

Theory of the Anomalous Intensities in the Vibrational Raman Spectra of Solid Hydrogen and Deuterium

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The coupling between the vibrational motions in neighboring molecules in solid hydrogen and deuterium, arising from the isotropic intermolecular interaction, is shown to be responsible for the anomaly in the ratio of the Raman scattering cross sections of the $Q_1(0)$ and $Q_1(1)$ vibrational lines, observed by McKague, Rosevaer, Whiting, and Allin. The vibrational impurity states associated with molecules of one nuclear species imbedded in a matrix of the other species are imperfectly localized, having an extent determined by the ratio of the vibrational coupling to the difference in the vibrational resonance frequencies of the two species. The $Q_1(1)$ intensity due to orthohydrogen "impurities" is enhanced by (in classical terms) in-phase contributions of surrounding para molecules, whereas the $Q_1(0)$ intensity due to parahydrogen "impurities" is reduced by out-of-phase contributions from adjacent ortho molecules. The enhancement factors for small impurity concentrations are expressed in terms of Green functions describing the vibrational impurity states, and are evaluated by means of the walk-counting method. In the limit $c=0$ of small ortho concentrations, the computed enhancement factor for the $Q_1(1)$ intensity is 3.42; as c approaches 1, the $Q_1(0)$ intensity is reduced by a factor of 2.29. Both results are in excellent agreement with experiment. In solid deuterium the anomaly is larger because the difference between the resonance frequencies of the two species is smaller. In the limit $c=0$ of very small para ($J=1$) concentrations, the calculated $Q_1(1)$ intensity is enhanced by a factor 55, whereas in the limit $c=1$ the $Q_1(0)$ intensity is reduced by a factor 4.86. At the lowest para concentration ($c=3.7\%$) at which observations have been made, the para-impurities cannot be regarded as independent because of the poor localization of the vibrational impurity states. The theory has been extended to a finite concentration of impurities arranged in a regular superlattice. The calculated intensity ratio at $c=3.7\%$ is 49, in good agreement with the experimental value of about 50.

I. INTRODUCTION

SOLID hydrogen is an ideal example of a molecular crystal, the cohesive energy per molecule, 0.0083 eV, being very small compared with the energy, 4.48 eV, required to separate a hydrogen molecule into its component atoms. It is also the crystal that conforms most nearly to the ideal of free molecular rotation. The energy of the anisotropic intermolecular coupling is so small compared with the separations between the rotational levels that states corresponding to different values of the rotational quantum number J are not mixed appreciably. Thus, J is a good quantum number in the solid at all temperatures. This does not appear to be the case, for all J , in any crystal except solid hydrogen and its isotopes.

Solid hydrogen can thus be regarded as an assembly of para and ortho molecules held together in a crystalline lattice by weak central forces and subject to still weaker forces depending on the orientations and internuclear distances of the molecules. The resulting rotational and vibrational energy levels and their infrared and Raman spectra have been investigated extensively in recent years, both experimentally¹⁻⁴ and theoretically.⁵⁻⁹ The

energy levels of the isolated molecules are replaced in the solid by narrow energy bands corresponding to travelling rotational and vibrational excitations. A complete analysis of these levels in solid parahydrogen has recently been completed,¹⁰ and from this analysis accurate empirical values of the small coupling constants can be obtained.

The present paper deals with the vibrational excitations in solid hydrogen and deuterium, and in particular with the structure of the imperfectly localized vibrational states arising in crystals with low ortho or low para concentrations. This work has grown out of study of the observed¹¹ unexpectedly large difference in the intensity ratio of the $Q_1(0)$ and $Q_1(1)$ Raman lines (due to transitions $v=0 \rightarrow v=1$, $\Delta J=0$) for gaseous and solid hydrogen. A similar but more pronounced effect is observed¹¹ for deuterium. The cross section $\sigma(J)$ per molecule in the state J , for the Raman scattering arising

⁴ V. Soots, E. J. Allin, and H. L. Welsh, *Can. J. Phys.* **43**, 1985 (1965).

⁵ J. Van Kranendonk, *Physica* **25**, 1080 (1959).

⁶ J. Van Kranendonk, *Can. J. Phys.* **38**, 240 (1960).

⁷ H. P. Gush and J. Van Kranendonk, *Can. J. Phys.* **40**, 1461 (1962).

⁸ V. F. Sears and J. Van Kranendonk, *Can. J. Phys.* **42**, 980 (1964).

⁹ J. Van Kranendonk and V. F. Sears, *Can. J. Phys.* **44**, 313 (1966).

¹⁰ J. Van Kranendonk and G. Karl, *Phys. Rev.* (to be published).

¹¹ V. Soots, E. J. Allin, and H. L. Welsh, *Can. J. Phys.* **43**, 1985 (1965); A. H. McKague, Rosevaer, G. Whiting, and E. J. Allin, *ibid.* (to be published).

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¹ H. P. Gush, W. F. J. Hare, E. J. Allin, and H. L. Welsh, *Can. J. Phys.* **38**, 176 (1960).

² H. P. Gush, *J. Phys. Radium* **22**, 149 (1961).

³ S. S. Bhatnagar, E. J. Allin, and H. L. Welsh, *Can. J. Phys.* **40**, 9 (1962).

from the transitions $v=0 \rightarrow v=1$, $J \rightarrow J$, in isolated H_2 and D_2 molecules is practically independent of J . This can be seen most easily in the polarizability approximation.¹² For freely rotating molecules, the cross section $\sigma(J)$ is equal to the sum of an isotropic and an anisotropic part,

$$\sigma(J) = \sigma_{\text{is.}}(J) + \sigma_{\text{anis.}}(J), \quad (1.1)$$

which are due to the average polarizability,

$$\alpha = \frac{1}{3}(\alpha_{11} + 2\alpha_{\perp}),$$

and the anisotropy, $\gamma = \alpha_{11} - \alpha_{\perp}$, respectively, where α_{11} and α_{\perp} are the polarizabilities along the principal axes. The isotropic cross section is given by

$$\sigma_{\text{is.}}(J) = A |\langle 1J | \alpha | 0J \rangle|^2, \quad (1.2)$$

where $|vJ\rangle$ is a rotation-vibration state, and all factors independent of J have been absorbed in the quantity A . The matrix elements appearing in Eq. (1.2) show a slight dependence on J , because of the stretching of the molecule by the centrifugal forces, but this effect is very small. When we neglect this dependence on J , and denote $\langle 1J | \alpha | 0J \rangle$ by α_{01} , we obtain for the isotropic cross section

$$\sigma_{\text{is.}} = A\alpha_{01}^2. \quad (1.3)$$

The anisotropic cross section is given by

$$\sigma_{\text{anis.}}(J) = A\gamma_{01}^2 \frac{4J(J+1)}{45(2J-1)(2J+3)}, \quad (1.4)$$

where $\gamma_{01} = \langle 1J | \gamma | 0J \rangle$ may also be assumed to be independent of J . The quantity $\sigma_{\text{anis.}}$ is strongly dependent on J , but its magnitude is negligible compared with that of $\sigma_{\text{is.}}$. From Eq. (1.4) we get $\sigma_{\text{anis.}}(0) = 0$ and $\sigma_{\text{anis.}}(1)/\sigma_{\text{is.}} = (8/225)(\gamma_{01}/\alpha_{01})^2$; for H_2 this ratio has the value ≈ 0.02 . Within the accuracy of present experiments the vibrational Raman cross section is therefore independent of J . This is confirmed by the measurements of Stoicheff¹³ of the intensities of the vibrational Raman lines in gaseous H_2 , and this should also be true in D_2 .

It has recently been discovered experimentally¹¹ that in liquid and solid H_2 and D_2 the total cross section σ is quite different for $J=0$ and $J=1$. Since the absolute intensities of the lines have not been measured, we can express the results most conveniently by writing

$$\sigma(1) = \xi\sigma(0). \quad (1.5)$$

In solid H_2 the ratio ξ varies from about 3 at small ortho ($J=1$) concentrations to about 2 at higher concentrations. In solid D_2 the ratio ξ is about 30–50 at small para ($J=1$) concentrations and falls to about 9 at 33% para concentration. It is clear that these large deviations of ξ from 1 cannot be due to the effect of a possible orientational ordering of the molecules in the condensed phases, since the anisotropic cross section is

negligibly small. Moreover, such an ordering should exist only at low temperatures and high concentrations of the $J=1$ molecules, whereas the effect is also present at low concentrations and at such high temperatures that orientational ordering is not to be expected.

It will be shown in this paper that the anomalous intensity ratios are due to the coupling of the vibrations in neighboring molecules arising from the intermolecular forces. The rotational degrees of freedom play no role in the effect, and it is sufficient to regard the molecules as coupled oscillators and to ignore the angular coordinates. Since the vibrational frequencies of the $J=0$ and $J=1$ species are slightly different, a molecule of one species in a matrix of molecules of the other species acts as an impurity on the vibrational energy band in the host crystal. The problem of calculating the energy and the wave function of the resulting bound state is similar to that considered by Koster and Slater¹⁴ for an electron in an energy band, but the treatment has here been carried through for the cubic and hexagonal close-packed lattices that occur for H_2 , whereas Koster and Slater discuss only the simple cubic case. Consideration of the very large intensity ratio in D_2 leads to a study of the effect of finite concentrations of vibrational impurities. In the present paper this discussion is limited to a particular regular superlattice of impurities.

The effect on the intensities of the infrared Q lines in solid H_2 of the imperfect localization of the excitation on a vibrational impurity has been discussed in a previous paper,⁸ where it is shown that this effect is quite small (of the order of 6%). The reason for the different behavior of the infrared and Raman Q lines is that the induced dipole moments that come into play when the vibrational excitation moves to the neighboring molecules of the impurity tend to cancel each other, whereas in the Raman transition a mutual reinforcement of the effects of the neighbors occurs.

In Sec. II the model of solid H_2 and D_2 used in the calculation of the Raman intensities is described and the basic equations of the theory are developed. A calculation based on the assumption that the localized impurity states involve only one impurity and its immediate neighbors is presented in Sec. III. This calculation brings out the physical ideas required for an understanding of the observed intensity ratios, but yields only poor quantitative agreement with the experimental data. In Sec. IV a more accurate treatment based on the counting of walks on the lattice is applied to the case of effectively isolated impurities. For H_2 the calculated intensity ratios ξ correspond well to observation. The nature of the results with the parameters appropriate to D_2 show that in this crystal, even at the lowest $J=1$ concentration for which observations have been made, it is not satisfactory to treat the impurities as isolated. In Sec. V a method for the treatment of interacting impurities is indicated, and an illustrative calculation is made for a periodic distribu-

¹² G. Placzek, *Handbuch der Radiologie* VI, 2, 209 (1934).

¹³ B. P. Stoicheff, *Can. J. Phys.* **35**, 730 (1957).

¹⁴ G. F. Koster and J. C. Slater, *Phys. Rev.* **95**, 1167 (1954).

tion of $J=1$ molecules with concentration corresponding to that at which the highest values of ξ have been observed; the agreement with observation is satisfactory.

II. BASIC EQUATIONS FOR THE COUPLED-OSCILLATOR MODEL

Since the Raman transitions do not involve any phonon transitions, we shall ignore the lattice vibrations and treat the crystal as a collection of interacting molecules with centers of mass fixed on the points of a rigid fcc or hcp lattice. The Raman transitions involve no rotational transitions, so that we need not consider the excited rotational states. Neglecting the ortho-para conversion, which is very slow in the solid, we may regard the crystal as a permanent mixture of two species of molecules, with $J=0$ and $J=1$. The concentration of the $J=1$ species will be denoted by c , so that c denotes the ortho concentration in H₂ and the para concentration in D₂.

The main interaction between the molecules is due to the van der Waals (vdW) forces, consisting of the repulsive overlap and the attractive dispersion forces, and the electrostatic quadrupole-quadrupole (QQ) forces. In the absence of orientational ordering in the crystal, the averages of the anisotropic vdW and the QQ interactions vanish, and only the isotropic vdW interaction remains. The potential of the isotropic interaction between two molecules 1 and 2 can be expanded in powers of r_1-r_e and r_2-r_e :

$$V = V_0 + (r_1-r_e)V_1 + (r_2-r_e)V_2 + \frac{1}{2}(r_1-r_e)^2V_{11} + \dots + (r_1-r_e)(r_2-r_e)V_{12} + \dots, \quad (2.1)$$

where r_1 and r_2 are the internuclear separations and r_e is the equilibrium value of r_1 and r_2 . The terms in the first line of Eq. (2.1) are responsible for the bulk of the shifts in the energies of the rotational and vibrational levels in the solid, as compared with those in the isolated molecules. These shifts are discussed in detail elsewhere,¹⁰ but are of no interest here. The mixed term in Eq. (2.1) is the main vibrational-coupling term. It will be written in the form

$$V(r_1, r_2) = -\epsilon'(r_1-r_e)(r_2-r_e)/l^2, \quad (2.2)$$

where $l = (\hbar/m\omega_0)^{1/2}$ is the amplitude of vibration in the state $v=0$, m being the reduced mass and ω_0 the resonance frequency of the $v=0 \rightarrow v=1$ transition. This coupling is appreciable only for nearest neighbors, and ϵ' is the coupling constant for nearest neighbors. An empirical value of ϵ' can be obtained¹⁰ from the difference in the frequencies of the $Q_1(0)$ infrared and Raman lines for $c=0$, and from the concentration dependence of the $Q_1(0)$ and $Q_1(1)$ Raman lines.⁴ From the measured frequencies¹⁻⁴ for H₂ we obtain $\epsilon'(H_2) = (0.49 \pm 0.01) \text{ cm}^{-1}$. For D₂ only the first method can be used, since the data on the concentration dependence are too scarce to be useful. From the measurements of Crane and Gush¹⁵ in 97% D₂, we obtain $\epsilon'(D_2) = (0.37 \pm 0.01) \text{ cm}^{-1}$.

¹⁵ A. Crane and H. P. Gush, Can. J. Phys. 44, 373 (1966).

A theoretical estimate of $\epsilon'(H_2)$ can be obtained by assuming that the coupling [Eq. (2.2)] is due entirely to the dispersion forces. This assumption is not unreasonable, since solid H₂ is blown up considerably by the zero-point lattice vibrations. Assuming an exp-6 potential, one finds⁹ that the zero of the potential comes at 3.10 Å and the lattice constant for the classical crystal would be 3.41 Å, whereas the observed lattice constant is 3.75 Å. Assuming that only the R^{-6} dispersion forces contribute to Eq. (2.2), we get⁵ $\epsilon'(H_2) = 0.4 \text{ cm}^{-1}$, in good order of magnitude agreement with the experimental value. The ratio $\epsilon'(D_2)/\epsilon'(H_2)$ for the R^{-6} forces is given by $(m\omega_0V)_{H_2}/(m\omega_0V)_{D_2} = 0.90$, where V is the volume per mole, whereas the empirical value of this ratio is $(0.37/0.49) = 0.76$. The discrepancy is presumably due to the fact that in D₂, which is less blown up by the zero-point lattice vibrations, the overlap forces make a larger contribution to the coupling than in H₂. In the present calculations we shall adopt the values $\epsilon'(H_2) = 0.49 \text{ cm}^{-1}$ and $\epsilon'(D_2) = 0.37 \text{ cm}^{-1}$, which will be seen to give excellent agreement between the observed and calculated Raman intensities.

The Hamiltonian for the internal vibrational motion of the molecules in the solid is

$$H = \sum_i H_i(r_i) + \sum_{(i,j)} V(r_i, r_j), \quad (2.3)$$

where V is given by Eq. (2.2) and is assumed to be independent of the rotational states of the molecules; the sum over (i,j) runs over all pairs of neighbors, and H_i is the vibrational energy of molecule i , which depends on J because of the rotation-vibration interaction. The difference in the vibrational excitation energy of a $J=0$ and a $J=1$ molecule, $\Delta E(J) = E_1(J) - E_0(J)$, can be obtained from the Raman spectra in the gas,¹³ and is given by

$$\begin{aligned} \Delta E(0) - \Delta E(1) &= 6.0 \text{ cm}^{-1} \quad \text{for } H_2, \\ \Delta E(0) - \Delta E(1) &= 2.1 \text{ cm}^{-1} \quad \text{for } D_2. \end{aligned} \quad (2.4)$$

In the absence of vibrational coupling the wave functions are products of single-oscillator wave functions,

$$\langle r_1 \cdots r_N | \{v_i\} \rangle = \prod_i \phi_i(v_i; r_i). \quad (2.5)$$

In the ground state all v_i are equal to 0, and this state will be denoted by $|0\rangle$. In the first vibrationally excited states one v_i is equal to 1, giving two closely spaced levels, corresponding to $J=1$ and $J=0$, separated by the energy in Eq. (2.4) and with vibrational degeneracies equal to cN and $(1-c)N$, respectively. We denote the state of the crystal in which the molecule at \mathbf{R}_i is in the state $v_i=1$ by $|\mathbf{R}_i\rangle$, the wave function of this state being

$$\langle r_1 \cdots r_N | \mathbf{R}_i \rangle = \phi_i(1; r_i) \prod_{j \neq i} \phi_j(0; r_j). \quad (2.6)$$

In the presence of the vibrational coupling the ground

state $|0\rangle$ will be unaltered, if we neglect mixing of states corresponding to different values of $\sum_i v_i$, but the first group of excited states will be linear combinations of the states $|\mathbf{R}_i\rangle$. Denoting one of these states by $|\tau\rangle$, we write

$$|\tau\rangle = \sum_i U_\tau(\mathbf{R}_i) |\mathbf{R}_i\rangle, \quad (2.7)$$

where $U_\tau(\mathbf{R}_i)$ is the wave function⁵ describing the motion of the $v=1$ excitation through the lattice in the state τ . In the subspace of Hilbert space corresponding to $\sum_i v_i=1$, the Schrödinger equation, $H|\tau\rangle = E|\tau\rangle$, reduces to the set of difference equations^{5,14}

$$-\frac{1}{2}\epsilon' \sum_{\mathbf{d}_i} U_\tau(\mathbf{R}_i + \mathbf{d}_i) + W \sum_{\rho} \delta(\mathbf{R}_i, \mathbf{R}_\rho) U_\tau(\mathbf{R}_\rho) = E_\tau U_\tau(\mathbf{R}_i). \quad (2.8)$$

The first sum runs over all the vectors \mathbf{d}_i connecting molecule i to its nearest neighbors, and the second sum extends over all molecules of one species ($J=0$ or $J=1$) regarded as impurity molecules in a pure crystal of the other species. E_τ is the energy of state τ relative to that of the pure crystal in the absence of the vibrational coupling, and W is given by

$$W = \Delta E(\text{impurity}) - \Delta E(\text{matrix}). \quad (2.9)$$

For a pure crystal the second sum drops out, and if there is one molecule per unit cell, as in the fcc lattice, the solutions of Eq. (2.8) with periodic boundary conditions are the Bloch waves,

$$U(\mathbf{k}; \mathbf{R}_i) = N^{-1/2} \exp(i\mathbf{k} \cdot \mathbf{R}_i), \quad (2.10)$$

with energy

$$E(\mathbf{k}) = -\frac{1}{2}\epsilon' \sum_{\mathbf{d}} \cos(\mathbf{k} \cdot \mathbf{d}). \quad (2.11)$$

To calculate the Raman intensities, we neglect the anisotropic scattering and assume that the polarizability of the crystal is equal to the sum of the polarizabilities of the molecules. Assuming further that the matrix element $\alpha_{01} = \langle 1J|\alpha|0J\rangle$ is independent of J , we obtain for the Raman transition element between the ground state $|0\rangle$ and the Bloch state $|\mathbf{k}\rangle$,

$$\langle \mathbf{k} | \sum_i \alpha_i | 0 \rangle = N^{1/2} \delta(\mathbf{k}) \alpha_{01}. \quad (2.12)$$

Thus only the $\mathbf{k}=0$ state of the vibrational band in a pure crystal is Raman active and the intensity is N times that for a single molecule. (We have assumed that the wavelength of the exciting radiation is large compared with the size of the crystal.) The total intensity of the Raman scattering per molecule is therefore the same as in the gas.

The nature of the solutions of the set of difference equations, Eqs. (2.8), for a single impurity in a simple cubic lattice has been discussed by Koster and Slater.¹⁴ If $|W|$ is sufficiently large, there is a localized impurity state for which $U(\mathbf{R}_i)$ decreases rapidly with increasing

distance of \mathbf{R}_i from the impurity. The energy of this bound state lies below or above the energy band of the pure crystal, depending on whether W is negative or positive. The remaining states are scattering states and are not localized [in fact, $U(\mathbf{R}_i)$ for these states decreases near the impurity], and their energies form a band which in the limit of an infinite crystal has the same density of states as in the pure crystal. The Raman transition element to either the localized or the scattering states is given by

$$\langle \tau | \sum_i \alpha_i | 0 \rangle = \alpha_{01} \sum_i U_\tau(\mathbf{R}_i), \quad (2.13)$$

where we have again neglected the small dependence of α_{01} on J . The ratio of the Raman intensity for this transition to that for a transition in one isolated molecule is therefore given by

$$\eta_\tau^2 = \left| \sum_i U_\tau(\mathbf{R}_i) \right|^2. \quad (2.14)$$

Since the quantities $U_\tau(\mathbf{R}_i)$ are the coefficients of a unitary transformation, Eq. (2.7), we have the sum rule

$$\sum_\tau \eta_\tau^2 = N. \quad (2.15)$$

Thus a principle of spectroscopic stability holds: The total intensity of the $Q_1(0)$ and $Q_1(1)$ lines is independent of the ortho-para concentration and of the strength of the vibrational coupling.

If the impurity concentration is very small, it is clearly sufficient to regard the impurities as isolated from each other. The intensity of the matrix Q_1 line, per molecule, will then be little affected by the impurities and may be assumed to be the same as for an isolated molecule. If l denotes the localized state for one impurity in an infinite matrix, the intensity of the impurity Q_1 line, per impurity molecule, for very small concentrations, is equal to

$$\eta_l^2 = \left| \sum_i U_l(\mathbf{R}_i) \right|^2 \quad (2.16)$$

times that of a single molecule. For very small concentrations of the $J=1$ species, $c \approx 0$, the ratio $\xi = \xi(c)$ defined by Eq. (1.5) is

$$\xi(0) = \eta_l^2, \quad (2.17)$$

where $l=1$ refers to the localized state due to a $J=1$ impurity in a $J=0$ matrix. For very small concentrations of the $J=0$ species, $c \approx 1$, this ratio is given by

$$\xi(1) = \eta_0^{-2}, \quad (2.18)$$

where $l=0$ refers to the localized state due to a $J=0$ impurity in a $J=1$ matrix. In the next section, a simple calculation will be given to show that both $\xi(0)$ and $\xi(1)$ are larger than 1, in agreement with the observed enhancement of the $Q_1(1)$ line relative to the $Q_1(0)$ line for all concentrations.

III. A PRELIMINARY ILLUSTRATIVE CALCULATION

The degree of localization of the bound impurity states is determined by a balance of conflicting tendencies: that of the vibrational coupling, measured by ϵ' , to transmit the excitation from the impurity to its neighbors, and that of the energy difference W between the two species of molecule to localize the excitation on the impurity. In this section we assume that the excitation will not be found beyond the nearest neighbors of the impurity. This is true for small values of (ϵ'/W) , for which one can carry out a perturbation calculation.⁸ If p is the probability of finding the excitation on one of the neighbors, we get for a fcc or a hcp lattice

$$\begin{aligned} U_i(\mathbf{R}_0) &= (1-12p)^{1/2}, \\ U_i(\mathbf{R}_0+\mathbf{a}) &= \pm p^{1/2}, \end{aligned} \quad (3.1)$$

where \pm corresponds to $W = \mp |W|$. In either case, p is given by

$$p = (\epsilon'/2W)^2. \quad (3.2)$$

From Eq. (2.16) we then obtain

$$\begin{aligned} \eta_1^2 &= [(1-12p)^{1/2} + 12p^{1/2}]^2, \\ \eta_0^2 &= [(1-12p)^{1/2} - 12p^{1/2}]^2. \end{aligned} \quad (3.3)$$

For H₂ we assume $\epsilon' = 0.49$ cm⁻¹ and $|W| = 6.0$ cm⁻¹, and get $p^{1/2} = 0.041$ and $p = 0.0017$. The enhancement factors [Eqs. (2.17) and (2.18)] then have the values

$$\begin{aligned} \xi(0) &= 2.2, \\ \xi(1) &= 4.0. \end{aligned} \quad (3.4)$$

These large factors result from the fact that, although p is small, the quantity $12p^{1/2}$ is not particularly small. Thus, although the excitation spends only a fraction $12p = 0.02$ of its time away from the impurity, the resulting increase in the intensity ratio of $Q_1(1)$ and $Q_1(0)$ Raman lines is about a factor 3. The corresponding change in the intensities of the infrared lines amounts to only about 6%,⁸ since the term $12p^{1/2}$ in Eq. (3.3) is replaced for the infrared lines by $\alpha p^{1/2}$, where α is of order 1. This different behavior is due to the fact that in the Raman case one sums a scalar quantity, the isotropic polarizability, over the 12 neighbors, with the probability amplitude as weight factor, whereas in the infrared case one sums vector quantities, the induced dipole moments, and these tend to cancel each other.

We remark that a simple classical interpretation of the enhancement effect can be given. During a Raman scattering process from a $J=1$ molecule in a $J=0$ matrix, the $J=1$ molecule vibrates at its resonance frequency, which is just below the resonance frequency of the surrounding $J=0$ molecules. In the presence of the vibrational coupling, the $J=1$ molecule drives the $J=0$ molecules, and, since the coupling constant ϵ' in Eq. (2.2) is positive, the $J=0$ molecules respond in phase with the central molecule. The result is an enhancement

of the modulation of the total polarizability associated with the vibration in the $J=1$ molecule, leading to an enhancement of the $Q_1(1)$ line. For a $J=0$ molecule in a $J=1$ matrix, the surrounding molecules are driven by the central molecule just above their resonance frequency, and their response will be out of phase with the central molecule, resulting in a reduction of the $Q_1(0)$ intensity. In the quantum theory, the in- and out-of-phase response corresponds to the \pm sign in Eq. (3.1).

In the case of D₂ we have $\epsilon' = 0.37$ cm⁻¹ and $|W| = 2.1$ cm⁻¹, giving $12p^{1/2} = 1.06$. The contribution of the twelve neighboring molecules to the Raman transition element is hence greater than that of the central molecule. This is a clear indication that the approximation on which the calculations in this section are based is inadequate for the case of D₂. In the next section we shall therefore apply a more accurate theory of the impurity states.

IV. RAMAN INTENSITIES DUE TO ISOLATED IMPURITIES

In this section attention will be limited to such low impurity concentrations that the impurities may be regarded as effectively isolated from each other. At the low temperatures at which the Raman intensities of solid H₂ and D₂ have been measured, the lattice is hexagonal close-packed when $c=0$ and the molecules with $J=1$ are to be regarded as the impurities, but is cubic close-packed when $c=1$ and the molecules with $J=0$ are the impurities. Fortunately, this change in the lattice does not complicate matters. It has been shown by one of us¹⁶ that, for the model considered here, the energy level distribution in the pure crystal and the energy levels due to the isolated impurities are determined by the number of closed walks of n steps (all n) on the lattice, and that the number of such walks is the same for all close-packed lattices. It will here be shown that this is also true of all quantities that enter the calculation of the Raman intensities. It is therefore possible to do all calculations for the simpler fcc lattice, knowing that the result will be valid also for the hcp lattice.

In the fcc lattice, the displacement vectors \mathbf{d} from any molecule to its neighbors are given by $(\pm a, \pm a, 0)$, $(\pm a, 0, \pm a)$, $(0, \pm a, \pm a)$, where a is half the cube edge and the signs are to be chosen independently. Since all molecules are equivalent, the first excited vibrational states of the pure crystal form a single band¹⁷ with energies [Eq. (2.11)]

$$E_{\mathbf{k}} = -2\epsilon' [\cos(k_x a) \cos(k_y a) + \cos(k_y a) \cos(k_z a) + \cos(k_x a) \cos(k_z a)]. \quad (4.1)$$

This band extends from $-6\epsilon'$ at $\mathbf{k}=0$ to $+2\epsilon'$ attained for many nonequivalent choices of \mathbf{k} ; for instance, for

¹⁶ H. M. James, preceding paper, Phys. Rev. **164**, 1153 (1967).

¹⁷ In the hcp lattice there are two bands, two energies for each \mathbf{k} , but the over-all level density is the same as for the fcc lattice.

$\cos k_x a = -\cos k_y a = \pm 1$ and arbitrary k_z . Since $\epsilon' > 0$, the bottom of the band corresponds to a nondegenerate level, the top to a degenerate one.

For a fcc lattice with a single impurity at the origin, Eq. (2.8) can be written as

$$U(\mathbf{R}_i) = \alpha U(\mathbf{R}_i) + \beta \sum_{\mathbf{d}} U(\mathbf{R}_i + \mathbf{d}) + \gamma \delta(\mathbf{R}_i, 0) U(0). \quad (4.2)$$

Here

$$\begin{aligned} \alpha &= -c(\lambda - c)^{-1}, \\ \beta &= (\lambda - c)^{-1}, \end{aligned} \quad (4.3)$$

$$\gamma = -(2W/\epsilon')(\lambda - c)^{-1},$$

where

$$\lambda = -2E/\epsilon', \quad (4.4)$$

and c is an arbitrary numerical constant, corresponding to a change in the zero of energy in Eq. (2.8), which has been introduced for later use. The solutions of Eq. (4.2) can be written in the form

$$U(\mathbf{R}_i) = \gamma G(\mathbf{R}_i; 0) U(0), \quad (4.5)$$

where G is the Green's function belonging to Eq. (4.2), which is a solution of the equation

$$U(\mathbf{R}_i) = \alpha U(\mathbf{R}_i) + \beta \sum_{\mathbf{d}} U(\mathbf{R}_i + \mathbf{d}) + \delta(\mathbf{R}_i; 0). \quad (4.6)$$

The energy E , which is involved in the parameters α , β , γ , is determined by the condition

$$1 = \gamma G(0; 0). \quad (4.7)$$

One of us¹⁶ has expressed the solutions of Eq. (4.2) in terms of the quantities $P_k(\mathbf{R}_i; 0)$, the number of distinct walks of k steps from the origin to the lattice point \mathbf{R}_i . The simplest form is obtained by choosing $c = \alpha = 0$:

$$G(\mathbf{R}_i; 0) = \sum_{k=0}^{\infty} P_k(\mathbf{R}_i; 0) \beta^k. \quad (4.8)$$

Within its range of convergence, this series goes to zero if $|\mathbf{R}_i|$ goes to infinity. The wave function given by Eq. (4.5) will thus represent a localized impurity state, provided Eq. (4.7) is satisfied. It will be convenient for the moment to normalize $U(\mathbf{R}_i)$ by taking $U(0) = 1$. Then

$$U(\mathbf{R}_i) = (W/E) \sum_{k=0}^{\infty} P_k(\mathbf{R}_i; 0) \beta^k. \quad (4.9)$$

The condition (4.7) for the energy can be written as

$$-(\epsilon'/2W) = \sum_{k=0}^{\infty} P^k(0; 0) \beta^{k+1}. \quad (4.10)$$

Since

$$\sum_i P_k(\mathbf{R}_i; 0) = 12^k, \quad (4.11)$$

Eq. (4.9) yields the results

$$\sum_i U(\mathbf{R}_i) = (W/E)(1 - 12\beta)^{-1} = W(E + 6\epsilon')^{-1}, \quad (4.12)$$

$$\mathfrak{U}^2 \equiv \sum_i |U(\mathbf{R}_i)|^2 = (W/E)^2$$

$$\times \sum_{n=0}^{\infty} \left[\sum_i \sum_{k=0}^n P_k(\mathbf{R}_i; 0) P_{n-k}(\mathbf{R}_i; 0) \right] \beta^n. \quad (4.13)$$

The sum over k is the total number of times that all closed walks of n steps beginning and ending at the origin pass through \mathbf{R}_i . Summing over all the sites i , one counts each such walk $n+1$ times to obtain $(n+1)P_n(0; 0)$. Thus we obtain

$$\mathfrak{U}^2 = (W/E)^2 \sum_{n=0}^{\infty} (n+1)P_n(0; 0)\beta^n. \quad (4.14)$$

To normalize the function $U(\mathbf{R}_i)$ in the usual way one must divide it by \mathfrak{U} . Then Eq. (2.16) yields, on use of Eqs. (4.12) and (4.14),

$$\eta^{-2} = (1 - 12\beta)^2 \sum_{k=0}^{\infty} (k+1)P_k(0; 0)\beta^k. \quad (4.15)$$

Equations (4.10) and (4.15) provide a parametric relation between the relative coupling strength ϵ'/W and the enhancement factor η^2 .

Since $P_k(0; 0)$ increases about proportionally to $(12)^k/k^{3/2}$, the above equations diverge if $|12\beta| > 1$, or $|E| < 6\epsilon'$. They can be used for impurity states everywhere below the band described by Eq. (4.1), but not for the impurity states in the range $2\epsilon' < E < 6\epsilon'$ above the band. One of us has shown¹⁶ that series expansions valid for all localized impurity states can be obtained by choosing as the zero of energy not the band origin but the energy midway between the bottom and the top of the band. This corresponds to the choice $c = 4$, giving

$$\begin{aligned} \alpha &= 2\epsilon'(E + 2\epsilon')^{-1}, \\ \beta/\alpha &= -0.25, \\ \gamma &= W(E + 2\epsilon')^{-1}. \end{aligned} \quad (4.16)$$

The solution with $U(0) = 1$ is then given by

$$U(\mathbf{R}_i) = W(E + 2\epsilon')^{-1} \sum_{k=0}^{\infty} Q_k(\mathbf{R}_i; 0) \alpha^k, \quad (4.17)$$

where

$$Q_k(\mathbf{R}_i; 0) = \sum_{s=0}^k \frac{k!}{s!(k-s)!} P_s(\mathbf{R}_i; 0) (\beta/\alpha)^s. \quad (4.18)$$

The function $U(\mathbf{R}_i)$ represents a localized impurity state if the energy condition

$$(2\epsilon'/W) = \sum_{k=0}^{\infty} Q_k(0; 0) \alpha^{k+1} \quad (4.19)$$

is satisfied. By summing Eq. (4.2) or Eq. (4.17) over i ,

one easily finds

$$\sum_i U(\mathbf{R}_i) = W(E + 6\epsilon')^{-1}, \quad (4.20)$$

in accord with Eq. (4.12). A calculation similar to that leading to Eq. (4.14) yields

$$\mathfrak{N}^2 = \left(\frac{W}{E + 2\epsilon'} \right)^2 \sum_{n=0}^{\infty} (n+1) Q_n(0; 0) \alpha^n, \quad (4.21)$$

on use of the relation

$$\sum_{k=0}^n \frac{k!}{s!(k-s)!} \frac{(n-k)!}{(v-s)!(n-k-v+s)!} = \frac{(n+1)!}{(v+1)!(n-v)!}, \quad (4.22)$$

which can be derived by showing that each side gives the coefficient of $\alpha^s \beta^{v-s}$ in $\sum_{k=0}^n (1+\alpha)^k (1+\beta)^{n-k}$. One thus finds

$$\eta^{-2} = (1+2\alpha)^2 \sum_{n=0}^{\infty} (n+1) Q_n(0; 0) \alpha^n. \quad (4.23)$$

Equations (4.19) and (4.23) now provide the parametric relation between (ϵ'/W) and η^2 .

It is easy to compute $P_n(0; 0)$ for a fcc lattice by constructing a generating function, a polynomial F_n in x, y, z such that the coefficient of $x^\alpha y^\beta z^\gamma$ is the number of walks of n steps that result in a displacement αa in the x direction, βa in the y direction, and γa in the z direction. The generating function for a single step is

$$F_1 = \left(x + \frac{1}{x} \right) \left(y + \frac{1}{y} \right) + \left(y + \frac{1}{y} \right) \left(z + \frac{1}{z} \right) + \left(z + \frac{1}{z} \right) \left(x + \frac{1}{x} \right), \quad (4.24)$$

and for a walk of n steps it is

$$F_n = F_1^n. \quad (4.25)$$

In this product of n factors, the terms arising from taking the first term in F_1 p times, the second term q times, and the third term r times give a contribution to F_n equal to

$$\frac{n!}{p!q!r!} \left(x + \frac{1}{x} \right)^{n-q} \left(y + \frac{1}{y} \right)^{n-r} \left(z + \frac{1}{z} \right)^{n-p}. \quad (4.26)$$

The coefficient of $x^0 y^0 z^0$ in this expression will be zero unless the exponents are all even. Let

$$2\lambda = n - q, \quad 2\mu = n - r, \quad 2\nu = n - p. \quad (4.27)$$

Then

$$0 \leq \lambda, \mu, \nu \leq \left[\frac{1}{2}n \right],$$

where $\left[\frac{1}{2}n \right]$ denotes the largest integer not exceeding $\frac{1}{2}n$;

TABLE I. The number of closed walks of unit steps on a close-packed lattice, $P_n(0; 0)$, and the function $Q_n(0; 0)$ for $\beta/\alpha = -0.25$.

n	$P_n(0,0)$	$Q_n(0,0)$
0	1	1.0
1	0	1.0
2	12	1.75
3	48	2.50
4	540	4.609375
5	4 320	7.328125
6	42 240	13.890625
7	403 200	23.3125
8	4 038 300	44.900818
9	40 958 400	77.86347
10	423 550 512	151.4646

also

$$\lambda + \mu + \nu = n.$$

Summing the coefficients of the terms $x^0 y^0 z^0$ in the various products (4.26), one obtains

$$P_n(0,0) = \sum_{\lambda=0}^{\left[\frac{1}{2}n \right]} \sum_{\mu=0}^{\left[\frac{1}{2}n \right]} \sum_{\nu=0}^{\left[\frac{1}{2}n \right]} \frac{n! \delta(\lambda + \mu + \nu, n)}{(n-2\lambda)!(n-2\mu)!(n-2\nu)!} \times \frac{(2\lambda)!(2\mu)!(2\nu)!}{(\lambda! \mu! \nu!)^2}. \quad (4.28)$$

Since the summand is invariant under permutations of the values of λ, μ, ν , the number of terms to be considered is relatively small, and the calculation is simple.¹⁸

Values of $P_n(0; 0)$ and $Q_n(0; 0)$ for n up to 10 are given in Table I. Table II summarizes the results of

TABLE II. The intensity ratio $\xi = \sigma(1)/\sigma(0)$ of the Raman scattering cross sections, for vanishing impurity concentration, as a function of the effective coupling $(2\epsilon'/W)$. $\xi = \eta^2$ for $W < 0$ ($J = 1$ impurity in a $J = 0$ matrix), and $\xi = \eta^{-2}$ for $W > 0$ ($J = 0$ impurity in a $J = 1$ matrix).

$$\text{Intensity ratio: } \xi = \frac{I[Q_1(1)]/c(J=1)}{I[Q_1(0)]/c(J=0)}.$$

α	$2\epsilon'/W$	$E/2\epsilon'$	η^2	ξ	η^{-2}
0.0	0.0	$-\infty$	1.00		
-0.05	-0.048	-21	1.35		
-0.10	-0.092	-11.0	1.85		
-0.15	-0.132	-7.67	2.57		
-0.20	-0.171	-6.00	3.67		
-0.25	-0.211	-5.00	5.44		
-0.30	-0.245	-4.33	8.54		
-0.35	-0.282	-3.86	14.6		
-0.40	-0.320	-3.50	28.8		
-0.45	-0.367	-3.22	81		
-0.50	-0.42	-3.0	∞		
0.05	0.053	19		1.35	
0.10	0.112	9.0		1.82	
0.15	0.180	5.67		2.48	
0.20	0.260	4.00		3.43	
0.25	0.357	3.00		4.87	
0.30	0.481	2.33		7.20	
0.35	0.647	1.86		11.3	

¹⁸ An alternative expression for $P_n(0,0)$ has been given by C. Domb, *Advan. Phys.* **9**, 149 (1960), in Appendix II. Domb also tabulates $P_n(0,0)$ for n up to 9.

calculations using Eqs. (4.19) and (4.23). Values of terms in the series with $n > 10$ have been estimated by taking note of the smooth approach of Q_n/Q_{n-2} to its limiting value 4 as n increases indefinitely. The value of the intensity ratio ξ is given by η^2 or η^{-2} according as W is negative or positive. The two sections of the table show how ξ increases as the impurity state approaches the band edges at $E = -6\epsilon'$ and $E = 2\epsilon'$ and becomes less and less localized.

For negative W the band edge is reached, and ξ goes to infinity, for a finite W , $(2\epsilon'/W) = -0.42$, as obtained by an extrapolation that may be in error by ± 0.01 . For positive W a plot of E against W suggests that the localized state disappears only when W goes to zero. This can be verified by a more formal argument. One of us has shown¹⁶ that the impurity level will approach a band edge for a finite W or as W goes to zero according as the level density at that band edge is zero or finite. In the present case, by Eq. (4.1), the lower band edge corresponds to one point in \mathbf{k} space; the surfaces of constant E_k approach spherical form near this point and the level density goes to zero proportionally to k . Thus the discrete level vanishes for finite W , and a finite minimum value of W is required to produce a discrete level. On the other hand, the energies at the upper band edge are attained along lines in \mathbf{k} -space, the surfaces of constant E_k approach cylindrical form nearby, and the level density remains finite as the band edge is approached; thus the impurity level vanishes only as W vanishes.

In the case of H_2 , for which $|2\epsilon'/W| = 0.163$, interpolation yields $\xi = 3.42$ for low $J=1$ concentrations ($W < 0$), and $\xi = 2.29$ for low $J=0$ concentrations ($W > 0$). The experimental values¹¹ are 3.5 ± 0.4 and 2.4 ± 0.4 , respectively, and the agreement between the theoretical and experimental values seems to be entirely satisfactory.

In the case of D_2 , the estimated value of $|2\epsilon'/W|$ is 0.352. For low ortho ($J=0$) concentrations we have $W > 0$, and from Table II we get $\eta_0^{-2} = 4.86$. In the limit $c=1$ of pure para deuterium the intensity ratio is therefore given by $\xi(1) = 4.86$. The largest para concentration at which measurements have been made is 50%, and the experimental value of ξ at this concentration is $\xi(\frac{1}{2}) = 9.2 \pm 0.5$.¹¹ However the slope of the curve $\xi = \xi(c)$ is negative, and the theoretical value $\xi(1) = 4.86$ is not inconsistent with the data. For low para ($J=1$) concentrations, we have $W < 0$, and interpolation yields the value $\eta_1^2 = 55$. If we assume that the intensity of the $Q_1(0)$ line is not affected by the para impurities, the intensity ratio is $\xi = 55$, and this is the value of ξ in the limit of vanishing para concentration. This large value compares well with the value $\xi = 50 \pm 10$ observed¹¹ at a para concentration $c = 3.7\%$, but this agreement cannot be regarded as significant. According to the principle of spectroscopic stability [Eq. (2.15)], in a mixture containing one para molecule in 27, one could not have $\eta_1^2 = 27$ unless the $Q_1(0)$ line were to disappear

completely, and in that case one would have $\xi = \infty$. The large value, $\eta_1^2 = 55$, calculated for a single para impurity indicates that the impurity states in solid deuterium are so poorly localized that the interaction between the vibrational states due to the impurities cannot be neglected even at the lowest concentration ($c = 3.7\%$) for which observations have been made. Moreover, it is evident that when the intensity of the $Q_1(1)$ line is greatly enhanced one must take account of the reduction in the intensity of the $Q_1(0)$ line of the host lattice in computing the intensity ratio ξ . These matters are dealt with in Sec. V, in relation to D_2 . For H_2 the corrections are unimportant at the lowest concentrations used in the experiments.

V. RAMAN INTENSITIES DUE TO INTERACTING IMPURITIES

When impurities are present at a number of sites R_ρ , the impurity state amplitudes are given by [James,¹⁶ Eq. (24)]

$$U(\mathbf{R}_i) = \gamma \sum_{\rho} G(\mathbf{R}_i; \mathbf{R}_\rho) U(\mathbf{R}_\rho). \quad (5.1)$$

The amplitudes at the impurity sites must satisfy the conditions

$$U(\mathbf{R}_\rho) = \gamma \sum_{\rho'} G(\mathbf{R}_\rho; \mathbf{R}_{\rho'}) U(\mathbf{R}_{\rho'}), \quad (5.2)$$

which determine the energies of the impurity states.

In making calculations to compare with available measurements on deuterium it is convenient and satisfactory to put $c=0$ in Eq. (4.3) and to use the obvious generalization of Eq. (4.8):

$$G(\mathbf{R}_i; \mathbf{R}_\rho) = \sum_{k=0}^{\infty} P_k(\mathbf{R}_i; \mathbf{R}_\rho) \beta^k. \quad (5.3)$$

Equation (5.2) can then be written as

$$EU(\mathbf{R}_\rho) = \sum_{\rho'} H_{\rho\rho'} U(\mathbf{R}_{\rho'}), \quad (5.4)$$

where

$$H_{\rho\rho'} = W \sum_{k=0}^{\infty} P_k(\mathbf{R}_\rho; \mathbf{R}_{\rho'}) \beta^k. \quad (5.5)$$

The problem thus assumes a standard form, with attention focussed on the impurities, except that the effective coupling matrix elements $H_{\rho\rho'}$ depend on E , through $\beta = -(\epsilon'/2E)$, as well as on the form of the lattice and the arrangement of the impurities, through the P 's.

We restrict our attention to the case of a periodic matrix and a periodic array of impurities at equivalent sites, one of which is the origin. Periodic boundary conditions can then be applied and there is a translational symmetry in the system that assures the existence of solutions of the form

$$U(\mathbf{R}_\rho) = \exp(ik \cdot \mathbf{R}_\rho). \quad (5.6)$$

In the state $\mathbf{k}=0$ all $U(\mathbf{R}_\rho)$ are equal, and this state is Raman active. All other states have $\sum_\rho U(\mathbf{R}_\rho)=0$, and are not Raman active.

We now focus attention on the Raman active state. From Eqs. (5.4) and (5.5) it follows that

$$E=W \sum_{n=0}^{\infty} S_n \beta^n, \quad (5.7)$$

where

$$S_n = \sum_\rho P_n(\mathbf{R}_\rho; 0) \quad (5.8)$$

is the total number of walks of n steps from the origin to any one of the impurities, including the one at the origin. Equation (5.1) becomes

$$U(\mathbf{R}_i) = U(0) \gamma \sum_{n=0}^{\infty} \sum_\rho P_n(\mathbf{R}_i; \mathbf{R}_\rho) \beta^n, \quad (5.9)$$

from which it follows that

$$\sum_i U(\mathbf{R}_i) = U(0) \gamma I (1-12\beta)^{-1}, \quad (5.10)$$

where the sum is over all N molecules in a period containing I impurities and $N-I$ matrix molecules. By the method previously illustrated, one finds easily

$$\mathfrak{X}^2 = |U(0) \gamma|^2 I \sum_{n=0}^{\infty} (n+1) S_n \beta^n. \quad (5.11)$$

Since there are I impurities per period, the ratio of the intensity of the impurity line per impurity molecule to that due to an isolated molecule is

$$\begin{aligned} \eta_i^2 &= \left| \sum_i U(\mathbf{R}_i) \right|^2 / I \mathfrak{X}^2 \\ &= [(1-12\beta)^2 \sum_{n=0}^{\infty} (n+1) S_n \beta^n]^{-1}. \end{aligned} \quad (5.12)$$

$$P_n(\mathbf{R}_\rho; 0) = \sum_{\lambda=0}^{\lfloor \frac{1}{2}(n-\alpha) \rfloor} \sum_{\mu=0}^{\lfloor \frac{1}{2}(n-\beta) \rfloor} \sum_{\nu=0}^{\lfloor \frac{1}{2}(n-\gamma) \rfloor} \left\{ \frac{n! \delta(\lambda+\mu+\nu+\frac{1}{2}[\alpha+\beta+\gamma], n)}{(n-\alpha-2\lambda)! (n-\beta-2\mu)! (n-\gamma-2\nu)! (\lambda+\alpha)! (\mu+\beta)! (\nu+\gamma)! \gamma!} \right\}. \quad (5.15)$$

Values of $P_n(\mathbf{R}_\rho; 0)$ are readily computed for an impurity in each of the successive shells about the origin. These numbers, multiplied by the number of equivalent impurities in a shell, constitute the contributions of the respective shells to S_n . The last-named quantities are given in Table III for all shells contributing to S_n for $n \leq 10$. It will be noted that even for $n=5$ the contributions from walks to nearest-neighbor impurities exceed the contribution from closed walks, and that for $n=10$ the third shell of impurities plays an important role in determining S_n . It is evident that 3.7% of impurities does not constitute a small concentration, in the sense that the impurities are effectively isolated, unless β is so small that terms beyond $n=2$ make only a small contribution to the series in Eqs. (5.7) and (5.12). This conclusion is reinforced by the consideration that the present model, with its regular arrangement of im-

By the principle of spectroscopic stability, any increase in the total intensity of the impurity line is matched by a decrease in the total intensity of the matrix line. Thus the ratio of the intensity of the matrix line per matrix molecule to that due to an isolated molecule is

$$\eta_m^2 = (N - I \eta_i^2) (N - I)^{-1}. \quad (5.13)$$

Finally, the observed quantity, the ratio of the intensity of the impurity line per impurity molecule to the intensity of the matrix line per matrix molecule, is given by

$$\xi = (\eta_i^2 / \eta_m^2) = (N - I) \eta_i^2 (N - I \eta_i^2)^{-1}. \quad (5.14)$$

We now consider the lowest para-deuterium concentration, $c=3.7\%$, at which measurements have been made,¹¹ corresponding to one impurity molecule in 27. One can arrange such a concentration of impurities in a fcc matrix in a very symmetric way in which every third molecule on any given line is an impurity. For a hcp matrix it is not possible to arrange this concentration of impurities in such a symmetric way, and the calculation of the number of walks between impurities would be appreciably more complex. We shall calculate the Raman intensities assuming a regular lattice of impurities in a fcc lattice, even though the material on which the observations were made is hcp. The approximation of using the wrong close-packed matrix can be expected to affect the results less than the rather drastic assumption that the impurities form a regular superlattice.

In this model the impurities occupy lattice points separated by steps $(\pm 3a, \pm 3a, 0)$, $(\pm 3a, 0, \pm 3a)$, $(0, \pm 3a, \pm 3a)$. A slight generalization of the argument used in deriving Eq. (4.28) shows that the number of walks of n steps from the origin to the impurity at $\mathbf{R}_\rho = (\alpha a, \beta a, \gamma a)$ is

purities, neglects the effects of neighboring impurity pairs having less-than-average separations. Inspection of the values of S_n given in Table IV shows that neglect of impurity interactions would be reasonable for 3.7% impurity in H₂, for which $\beta = (\epsilon'/2W) \cong 0.04$, but that it is much less satisfactory for D₂, for which (as will appear in the next paragraph) $\beta \cong 0.076$, and for which even the terms with $n > 10$ contribute significantly, particularly to the calculation of \mathfrak{X}^2 .

Table V gives the calculated values of

$$-(\epsilon'/2W) = \sum_{n=0}^{\infty} S_n \beta^{n+1}, \quad (5.16)$$

$$\mathfrak{X}^2 / U(0)^2 \gamma^2 I = \sum_{n=0}^{\infty} (n+1) S_n \beta^n, \quad (5.17)$$

TABLE III. Contributions to S_n from neighboring impurities. The first column gives the position $(\alpha\alpha,\beta\alpha,\gamma\alpha)$ with respect to the origin of one impurity and the number of equivalent impurities; the remaining columns give the total contribution to S_n for all the equivalent impurities.

α, β, γ	0	1	2	3	4	5	6	n	7	8	9	10
0, 0, 0 (1)	1	0	12	48	540	4320	42 240	403 200	4 038 300	40 958 400	423 550 512	
3, 3, 0 (12)				12	288	4860	66 000	846 972	10 350 144	123 769 296	1 456 781 760	
6, 0, 0 (6)							2 400	50 400	887 040	13 345 920	187 336 800	
6, 3, 3 (24)							480	25 200	612 864	11 745 216	195 320 160	
6, 6, 0 (12)							12	1 008	41 760	1 094 400	22 710 780	
9, 3, 0 (24)										169 344	6 531 840	
6, 6, 6 (8)										13 440	604 800	
9, 6, 3 (48)										4 032	440 640	
9, 9, 0 (12)										12	2 160	

and of the intensity ratios η_i^2 and η_i^2/η_m^2 for a range of values of β appropriate to D_2 . Table IV shows that S_n/S_{n-1} rapidly approaches the limiting value 12 as n increases, and has effectively attained this limit at $n=10$. The calculations include contributions from terms with $n>10$, computed using this ratio, ranging from 3% in $(-\epsilon'/2W)$ for $\beta=0.070$ to 88% in \mathfrak{R}^2 for $\beta=0.080$.

TABLE IV. Number of walks of n steps from a given impurity to any other impurity, including the original one, for a superlattice of impurities of 1 in 27 in an fcc lattice.

n	S_n	S_n/S_{n-1}
0	1	
1	0	
2	12	
3	60	5.000
4	826	13.800
5	9 180	11.087
6	111 132	12.106
7	1 326 780	11.939
8	15 930 108	12.007
9	191 100 060	11.996
10	2 293 279 452	12.000

TABLE V. Results of calculations for 3.7% para- D_2 in solid deuterium.

$\beta = -\epsilon'/2E$	0.07	0.074	0.075	0.076	0.080
$-\epsilon'/2W$	0.0837	0.0960	0.1003	0.1056	0.152
$\mathfrak{R}^2/U(0)^2\gamma^2I$	2.447	3.962	4.715	5.797	24.173
η_i^2	16.0	20.1	21.2	22.3	25.9
η_i^2/η_m^2	37.6	76	95	123	590

The estimated value of $(-\epsilon'/2W)$ for D_2 , 0.088, corresponds to $\beta=0.0715$ and to $E=-2.59$ cm^{-1} , as compared with $E=-2.44$ cm^{-1} for an isolated impurity. The lower edge of the band in the pure crystal lies at $E=-6\epsilon'=-2.22$ cm^{-1} . Thus, the interaction between the impurity states increases the separation of the Raman active frequency from the band edge, and improves the convergence of the calculation with the convenient choice of the parameter c as zero. Interpolation on a plot of η_i^2 against $\epsilon'/2W$ shows that $\eta_i^2=17.6$, well below the upper limit 27 for this concentration, and that

$$\xi = (\eta_i^2/\eta_m^2) = \frac{26 \times 17.6}{26 - 17.6} = 49.$$

This final result illustrates the considerable effect of the reduction of the $Q_1(0)$ intensity, along with the increase of the $Q_1(1)$ intensity. Agreement with the observed value, $\xi=50 \pm 10$, is satisfactory, as would be the somewhat smaller value that would be expected to follow from a calculation with a random distribution of impurities, in which the effect of impurity interactions would be increased.

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