagate from a site adjacent to i to one adjacent to k. But since only the total momentum of the vibron plus libron(s) is fixed to be zero, the vibron momentum ranges over the entire Brillouin zone. Propagation is then an in-



$$= \frac{1}{E_L^2} \sum_{m'',n}' \sum_j \zeta_{ij}^{m''-m,n} \left(\zeta^{m''-m',n}\right)^* \quad \text{(C 5a)}$$

$$= \delta_{m,m'} \; 84.79 \, \Gamma^2/E_L^2 \quad \text{(C 5b)}$$

FIG. 9. Diagrammatic Eqs. (C5a) and (C5b).

coherent process and the nonlocal matrix element will be averaged approximately to be zero. Hence, we estimate J_2 from diagram 8(c) and I_2 for diagrams 8(a) and 8(b).

From the work of Ref. 1 we see that in estimating total intensities in the two-libron band we may set the relations (C5a) and (C5b) shown in Fig. 9. Using this result and comparing Figs. 6(b) and 8(c), we have that

$$J_2/J_1 = 84.79\Gamma^2/E_L^2 \ . \quad \text{(C6)}$$

A similar calculation enables us to evaluate the contribution from Fig. 8(a). To evaluate Fig. 8(b) we need the explicit form of $A^R_{i,m}(A^R_{j,m'})^*$. For the Raman spectrum on a powder sample the result given in Ref. 1 may be written

$$A^R_{i,m}(A^R_{j,m'})^* = D^{(2)}_{m',m}(\chi_{ji})^* \ , \quad \text{(C7)}$$

where D is a rotation matrix and χ_{ji} is the set of Euler angles which take the coordinate system based on the equilibrium orientation of the jth molecule into that of the ith molecule. Thus,

$$\frac{I_2}{I_1} = \frac{84.79\Gamma^2}{E_L^2} + \sum_j \sum_{mm'} \sum_{nn'} D^{(2)}_{m',m}(\chi_{ji})^* \times \zeta_{ij}^{n'-m,n}(\zeta_{ij}^{n',n-m'})^*/E_L^2 \sum_{jm} D^{(2)}_{m,m}(\chi_{jj}) \quad \text{(C8a)}$$

$$= 84.79\Gamma^2/E_L^2 - 30.18\Gamma^2/E_L^2 = 54.61\Gamma^2/E_L^2 \ . \quad \text{(C8b)}$$

So in all,

$$\frac{J_2/J_1}{I_2/I_1} = \frac{84.79}{54.61} = 1.55 \ . \quad \text{(C9)}$$

This result suggests that the two-libron processes should be rather more prominent in the infrared spectrum than in the Raman spectrum. From the experimental results of Refs. 3 and 6 we have $I_2/I_1 \approx 0.2$ and $J_2/J_1 \approx 0.5$ so that experimentally the ratio in Eq. (C9) is found to be about 2.5.

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*The portion of the work done at the University of Pennsylvania was supported in part by the National Science Foundation; the work done at Duke University was supported in part by the U.S. Army Research Office (Durham) and the Office of Naval Research.

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