

## Theoretical analysis of inelastic neutron scattering in solid hydrogen\*

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(Received 11 August 1975)

The inelastic-neutron-scattering cross section of ( $J = 1$ ) solid hydrogen is studied and the experimental data of Stein and co-workers analyzed. The rms displacement  $\langle u^2 \rangle^{1/2}$  is deduced from the data via different methods and mutually consistent values of order 0.65 Å are obtained. The enhancement of the cross section at the libron energy due to libron-phonon interactions is found to be the same, about 40% each for both one- and two-libron processes, in agreement with the neutron scattering data. The rms splitting at the libron-phonon crossovers is found to be about  $1 \text{ cm}^{-1}$ , somewhat smaller than found by Mertens and Biem. A sum rule for the  $J = 1$  to  $J = 0$  cross section is given which relates the average energy of this transition to the orientational internal energy. Using high-temperature expansions and experimental data for the specific heat, we obtain a qualitative fit to the neutron scattering data in the orientationally disordered phase. In the ordered phase both the sum rule and a direct calculation indicate the existence of a libron sideband above the main  $J = 1$  to  $J = 0$  line having an intensity of 10% of the main line. The energy of the main line at zero temperature is calculated including (a) tipping corrections, (b) virtual excitations with  $J$  not conserved, and (c) modified zero-point energy. The value of the electrostatic quadrupole-quadrupole coupling constant deduced from the data of Stein and co-workers using this calculation is in agreement with that obtained from other experiments.

### I. INTRODUCTION

In the past several years there has been great interest in the orientational ordering of the molecules in the solid hydrogens,  $\text{H}_2$  and  $\text{D}_2$ , and in the elementary excitations out of the ground state. These orientational excitations, called librions, were first studied by Homma *et al.*<sup>1</sup> and by Ueyama and Matsubara.<sup>2</sup> Subsequently, a number of calculations appeared,<sup>3,4</sup> essentially confirming the spectrum of Ueyama and Matsubara, who considered nearest-neighbor electrostatic quadrupole-quadrupole (EQQ) interactions within a harmonic theory in which the rotational quantum number  $J$  is conserved, which is analogous to that given for spin waves.<sup>5</sup> Later, extensions to include farther-neighbor EQQ interactions were given.<sup>6-8</sup>

More recently, it was shown<sup>9-11</sup> that even a qualitative understanding of the optically observed<sup>12,13</sup> libron spectrum required the inclusion of libron-libron interactions, which are predominantly cubic in the libron amplitudes.<sup>7,10</sup> In addition, it was shown<sup>14</sup> the virtual states in which  $J$  is not conserved produce effects which can be important, especially for the orientationally ordered state and/or for solid  $\text{D}_2$ .

In all these works, the coupling between librions and phonons was unimportant. However, with the advent of neutron scattering experiments<sup>15-23</sup> on solid hydrogen, libron-phonon interactions

have become potentially observable, as was indicated by Stein *et al.*,<sup>21</sup> who showed that for the momentum transfer of their experiment the ratio of the cross section of phonons to that of librions is of order 500. Thus, even small phonon admixtures into the libron modes might be detectable.

Some calculations of the effects of libron-phonon coupling have already been done<sup>24,25</sup> using a Hartree formulation for quantum crystals. These calculations are numerically quite complicated, because, for the coupled system, there are 20 normal modes, 12 phonons, and 8 librions. There are two reasons why we give here a numerically simplified treatment in the face of existing detailed numerical work. First of all, in our calculation we can include a variety of interactions. In particular, cubic anharmonic interactions where either one phonon or one libron decays into two librions are handled in our calculation. Second, using a simple two-mode Hamiltonian we get an idea of the order of magnitude and of the details of the mechanism which numerical work does not always elucidate. This is especially true in the calculation of the phononlike admixtures into the libron modes, which we find to be an order of magnitude smaller than those of Bickermann *et al.*<sup>25</sup>

Neutron scattering provides other types of useful information. In particular, we reexamine the analysis of the phonon spectrum and remove the

inconsistencies in the values of the mean-square displacement  $\langle u^2 \rangle$  which Stein *et al.* have deduced from their experiment.<sup>21</sup> Also, we calculate the position of the conversion line, both in the fcc ordered phase and in the hcp disordered phase. The former calculation includes a number of effects suggested previously,<sup>14</sup> and leads to a determination of the EQQ coupling constant  $\Gamma$  which agrees with values obtained from other experiments.<sup>26</sup> The latter calculation relates the average energy associated with ortho-para conversion,  $\langle E_c \rangle$ , to  $U(x, T)$ , where  $x$  is the ortho concentration and  $U(x, T)$  is essentially the orientational internal energy. By using high-temperature expansions<sup>27</sup> and experimental data<sup>28,29</sup> for the specific heat, we obtain qualitative agreement between our sum rule and the experimental data of Stein *et al.*<sup>21</sup> The sum rule also indicates the existence of a libron sideband above the conversion line, an effect which is corroborated by direct calculation.

Our main conclusion is that the inelastic-neutron-scattering cross section of solid H<sub>2</sub> is qualitatively understood, although some details remain to be settled. However, new experiments at higher resolution are needed to better define the experimental situation.

Briefly, this paper is organized as follows. In Sec. II we reanalyze the phonon cross section and show that the various methods for deducing  $\langle u^2 \rangle$  are mutually consistent. Sections III–V are concerned with libron-phonon coupling. The form of the coupling is given in Sec. III. Calculations of the average splitting at the libron-phonon crossover are presented in Sec. IV. The enhancement of the neutron scattering cross section of librions due to libron-phonon coupling is discussed via a simple model in Sec. V and in more detail in Appendices B and D. In Sec. VI we obtain the sum rule relating the average energy associated with ortho-para conversion to the orientational internal energy, and specific-heat data and high-temperature expansions are used to evaluate the sum rule. In Sec. VII we calculate the conversion energy and the intensity of the libron sideband in the ordered phase at zero temperature. Our conclusions are summarized in Sec. VIII. In appendices we discuss the evaluation of the libron-phonon force constants and some details of the calculation of the conversion energy at zero temperature in the ordered phase.

## II. REANALYSIS OF PHONON AND LIBRON SCATTERING CROSS SECTIONS

Incoherent-neutron-scattering experiments offer very detailed information about the elemen-

tary excitations of a solid because they probe the entire momentum range of the excitation spectra. In solid ortho-hydrogen in the ordered state, these excitations include phonons, librions, and transitions between rotational states ( $J = 1 \rightarrow 0$ ). To the extent that the translational and rotational degrees of freedom are uncoupled, the neutron spectrum which is observed is just a simple superposition of spectra caused by various combinations of these excitations. Thus the number  $N(K, \omega)$  of neutrons scattered per unit solid angle and per unit energy range for energy and momentum transfers  $\hbar\omega$  and  $\hbar K$  is given by

$$N(K, \omega) = \frac{K_F}{K_I} I_0 S(K, \omega) \equiv \frac{K_F}{K_I} \psi(K, \omega), \quad (2.1a)$$

where  $\hbar K_I$  and  $\hbar K_F$  are the incident and final momenta of the neutron,  $I_0$  depends on the spin-dependent part of the interaction of the neutron with the proton, on the incident neutron flux and the geometry of the detector, and  $S(K, \omega)$  is the normalized scattering function for which we adopt the approximation

$$S(K, \omega) = e^{-2W(K)} [S_{el}(K, \omega) + S_J(K, \omega) + S_P(K, \omega) + S_L(K, \omega) + S_{JP}(K, \omega)], \quad (2.1b)$$

where  $e^{-2W(K)}$  is the Debye-Waller factor. The second equality in Eq. (2.1a) defines a cross section normalized by  $I_0$ . In the harmonic approximation  $W$  is given by<sup>30</sup>

$$2W = \frac{1}{3} K^2 \langle u^2 \rangle, \quad (2.2)$$

where  $\langle u^2 \rangle$  is the mean-square average displacement of the hydrogen molecule.

The various terms in the square brackets of Eq. (2.1b) have the values (for  $T=0$ , in a linear theory)

$$S_{el}(K, \omega) = \frac{1}{2} [j_0^2(y) + \frac{4}{5} j_2^2(y)] \delta(\hbar\omega), \quad (2.3a)$$

$$S_J(K, \omega) = \frac{1}{4} j_1^2(y) \delta(\hbar\omega + E_{10}), \quad (2.3b)$$

$$S_P(K, \omega) = \left( \frac{\hbar^2 K^2}{4M} \right) [j_0^2(y) + \frac{4}{5} j_2^2(y)] \frac{g(\hbar\omega)}{\hbar\omega}, \quad (2.3c)$$

$$S_L(K, \omega) = \frac{3}{5} j_2^2(y) G(\hbar\omega), \quad (2.3d)$$

$$S_{JP}(K, \omega) = \frac{\hbar^2 K^2}{8M} j_1^2(y) \frac{g(\hbar\omega + E_{10})}{\hbar\omega + E_{10}}, \quad (2.3e)$$

as is discussed in Ref. 21. These terms correspond, respectively, to elastic scattering, scattering induced by a  $J = 1 \rightarrow 0$  transition, creation of a phonon, creation of a libron, and phonon creation in the presence of a  $J = 1 \rightarrow 0$  transition. The quantity  $y$  is given by  $y = \frac{1}{2} K\rho$ , where  $\rho = 0.735 \text{ \AA}$  is the

internuclear separation of the  $H_2$  molecule and  $M$  is the mass of a hydrogen molecule. The functions  $j_n(y)$ ,  $n=0, 1, 2$ , are the spherical Bessel functions of order  $n$ , and  $g(\hbar\omega)$  and  $G(\hbar\omega)$  are, respectively, the phonon and libron densities of states normalized so that their integral over energy is equal to 1;  $E_{10}$  is the energy released by the transition  $J=1-0$ . In Eq. (2.3c) we may replace  $j_0^2(y) + \frac{4}{5}j_2^2(y)$  by  $j_0^2(y)$  with an error of about 1% for the value of  $K$  of interest here.

Within the limits of the approximation which we have made, Eqs. (2.1)–(2.3) enable us to interpret an experimental spectrum and to extract the following information: (i) the constant  $I_0$  which is characteristic of the experimental apparatus [knowledge of this constant allows us to properly normalize the experimental data,  $\psi(K, \omega)$  in order to obtain  $S(K, \omega)$ ]; (ii) the value of  $\langle u^2 \rangle$ ; (iii) the normalized phonon density of states  $g(\hbar\omega)$ ; (iv) the normalized libron density of states  $G(\hbar\omega)$ .

We base our analysis upon the neutron scattering data of Stein *et al.* for the unnormalized cross section  $\psi(K, \omega)$  for 95% ortho-hydrogen at 1.1 K. These data are shown in Fig. 1. As can be seen, the contributions to  $\psi(K, \omega)$  from the various processes in Eq. (2.3) are separable and we write

$$\psi(K, \omega) = \sum_{\alpha} \psi_{\alpha}(K, \omega), \quad (2.4)$$

where  $\psi_{\alpha}(K, \omega) = I_0 e^{-W(K)} S_{\alpha}(K, \omega)$ , where  $\alpha$  ranges over the labels el,  $J, P$ , etc. The experiment was performed using a fixed-angle spectrometer with the initially monochromatic beam of neutrons being scattered through an angle of  $110^\circ$ . The incident energy was  $E_I = 8.8$  meV, and the momentum transfer is given by

$$\hbar K = [(\hbar K_I - \hbar K_F)^2 + 4\hbar^2 K_I K_F \sin^2 55^\circ]^{1/2}, \quad (2.5)$$

where

$$\hbar K_I = (2mE_I)^{1/2}, \quad (2.6a)$$

$$\hbar K_F = [2m(E_L - \hbar\omega)]^{1/2}, \quad (2.6b)$$

and  $m$  is the neutron mass. For elastic scattering  $\hbar\omega = 0$  and Eq. (2.5) becomes

$$\hbar K_{el} = 2 \sin 55^\circ (2mE_I)^{1/2}, \quad (2.7)$$

and  $K_{el} = 3.38 \text{ \AA}^{-1}$ .

To obtain the overall normalization of the scattering function, we begin by examining the elastic line, which has the desirable properties of being (i) very intense, so that the number of neutrons counted is statistically significant, and (ii) very narrow, so that the variation of  $K$  across its width is negligible. A convenient way to integrate the elastic line is to approximate it by a Gaussian curve of suitable height and width. An excellent approximation to the experimental data is obtained by putting

$$\begin{aligned} \psi_{el}(K, \omega) &\approx I_0 e^{-2W(K_{el})} S_{el}(K_{el}, \omega) \\ &= 2356 e^{-16.1(\hbar\omega)^2} / \text{meV} \end{aligned} \quad (2.8)$$

for  $\hbar\omega$  in meV. Integrating over energy and evaluating  $j_0(y_{el})$  and  $j_2(y_{el})$  we obtain the result

$$I_0 e^{-2W(K_{el})} = 3545. \quad (2.9)$$

Clearly we cannot yet evaluate the normalization constant  $I_0$  since we do not know  $\langle u^2 \rangle$  and thus cannot evaluate the Debye-Waller factor.

To proceed further it is necessary to compare the theoretical expressions Eq. (2.1)–(2.3) to some other feature of the experimental spectrum; and, in order for our determination of  $I_0$  and  $\langle u^2 \rangle$  to be reliable, this comparison should involve those features of the experiment which we understand the best. There are two aspects of the spectrum which we understand moderately well. These are (a) the intensity of the ortho-para conversion line, which is given by Eq. (2.3b), and (b) the gross features of the phonon scattering functions  $S_P$  and  $S_{JP}$ , namely, that  $S_P$  and  $S_{JP}$  both depend on the same function  $g(\hbar\omega)$ . As we shall see, the respective values of  $\langle u^2 \rangle$  obtained from the two features are quite consistent.

We continue our analysis by first using (a). The ortho-para conversion line may also be approximated by a Gaussian curve,

$$\psi_J(K, \omega + \hbar^{-1}E_{10}) \approx 30 e^{-1.34(\hbar\omega)^2} / \text{meV}, \quad (2.10)$$

and if we evaluate the Bessel function in Eq. (2.3b) using  $K_{10}$  obtained from Eqs. (2.5) and (2.6), we find that

$$I_0 e^{-2W(K_{10})} = 1090, \quad (2.11)$$

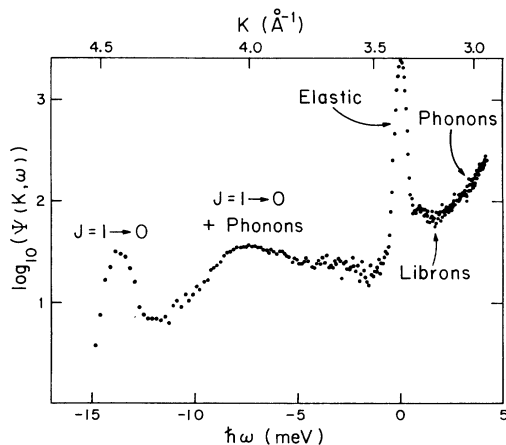


FIG. 1. Experimental values (Ref. 21) of  $\Psi(K, \omega) \equiv I_0 S(K, \omega)$  versus  $\omega$ . Note that  $K$  varies according to Eq. (2.5) as  $\omega$  is varied, since the incident energy is constant.

where  $K_{10} = 4.45 \text{ \AA}^{-1}$  is the value of  $K$  at the conversion line.

Comparing Eqs. (2.9) and (2.11) and using the definition of  $W(K)$  in Eq. (2.2) we obtain  $\langle u^2 \rangle = 0.42 \text{ \AA}^2$  and  $I_0 = 17\,200$ . The accuracy of these numerical results depends on our theoretical understanding of the ortho-para transition. In fact, in Sec. VII [see the discussion following Eq. (7.15)] we show that about 10% of the intensity associated with ortho-para conversion is shifted out of the main conversion line described by Eq. (2.10) into a libron sideband. This result suggests that we enhance the observed integrated intensity in Eq. (2.11) by 10%. This procedure yields

$$\langle u^2 \rangle = 0.39 \text{ \AA}^2, \quad (2.12a)$$

$$I_0 = 15\,000. \quad (2.12b)$$

Another way of getting at  $\langle u^2 \rangle$  and  $I_0$  involves the shape of the phonon curves  $S_P$  and  $S_{JP}$  at low energy. If we knew the value of  $\langle u^2 \rangle$  then we could evaluate the function  $I_0 g(\hbar\omega)$  independently from the two phonon scattering curves. Thus one way of evaluating  $\langle u^2 \rangle$  is to choose it by requiring that the densities of states evaluated from the two different scattering functions be equal. This is a more stringent requirement on  $\langle u^2 \rangle$  than requiring that  $g(\hbar\omega) \sim \omega^2$ , as was done in Ref. 21. In fact, instead of working with the density of states it will be more convenient to work with the functions

$$f_P(\omega, \eta^2) \equiv \left\{ (\hbar^2 K^2 / 4M) [j_0^2(y) + \frac{4}{5} j_2^2(y)] \right\}^{-1} \\ \times e^{K^2 \eta^2 / 3} \psi_P(K, \omega), \quad (2.13a)$$

$$f_{JP}(\omega, \eta^2) \equiv \left[ (\hbar^2 K^2 / 8M) j_1^2(y) \right]^{-1} \\ \times e^{K^2 \eta^2 / 3} \psi_{JP}(K, \omega - \hbar^{-1} E_{10}). \quad (2.13b)$$

Thus when  $\eta$  is chosen so that

$$f_P(\omega, \eta^2) = f_{JP}(\omega, \eta^2), \quad (2.14)$$

then

$$\eta^2 = \langle u^2 \rangle, \quad (2.15)$$

and

$$f_P(\omega, \langle u^2 \rangle) = f_{JP}(\omega, \langle u^2 \rangle) = I_0 g(\hbar\omega) / \hbar\omega. \quad (2.16)$$

The numerical work was based on a comparison of data points at energies between 2 and 3 meV to the right of the elastic and conversion lines. This choice was dictated by the fact that below 2 meV the scattering curve above the elastic line also contained a part due to librions. For energies more than 3 meV to the right of the elastic line, the scattering intensity increases so quickly as to be inconsistent with the curve  $S_{JP}$  for any reasonable value of  $\langle u^2 \rangle$ . Accordingly, we discarded the data points to the right of 3 meV. The data points for the chosen energy intervals were renor-

malized according to Eqs. (2.13) for some choice of  $\eta$  and fit to smooth functions  $\hat{f}_P(\omega, \eta^2)$  and  $\hat{f}_{JP}(\omega, \eta^2)$ . We then computed the variance

$$V(\eta^2) = \int_{2\text{meV}}^{3\text{meV}} [\hat{f}_P(\omega, \eta^2) - \hat{f}_{JP}(\omega, \eta^2)]^2 d(\hbar\omega). \quad (2.17)$$

A minimum value of  $V$  was obtained for

$$\eta^2 = \langle u^2 \rangle = 0.35 \text{ \AA}^2. \quad (2.18a)$$

We will use this value of  $\langle u^2 \rangle$  in the calculations which follow, rather than Eq. (2.12a), because it implies a more reasonable normalization of the phonon density of states. Both equations (2.12a) and (2.18a) disagree with the value  $\langle u^2 \rangle = 1.0 \pm 0.1 \text{ \AA}^2$  given in Ref. 21. There it was mentioned that comparison of elastic to conversion intensities gave  $\langle u^2 \rangle = 0.47 \text{ \AA}^2$ , which is about 10% higher than our value deduced from the same data. We can find no basis for the value  $\langle u^2 \rangle = 1 \text{ \AA}^2$ , especially since our analysis of the phonon curves gives the considerably smaller result of Eq. (2.18a). In addition our values for  $\langle u^2 \rangle$  are in agreement with that of Schott,<sup>17</sup> who found  $\langle u^2 \rangle = 0.346 \text{ \AA}^2$  for 68% ortho-H at 4.3 K and are comparable to that of Nielsen,<sup>23</sup> who found  $\langle u^2 \rangle = 0.48 \text{ \AA}^2$  for para-H<sub>2</sub> at  $T = 5.4$  K.

We now determine the phonon density of states from the scattering function  $S_{JP}$  by

$$g(\hbar\omega) = \left[ I_0 e^{-K^2 \langle u^2 \rangle / 3} \left( \frac{\hbar^2 K^2}{8M} \right) j_1^2 \left( \frac{K\rho}{2} \right) \right]^{-1} \\ \times \hbar\omega \psi_{JP}(K, \omega - \hbar^{-1} E_{10}). \quad (2.19)$$

To properly normalize  $g(\hbar\omega)$  we must determine  $I_0$ . Henceforth we will use the elastic line, Eq. (2.9), to fix  $I_0$ . Using Eqs. (2.9) and (2.18a) we find

$$I_0 = 13\,100. \quad (2.18b)$$

Determining  $I_0$  from the conversion line by Eq. (2.11) leads to different normalizations.

$G_T = \int g(\hbar\omega) \hbar d\omega$  and different values of  $\Theta_D$ , where  $\Theta_D$  is defined by  $g(\hbar\omega) \sim 3(\hbar\omega)^2 / (k\Theta_D)^3$  for small  $\omega$ . For a fixed value of  $\langle u^2 \rangle$  one has

$$G'_T / G_T = \exp \left[ \frac{1}{3} (K_{10}^2 - K_{a1}^2) (0.42 \text{ \AA}^2 - \langle u^2 \rangle) \right], \quad (2.20a)$$

$$\Theta'_D / \Theta_D = (G'_T / G_T)^{-1/3}, \quad (2.20b)$$

where the primed quantities are based on  $I_0$  determined from Eq. (2.11) and the unprimed from Eq. (2.9).

To determine  $\psi_{JP}(K, \omega)$  we subtracted from the raw experimental data the fit given in Eq. (2.10) to the conversion line and that given in Eq. (2.8) to the elastic line. This procedure leads to the

solid curve for  $g(\hbar\omega)$ , shown in Fig. 2. However, the large peak at high energy is not observed<sup>23</sup> and we attribute it to an inaccuracy in the subtraction of the elastic line. Indeed, the approximation of Eq. (2.8) appears to break down in the wings of the elastic line. Accordingly, we will use an improved fit to the elastic line given by

$$\psi_{el}(K, \omega) = (2312 e^{-16.8(\hbar\omega)^2} + 41 e^{-0.64(\hbar\omega)^2})/\text{meV}, \quad (2.21)$$

with  $\hbar\omega$  in meV when subtracting from the experimental data of Ref. 21. Applying Eq. (2.19) to the data points so analyzed we obtain the corresponding "experimental" values of  $g(\hbar\omega)$  shown in Fig. 2.

Also shown in Fig. 2 is the theoretical phonon density of states based on the calculation of Mertens.<sup>31</sup> For the case of hcp para-hydrogen, Mertens's theory is in good agreement with experiment if the energy scale is renormalized by a factor of about 0.82. For fcc ortho-hydrogen, we can fix the energy scale by comparing the theoretical value of the energy of the lowest  $k=0$  optical phonon to the infrared absorption data of Hardy *et al.*<sup>32</sup> From this comparison we infer that Mertens's energy scale should be multiplied by a factor of 0.794. The theoretical density-of-states histogram which results is in excellent agreement with the density of states which is derived from the neutron data. The integrated area under the points derived from the neutron data is about 1.3, which is somewhat larger than its theoretical value of 1.0. This  $g(\hbar\omega)$  gives  $\Theta_D$  to be 113 K, somewhat lower than the accepted val-

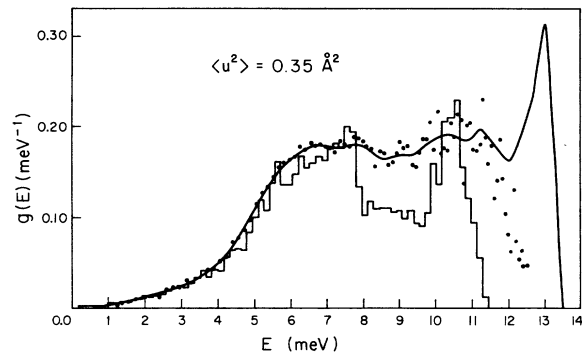


FIG. 2. Phonon density of states versus energy. The dots are values obtained from the data points of Fig. 1 using Eqs. (2.19) and (2.21) with  $\langle u^2 \rangle$  and  $I_0$  as given in Eq. (2.18). The solid line (histogram) is the theory of Mertens (Ref. 31) with the energy renormalized by a factor 0.794 as discussed in the text. The smooth solid curve is obtained from the data by using the less-satisfactory single-Gaussian approximation, Eq. (2.8), for the elastic line.

TABLE I. Values of various constants.

Symbol	Value	Ref.
$R_0 \equiv a/\sqrt{2}$	3.75 Å	37, 38
$\Gamma_0 \equiv 6e^2Q^2/25R_0^5$	0.654 cm <sup>-1</sup>	42
$\Gamma \equiv \xi\Gamma_0$	0.58 cm <sup>-1</sup>	10, 14
$E_L \approx 16.0\Gamma$	8.7 cm <sup>-1</sup>	10
$\hbar\omega_D$	10.4 meV	29, 41
$\Theta_D$	120	29, 41
$\omega_D R_0/c$	4.56	23
$M\omega_D^2 R_0^2$ <sup>a</sup>	5810 cm <sup>-1</sup>	29, 41
$i_1$	0.467 cm <sup>-1</sup>	40
$\beta_2$	0.694 cm <sup>-1</sup>	40
$\alpha$	1.77 Å <sup>-1</sup>	40
$B(R_0)$	-0.227 cm <sup>-1</sup>	40
$R_0 B'(R_0) \equiv R_0 \frac{dB(R_0)}{dR_0}$	-2.05 cm <sup>-1</sup>	40

<sup>a</sup> Based on  $c = 1.3 \times 10^5$  cm/sec from Ref. 23.

ue,<sup>29,41</sup> 120 K. The values of  $\Theta_D$  and other constants used are listed in Table I. It is probable that these discrepancies are in part due to an error in the determination of  $I_0$  [see Eq. (2.20)]. In addition some of this "extra" intensity may be due to residual effects at the elastic scattering.

It is interesting to consider how the density of states obtained using Eq. (2.19) depends on the value assumed for  $\langle u^2 \rangle$ . The results for  $\langle u^2 \rangle = 0.48 \text{ \AA}^2$  and for  $\langle u^2 \rangle = 1.0 \text{ \AA}^2$  are shown in Fig. 3. The area  $G_T$  is 1.6 for  $\langle u^2 \rangle = 0.48 \text{ \AA}^2$  and 3.0 for  $\langle u^2 \rangle = 1.0 \text{ \AA}^2$ . Within harmonic phonon theory this quantity should be unity. Had we normalized  $I_0$  to the conversion line we would have had areas of 1.4 and 0.6 for  $\langle u^2 \rangle = 0.48 \text{ \AA}^2$  and  $1.0 \text{ \AA}^2$ , respectively [see Eq. (2.20)].

Finally we may conclude this analysis by evaluating the libron scattering cross section. This is shown by the dots in Fig. 4. Also shown in Fig. 4 is the theoretical density of states of Ref. 33, which is normalized so that its area is 1, and we have replaced  $\Gamma$  by  $x\Gamma = 0.068$  meV for 95% ( $y = 0.95$ ) ortho-hydrogen as discussed in Ref. 14. The agreement here is not very satisfactory. The neutron data give an integrated density of states of 1.4 and it is clear from the figure that most of this extra intensity is on the low-energy side. In the absence of libron-phonon coupling, Raman scattering experiments<sup>12,13</sup> provide a very accurate lower bound to the libron band because the lowest-energy libron mode is Raman active. For ortho concentrations of greater than 92% this energy is greater than 0.79 meV. Libron-phonon interactions would shift some of the libron scatterings to lower energy. However, the large shift required to explain the data would lead to a concomitant dip at higher energy which is not ob-

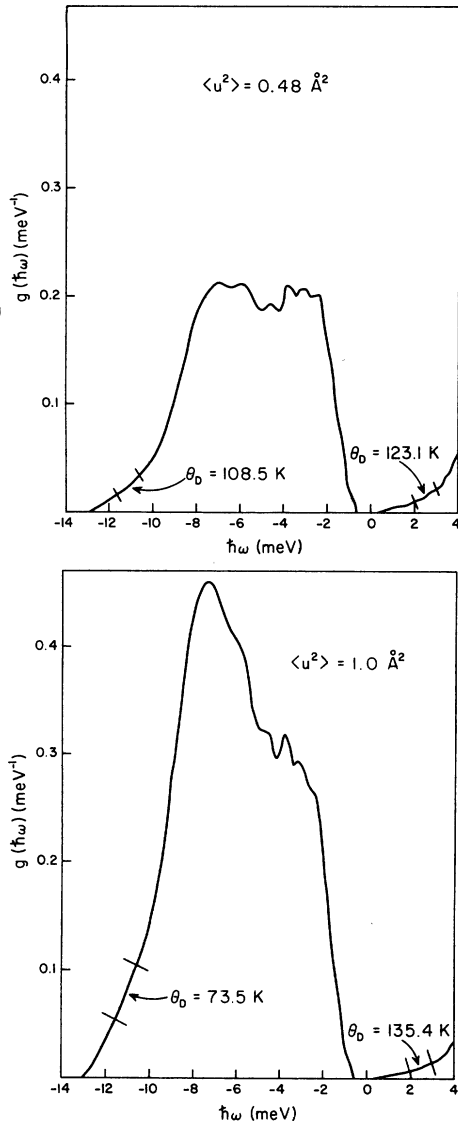


FIG. 3. Phonon density of states for values of  $\langle u^2 \rangle$  indicated. Equation (2.21) was used for the subtraction of the elastic line, Eq. (2.9) was used for normalization, Eq. (2.19) was used for negative energy, and the analog of Eq. (2.19) was used for positive energy. The values of  $\theta_D$  are obtained from  $g(\hbar\omega) \sim 3(\hbar\omega)^2 / (k\theta_D)^3$  over regions at low energy between the transverse lines. As expected, our result for  $\langle u^2 \rangle = 1.0 \text{ \AA}^2$  agrees with the previous result shown in Fig. 5 of Ref. 21 and Fig. 2 of Ref. 22.

served. Thus, even in light of the rather large resolution width, some of the neutron intensity below 0.8 meV is anomalous. We should point out, however, that this intensity might be attributed to the wings of the elastic line as may also have been the case for the extra intensity on the high-energy side of the phonon density of states.

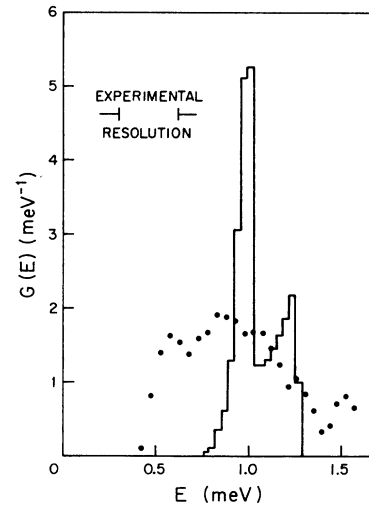


FIG. 4. Libron density of states versus energy. The dots are smoothed values obtained assuming Eq. (2.3d) is a valid description of the cross section which is not attributable to quasiharmonic phonons as described by Eq. (2.3c). The solid curve (histogram) is the anharmonic density of states of Ref. 33 taking (Ref. 14)  $\times \Gamma = 0.068 \text{ meV}$ .

It is also possible, as suggested in Ref. 21, that some of the intensity may be due to the multiphonon tail of the phonon spectrum extending through the elastic line.

### III. LIBRON-PHONON COUPLING

At zero pressure the dominant orientationally dependent interaction between molecules is the electrostatic quadrupole-quadrupole (EQQ) interaction.<sup>34,35</sup> For pure  $J=1$  solid  $\text{H}_2$  we write the EQQ Hamiltonian  $H_Q$  as<sup>10</sup>

$$H_Q = \frac{1}{2} \sum_{ij} \sum_{MN} \zeta_{ij}^{MN} O_i^M O_j^N, \quad (3.1)$$

where the operators  $O_i^M$  are

$$O_i^2 = (O_i^{-2})^\dagger = c_{i1}^\dagger c_{i,-1}, \quad (3.2a)$$

$$O_i^1 = -(O_i^{-1})^\dagger = [c_{i1}^\dagger(1-n_i) - (1-n_i)c_{i,-1}], \quad (3.2b)$$

$$O_i^0 = -\frac{2}{3} + n_i, \quad (3.2c)$$

where  $c_{iM}^\dagger$  creates a libron of polarization  $M$  on the  $i$ th site, referred to the local axes listed in Table II.  $M = \pm 1$  and  $n_i = c_{i1}^\dagger c_{i1} + c_{i,-1}^\dagger c_{i,-1}$ . The coefficients  $\zeta_{ij}^{MN}$  are proportional to the EQQ coupling constant  $\Gamma_0 = 6e^2Q^2/25R_0^5$ , where  $eQ$  is the molecular quadrupole moment<sup>36</sup> and  $R_0$  the nearest-neighbor separation.<sup>37,38</sup> Some of the values of the coefficients  $\zeta_{ij}^{MN}$  were tabulated by Berlinsky and Harris<sup>11</sup> and by Coll<sup>39</sup> and are given in Table

TABLE II. Quantization axes for the four sublattices in terms of the cubic crystal axes. See Refs. 42-44.

$\beta^a$	$\vec{\tau}_\beta^b$	Direction of z axis	Direction of x axis	Direction of y axis
1	$(a/2)(0, 0, 0)$	[111]	[11 $\bar{2}$ ]	[ $\bar{1}$ 10]
2	$(a/2)(1, 1, 0)$	[ $\bar{1}$ 11]	[ $\bar{1}$ 1 $\bar{2}$ ]	[ $\bar{1}$ 10]
3	$(a/2)(0, 1, 1)$	[1 $\bar{1}$ 1]	[1 $\bar{1}$ 2]	[110]
4	$(a/2)(1, 0, 1)$	[11 $\bar{1}$ ]	[ $\bar{1}$ 1 $\bar{2}$ ]	[ $\bar{1}$ 10]

<sup>a</sup> Here  $\beta$  labels the sublattice.

<sup>b</sup> The position of a molecule on sublattice  $\beta$  can be written as  $\vec{R} + \vec{\tau}_\beta$ , where  $\vec{R}$  is a lattice vector. Here  $a = \sqrt{2}R_0$ , where  $R_0$  is the nearest-neighbor separation.

III. The others may be obtained using the symmetry operations of the crystal.<sup>7</sup> The non-EQQ interactions, and especially the single-molecule terms, are not reliably known, although they are believed to be much smaller than  $H_Q$ .<sup>34,35</sup> However, in order to make comparisons with quantum crystal treatments of libron-phonon interactions,<sup>24,25</sup> we include the single-molecule terms, which are of the form

$$V = \sum_j V_j, \quad (3.3a)$$

$$V_j = \sum_i B(R_{ij}) [3(\hat{n}_j \cdot \hat{R}_{ij})^2 - 1], \quad (3.3b)$$

where the carets indicate unit vectors and  $\hat{n}_j$  is the orientation of molecule  $j$ . A semiempirical form for  $B(R)$  is<sup>40</sup>

$$B(R) = \beta_1 e^{-2\alpha(R-R_0)} - \beta_2 (R_0/R)^6, \quad (3.4)$$

where  $R_0$  is the nearest-neighbor separation and the estimated values of the constants are given in Table I.<sup>41,42</sup> A libron expansion of  $V_j$  yields

$$V_j = \sum_M \Lambda_j^M O_j^M, \quad (3.5)$$

where

$$\Lambda_j^M = \frac{8\pi}{5} \sum_i B(R_{ij}) Y_2^M(\hat{R}_{ij}) \dagger A_M, \quad (3.6)$$

where  $Y_2^M(\hat{R}_{ij})$  is a spherical harmonic referred

to the local axes based on the equilibrium orientation<sup>42-44</sup> of the sublattice containing the site  $j$  (see Table II) and the  $A_M$ 's are given as

$$A_{\pm 2} = -(3/10\pi)^{1/2}, \quad (3.7a)$$

$$A_{\pm 1} = (3/20\pi)^{1/2}, \quad (3.7b)$$

$$A_0 = -(9/20\pi)^{1/2}. \quad (3.7c)$$

In Eq. (3.6) we will restrict the sum to sites which are nearest neighbors of site  $j$ .

The representation of Eq. (3.2) provides a simple classification of terms according to the number of librions involved. For instance, the single-libron terms are those involving  $O_i^M$  with  $M = \pm 1$ . Thus the linear libron-phonon coupling is the one-phonon contribution to such terms in (3.1) and (3.5). Denoting these terms by superscripts 1, 1 we have

$$H_Q^{1,1} = -\frac{2}{3} \sum_{\alpha ij} \sum_{M=\pm 1} (u_i^\alpha - u_j^\alpha) \times \nabla_i^\alpha \zeta_{ij}^{0M} (c_{jM}^\dagger - c_{j,-M}^\dagger), \quad (3.8a)$$

$$V_j^{1,1} = \frac{4}{5} \left(\frac{3\pi}{5}\right)^{1/2} \sum_{\alpha ij} \sum_{M=\pm 1} (u_i^\alpha - u_j^\alpha) \times \nabla_i^\alpha [B(R_{ij}) Y_2^M(\hat{R}_{ij}) \dagger] \times (c_{jM}^\dagger - c_{j,-M}^\dagger), \quad (3.8b)$$

where  $\alpha = x, y, \text{ or } z$  and  $\vec{\nabla}_i$  is the gradient with respect to  $\vec{R}_i$ .

Likewise we can enumerate the terms which describe one phonon interacting with two librions. Denoting these by superscripts 1, 2 we write

$$H_Q^{1,2} = \frac{1}{2} \sum_{i j \alpha} \sum_{M, N=\pm 1} (u_i^\alpha - u_j^\alpha) \nabla_i^\alpha \zeta_{ij}^{MN} \times (c_{iM}^\dagger c_{jN}^\dagger + c_{i,-M} c_{j,-N}), \quad (3.9a)$$

$$V_j^{1,2} = 0. \quad (3.9b)$$

Here we neglect the effect of phonon-modulated libron scattering (viz., terms of the type  $uc^\dagger c$ ), since these lead to corrections of order  $e^{-\Delta/T}$ , where  $\Delta$  is the libron energy gap.

To take account of the large amplitude fluctuations characteristic of quantum crystals, we

TABLE III. Values of  $\zeta_{kj}^{MN}/\Gamma$ , where  $\vec{R}_k = (0, 0, 0)$  and  $\vec{R}_j = \frac{1}{2}a(1, 1, 0)$ . Here  $(x, y)$  denotes  $x + iy$ .

$M \setminus N$	2	1	0	-1	-2
2	(-1.3472, -0.9623)	(-0.9444, 0.2887)	(-0.9583, 0.5774)	(-0.3889, 0.4811)	(-0.0139, 0.5773)
1	(-2.1944, -0.2887)	(-0.5556, 0.2406)	(-1.4167, -0.2887)	(-0.7778, 0.1443)	(-0.8611, 0.4811)
0	(-2.2083, 2.3094)	(-0.1667, -1.1547)	(-2.3750, -0.0000)	(0.1667, -1.1547)	(-2.2083, -2.3094)
-1	(0.8611, 0.4811)	(-0.7778, -0.1443)	(1.4167, -0.2887)	(-0.5556, -0.2406)	(2.1944, -0.2887)
-2	(-0.0139, -0.5773)	(0.3889, 0.4811)	(-0.9583, -0.5773)	(0.9444, 0.2887)	(-1.3472, 0.9622)

should really replace the force constants  $\nabla\zeta$  and  $\nabla B$  in (3.8) and (3.9) by averages of these quantities over the displacement distribution function.<sup>25,45,46</sup> Such an average leads to a reduction in  $\zeta$  of order 15%.<sup>47-49,26</sup> We therefore replace  $\Gamma_0$  by its phonon-renormalized value  $\Gamma$ . More important renormalizations may occur when  $B$  is averaged in this way.<sup>49,50</sup> We will assume that  $\zeta$  and  $\nabla\zeta$  are renormalized in the same ratio, so that  $\zeta$  may be interpreted as its phonon-renormalized value. Since  $B$  is not well known, the additional uncertainty introduced by the renormalization is not significant. As we shall see, the effect of  $B$  on the libron-phonon coupling is small, assuming reasonable values for  $B$  and  $\nabla B$ .

A table of values of  $\nabla\zeta$  for one pair of nearest neighbors<sup>51</sup> is given in Appendix A and the symmetry operation needed to obtain the values of  $\nabla\zeta$  for any other pair of nearest neighbors is also discussed. The tabulations can also be used to treat libron-phonon interactions in classical solids with  $Pu3$  structure, such as solid  $N_2$ .<sup>52</sup>

#### IV. SPLITTINGS AT THE LIBRON-PHONON CROSSOVERS

Apart from the renormalization effects we neglect the phonon anharmonicity. Furthermore, if we neglect the effect of orientational interactions on the phonon wave functions we may describe the phonons in an fcc basis.<sup>53</sup> (We can still include some effects of orientational interactions on the phonon energies.) Using this approach we write

$$u_i^\alpha = \left( \frac{\hbar}{2MN} \right)^{1/2} \times \sum_{\vec{q} \in \text{fcc}} \sum_{\mu=1}^3 \xi_\mu^\alpha(\vec{q}) \times [\omega_\mu(\vec{q})]^{-1/2} e^{i\vec{q} \cdot \vec{R}_i} (a_{\vec{q}\mu}^\dagger + a_{-\vec{q}\mu}^\dagger), \quad (4.1)$$

where  $\vec{q} \in \text{fcc}$  indicates that  $\vec{q}$  is summed over the fcc Brillouin zone,  $N$  is the number of molecules,

$$\Delta^2 = \frac{\hbar}{27MN} \sum_{M=\pm 1} \sum_{i,i',j} \sum_{\alpha,\alpha'} \sum_{\mu=1,3} \xi_\mu^{\alpha'}(q) \xi_\mu^\alpha(q) \omega_\mu(q^*) \times (\nabla_i^\alpha \xi_{i'j}^{\alpha'}) (\nabla_{i'} \xi_{i'j}^{\alpha'})^* \{ \exp[i\vec{q} \cdot (\vec{R}_j - \vec{R}_i)] - 1 \} \{ \exp[-i\vec{q} \cdot (\vec{R}_j - \vec{R}_i)] - 1 \}. \quad (4.5)$$

We introduce the following approximations which lead to a simple result, but which do not cause any great error: (i) We set  $\omega_\mu(q) = \omega(q)$ ; i.e., we do not distinguish between acoustic modes. (ii) We set

$$e^{i\vec{q} \cdot (\vec{R}_j - \vec{R}_i)} - 1 = i\vec{q} \cdot (\vec{R}_j - \vec{R}_i). \quad (4.6)$$

The error in this approximation is of order

and  $\vec{\xi}_\mu(\vec{q})$  is the polarization vector of the mode  $\mu$ , created by  $a_{\vec{q}\mu}^\dagger$ .

On the other hand, we cannot ignore the sublattice structure induced by orientational ordering when we discuss the librations. Thus we use the first Brillouin zone for a simple-cubic lattice having four molecules per unit cell. There are then eight libron modes and 12 phonon modes for each wave vector. Within the approximation of the preceding paragraph we see that the acoustic-phonon-mode operators, labeled  $a_{\vec{q}1}^\dagger$ ,  $a_{\vec{q}2}^\dagger$ , and  $a_{\vec{q}3}^\dagger$  are the same for the fcc and sc descriptions. If we insert Eq. (4.1) into the expression for  $H_Q^{1,1}$ , we obtain the term which describes the linear mixing of librations and phonons. The secular part of this term is of the form

$$H_Q^{1,1} = \sum_{\vec{q} \in \text{sc}} \sum_{\sigma=1}^8 \sum_{\mu=1}^{12} V_{\sigma\mu}(\vec{q}) c_{\vec{q}\sigma}^\dagger a_{\vec{q}\mu}^\dagger + \text{H.c.}, \quad (4.2)$$

where  $c_{\vec{q}\sigma}^\dagger$  is a libron creation operator for wave vector  $\vec{q}$  and mode index  $\sigma$ , and  $\vec{q} \in \text{sc}$  indicates that  $\vec{q}$  is summed over the first Brillouin zone for a simple-cubic lattice.

When the energy of a phonon mode  $\mu$  equals that of a libron mode  $\sigma$ , the interaction (4.2) leads to a splitting  $\Delta E_{\sigma\mu} \approx 2|V_{\sigma\mu}(\vec{q})|$ . Since the libron band is rather narrow,<sup>33</sup> we will neglect the fact that the phonon wave vector  $\vec{q}$  depends on the orientation of  $\vec{q}$  and on the crossover energy. We will denote the average wave vector at the crossover for  $1 \leq \mu \leq 3$  by  $q^*$ . With this approximation, we may write the mean-square splitting for EQQ interactions as

$$\Delta^2 = \frac{1}{24} \sum_{\sigma\mu} (\Delta E_{\sigma\mu})^2 \quad (4.3)$$

$$= \frac{1}{6} \sum_{\mu} \langle 0 | a_{q\mu} (H_Q^{1,1})^2 a_{q\mu}^\dagger | 0 \rangle_{|q=q^*}, \quad (4.4)$$

where  $|0\rangle$  denotes the vacuum state. The normalization in Eq. (4.3) is appropriate because there are 24 distinct crossovers for a general direction in  $q$  space. Explicitly, Eq. (4.4) is

$\frac{1}{6} q^2 R_0^2 = \frac{1}{12} a^2 q^2 \approx \frac{1}{12} (\pi E_L / \hbar \omega_D)^2 = 0.01 \ll 1$ , where  $E_L$  is the average libron energy.<sup>10</sup> We thereby obtain the result

$$\Delta^2 = \frac{1}{81} \frac{\hbar^2 q^{*2}}{NM \hbar \omega(q^*)} \sum_{M=\pm 1} \sum_{\mu,\alpha,j} |S_{\mu\alpha}^M(j)|^2, \quad (4.7)$$

where



$$S_{\mu\alpha}^M(j) = \sum_{\mathbf{i}} R_{ij}^{\mu} \nabla_{\mathbf{i}}^{\alpha} \xi_{ij}^{0M}. \quad (4.8)$$

The numerical values needed to evaluate this expression are given in Appendix A. Using these values we find that

$$\underline{S}^1 = -(\underline{S}^{-1})^* = \frac{5}{24} \Gamma \times \begin{pmatrix} -25 - 17\sqrt{3}i & -20 - 62\sqrt{3}i & 9 - 37\sqrt{3}i \\ -60 + 14\sqrt{3}i & -13 + 21\sqrt{3}i & -83 + 41\sqrt{3}i \\ 103 + 21\sqrt{3}i & 51 + 23\sqrt{3}i & 38 - 4\sqrt{3}i \end{pmatrix}, \quad (4.9)$$

so that

$$\Delta^2 \approx 56.6 \hbar (q^*)^2 \Gamma^2 / M\omega(q^*) = 56.6 E_L \Gamma^2 / Mc^2 \quad (4.10)$$

in terms of the average sound velocity  $c$  and the average libron energy  $E_L$ . For  $E_L$  we use the result of anharmonic-libron theory<sup>33</sup> that  $E_L = 16.0\Gamma$ . We take  $c = 1.3 \times 10^5$  cm/sec from neutron scattering experiments<sup>23</sup> rather than the somewhat smaller value obtained from sound-velocity<sup>54,55</sup> measurements, since the former cover the energy range of interest here. Then we obtain

$$\Delta = 0.70 \text{ cm}^{-1}. \quad (4.11)$$

For comparison we have taken the values of  $\Delta$  from the libron-phonon dispersion curves given by Mertens and Biem,<sup>24</sup>

$$\Delta = 0.88 \text{ cm}^{-1}, \quad \vec{k} \parallel \langle 100 \rangle, \quad (4.12a)$$

$$\Delta = 1.05 \text{ cm}^{-1}, \quad \vec{k} \parallel \langle 111 \rangle. \quad (4.12b)$$

The disagreement between our result, Eq. (4.11), and that of Mertens and Biem, Eq. (4.12), is not a result of the approximate method we have used. In fact we will now show that this disagreement results almost entirely from a difference in the choice of parameters used to describe the librions and phonons. In particular (a) they have not included libron-libron interactions which cause  $E_L$  to be less than the harmonic value  $E_L^0 = 21.2\Gamma$  and (b) their renormalization of  $\Gamma$  due to zero-point phonon motion is not sufficiently accurate. If  $\Gamma_0$  denotes the bare value of  $\Gamma$ , their treatment gives  $\Gamma/\Gamma_0 = 0.98$ , whereas experiment gives  $\Gamma/\Gamma_0 \approx 0.8$ . To show the basic agreement between the two calculations, we write Eq. (4.10) as

$$\Delta = K(E_L \Gamma^2 / Mc^2)^{1/2} \quad (4.13)$$

and our result is  $K = 7.5$ , whereas the treatment of Mertens and Biem<sup>23</sup> ( $\Gamma/\Gamma_0 = 0.98$ ,  $E_L = E_L^0$ , etc.) yields

$$K = 7.7, \quad \vec{k} \parallel \langle 111 \rangle, \quad (4.14a)$$

$$K = 8.1, \quad \vec{k} \parallel \langle 100 \rangle, \quad (4.14b)$$

where we took  $c = 1.5 \times 10^5$  cm/sec for  $\vec{k} \parallel \langle 111 \rangle$  and  $c = 1.9 \times 10^5$  cm/sec for  $\vec{k} \parallel \langle 100 \rangle$  from their dispersion curves. So the two calculations differ mainly in the way the unmixed librions and phonons are described, but otherwise yield nearly identical values of  $K$ . Our method has the advantage that renormalizations due to libron-libron interactions can easily be included.

The above calculation can be extended in a straightforward way to include the single-molecule interactions of (3.5). The result is that in (4.7)  $S_{\mu\alpha}^M(j)$  is replaced by  $[S_{\mu\alpha}^M(j) + T_{\mu\alpha}^M(j)]$ , where

$$T_{\mu\alpha}^M(j) = -\frac{6}{5} \left( \frac{3\pi}{5} \right)^{1/2} \sum_{\mathbf{i}} R_{ij}^{\mu} \nabla_{\mathbf{i}}^{\alpha} [B(R_{ij}) Y_2^M(\hat{R}_{ij})]. \quad (4.15)$$

We evaluate this as

$$\underline{T}^1(0) = -\underline{T}^{-1}(0)^* = \begin{pmatrix} \lambda^2 c_1 & c_2 & \lambda c_2 \\ c_2 & \lambda c_1 & \lambda^2 c_2 \\ \lambda c_2 & \lambda^2 c_2 & c_1 \end{pmatrix}, \quad (4.16)$$

where  $\lambda = e^{2\pi i/3}$  and

$$c_1 = -\frac{3}{5} [R_0 B'(R_0) + 6B(R_0)], \quad (4.17a)$$

$$c_2 = \frac{3}{5} [R_0 B'(R_0) + 2B(R_0)], \quad (4.17b)$$

with  $B'(R_0) = dB(R_0)/dR_0$ . Thus, including single-molecule and EQQ interactions we find that

$$\Delta^2 = (2E_L / 81Mc^2) \left[ \frac{110075}{48} \Gamma^2 + 3c_1^2 + 6c_2^2 + \Gamma \left( \frac{95}{2} c_1 - 100c_2 \right) \right]. \quad (4.18)$$

Using the values of Table I for the constants in Eq. (3.4) ( $c_1/\Gamma \approx 3.7$ ;  $c_2/\Gamma \approx -2.8$ ), we find that  $\Delta$  is about 10% larger than for EQQ interactions only.

## V. EFFECT OF LIBRON-PHONON INTERACTIONS ON THE NEUTRON SCATTERING CROSS SECTION

In Sec. IV we have calculated the rms splitting at the libron-phonon crossovers. Since these splittings are rather small, we conclude that the libron-phonon mixing is small, especially at points in reciprocal space far from the crossovers. Nevertheless, since the ratio of the cross section of phonons to that of librions

$$\frac{S_P(K, \omega)/g(h\omega)}{S_L(K, \omega)/G(h\omega)} \equiv \frac{V_P(K, \omega)}{V_L(K, \omega)},$$

is of order 500,<sup>21</sup> even a small admixture of phonons into a libron mode could significantly enhance the cross section of these modes. We will study this possibility by evaluating  $S_p(K, \omega)$ , including the effect of libron-phonon interactions.

Since the cross section we calculate is the total contribution from all libron modes, we do not need to take account of the detailed structure of these modes. That is, we take the uncoupled libron Hamiltonian  $H_L$  to be

$$H_L = \sum_{iM} E_L c_{iM}^\dagger c_{iM} \equiv \sum_{iM} \hbar \omega_L c_{iM}^\dagger c_{iM}. \quad (5.1)$$

Such a localized scheme was used previously<sup>7,10,11</sup> to obtain estimates of the effects of libron-libron interactions on the libron spectrum. Here we take  $E_L$  to be the average libron energy renormalized by libron-libron interactions.<sup>10</sup> Alternatively,  $E_L$  may be interpreted as an experimentally determined parameter.<sup>14</sup> The fact that the librions form a band of width  $\delta$  about  $E_L$  will be incorporated in a crude way later.

To study the effects of libron-phonon coupling on the neutron scattering cross section we will perform various calculations. In the first of these, we study the simplest possible model for linearly coupled modes. This calculation will be done completely and has the virtue that it leads in a simple way to qualitatively correct results in terms of a few parameters whose physical significance is obvious. However, this calculation does not properly describe the dependence of the libron-phonon interaction on either polarization or wave vector. A more realistic treatment of these effects is given in Appendix B. Owing to the complexity of the formulas we give approximate evaluations which show that linear libron-phonon coupling causes about a 40% enhancement in the neutron scattering cross section. This calculation, if done completely, would be equivalent to the treatment of Bickermann *et al.*, who found a 1100% enhancement.<sup>25</sup> Their result is implausible in view of the simple model calculation which follows. Furthermore, since the librions are known to be very anharmonic,<sup>9-11</sup> we also study in Appendix B the effect of interactions involving two librions and one phonon given in Eq. (3.9). We find that these anharmonic mixing terms lead to effects comparable to the linear mixing terms in the simpler models. These mixing terms are the most important contributions to the anharmonic term  $H'$  in the Hamiltonian of Eq. (II.1) of Ref. 25. Such terms are usually neglected in the random-phase approximation. The fact that their effects are comparable to those of the harmonic mixing terms underlines the importance of using a systematic approach based on pertur-

bation theory where different types of effects can be compared on an equal footing. It may be helpful to represent the various processes diagrammatically. The phonon scattering cross section  $S_p(K, \omega)$  includes all processes involving  $j_0(y)$ , viz.,  $a, c, d, f$ , and  $g$  of Fig. 5. In particular, without libron-phonon mixing the only phonon process is  $a$ . The mixing of one- and two-libron states to one-phonon states is responsible for processes  $c$  and  $d$ . We will comment on processes  $f$  and  $g$  later.

The simple model we use to describe linearly coupled modes is

$$H = \hbar \sum_K c K a_K^\dagger a_K + \omega_L b_K^\dagger b_K + g(\omega_L c K)^{1/2} (a_K^\dagger b_K + b_K^\dagger a_K), \quad (5.2)$$

where  $g$  is a dimensionless constant and  $a_K^\dagger$  and  $b_K^\dagger$  are to be identified as creation operators for phonons and librions, respectively. The wave vector is confined to the Debye sphere,  $|K| < \omega_D/c$ , and there are no polarization or sublattice indices in this model. In order to evaluate  $S(K, \omega)$  we write the analog of Eq. (2.3c) in the form<sup>56</sup>

$$S_p(K, \omega) = \frac{K^2}{2\pi} \frac{j_0^2(y)}{1 - e^{-\beta\hbar\omega}} \times \text{Im} \sum_{\alpha} \langle \langle u_i^\alpha; u_i^\alpha \rangle \rangle_{\omega - i0^+}, \quad (5.3)$$

where we have neglected the term in  $j_2^2(y)$  and  $\langle \langle u_i^\alpha; u_i^\alpha \rangle \rangle_{\omega}$  is the phonon Green's function.<sup>57</sup> In the energy region  $\omega \sim \omega_L$  we have  $e^{-\beta\hbar\omega} \ll 1$  and  $K^2$  and  $j_0(y)$  do not vary significantly over the libron band. Also, in view of Eq. (4.1) we may

PROCESS	MAGNITUDE	FORMULA
a)	$J_0 K u$	2.3c
b)	$J_2$	2.3d
c)	$J_0 K u (V_{LP}/E_L)$	B.5
d)	$J_0 K u (V_{LP}/E_L)$	B.30
e)	$J_2 (V_{LL}/E_L)$	—
f)	$J_0 K u (V_{LP}/E_L) (V_{LL}/E_L)$	—
g)	$J_0 K u (V_{LP}/E_L) (V_{LL}/E_L)$	—
h)	$J_1$	2.3b
i)	$J_1 K u$	2.3e
j)	$J_1 (V_{TIP}/E)$	7.20

LEGEND:   
 ●●●●● = NEUTRON   
 ~~~~~ = PHONON   
 - - - - - = LIBRON   
 - - - - - = (J·O) MOLECULE

FIG. 5. Diagrammatic representation of various processes which contribute to the inelastic cross section for neutron scattering in solid hydrogen. Here  $V_{LL}$  is the cubic libron-libron interaction (Refs. 9-11, 14),  $K$  is the average momentum transfer, and  $u = \langle u^2 \rangle^{1/2}$ .

identify  $S_p(K, \omega)$  as

$$S_p(K, \omega) = K^2 \int k^2 dk \left( \frac{1}{k} \text{Im} G_{aa}(k, \omega) \right), \quad (5.4)$$

where  $G_{aa}(k, \omega) = \langle \langle a_k; a_k^\dagger \rangle \rangle$ . Since  $V_p(K, \omega)/V_L(K, \omega) \approx 500$ , we can neglect the effect of libron-phonon interactions on  $S_L(K, \omega)$ .

The normal modes from the Hamiltonian of Eq. (5.2) are

$$\omega_{\pm}(k) = \frac{1}{2}(ck + \omega_L) \pm \frac{1}{2}[(ck - \omega_L)^2 + 4g^2\omega_L ck]^2. \quad (5.5)$$

This spectrum is shown in Fig. 6. Also we find

$$G_{aa}(k, \omega) = \frac{\omega_L - \omega_-(k)}{\omega_+(k) - \omega_-(k)} \frac{1}{\omega - \omega_-(k)} + \frac{\omega(k) - \omega_L}{\omega_+(k) - \omega_-(k)} \frac{1}{\omega - \omega_+(k)}. \quad (5.6)$$

Substituting this into Eq. (5.4) we find

$$S_p(K, \omega) = \frac{K^2}{c^2} \frac{\omega(\omega - \omega_L)^2}{(g^2\omega_L + \omega - \omega_L)^2}, \quad (5.7a)$$

$$0 \leq \omega \leq \omega_1 \text{ or } \omega_L < \omega < \omega_2 \quad (5.7b)$$

$$S_p(K, \omega) = 0, \quad (5.7b)$$

where  $\omega_1 = \omega_-(\omega_D/c)$  and  $\omega_2 = \omega_+(\omega_D/c)$ . The value of  $g$  is related to the size of the splitting at the libron-phonon crossover. At the crossover we have

$$(\omega_+ - \omega_-)/2 = g\omega_L, \quad (5.8)$$

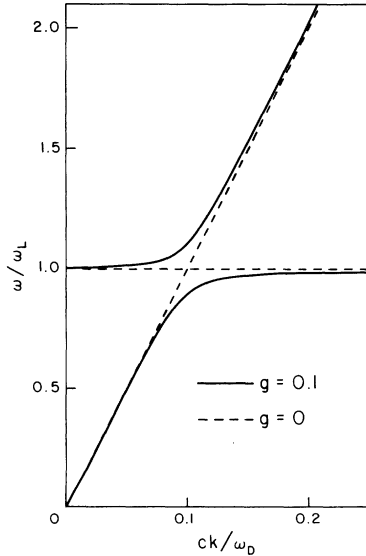


FIG. 6. Dispersion relation for the Hamiltonian of Eq. (5.2). The dashed lines are for the case  $g=0$ ; the solid lines are for  $g=0.1$ , as is appropriate to describe solid hydrogen.

so that we may identify  $g$  by

$$g = (\omega_+ - \omega_-)/2\omega_L. \quad (5.9)$$

Taking  $\omega_+ - \omega_- \approx 0.2$  meV and  $\omega_L = 1$  meV gives  $g \approx 0.1$ . This value of  $\omega_+ - \omega_-$  is at least as large as any that have been suggested either in Sec. IV above or previously.<sup>24,25</sup> The result for  $S_p(K, \omega)$  is shown by the dashed line in Fig. 7. Our units are such that when  $g=0$ ,

$$S_p^0(K, \omega) = (K^2/c^2)\omega. \quad (5.10)$$

We see from Fig. 7 that there is a significant effect in the cross section for  $|\omega - \omega_L| \ll \omega_L$ . The sharp dispersion in  $S_p(K, \omega)$  for  $\omega \sim \omega_L$  is an artifact of our model, which takes the libron bandwidth to be zero. To take account of the actual<sup>33</sup> bandwidth we should convolute  $S_p(K, \omega)$  with the libron density of states  $G(\hbar\omega)$ . For the present calculation we approximate  $G(\hbar\omega)$  by a square density of states:  $G(\hbar\omega) = (2E_L\delta)^{-1}$  for  $1 - \delta < \hbar\omega/E_L < 1 + \delta$  and  $G(\hbar\omega) = 0$  otherwise. Thus we set

$$S_p(K, \omega) = (2E_L\delta)^{-1} \int_{E_L(1-\delta)}^{E_L(1+\delta)} S_p(K, \omega; E'_L) dE'_L, \quad (5.11)$$

where  $S_p(K, \omega; E'_L)$  is the value of  $S_p(K, \omega)$  when the libron energy in Eq. (5.1) is  $E'_L$ . From Fig. 7 we see that  $S_p(K, \omega)$  has a contribution due to libron-phonon interactions which mirrors the libron density of states and whose maximum height is about 30% of the background,  $S_p^0(K, \omega)$  at that frequency. To get the total cross section we must add  $S_p(K, \omega)$  and  $S_L(K, \omega)$ . The former is scaled by  $K^2$  and the latter by  $j_2^2(\frac{1}{2}k\rho) \sim K^4$ . Thus, at small  $K$ ,  $S(K, \omega)$  will be similar in shape to the

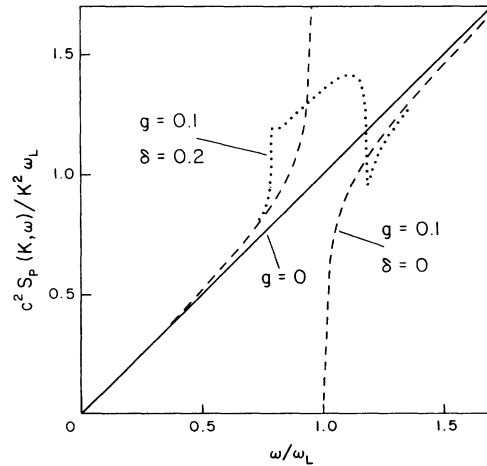


FIG. 7.  $S_p(K, \omega)$  from Eq. (5.10) (solid line), from Eq. (5.7) (dashed line) for  $g=0.1$ , and from (5.11) (dotted line) for  $g=0.1$  and  $\delta=0.2$ . In each case we have taken  $\omega_D = 10\omega_L$ .

dotted curve of Fig. 7. At large  $K$  the libronlike bump at  $\omega = \omega_L$  will be larger, owing to the contribution from  $S_L(K, \omega)$ .

A quantity of interest is

$$r = \frac{\int_0^{\omega_0} S_P(K, \omega) d\omega}{\int_0^{\omega_0} S_P^0(K, \omega) d\omega}, \quad (5.12)$$

which is a measure of the enhancement of the integrated cross section for  $\omega < \omega_0$  of  $S_P(K, \omega)$  due to libron-phonon interactions. Using Eq. (5.7) we find, for  $1 < \omega_0/\omega_L \ll \omega_D/\omega_L$ , that

$$r = 1 + g^2 \left[ 4 \left( \frac{\omega_L}{\omega_0} \right) \ln \frac{\omega_D}{\omega_0 - \omega_L} + 2 \frac{\omega_D \omega_L}{\omega_0^2} - \frac{\omega_L}{\omega_0} - 2 \left( \frac{\omega_L}{\omega_0} \right)^2 - 2 \frac{\omega_L^3}{\omega_0^2 \omega_D} \right]. \quad (5.13)$$

As discussed following Eq. (5.9), we set  $g \approx 0.1$ . Using this we find  $r \approx 1.11$ . Thus the mixing leads to an enhancement in the phonon cross section of about 10%. We may compare this additional phonon cross section with that due to librions since the two scattering mechanisms occur at the same energy. Thus we evaluate the quantity

$$r' = (r - 1) \frac{\int_0^{\omega_0} S_P(K, \omega) d\omega}{\int_0^{\omega_0} S_L(K, \omega) d\omega} \equiv (r - 1)R, \quad (5.14)$$

where  $K$  is taken to be the value at 1 meV and again we set  $\omega_0 = \frac{3}{2}$  meV. Note that  $r'$  is related to the quantity  $St$  of Eq. (IV.4) of Ref. 25 by  $r' = St - 1$ . Our simple model gives  $r' = 0.22$ , in contrast to the result of Bickermann *et al.*,  $r' = 11$ . (Their result means that phonon mixing leads to an addition to the libron cross section 11 times larger than the direct creation of librions. Our result corresponds to a 20% increase due to mixing.) Part of the difference between these two results comes from the values given to  $R$ : we take  $R = 2$  based on Eq. (2.3), whereas in Ref. 25 the value  $R = 8$  is taken. Regarding Ref. 25, it appears from their Eq. (III.11) that there is a factor  $\frac{1}{3}$  missing in Eq. (III.14). However, even allowing for this difference, the value of  $r'$  in Ref. 25 would be an order of magnitude larger than that found here.

Finally, in this simple model the number of "phonon" and "libron" modes are the same, whereas really the former are 50% more numerous than the latter. One might guess that with 50% more phonon modes available for mixing that  $r'$  would be 50% larger in the real case. In fact, our detailed calculations in Appendix B give  $r' \approx 0.37$ , which is surprisingly close to  $\frac{3}{2}r' = 0.33$ . However, the work of Appendix B also indicates that the mixing of two-libron and one-phonon states leads to a contribution to  $r'$  of about 0.37. Thus, the one- and two-libron processes must be treated

on an equal footing, as we do here. We should also note the dependence of  $r'$  on momentum transfer  $K$ . From Eq. (N26) we have  $r' \sim [KR_0 j_0(\frac{1}{2}K\rho)/j_2(\frac{1}{2}K\rho)]^2$ , so that  $r'$  increases  $\sim K^{-2}$  as  $K \rightarrow 0$ . For  $r' \geq 1$  the libron cross section is due to phonon admixture and the cross section should vary with  $K$  as  $I_{PL} \sim K^2$  rather than as  $K^4$  as expected at larger  $K$ .

## VI. SUM RULES FOR ORTHO-PARA CONVERSION SCATTERING

In this section we will study the inelastic neutron scattering associated with ortho-para, i.e.,  $J=1$  to  $J=0$ , conversion. We do this by obtaining a sum-rule formula for the average frequency of this transition. We thereby obtain a relation between this average frequency and the thermodynamic internal energy, which we discuss using high-temperature expansions and experimental data. In Sec. VII we will show that at low temperature the sum rule indicates the existence of a libron sideband above the conversion line.

The contribution of zero-phonon processes involving ortho-para conversion to the neutron scattering cross section is<sup>21</sup>

$$S_J(K, \omega) = \frac{1}{4} j_1^2(\frac{1}{2}K\rho) s_J(\omega), \quad (6.1)$$

where the reduced scattering cross section  $s_J(\omega)$  is

$$s_J(\omega) = \sum_{i,j,m,f} p_i \delta(\hbar\omega - E_f + E_i) |\langle f | Q_m^{(j)} | i \rangle|^2. \quad (6.2)$$

Here  $p_i$  is the probability associated with the initial state  $|i\rangle$ , and  $Q_m^{(j)}$  converts a  $J=1$ ,  $m_J = m$  state at the  $j$ th site into a  $J=0$  one in the final state  $|f\rangle$ . More correctly, we write

$$Q_m^{(j)} = (4\pi)^{1/2} Y_1^m(\omega_j)^*. \quad (6.3)$$

However, since we confine our attention to energies near the ortho-para transition, we interpret the  $Q_m$ 's as angular momentum destruction operators.

We can calculate the total cross section  $M_0$  as follows:

$$M_0 = \int_{-\infty}^{\infty} s_J(\omega) \hbar d\omega \quad (6.4a)$$

$$= \sum_{i,j,m,f} p_i |\langle f | Q_m^{(j)} | i \rangle|^2 \quad (6.4b)$$

$$= \sum_{i,j,m} p_i \langle i | (Q_m^{(j)})^\dagger Q_m^{(j)} | i \rangle. \quad (6.4c)$$

Since  $\sum_{j,m} Q_m^{(j)\dagger} Q_m^{(j)}$  is just the number of  $J=1$  molecules, we have

$$M_0 = Nx, \quad (6.5)$$

where  $x$  is the  $J=1$  concentration.

Likewise, we write the first moment of the scattering function  $M_1$  as

$$M_1 \equiv \int \hbar\omega s_J(\omega) \hbar d\omega \quad (6.6a)$$

$$= \sum_{ijm} p_i \langle i | (Q_m^{(j)})^\dagger [H, Q_m^{(j)}] | i \rangle. \quad (6.6b)$$

We write the Hamiltonian as

$$H = K + V, \quad (6.7)$$

where  $K$  is the kinetic energy,

$$K = 2B \sum_m (Q_m^{(j)})^\dagger Q_m^{(j)}, \quad (6.8)$$

and  $V$  is the potential energy,

$$V = \frac{1}{2} \sum_{ijMNmn} \zeta_{ij}^{MN} O_i^M O_j^N \times (Q_m^{(i)} Q_n^{(j)})^\dagger Q_m^{(i)} Q_n^{(j)}. \quad (6.9)$$

Here we have used the fact that  $J$  is either 1 or 0 at the temperatures of interest, so that  $\sum_m Q_m^{(j)\dagger} Q_m^{(j)}$  is an indicator function for  $J=1$  molecules. In Eq. (6.9) we have assumed that  $J$  is a good quantum number. The effect of processes which are off diagonal in  $J$  is not important<sup>14</sup> in the orientationally disordered phase which we consider in this section. These effects will be considered in our treatment of the low-temperature phase in Sec. VII.

We substitute Eq. (6.7) into Eq. (6.6b) and evaluate the commutator using

$$\sum_m [Q_m^{(j)\dagger} Q_m^{(j)}, Q_n^{(j')}] = -\delta_{j,j'} Q_n^{(j)\dagger} Q_n^{(j)}, \quad (6.10)$$

the result being

$$M_1 = -\sum_i p_i \langle i | K + 2V | i \rangle. \quad (6.11)$$

We write this as

$$M_1 = -2BNx - 2U(x, T), \quad (6.12)$$

where  $U(x, T)$  is the internal energy of the orientational system neglecting interactions nondiagonal in  $J$ .

The average energy of the ortho-para conversion line is therefore

$$\langle E \rangle = M_1/M_0 \quad (6.13a)$$

$$= -2B - 2U(x, T)/Nx. \quad (6.13b)$$

We now use this result to interpret the data of Stein *et al.*<sup>21</sup> in hcp solid H<sub>2</sub> at 4.2 K. As we have shown elsewhere,<sup>27</sup> the high-temperature orientational specific heat can be usefully represented by the Padé approximant

$$C(x, T) = \frac{140}{3} Nk_B \left( \frac{x\Gamma}{k_B T} \right)^2 \times \frac{1 + \alpha(\Gamma/k_B T)}{1 + \beta(\Gamma/k_B T) + \gamma(\Gamma/k_B T)^2}, \quad (6.14)$$

where the coefficients  $\alpha$ ,  $\beta$ , and  $\gamma$  are given by

$$\beta = (C - AB)/(A^2 - B), \quad (6.15a)$$

$$\gamma = -B - A\beta, \quad (6.15b)$$

$$\alpha = A + \beta, \quad (6.15c)$$

where  $A$ ,  $B$ , and  $C$  are the concentration-dependent coefficients in the high-temperature expansion

$$C(x, T) = \frac{140}{3} Nk_B \left( \frac{x\Gamma}{k_B T} \right)^2 \times \left[ 1 + A \left( \frac{\Gamma}{k_B T} \right) + B \left( \frac{\Gamma}{k_B T} \right)^2 + C \left( \frac{\Gamma}{k_B T} \right)^3 \cdots \right], \quad (6.16)$$

and are given in Ref. 27. Integrating (6.14) we obtain  $U(x, T)$  as

$$U = \frac{140}{3} Nx^2 \Gamma \left\{ -\frac{\alpha}{2\gamma} \ln \left[ 1 + \frac{\beta\Gamma}{k_B T} + \gamma \left( \frac{\Gamma}{k_B T} \right)^2 \right] - \frac{1 - \alpha\beta/2\gamma}{\gamma - \frac{1}{4}\beta^2} \tan^{-1} \frac{\gamma - \frac{1}{4}\beta^2}{k_B T/\Gamma + \frac{1}{2}\beta} \right\}. \quad (6.17)$$

We have used this approximation for  $U(x, T)$  to calculate  $\langle E \rangle + 2B$  according to Eq. (6.13b) with  $\Gamma = 0.58 \text{ cm}^{-1}$  and the result is shown in Fig. 8. Also shown are the experimental values of Stein *et al.*<sup>21</sup> for  $\langle E \rangle_{x=0} - \langle E \rangle_x$ .

There are several reasons why these two quantities might not agree as expected. First, the approximation for  $U(x, T)$  in Eq. (6.17) becomes less reliable as the temperature is lowered. However, this difficulty is less serious for  $U(x, T)$  than for  $C(x, T)$ .<sup>27</sup> To avoid this approximation we have used the experimental values<sup>28,29</sup> of  $C(x, T)$  to calculate  $U(x, T)$  to  $T = 4 \text{ K}$  and the result is also shown in Fig. 8. Second the determination of  $\langle E \rangle_{x=0}$  from the experimental data is open to question. The variation in  $\langle E \rangle$  at small  $x$  is expected to be linear, but the extrapolation of  $\langle E \rangle_x$  to  $x=0$  was performed by fitting  $\langle E \rangle_{x=0} - \langle E \rangle_x$  to a term proportional to  $x^2$ . If a linear extrapolation is used, one obtains  $\langle E \rangle_{x=0} \approx 14.84 \text{ meV}$  rather than  $14.74 \text{ meV}$  given in Ref. 21.

It is not clear which of these two values is more correct. Taking  $\langle E \rangle_{x=0} = 14.74 \text{ meV}$  leads to the result  $\langle E \rangle_{x=0} - \langle E \rangle_{x=0.2} \approx 0.03 \text{ meV}$ . This result cannot be understood theoretically. For instance, one can underestimate this quantity by considering

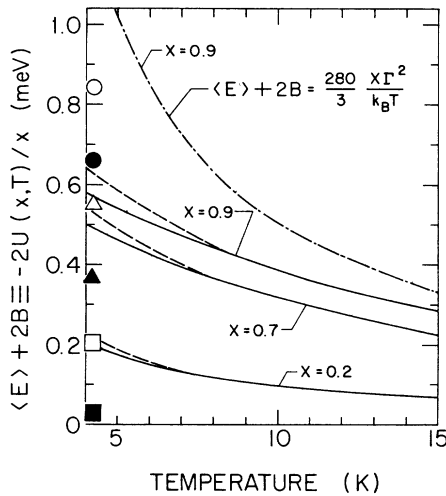


FIG. 8. Average energy  $\langle E \rangle$  of the ortho-para conversion line. The squares, triangles, and circles are the experimental values for  $x=0.2$ ,  $x=0.7$ , and  $x=0.9$ , respectively. The open symbols are the values obtained assuming  $\langle E \rangle_{x=0} = 14.89$  MeV, whereas the filled symbols correspond to  $\langle E \rangle_{x=0} = 14.74$  meV as given in Ref. 21. The solid curves are from Eqs. (6.17) and (6.13). The dashed curves are based on Eq. (6.13) but using experimental values to extrapolate  $U(x, T)$  to 4 K. The uppermost curve is for  $x=0.9$  using only the leading term in the high temperature expansion for  $U(x, T)$ .

only nearest-neighboring pairs of  $J=1$  molecules.<sup>58</sup> Then one has

$$\langle E \rangle_{x=0} - \langle E \rangle_x = zx |U_{\text{pair}}(T)|, \quad (6.18)$$

where  $z$  is the number of nearest neighbors ( $z=12$ ) and<sup>59</sup>

$$\frac{-U_{\text{pair}}(T)}{\Gamma} = \frac{8 - 2e^{-5y} - 6e^{-10y}}{2 + 4e^{-4y} + 2e^{-5y} + e^{-10y}} \quad (6.19)$$

is the thermal energy of a  $J=1$  pair with  $y = \Gamma/k_B T$ . For  $T=4.2$  K,  $y=0.2$  and we find  $U_{\text{pair}}(T) = -1.38\Gamma$ , which gives  $\langle E \rangle_{x=0} - \langle E \rangle_x = 3.3\Gamma \approx 0.20$  meV. In contrast, linear extrapolation yields better agreement between theory and experiment, especially for  $x=0.2$ . (See Fig. 8.)

A naive interpretation would set  $\langle E \rangle_{x=0} = 2B$ , in which case the linear extrapolation used above leads to significantly larger values of  $B$  than are found from optical data in the solid and gas phases. For instance, in the solid phase Bhatnagar *et al.*<sup>60</sup> give the  $J=0$  to  $J=2$  energy as  $353.35 \text{ cm}^{-1}$  ( $43.813 \text{ meV}$ ), if one uses the theory of Van Kraneendonk<sup>61</sup> for the center of gravity of the Raman triplet. Assuming  $E_J = BJ(J+1)$  this result implies  $E_1 - E_0 = 14.60 \text{ meV}$ . In the gas phase Stoicheff<sup>62</sup> found this energy to be  $354.381 \text{ cm}^{-1}$  ( $43.938 \text{ meV}$ ) and deduced the  $J=0$  to  $J=1$  energy to be  $118.494 \text{ cm}^{-1}$  ( $14.69 \text{ meV}$ ). Theoretical predictions for the differences in  $B$  between the

solid and the gas phases have been given<sup>63,64</sup> and lead to the conclusion that  $B$  is smaller in the solid than in the gas.

Clearly, a clarification of the experimental situation in this regard is needed.

## VII. CONVERSION CROSS SECTION AT ZERO TEMPERATURE

We now calculate the zero-phonon conversion cross section at zero temperature. The process we consider is shown schematically in Fig. 9. Initially the system is in the ground state for the system of  $N_1 J=1$  molecules. The final state can be either the ground state of  $N_1 - 1 J=1$  molecules or, with smaller probability, an excited state. The fact that the sum-rule value of the average energy lies above the lowest-energy final state indicates the presence of a libron sideband of smaller amplitude as shown.

We first ignore effects off diagonal in  $J$  and will treat the case of pure  $J=1 \text{ H}_2$ , so that  $N_1 = N$ . The calculation of the ground-state energies  $E_0(N)$  and  $E_0(N-1)$  has been performed previously by Nakamura<sup>65</sup> and our treatment is quite similar to his.

The Hamiltonian for librions was given in (3.1) and we write it as

$$H = H_0 + V, \quad (7.1)$$

where, as in Eq. (5.1),

$$H_0 = \sum_{iM} E_L c_{iM}^\dagger c_{iM} + E_0^0(N), \quad (7.2)$$

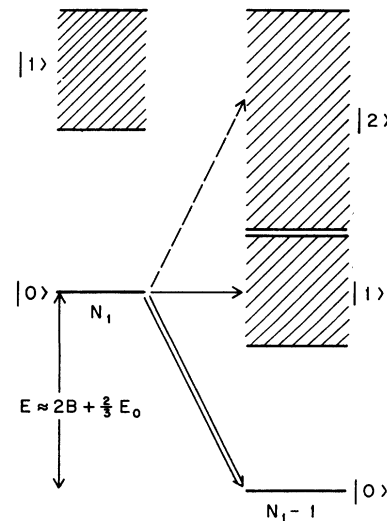


FIG. 9. Various processes involving ortho-para conversion. The dominant process connects the ground states of the system with  $N_1 J=1$  molecules to that with  $N_1 - 1 J=1$  molecules. Less important processes lead to final states with one or more librions, as shown.

where

$$E_0^0(N) = \frac{1}{2} \sum_{ij} \xi_{ij}^{00} \left(-\frac{2}{3}\right)^2 \quad (7.3a)$$

$$= -\frac{1}{3}NE_L^0, \quad (7.3b)$$

where  $E_L^0 = 21.2\Gamma$  is the average harmonic libron energy.<sup>6,10</sup> Treating the nearest-neighbor libron-pair creation terms in second-order perturbation theory we find the ground-state energy to be

$$E_0(N) = -\frac{1}{3}NE_L^0 - \frac{1}{2} \sum_{ij} \sum_{M,N=\pm 1} |\xi_{ij}^{MN}|^2 (2E_L)^{-1} \quad (7.4a)$$

$$= -\frac{1}{3}NE_L^0 - \frac{Nz}{4E_L} S_2, \quad (7.4b)$$

where  $E_L = 16.0\Gamma$  is the average anharmonic libron energy,<sup>33</sup> and

$$S_2 = \sum_{M,N=\pm 1} |\xi_{ij}^{MN}|^2 = \frac{643}{324}. \quad (7.5)$$

Here we take the energy denominator to be  $2E_L$  rather than  $2E_L^0 + \xi_{ij}^{00}$  as Nakamura<sup>65</sup> has done. The factor  $\xi_{ij}^{00}$  takes account of the fact that the two virtual librons are on neighboring sites. This effect is much smaller than that due to replacing<sup>10</sup>  $E_L^0$  by  $E_L$ . Since it is hard to include both effects self-consistently, we ignore the interaction in the virtual state.

When a single  $J=1$  molecule is replaced by a  $J=0$  one at the origin, the terms analogous to (7.3) and (7.4) are

$$E_0^0(N-1) = \frac{1}{2} \sum_{i \neq 0, j \neq 0} \xi_{ij}^{00} \left(-\frac{2}{3}\right)^2 \quad (7.6a)$$

$$= -\frac{1}{3}(N-2)E_L^0 \quad (7.6b)$$

and

$$E_0(N-1) = E_0^0(N-1) - \frac{1}{2} \sum_{i \neq 0, j \neq 0} \sum_{M,N=\pm 1} |\xi_{ij}^{MN}|^2 (E_i + E_j)^{-1}. \quad (7.7)$$

We set

$$E_i = E_L(1 - 1/z), \quad i = n(0) \quad (7.8a)$$

$$E_i = E_L, \quad i \neq n(0), \quad (7.8b)$$

where " $=n(0)$ " means "is a neighbor of the  $J=0$  molecule." We evaluate Eq. (7.7) to lowest order in  $z^{-1}$  and find

$$E_0(N-1) = -\frac{1}{3}(N-2)E_L^0 + S_2 \left( -\frac{Nz}{4E_L} + \frac{13}{4E_L} \right). \quad (7.9)$$

Also, in the case when a  $J=0$  molecule is present we must consider the "tipping" corrections which cause molecules near the  $J=0$  one to reorient.<sup>65</sup> These come from the terms

$$V_{\text{tip}} = \sum_{j,M=\pm 1} (c_{jM}^\dagger - c_{j,-M}) \sum_i \left(-\frac{2}{3} \xi_{ij}^{0M}\right). \quad (7.10)$$

In the pure  $J=1$  system the sum over  $i$  vanishes. Therefore, in the presence of a single  $J=0$  molecule Eq. (7.10) becomes

$$V_{\text{tip}} = \frac{2}{3} \sum_{j,M=\pm 1} \xi_{0j}^{0M} (c_{jM}^\dagger - c_{j,-M}), \quad j = n(0) \quad (7.11)$$

which leads to a perturbation energy  $\Delta E_{\text{tip}}$ , of

$$\Delta E_{\text{tip}} = -\frac{1}{E_L} \sum_j \sum_{M=\pm 1} \frac{4}{9} |\xi_{0j}^{0M}|^2 \quad (7.12a)$$

$$\approx -1.14\Gamma, \quad (7.12b)$$

similar to Nakamura's result.<sup>65</sup> Collecting the above results we have

$$\Delta E_0 \equiv E_0(N-1) - E_0(N) = \frac{2}{3}E_L^0 + 13S_2/4E_L - 1.14\Gamma \quad (7.13a)$$

$$= 13.40\Gamma. \quad (7.13b)$$

According to the sum rule of Sec. VI the average energy  $\langle E \rangle$  of the transition is

$$\langle E \rangle = -2E_0(N)/N \quad (7.14a)$$

$$= \frac{2}{3}E_L^0 + zS_2/2E_L = 14.9\Gamma. \quad (7.14b)$$

Since

$$(\langle E \rangle - \Delta E_0)/E_L = 0.10, \quad (7.15)$$

we expect that the libron sideband has an intensity of order 10% of that of the main conversion line. Of course, this intensity is spread over the width of the single libron band and may not be easy to observe.

We should modify Eq. (7.13) by including effects which are off diagonal in  $J$ . These effects have been shown to be significant in other contexts.<sup>14</sup> Here, however, we find that they are small, and their calculation is described in Appendix C. The result is that

$$E_{1,3}(N-1) - E_{1,-3}(N) = 78\Gamma^2/B, \quad (7.16a)$$

$$E_{0,2}(N-1) = -59\Gamma^2/B, \quad (7.16b)$$

where  $E_{J,J'}(L)$  is the contribution to the energy of the system of  $L J=1$  molecules from virtual processes into the state  $J'$  from the state  $J$ .

Thus, we obtain

$$\Delta E_0 = 13.40\Gamma + 19\Gamma^2/B \quad (7.17a)$$

$$\approx 13.59\Gamma, \quad (7.17b)$$

since  $\Gamma/B \approx 0.01$ . The various corrections tend

to cancel one another, so the final result, Eq. (7.17b), differs by only 5% from the "bare" value  $-2E_L^0/3 = 14.14\Gamma$ . One can include phonon renormalization<sup>47-49</sup> by replacing  $\Gamma$  by  $\xi\Gamma_0$ , where  $\Gamma_0$  is the bare value of  $\Gamma$  and  $\xi$  is expected to differ from unity only for nearest neighbors. Thus  $E_L^0 = 21.21\Gamma$  is replaced by

$$E_L^0 = (19\xi + 2.21)\Gamma_0 \quad (7.18)$$

and  $\Delta E_0$  in Eq. (7.17) is approximated by

$$\Delta E_0 = (12.12\xi + 1.47)\Gamma_0. \quad (7.19)$$

Using the quadratic extrapolation of  $E_{10}$  to pure para- $H_2$  discussed in Sec. VI, Stein *et al.*<sup>21</sup> give  $\Delta E_0 = 8.1 \text{ cm}^{-1}$ . Taking  $\Gamma_0 = 0.698 \text{ cm}^{-1}$  we find  $\xi = 0.84$ , which agrees with other determinations.<sup>26</sup> There are some residual uncertainties in this determination, however. It is clear that the extrapolation to pure  $J=0 H_2$  leads to an uncertainty of order 10% in  $\Delta E_0$  or  $\xi$ . In fact the linear extrapolation of  $E_{10}$  to 14.84 meV for pure para- $H_2$  gives  $\Delta E_0 = 8.9 \text{ cm}^{-1}$  and  $\xi = 0.93$ . Also in our calculation, the approximations we have made could lead to errors of a few percent.

Finally, we give a direct calculation of the cross section for ortho-para conversion plus libron creation. Let  $V_c$  be the perturbation which causes ortho-para conversion in neutron scattering. Then, owing to the final-state interactions from  $V_{\text{tip}}$  of Eq. (7.11), there is an effective matrix element  $V_{\text{eff}}$  for ortho-para conversion plus libron creation given by

$$V_{\text{eff}} = V_{\text{tip}}(1/E_L)V_c. \quad (7.20)$$

Thus, if  $I_c$  is the total cross section for conversion,  $I_{1c}$  that for conversion plus libron creation, and  $|0, N-1\rangle$  is the libron vacuum for  $N-1 J=1$  molecules, we have

$$I_{1c}/I_c = E_L^{-2} \langle 0, N-1 | V_{\text{tip}}^2 | 0, N-1 \rangle \quad (7.21a)$$

$$= \Delta E_{\text{tip}}/E_L \approx 0.07. \quad (7.21b)$$

We expect successively smaller amplitudes for creation of successively more librions. These small amplitudes for multiple creation probably explain the difference between the relative intensities given in Eqs. (7.15) and (7.21).

### VIII. CONCLUSIONS

We may summarize our main conclusions as follows.

(i) We have reanalyzed the phonon contribution to the inelastic-neutron-scattering cross section. The values of  $\langle u^2 \rangle$  we deduce from the experimental cross section of Stein *et al.*<sup>21</sup>  $\langle u^2 \rangle \approx 0.37$

$\text{\AA}^2$ ) are mutually self-consistent and agree qualitatively with those obtained from other inelastic-neutron experiments.<sup>17,23</sup>

(ii) We have calculated the rms libron-phonon splitting  $\Delta$  and our analytic result shows that  $\Delta^2 \propto E_L \Gamma^2 / Mc^2$ , where  $E_L$  is the average anharmonic libron energy,  $\Gamma$  the quadrupolar coupling constant,  $M$  the molecular mass, and  $c$  the average sound velocity. Our result for  $\Delta$  is about  $0.8 \text{ cm}^{-1}$ , which is about 10% smaller than that of Mertens and Biem.<sup>24</sup>

(iii) We have calculated the enhancement of the neutron scattering cross section for energies within the libron band due to the decay of a phonon into one or two librions. Each of these processes has a cross section of about 40% of that for direct libron production, at  $K \sim 3.3 \text{ \AA}^{-1}$ .

(iv) Sum rules for the zero-phonon ortho-para conversion cross section for neutron scattering are given. The sum rules yield a relation between the average energy  $\langle E \rangle$  of this process and the orientational internal energy. By integrating the high-temperature expansions and experimental values for the specific heat we obtain an order-of-magnitude fit to the experimental values of  $\langle E \rangle$  found by Stein *et al.*<sup>21</sup> at 4.2 K.

(v) The ortho-para conversion energy for pure ortho- $H_2$  at zero temperature is calculated including a number of effects suggested previously.<sup>14</sup> Comparing this calculation to the experimental value of Stein *et al.*<sup>21</sup> we find  $\Gamma = 0.58 \pm 0.06 \text{ cm}^{-1}$ , in agreement with other determinations.<sup>14,26</sup> The large uncertainty in this value of  $\Gamma$  results from the uncertainty in the extrapolation to  $x=0$ .

(vi) We predict the cross section associated with ortho-para conversion plus creation of a libron at zero temperature to be about 7% of the conversion cross section. We therefore expect a libron sideband above the conversion line having a shape similar to the libron density of states with an intensity  $\sim 7\%$  of that of the conversion line. This result is consistent with the sum rules for  $\langle E \rangle$ .

### ACKNOWLEDGMENTS

We would like to thank Dr. H. Stein, Professor H. Stiller, and Dr. R. Stockmeyer for helpful discussions and correspondence concerning their data, and for supplying tabulations of their results. We also wish to thank Dr. C. F. Coll, III for his tabulations of quadrupolar coupling constants. Also we wish to acknowledge the suggestions of Professor W. Hardy concerning the discussion of the values of  $B$  given in Sec. VI. We appreciate many constructive suggestions and discussions from Professor H. Meyer.



TABLE IVa. Values of  $\frac{1}{2}(a/\Gamma)(\partial/\partial x_j - i\partial/\partial y_j)\zeta_{kj}^{MN}$ , where  $\vec{R}_k = (0, 0, 0)$  and  $\vec{R}_j = \frac{1}{2}a(1, 1, 0)$ . Here  $(x, y)$  denotes  $x + iy$ .

| $M \setminus N$ | 2                  | 1                  | 0                 | -1                | -2                 |
|-----------------|--------------------|--------------------|-------------------|-------------------|--------------------|
| 2               | (10.2527, -3.2192) | (3.1659, -5.1648)  | (2.6450, -7.1984) | (0.0558, -3.5726) | (-1.2425, -2.7553) |
| 1               | (9.1776, -8.2898)  | (2.7492, -3.3965)  | (6.3726, -5.7625) | (2.4442, -2.8881) | (2.3475, -3.6420)  |
| 0               | (1.4399, -14.6535) | (5.4126, -0.4725)  | (8.4375, -3.4375) | (5.4126, 1.1942)  | (7.9351, 1.9452)   |
| -1              | (-3.0692, -0.4476) | (1.7225, -0.7230)  | (0.1226, 2.1541)  | (0.5841, 1.1742)  | (-1.2390, 3.2380)  |
| -2              | (0.2008, 1.5748)   | (-0.7775, -0.5170) | (0.4800, 0.7401)  | (-1.0008, 0.1130) | (-1.2943, -1.2947) |

TABLE IVb. Values of  $(1/\sqrt{2})(a/\Gamma)(\partial/\partial z_j)\zeta_{kj}^{MN}$ , where  $\vec{R}_k = (0, 0, 0)$  and  $\vec{R}_j = \frac{1}{2}a(1, 1, 0)$ . Here  $(x, y)$  denotes  $x + iy$ .

| $M \setminus N$ | 2                   | 1                  | 0                 | -1                 | -2                 |
|-----------------|---------------------|--------------------|-------------------|--------------------|--------------------|
| 2               | (4.9105, -1.0206)   | (0.3928, -0.1701)  | (2.9463, 2.0412)  | (1.9642, 0.5103)   | (2.5534, -0.3402)  |
| 1               | (1.2767, -5.4433)   | (-0.9821, 2.0412)  | (1.4731, 2.0412)  | (-0.1964, 2.7216)  | (2.4552, 4.0825)   |
| 0               | (-11.1958, -5.1031) | (2.3570, 2.5515)   | (-8.8388, 0.0000) | (-2.3570, 2.5515)  | (-11.1958, 5.1031) |
| -1              | (-2.4552, 4.0825)   | (-0.1964, -2.7216) | (-1.4731, 2.0412) | (-0.9821, -2.0412) | (-1.2767, -5.4433) |
| -2              | (2.5534, 0.3402)    | (-1.9642, 0.5103)  | (2.9463, -2.0412) | (-0.3928, -0.1701) | (4.9104, 1.0206)   |

APPENDIX A: TABULATION OF  $\vec{\nabla}\zeta$ 

In Tables III and IV we present values of  $\zeta_{ij}^{MN}$  and  $\nabla_j^\alpha \zeta_{ij}^{MN}$  for the case when  $i$  is the molecule at the origin and  $j$  is that at  $\frac{1}{2}a(1, 1, 0)$ . The components of the gradient are taken with respect to a coordinate system based on the sc unit cell and the orientation of the molecules is as specified in Table II. We now discuss the evaluation of  $\nabla_n^\alpha \zeta_{n0}^{MN}$  for  $2 \leq n \leq 12$  from the data of Table IV. Here we label the 12 nearest neighbors of the molecule 0 (at the origin) as shown in Table V.

It is clear from inversion symmetry that

$$\vec{\nabla}_{n+6} \zeta_{n+6,0}^{MN} = -\vec{\nabla}_n \zeta_{n,0}^{MN}, \quad (\text{A1})$$

so we need only consider the cases  $2 \leq n \leq 6$ . We use the symmetry relations<sup>7</sup>

$$\zeta_{20}^{MN}(\vec{R}_2 + \vec{u}) = \zeta_{10}^{NM}(\vec{R}_1 + \sigma_x \vec{u})^*, \quad (\text{A2a})$$

$$\zeta_{30}^{MN}(\vec{R}_3 + \vec{u}) = \zeta_{10}^{MN}(\vec{R}_1 + \mathcal{R}^2 \vec{u}) e^{2\pi i(M-N)/3}, \quad (\text{A2b})$$

$$\zeta_{40}^{MN}(\vec{R}_4 + \vec{u}) = \zeta_{10}^{NM}[\vec{R}_{10} + \sigma_x(\mathcal{R}^2 \vec{u})]^* e^{2\pi i(M-N)/3}, \quad (\text{A2c})$$

$$\zeta_{50}^{MN}(\vec{R}_5 + \vec{u}) = \zeta_{10}^{MN}(\vec{R}_1 + \mathcal{R} \vec{u}) e^{\pi i(M+2N)/3}, \quad (\text{A2d})$$

$$\zeta_{60}^{MN}(\vec{R}_6 + \vec{u}) = \zeta_{10}^{NM}[\vec{R}_1 + \sigma_x(\mathcal{R} \vec{u})]^* e^{\pi i(M+2N)/3}, \quad (\text{A2e})$$

where  $\sigma_x$  and  $\mathcal{R}$  are operators defined by

$$\sigma_x(A\hat{i} + B\hat{j} + C\hat{k}) = -A\hat{i} + B\hat{j} + C\hat{k}, \quad (\text{A3a})$$

$$\mathcal{R}(A\hat{i} + B\hat{j} + C\hat{k}) = C\hat{i} + A\hat{j} + B\hat{k}. \quad (\text{A3b})$$

From (A2) we obtain the relations

$$\vec{\nabla}_2 \zeta_{20}^{MN} = \sigma_x(\nabla_1 \zeta_{10}^{NM})^*, \quad (\text{A4a})$$

$$\vec{\nabla}_3 \zeta_{30}^{MN} = \mathcal{R}(\nabla_1 \zeta_{10}^{MN}) e^{2\pi i(M-N)/3}, \quad (\text{A4b})$$

$$\vec{\nabla}_4 \zeta_{40}^{MN} = \mathcal{R}[\sigma_x(\nabla_1 \zeta_{10}^{NM})^*] e^{2\pi i(M-N)/3}, \quad (\text{A4c})$$

$$\vec{\nabla}_5 \zeta_{50}^{MN} = \mathcal{R}^2(\nabla_1 \zeta_{10}^{MN}) e^{\pi i(M+2N)/3}, \quad (\text{A4d})$$

$$\vec{\nabla}_6 \zeta_{60}^{MN} = \mathcal{R}^2[\sigma_x(\nabla_1 \zeta_{10}^{NM})^*] e^{\pi i(M+2N)/3}. \quad (\text{A4e})$$

The gradients of  $\zeta$ 's involving other sublattices can also be obtained using symmetry relations as discussed in Ref. 7. The components of the gradient of  $\zeta$  which are not given in Table IV can be constructed using the relation

$$\left(\frac{\partial}{\partial x_j} + i\frac{\partial}{\partial y_j}\right)\zeta_{kj}^{MN} = (-1)^{M+N} \left[\left(\frac{\partial}{\partial x_j} - i\frac{\partial}{\partial y_j}\right)\zeta_{kj}^{-M,-N}\right]^* \quad (\text{A5})$$

We may evaluate  $S_{\mu\nu}^1(0)$ , where

$$S_{\mu\nu}^M(0) = 2 \sum_{i=1}^6 \frac{R_i^\mu}{a} (a\nabla_i^\nu \zeta_{i0}^{0M}), \quad (\text{A6})$$

where we have used (A1) to simplify (4.8). Using the data of Table II and the relations (A4) we

TABLE V. Position vectors of nearest neighbors of the molecule at  $(0, 0, 0)$ . Here  $a$  is the lattice parameter for the cubic cell,  $a = \sqrt{2}R_0$ , where  $R_0$  is the nearest-neighbor separation; and  $\bar{1} = -1$ .

|                                    |                                             |
|------------------------------------|---------------------------------------------|
| $(2/a)\vec{R}_1 = (1, 1, 0)$       | $(2/a)\vec{R}_7 = (\bar{1}, \bar{1}, 0)$    |
| $(2/a)\vec{R}_2 = (\bar{1}, 1, 0)$ | $(2/a)\vec{R}_8 = (1, \bar{1}, 0)$          |
| $(2/a)\vec{R}_3 = (0, 1, 1)$       | $(2/a)\vec{R}_9 = (0, \bar{1}, \bar{1})$    |
| $(2/a)\vec{R}_4 = (0, \bar{1}, 1)$ | $(2/a)\vec{R}_{10} = (0, 1, \bar{1})$       |
| $(2/a)\vec{R}_5 = (1, 0, 1)$       | $(2/a)\vec{R}_{11} = (\bar{1}, 0, \bar{1})$ |
| $(2/a)\vec{R}_6 = (1, 0, \bar{1})$ | $(2/a)\vec{R}_{12} = (\bar{1}, 0, 1)$       |

evaluate the matrix  $\underline{S}^{-1}$  as

$$\underline{S}^{-1} = \begin{pmatrix} S_x + \lambda_+ S_y & A_y + \lambda_+ S_z & A_z + \lambda_+ A_x \\ A_x + \lambda_- A_z & S_y + \lambda_- S_x & S_z + \lambda_- A_y \\ \lambda_- S_z + \lambda_+ A_y & \lambda_- A_x + \lambda_+ A_z & \lambda_- S_y + \lambda_+ S_x \end{pmatrix}, \quad (\text{A7})$$

where  $\lambda_{\pm} = e^{\pm 2\pi i/3}$  and

$$S_{\alpha} = a \nabla_1^{\alpha} [\zeta_{10}^{\alpha}(R_1) + \zeta_{10}^{\alpha}(R_1)^*], \quad (\text{A8a})$$

$$A_{\alpha} = a \nabla_1^{\alpha} [\zeta_{10}^{\alpha}(R_1) - \zeta_{10}^{\alpha}(R_1)^*]. \quad (\text{A8b})$$

Using the values of  $\nabla_1^{\alpha} \zeta_{10}^{\alpha}$  from Table IV we obtain (4.9).

$$V_{iM; \vec{q}\mu} = \left( \frac{\hbar}{2MN\omega_{\mu}(\vec{q})} \right)^{1/2} \sum_{jB} (e^{-i\vec{q} \cdot \vec{R}_i} - e^{-i\vec{q} \cdot \vec{R}_j}) \xi_{\mu}^{\beta}(\vec{q}) \left\{ -\frac{2}{3} \nabla_j^{\beta} \zeta_{ji}^{\alpha M} + \frac{4}{5} \left( \frac{3}{5} \pi \right)^{1/2} \nabla_j^{\beta} [B(R_{ij}) Y_2^M(\hat{R}_{ij})^*] \right\}. \quad (\text{B2})$$

In the presence of the perturbation (B1) the libron states are

$$|iM\rangle = c_{iM}^{\dagger} |0\rangle^0 - \sum_{\vec{q}\mu} \frac{V_{iM; \vec{q}\mu}^{\dagger} a_{\vec{q}\mu}^{\dagger}}{\hbar [\omega_{\mu}(\vec{q}) - \omega_L]} |0\rangle^0, \quad (\text{B3})$$

where  $|0\rangle^0$  denotes the vacuum state. The ground state  $|0\rangle$  is

$$|0\rangle = |0\rangle^0 - \sum_{iM} \sum_{\vec{q}\mu} \frac{V_{iM; \vec{q}\mu} c_{iM}^{\dagger} a_{\vec{q}\mu}^{\dagger}}{\hbar [\omega_{\mu}(\vec{q}) + \omega_L]} |0\rangle^0. \quad (\text{B4})$$

We denote the integrated contribution to  $S_p(K, \omega)$  from these libronlike states, due to the small

$$I_{PL}^+ = \frac{2K^2}{3\hbar^4} j_0^2 \left( \frac{1}{2} K\rho \right) \sum_{iM\alpha} \left| \sum_{\vec{q}\mu} \frac{V_{iM; \vec{q}\mu} [\hbar \omega_{\mu}(\vec{q})]}{\omega_{\mu}(\vec{q})^2 - \omega_L^2} \langle a_{\vec{q}\mu}^{\dagger} u_{\vec{s}}^{\alpha} \rangle \right|^2. \quad (\text{B6})$$

We now insert (B2) into (B6) and have

$$I_{PL}^+ = \frac{2}{3} K^2 j_0^2 \left( \frac{1}{2} K\rho \right) \sum_{iM\alpha} \sum_{\vec{q}\mu} \sum_{\vec{q}'\mu'} \sum_{jB} \sum_{j'B'} [\omega_{\mu}(\vec{q})^2 - \omega_L^2]^{-1} \xi_{\mu}^{\beta}(\vec{q}) \xi_{\mu'}^{\beta'}(\vec{q}') \xi_{\mu}^{\alpha}(\vec{q}) \xi_{\mu'}^{\alpha}(\vec{q}') [\omega_{\mu'}(\vec{q}')^2 - \omega_L^2]^{-1} \\ \times (2MN)^{-2} X_{ij'}^{\beta M} (X_{ij'}^{\beta' M})^* (e^{i\vec{q} \cdot \vec{R}_i} - e^{i\vec{q} \cdot \vec{R}_j}) \\ \times (e^{-i\vec{q}' \cdot \vec{R}_i} - e^{-i\vec{q}' \cdot \vec{R}_j}) e^{i(\vec{q}' \cdot \vec{s} - \vec{q} \cdot \vec{s})}, \quad (\text{B7})$$

where  $X_{ij'}^{\beta M}$  denotes the curly brackets in (B2). Since the result must be independent of  $\vec{s}$ , we may average over  $\vec{s}$ , whence  $\vec{q} = \vec{q}'$ . Also we neglect the dependence of  $\omega_{\mu}(\vec{q})$  on  $\mu$ . Then we find

$$I_{PL}^+ = \frac{K^2 j_0^2 \left( \frac{1}{2} K\rho \right)}{6M^2 N^2} \sum_{iMB} \sum_{\vec{q}j'} (1 - e^{i\vec{q} \cdot (\vec{R}_j - \vec{R}_i)}) (1 - e^{-i\vec{q} \cdot (\vec{R}_j' - \vec{R}_i)}) X_{ij'}^{\beta M} (X_{ij'}^{\beta M})^* [\omega^2(\vec{q}) - \omega_L^2]^{-2}. \quad (\text{B8})$$

Since  $X_{ij'}^{\beta M}$  is an odd function of  $\vec{R}_{ij'}$ , we may write (B8) as

$$I_{PL}^+ = \frac{2K^2 j_0^2 \left( \frac{1}{2} K\rho \right)}{3M^2 N} \sum_{M=\pm 1} \sum_{\vec{q}B} \sum_{j, j'=1}^6 \frac{\sin \vec{q} \cdot \vec{R}_j \sin \vec{q} \cdot \vec{R}_{j'}}{[\omega^2(\vec{q}) - \omega_L^2]^2} X_{0j'}^{\beta M} (X_{0j'}^{\beta M})^*, \quad (\text{B9})$$

where we have numbered the nearest neighbors of the origin ( $i=0$ ) according to Table V of Appendix A. Furthermore, since the origin has a threefold symmetry axis along the (1, 1, 1) direction and there is time-

## APPENDIX B: EFFECT OF LIBRON-PHONON INTERACTIONS ON THE NEUTRON SCATTERING CROSS SECTION

In this appendix we evaluate the effect on the neutron scattering cross section at  $\approx \omega_L$  of libron-phonon interactions. In subsection 1 we consider linear libron-phonon mixing and in subsection 2 we study anharmonic mixing.

### 1. Linear libron-phonon mixing

The process we evaluate now is that of diagram *c* of Fig. 5. For this calculation we write the linear libron-phonon coupling as

$$V_{LP} = \sum_{iM} \sum_{\vec{q}\mu} V_{iM; \vec{q}\mu} (c_{iM}^{\dagger} - c_{i, -M}) (a_{-\vec{q}\mu}^{\dagger} - a_{\vec{q}\mu}), \quad (\text{B1})$$

where  $\vec{q}$  is summed over the fcc Brillouin zone and

admixture of phonon amplitude,  $I_{PL}^+$ . Then,

$$I_{PL}^+ = \frac{1}{2} j_0^2 \left( \frac{1}{2} K\rho \right) \sum_{iM} |\langle iM | \vec{K} \cdot \vec{u}_{\vec{s}} | 0 \rangle|^2 \quad (\text{B5a})$$

$$= \frac{1}{6} K^2 j_0^2 \left( \frac{1}{2} K\rho \right) \sum_{iM\alpha} |\langle iM | u_{\vec{s}}^{\alpha} | 0 \rangle|^2, \quad (\text{B5b})$$

where  $u_{\vec{s}}^{\alpha}$  is the displacement of the molecule at  $\vec{s}$ . As mentioned in Sec. V we may neglect the effect of libron-phonon interactions on  $S_L(K, \omega)$ . Using the wave functions of (B3) and (B4) we obtain

reversal invariance, we may write (B9) as

$$I_{PL}^+ = \frac{4K^2 j_0^2 (\frac{1}{2}K\rho)}{M^2 N} \sum_{\vec{q}\beta} \sum_{j=1}^2 \sum_{j'=1}^6 \frac{\sin\vec{q} \cdot \vec{R}_j \sin\vec{q} \cdot \vec{R}_{j'}}{[\omega^2(\vec{q}) - \omega_L^2]^2} X_{0j}^{\beta 1} (X_{0j'}^{\beta 1})^* \quad (\text{B10})$$

This result represents the additional phononlike scattering which occurs at  $\hbar\omega \approx E_L$ : Clearly, when averaged over all energy, a comparable amount of intensity is removed from the phonon part of the cross section. The enhanced scattering calculated in Eq. (B10) is superimposed on a depletion of the phonon scattering which is spread over the entire phonon spectrum. Thus, in calculating the enhancement near  $E_L$  it is necessary to take account of that part of the depletion which occurs over the energy interval under consideration, i.e., the libron band. The calculation of this effect is most naturally carried out using Green's functions, as we now do.

To begin with it is useful to note that the result, Eq. (B10), can also be obtained using Green's functions,<sup>56</sup> as outlined in Appendix D. There the perturbed phonon frequency  $\tilde{\omega}(q)$  is obtained as

$$\tilde{\omega}(\vec{q}) = \omega(\vec{q}) + [\hbar/(2M\omega(\vec{q}))]\Sigma(\vec{q}, \omega), \quad (\text{B11})$$

where  $\Sigma(\vec{q}, \omega)$  is the self-energy given in Eq. (D3). In Fig. 10 we show  $\Sigma(\vec{q}, \omega)$  and  $\tilde{\omega}(\vec{q})$ . In Eq. (D3) there is a singularity at  $\omega = \omega_L$  which would not occur if we had taken proper account of the bandwidth  $\delta$  of the librions.<sup>33</sup> A simple way to proceed is to replace  $\omega$  by  $\omega - i\delta$  as we have done in Fig. 10. From this figure we also see the depletion effect on  $S_p(K, \omega)$ ; namely, the energy shift in Eq. (B11) leads to a decrease in the total number of phonon states within the libron band. In the simple model treated in Sec. V this effect is taken into account via the coefficients appearing in Eq. (5.6). The easiest way to discuss this effect is to calculate the increase  $\Delta n$  in the number of phonon states having frequencies outside the libron band. Because of the momentum dependence of the scattering cross section, it suffices to calculate  $\Delta n$  for energies above the upper edge of the libron band at frequency  $\omega_L + \delta$ . We have, using Eq. (D4),

$$\Delta n = g(\hbar\omega_{\max}) \langle \Sigma(\vec{q}, \omega_{\max}) \rangle \hbar^2 / 2M\omega_{\max}, \quad (\text{B12})$$

where  $\langle \rangle$  indicates an average over all  $\vec{q}$ 's having  $\omega(\vec{q}) = \omega_{\max}$ . According to Eq. (2.3c), the change in the cross section, which we denote  $I_{PL}^-$ , within the libron band due to removing this number of phonon states is

$$I_{PL}^- = -\frac{1}{2} g(\hbar\omega_{\max}) \langle \hbar\Sigma(q, \omega_{\max}) \rangle \times [(\hbar K/2M\omega_{\max}) j_0(\frac{1}{2}K\rho)]^2, \quad (\text{B13})$$

and we write the total change in the cross section attributable to libron-phonon interactions  $I_{PL}$  as

$$I_{PL} = I_{PL}^+ + I_{PL}^-. \quad (\text{B14})$$

Since the effect of  $I_{PL}^-$  is to cancel almost all of the contribution to  $I_{PL}^+$  from low-frequency phonons, the dominant contribution to  $I_{PL}$  comes from high-frequency phonons, for which we use the approximation  $\omega^2(q) - \omega_L^2 = \omega_{\text{eff}}^2$ , with  $\omega_{\text{eff}} \approx \omega_D$ , and neglect  $I_{PL}^-$  altogether. Within this approximation the sum over  $\vec{q}$  in (B10) vanishes unless  $j=j'$ , so that

$$I_{PL} = 2 \left[ \frac{KR_0 j_0(\frac{1}{2}K\rho)}{M\omega_{\text{eff}}^2 R_0^2} \right]^2 R_0^2 \sum_{j=1}^2 \sum_{\beta} |X_{0j}^{\beta 1}|^2. \quad (\text{B15})$$

Using the data of Appendix A we evaluate this as

$$I_{PL} = \left( \frac{KR_0 j_0(\frac{1}{2}K\rho)}{M\omega_{\text{eff}}^2 R_0^2} \right)^2 \left[ \frac{22625}{162} \Gamma^2 + \frac{68}{9} \Gamma R_0 B' + \frac{20}{9} \Gamma B + \frac{8}{25} (R_0 B')^2 + \frac{64}{25} B^2 \right]. \quad (\text{B16})$$

The contribution of the non-EQQ terms are of

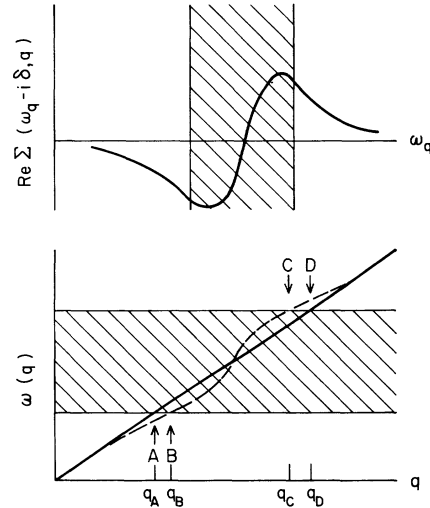


FIG. 10. Top: Schematic graph of the phonon self-energy  $\text{Re}\Sigma(\omega - i\delta, q)$  versus  $\omega$  for fixed wave vector  $q$  with  $\delta$  approximately equal to the libron bandwidth. The shaded region is the libron band. Bottom: Phonon frequency  $\omega(q)$  versus  $q$  with (dashed line) and without (solid line) libron-phonon interactions. The libron band is shaded. The total number of phonon states within the libron band is  $\sim q_D^3 - q_A^3$  in the absence of libron-phonon interactions and is  $\sim q_C^3 - q_B^3$  in the presence of interactions.

relative order 10% if the values of the potential parameters of Table I are used. Omitting these terms yields the result

$$r' \equiv \frac{I_{PL}}{I_L} = \frac{181}{6} \left( \frac{25j_0(\frac{1}{2}K\rho)\Gamma KR_0}{9j_2(\frac{1}{2}K\rho)M\omega_{\text{eff}}^2 R_0^2} \right)^2, \quad (\text{B17})$$

where  $I_L$  is the integrated scattering cross section of librons in the absence of libron-phonon coupling. We now evaluate this expression using experimental values appropriate to the experiment of Stein *et al.*<sup>21</sup> There the momentum transfer corresponding to the average libron energy of 1 meV was  $K=3.28 \text{ \AA}^{-1}$ , for which value  $j_0(\frac{1}{2}K\rho)/j_2(\frac{1}{2}K\rho)=8.9$ . Setting  $\omega_{\text{eff}}=\omega_D$  and taking the remaining values from Table I we obtain

$$r' = 0.028. \quad (\text{B18})$$

We now make a more complete evaluation of

$$I_{PL}^+ = \frac{1}{N} \left( \frac{4Kj_0(\frac{1}{2}K\rho)}{3MN} \right)^2 \sum_q [\omega(q)^2 - \omega_L^2]^{-2} \{ \sin^2 \vec{q} \cdot \vec{R}_{10} (\vec{v}_1 \cdot \vec{v}_1^* + \vec{v}_2 \cdot \vec{v}_2^* + \sin \vec{q} \cdot \vec{R}_{10} \sin \vec{q} \cdot \vec{R}_{30} [ \vec{v}_1 \cdot (\vec{v}_3 - \vec{v}_4 + \vec{v}_5 + \vec{v}_6)^* + \vec{v}_2 \cdot (\vec{v}_3 - \vec{v}_4 - \vec{v}_5 - \vec{v}_6)^* ] \} \}. \quad (\text{B21})$$

Substituting the values of Eq. (B20) we obtain

$$I_{PL}^+ = \left( \frac{5j_0(\frac{1}{2}K\rho)KR_0\Gamma}{9M\omega_D^2 R_0^2} \right)^2 \frac{1}{2N} \sum_q \frac{\omega_D^4}{[\omega(q)^2 - \omega_L^2]^2} (1810 \sin^2 \vec{q} \cdot \vec{R}_{10} + 783 \sin \vec{q} \cdot \vec{R}_{10} \sin \vec{q} \cdot \vec{R}_{30}). \quad (\text{B22})$$

In evaluating Eq. (B22) we only consider processes which shift weight into the libron band from phonons whose energy lies above the top of the libron band at energy  $\hbar\omega_{\text{max}}$ . We take  $\hbar\omega_{\text{max}}=2 \text{ meV}$  and approximate the sum over  $q$  by an integral over the Debye sphere. Thus we obtain

$$I_{PL}^+ = 1810 \left( \frac{5j_0(\frac{1}{2}K\rho)KR_0\Gamma}{18M\omega_D^2 R_0^2} \right)^2 \Lambda, \quad (\text{B23})$$

where

$$\Lambda = \int_{\omega_{\text{max}}}^{\omega_D} \frac{3\omega^2 \omega_D}{(\omega^2 - \omega_L^2)^2} d\omega \times \left\{ 1 - j_0 \left( \frac{2\omega R_0}{c} \right) + \frac{783}{1810} \left[ j_0 \left( \frac{\omega R_0}{c} \right) - j_0 \left( \frac{\sqrt{3}\omega R_0}{c} \right) \right] \right\}. \quad (\text{B24})$$

The result (B18) is obtained by neglecting  $I_{PL}^-$  and setting  $\Lambda=1$ . This is a rather poor approximation. Numerically we found  $\Lambda=16.05$ . The effect of admixture of phonon modes having energy less than the libron gap was estimated by computing the integral of (B24) between the limits 0 and 0.5 meV, which gives  $\Lambda=0.03$ . Thus the

$I_{LP}$  but, for simplicity, we neglect the terms involving  $B$ . We set

$$\vec{v}_j = \vec{v}_j \zeta_{j0}^{01} \quad (\text{B19})$$

and the data of Appendix A yield

$$\begin{aligned} \vec{v}_1 &= \lambda \mathcal{R}^2 \vec{v}_3 = \lambda^2 \mathcal{R} \vec{v}_5 \\ &= \frac{5\sqrt{2}\Gamma}{24R_0} (15 - 5\sqrt{3}i, 19 + 9\sqrt{3}i, 5 + 4\sqrt{3}i), \end{aligned} \quad (\text{B20a})$$

$$\begin{aligned} \vec{v}_2 &= \lambda \mathcal{R}^2 \vec{v}_4 = \lambda^2 \mathcal{R} \vec{v}_6 = \\ &= \frac{5\sqrt{2}\Gamma}{24R_0} (\sqrt{3}i, 4 - 15\sqrt{3}i, 8 - 5\sqrt{3}i), \end{aligned} \quad (\text{B20b})$$

where  $\mathcal{R}$  is a rotation operator defined in Eq. (A3b). Using the symmetry of the momentum sums we write Eq. (B10) as

admixture of low-frequency phonons is negligible.

A similar evaluation of Eq. (B13) based on Eq. (D3) leads to the result

$$I_{PL}^- = -\frac{181}{10} \left( \frac{25j_0(\frac{1}{2}K\rho)\Gamma KR_0}{9M\omega_D^2 R_0^2} \right)^2 \frac{\omega_D \omega_L \omega_{\text{max}}^2 R_0^2}{c^2 (\omega_{\text{max}}^2 - \omega_L^2)}. \quad (\text{B25})$$

Combining Eqs. (B24) and (B25) we have

$$r' = \frac{I_{PL}^+ + I_{PL}^-}{I_L} = \frac{181}{6} \left( \frac{25j_0(\frac{1}{2}K\rho)\Gamma KR_0}{9j_2(\frac{1}{2}K\rho)M\omega_D^2 R_0^2} \right)^2 \times \left[ \Lambda - \left( \frac{\omega_L}{\omega_D} \right) \left( \frac{\omega_D R_0}{c} \right)^2 \frac{\omega_{\text{max}}^2}{\omega_{\text{max}}^2 - \omega_L^2} \right] \quad (\text{B26a})$$

$$= 0.37. \quad (\text{B26b})$$

Our result for  $r'$  contrasts with that of Bickermann,<sup>25</sup> who gives  $r' \approx 11$ . However, Eq. (B26a) is consistent with the evaluation  $r'=0.22$  of Sec. V for the simple model of linear mode mixing.

## 2. Two-libron effects

Now we calculate the two-libron contributions to the cross section corresponding to diagram  $d$  of Fig. 4. For this calculation the formalism

of Appendix D is convenient.

The coupling of one phonon to two librions is given in Eq. (3.9). The self-energy in second-order perturbation theory is

$$\begin{aligned} \Sigma_{\mu, \mu'}(\omega, \vec{q}) = & \frac{2\omega_L}{N\hbar^2} \sum_{i,j\alpha\beta} \sum_{M, N=\pm 1} |e^{i\vec{q}\cdot\vec{R}_i} - e^{i\vec{q}\cdot\vec{R}_j}|^2 \\ & \times \xi_\mu^\alpha(\vec{q}) \xi_{\mu'}^\beta(\vec{q}) \nabla_i^\alpha \xi_{ij}^{MN} \\ & \times \nabla_j^\beta (\xi_{ij}^{MN})^* (\omega^2 - 4\omega_L^2)^{-1}, \end{aligned} \quad (\text{B27})$$

where  $\mu$  and  $\mu'$  are polarization indices. In deriving this result we again neglect the mode structure of the librions, assuming Eq. (5.1). We now average over polarizations, since we always assume  $\omega_\mu(q) = \omega(q)$ . Then we obtain

$$\begin{aligned} \Sigma(\omega, \vec{q}) = & \frac{4\omega_L}{3N\hbar^2} \sum_{i,j\alpha} \sum_{M, N=\pm 1} (1 - \cos\vec{q}\cdot\vec{R}_{ij}) \\ & \times |\nabla_i^\alpha \xi_{ij}^{MN}|^2 (\omega^2 - 4\omega_L^2)^{-1}. \end{aligned} \quad (\text{B28})$$

To determine  $I_{PL}^+$  from  $\Sigma$  we note that the analog of Eq. (D7) for the two-libron case reads

$$W_q(2\omega_L)(2\omega_L) = -\frac{\hbar^2}{4M^2} \frac{1}{\omega} \left. \frac{\partial \Sigma}{\partial \omega} \right|_{\omega=\omega(q)}, \quad (\text{B29})$$

so that Eq. (D8) becomes

$$I_{PL}^+ = \frac{\hbar^2 K^2}{16M^2 \omega_L} j_0^2(\frac{1}{2}K\rho) \frac{1}{N} \sum_q \frac{1}{\omega} \left. \frac{\partial \Sigma}{\partial \omega} \right|_{\omega=\omega(q)}. \quad (\text{B30})$$

Substituting Eq. (B28) for  $\Sigma$  into this expression for  $I_{PL}^+$  and into (B13) for  $I_{PL}^-$  we obtain the two-libron contribution to  $r'$ , denoted  $r''$ , as

$$\begin{aligned} r'' = & 10S \left( \frac{KR_0 \Gamma j_0(\frac{1}{2}K\rho)}{6M\omega_D^2 R_0^2 j_2(\frac{1}{2}K\rho)} \right)^2 \\ & \times \left( \Lambda' - \frac{3\omega_L \omega_D}{\omega_{\max}^2 - 4\omega_L^2} \langle 1 - \cos\vec{q}\cdot\vec{R}_{10} \rangle \right), \end{aligned} \quad (\text{B31})$$

where

$$S = \left( \frac{R_0}{\Gamma} \right)^2 \sum_{j,\alpha} \sum_{M, N=\pm 1} |\nabla_i^\alpha \xi_{ij}^{MN}|^2 \approx 1221, \quad (\text{B32a})$$

and

$$\Lambda' = \frac{1}{N} \sum_q \frac{\omega_D^4 (1 - \cos\vec{q}\cdot\vec{R}_{10})}{[\omega(q)^2 - 4\omega_L^2]^2}. \quad (\text{B32b})$$

In Eq. (B31)  $\langle \rangle$  indicates an average over all  $\vec{q}$ 's having  $\omega(q) = \omega_{\max}$  and the evaluation of Eq. (B32a) was done using Table IV.

To evaluate Eq. (B31) we again consider phonon admixtures only from phonons having  $\omega > \omega_{\max}$  where now  $\hbar\omega_{\max}$  is the maximum two-libron energy, i.e.,  $\hbar\omega_{\max} \approx 2.5$  meV.<sup>66</sup> Also we integrate

over a Debye sphere, so that

$$\Lambda' = 3 \int_{\omega_{\max}}^{\omega_D} \frac{\omega_D \omega^2}{(\omega^2 - 4\omega_L^2)^2} \left[ 1 - j_0\left(\frac{\omega R_0}{c}\right) \right] d\omega \quad (\text{B33a})$$

$$= 11.37, \quad (\text{B33b})$$

and also

$$\langle 1 - \cos\vec{q}\cdot\vec{R}_{10} \rangle = 1 - j_0(2\omega_L R_0/c) \quad (\text{B33c})$$

$$= 0.14. \quad (\text{B33d})$$

These evaluations yield

$$r'' = 369 \left[ \frac{25j_0(\frac{1}{2}K\rho)\Gamma KR_0}{9j_2(\frac{1}{2}K\rho)M\omega_D^2 R_0^2} \right]^2 \quad (\text{B34a})$$

$$= 0.37. \quad (\text{B34b})$$

Here we took  $K = 3.17 \text{ \AA}^{-1}$  for  $\hbar\omega = 2$  meV and  $j_0(\frac{1}{2}K\rho)/j_2(\frac{1}{2}K\rho) = 9.6$ .

Thus, we conclude that for  $K \approx 3.3 \text{ \AA}^{-1}$  the enhancement to the cross section in the libron band due to libron-phonon interactions is about the same for one- and two-libron processes. The total enhancement due to both processes is about 74%. We have not discussed explicitly the effect of libron-libron interactions. In the absence of libron-phonon coupling the interactions cause a mixing of the one- and two-libron states<sup>9,11</sup>; that is, they shift libron spectral weight from the single-libron band into the two-libron band. (See Fig. 5, diagram *e*.) Accordingly, in the present case, some of the single-libron-enhanced cross section will be shifted into the two-libron band. (See Fig. 5, diagram *f*.) However, by the same mechanism (Fig. 5, diagram *g*), some of the two-libron-enhanced cross section will be shifted into the single-libron band. Since the enhancements are approximately equal, the two anharmonic shifts will be of the same order of magnitude and will tend to cancel.

#### APPENDIX C: PROCESSES OFF DIAGONAL IN $J$

In this appendix we consider virtual processes in which  $J$  is not conserved. Throughout we will use the procedure and notation of Appendix A of Ref. 14 and equations from there will be denoted (A1'), (A2'), etc. We will repeat that calculation for the case when there is a single  $J = 0$  molecule at the site  $s$ , confining our attention, however, to the ground-state energy.

Contributions to the ground-state energy come from terms in (A15'), (A31'), and (A32'). For instance, in the present case the terms in (A15') lead to an energy shift  $\Delta E$  given by

$$-10B(\Delta E) = \frac{1}{2} \sum_i \sum_{kt} \sum_{mm'} \xi_{ik}^{m0} \xi_{it}^{m'0} \left(-\frac{2}{3}\right)^2 \\ \times R_{mm'}^i (1 - \delta_{is}) \\ \times (1 - \delta_{ks})(1 - \delta_{ts}) \quad (C1)$$

$$= \frac{3}{7} (E_L^0)^2 (N-3) + \frac{2}{9} \sum_{im} |\xi_{is}^{m0}|^2 r_m. \quad (C2)$$

We note the appearance of the factor  $N-3$  for the three-molecule term. Since the terms in (A31') and (A32') which contribute to the ground-state energy are both two-molecule terms, with which we associate the factor  $N-2$ , one sees that in the present case, the final result, (A34'), becomes

$$-10B(\Delta E) = (N-3) \frac{3}{7} (E_L^0)^2 \\ + (N-2) \frac{\Gamma^2}{4} \sum_m \sum_{n \neq 0} S_{mn} r_m (t_n + \frac{1}{4} r_n) \\ + \frac{2}{9} \Gamma^2 \sum_m r_m S_{m0}. \quad (C3)$$

Thus, in the notation of (7.16) we write

$$E_{1,3}(N-1) - E_{1,3}(N) \\ = \frac{1}{10B} \left( \frac{3}{7} (E_L^0)^2 - \frac{2}{9} \Gamma^2 \sum_m r_m S_{m0} \right. \\ \left. + \frac{\Gamma^2}{2} \sum_m \sum_{n \neq 0} S_{mn} r_m (t_n + \frac{1}{4} \Gamma_n) \right). \quad (C4)$$

Next we consider the terms involving virtual  $J=2$  excitation. We note that  $\langle 00 | O_i^{-m} | 2m \rangle \times \langle 2m | O_i^m | 00 \rangle = (-1)^m (4\pi A_m^2)^{-1}$ , where  $A_m$  is given in (3.7). We write

$$E_{0,2}(N-1) = -\frac{1}{6B} \sum_{i \neq j} \sum_m \xi_{oi}^{m0} \xi_{oj}^{-m0} (4\pi A_m^2)^{-1} (-1)^m \left(-\frac{2}{3}\right)^2 - \frac{1}{6B} \sum_i \sum_{mn} \xi_{oi}^{mn} \xi_{oi}^{-m,-n} (4\pi A_m^2)^{-1} (-1)^m \langle O_i^n O_i^{-n} \rangle \\ - \frac{1}{6B} \sum_i \sum_{mn} \xi_{oi}^{mn} \xi_{oi}^{-m,-n} (4\pi A_m^2)^{-1} (-1)^m \langle O_i^n P_i O_i^{-n} \rangle, \quad (C5)$$

where  $\langle \rangle$  denotes an average in the ground state. The first term in (C5) is the contribution involving two distinct  $J=1$  molecules. The second and third terms involve a single  $J=1$  molecule. The virtual state of the  $J=1$  molecule is  $J=1$  for the second term and  $J=3$  for the third term. Doing the sums over lattice sites we obtain

$$E_{0,2}(N-1) = -\frac{1}{6B} \left( \frac{1}{-4\pi A_0^2} (E_L^0)^2 - \frac{1}{9\pi} \sum_m \frac{S_{m0}}{|A_m|^2} \right) \\ - \frac{1}{6B} \sum_{mn} \frac{1}{8\pi A_m^2} S_{mn} t_n \\ - \frac{1}{16B} \sum_{mn} \frac{1}{8\pi A_m^2} S_{mn} r_n \quad (C6)$$

in the notation of Ref. 14. Numerical evaluation of this result yields (7.16b).

$$\Sigma(\omega, \vec{q}) = \frac{16\omega_L}{\hbar^2} \sum_B \sum_{j=1}^2 \sum_{j'=1}^6 \frac{\sin \vec{q} \cdot \vec{R}_j \sin \vec{q} \cdot \vec{R}_{j'} X_{0j}^{\beta M} (X_{0j'}^{\beta M})^*}{\omega^2 - \omega_L^2}. \quad (D3)$$

The perturbed phonon frequency is determined from the pole in  $D(\omega, \vec{q})$  to be

$$\bar{\omega}_q^* = \omega(\vec{q}) + \frac{\hbar}{2M\omega(\vec{q})} \Sigma(\omega, \vec{q}) \Big|_{\omega=\omega_q^*} \quad (D4)$$

to lowest order in  $\Sigma$ . The perturbed oscillator

#### APPENDIX D: GREEN'S-FUNCTION ANALYSIS OF LIBRON-PHONON MIXING

Here we outline the Green's-function description of libron-phonon mixing. We write the displacement-displacement Green's function<sup>56</sup> for the unperturbed system as

$$D_{\mu\mu'}^0(\omega, \vec{q}) = \frac{\hbar}{m\{\omega^2 - [\omega(\vec{q})]^2\}} \delta_{\mu\mu'}, \quad (D1)$$

where  $\mu$  and  $\mu'$  are polarization indices. Since we have assumed  $\omega_\mu(\vec{q}) = \omega(\vec{q})$ , independent of  $\mu$ , all quantities will be diagonal in the polarization indices, which therefore will henceforth be omitted. Including the libron-phonon coupling in second-order perturbation theory, we obtain

$$D(\omega, \vec{q}) = \frac{\hbar}{m\{\omega^2 - [\omega(\vec{q})]^2\} - \hbar\Sigma(\omega, \vec{q})}, \quad (D2)$$

where  $\Sigma(\omega, \vec{q})$  is the self-energy. The work of Appendix (B1) corresponds to the approximation

$$\text{strength } W_q^*(\bar{\omega}_q^*) \text{ is the residue of } D(\omega, q) \text{ at } \omega = \bar{\omega}_q^* \text{ and to lowest order in } \Sigma \text{ is} \\ W_q^*(\omega_q^*) = \frac{\hbar}{2M\bar{\omega}(\vec{q})} \left( 1 + \frac{\hbar}{2M\omega(\vec{q})} \frac{\partial \Sigma(\omega, \vec{q})}{\partial \omega} \Big|_{\omega=\omega_q^*} \right)^{-1}. \quad (D5)$$

The oscillator strength of the phonon which is shifted into the libron band, denoted  $W_{\vec{q}}(\omega_L)$ , is conveniently calculated using the one-phonon sum rule<sup>30</sup>

$$\frac{1}{\pi} \int_0^{\infty} \text{Im} D(\omega - i0^+, \vec{q}) \omega d\omega = \frac{\hbar}{2m}. \quad (\text{D6})$$

This relation yields

$$W_{\vec{q}}(\omega_L) \omega_L = - \frac{\hbar^2}{4M^2 \omega(\vec{q})} \left. \frac{\partial \Sigma(\omega, \vec{q})}{\partial \omega} \right|_{\omega = \omega_{\vec{q}}}. \quad (\text{D7})$$

Thus, in this description  $I_{PL}^+$  is given as

$$I_{PL}^+ = - \frac{\hbar^2 K^2}{8M^2 \omega_L} j_0^2(\frac{1}{2} K \rho) \frac{1}{N_{\text{tot}}} \times \sum_{\vec{q}} \frac{1}{\omega_{\vec{q}}} \left. \frac{\partial \Sigma(\omega, \vec{q})}{\partial \omega} \right|_{\omega = \omega_{\vec{q}}}. \quad (\text{D8})$$

Using the expression (D3) for  $\Sigma$  one recovers (B10) of the text.

\*Work supported in part by the National Science Foundation.

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