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Optical Absorption by Dilute Solutions of H_2 in Liquid Argon

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It has been proposed that the infrared absorption spectra of diatomic molecules in simple liquids should exhibit effects of the collective excitations of liquid. On the other hand, it was suggested that the absorption line shapes for the H_2-Ar system are essentially determined by the diffusive motion of the hydrogen impurity. We have made a detailed study of the H_2-Ar system and find that both effects must be included to accurately describe the $S_1(1)$ vibrational absorption line shape. Numerical calculations based on a model that does not include diffusive effects yield a line of the right qualitative shape, but that is narrower than the observed line. Extension of the model to include these diffusive effects leads to a line shape in good agreement with experiment.

I. INTRODUCTION

Our primary motivation in undertaking this study was the hope that it might lead to a new tool with which the collective effects in liquids could be studied. Light-scattering experiments have enabled the study of small-wave-vector (i.e., long-wavelength) collective excitations of liquids, but the conservation of momentum laws make it unfeasible to study excitations with smaller wavelengths. The absorption process for an impurity coupled to the collective excitations of the host liquid does not suffer from this restriction since the impurity breaks the translational invariance. Thus the absorption process is sensitive to excitations of all wavelengths, but with unequal weighting which is determined by the coupling. One might hope that the situation would be similar to the case in some solids where the absorption spectrum has a central line accompanied by distinct sidebands. The sidebands correspond to an absorption process accompanied by creation or absorption of a phonon and give information on the density of states of these phonons.

A previous theoretical study[1] indicated that the H_2 in the liquid-argon system was likely to exhibit collective effects in the absorption spectrum. This theory predicts a line shape based only on the interaction of the impurity with the collective motions of the host liquid, neglecting the diffusive motion of the impurity. On the other hand, experiments by De Remigis *et al.*[2] report an inverse density dependence of the linewidth of the $S_1(1)$ absorption line which Zaidi and Van Kranendonk[3] attributed to the diffusive motion of the impurity. The experiments do not show distinct sidebands on the S_1 absorption line. In this paper we have studied the model of Ref. 1 and extended it to include diffusive effects. We will show that both the diffusive and collective effects are of importance in determining the line shape of the S_1 line of H_2 in Ar. We also find a detailed explanation for the absence of sidebands in the experiments. We note that the S_1 absorption line of H_2 is particularly convenient since it arises predominantly from the well-understood quadrupole-dipole interaction between the H_2 impurity and the argon host. Thus, we avoid the difficulties arising from lack of detailed knowledge of other contributions to the H_2-Ar interaction.

In Sec. II we extend the model of Ref. 1 to include diffusive effects, discussing briefly the approximations involved. In Sec. III we present the results of numerical calculation of the absorption line shape (for the S_1 line) with and without inclusion of effects of diffusion of the impurity and discuss the physical significance of these results. In Sec. IV we briefly summarize our findings.

II. FORM OF ABSORPTION COEFFICIENT AND METHOD OF CALCULATION

We present here a derivation of an approximate expression for the absorption coefficient of a diatomic molecule in a simple liquid. This derivation essentially parallels that of Ref. 1, but is more general in the sense that it takes into account diffusive motions of the impurity.

If the H_2-Ar solution is sufficiently dilute that interactions between impurities are small, then it is sufficient to consider only the effects of a single impurity. The absorption coefficient is given by

$$A(\omega)=(1-e^{-\beta\hbar\omega})J(\omega)\,, \tag{1}$$

where $J(\omega)$ is the Fourier transform of the dipole-moment autocorrelation function $\Phi(t)$ of the system. For the portion of the spectrum near an energy corresponding to a vibrational plus rotational transition of the free molecule, Φ is given by[1]

$$\Phi(t)=K\,e^{-i(\Omega_0+E_J-E_{J'})t/\hbar}\times\sum_{\sigma\nu}\int d\vec{r}\,d\vec{r}\,'\,d\vec{r}_I\,d\vec{r}_I\,'\,T^{\sigma\nu}(\vec{r}-\vec{r}_I)\,T^{\sigma\nu}(\vec{r}\,'-\vec{r}_I\,')\times L(\vec{r},\vec{r}\,',\vec{r}_I,\vec{r}_I\,',t)\,, \tag{2}$$

where Ω_0 is the vibrational energy, E_J and $E_{J'}$ are the rotational energies of the molecule characterized by rotational quantum numbers J and J', $T^{\sigma v}$ is the tensor describing the quadrupole-dipole interaction between impurity and host, L is a four-point correlation function defined below, and K is a constant. In deriving Eq. (2) it was assumed that exchange contributions to the impurity-host interaction are spherical[4] and that $\Delta J \neq 0$. In particular, we have in mind the $S_1(1)$ line for which $\Delta J = 2$. For this line and in the above approximation, only the quadrupole-dipole interaction contributes, and difficulties associated with lack of detailed information about the other interactions are avoided. Hereafter, we shall take $(\Omega_0 + E_J - E_{J'})/\hbar$ as the zero of our frequency (energy) scale.

We proceed to discuss the correlation function L, which is defined as

$$L(\vec{r}, \vec{r}\,', \vec{r}_I, \vec{r}_I\,', t) = \langle \rho_I^*(\vec{r}_I, t)\, \rho^*(\vec{r}, t),\ \rho_I^*(\vec{r}_I\,', 0)\, \rho^*(\vec{r}\,', 0)\rangle\rangle ,$$

where ρ_I^* and ρ^* describe the densities of the impurity and the host, respectively, and the angular brackets represent a statistical average. L is approximated here in the following way: We assume the center of mass of the impurity to be performing oscillatory motion in a cavity formed by the host liquid. The density fluctuations of the host and the motion of the impurity are assumed to be coupled only in the sense that the volume of the cavity is excluded to the host and that the impurity is constrained to be in the cavity. The motion of the cavity is supposed to be described independently of the density fluctuations of the host. Mathematically these assumptions take the form

$$\begin{aligned} L(\vec{r}, \vec{r}\,' \vec{r}_I, \vec{r}_I\,', t) &= \int d\vec{R}\, d\vec{R}' \langle \rho_I(\vec{r}_I - \vec{R}, t),\ \rho_I(\vec{r}_I\,' - \vec{R}', 0)\rangle\rangle \\ &\quad \times \bar{g}(\vec{r} - \vec{R})\, \bar{g}(\vec{r}\,' - \vec{R}')\, G(\vec{r} - \vec{r}\,', t) S_c(\vec{R} - \vec{R}', t) , \qquad (3) \end{aligned}$$

where $\bar{g}(r)$ describes the exclusion of the host from a cavity centered at the origin. ρ_I describes the density of the impurity with respect to the center of the cavity. S_c describes the motion of the cavity:

$$S_c(\vec{R} - \vec{R}', t) = \langle \rho_c(\vec{R}, t),\ \rho_c(\vec{R}', 0)\rangle\rangle ,$$

and finally G describes the dynamic pair correlation for the pure liquid:

$$G(\vec{r} - \vec{r}\,', t) = \langle \rho(\vec{r}, t),\ \rho(\vec{r}\,', 0)\rangle\rangle_{\text{pure liquid}} .$$

We note here that the function

$$\langle \rho_I(\vec{X}, t),\ \rho_I(\vec{Y}, 0)\rangle\rangle$$

is the same as function $L_I(\vec{X}, \vec{Y}, t)$ of Ref. 1. Furthermore, if we think of the cavity as being fixed, that is

$$S_c = \alpha\delta(\vec{R} - \vec{R}'), \quad (\alpha \text{ independent of } \vec{R},\ \vec{R}' \text{ and } t)$$

then Eq. (3) reduces to the form found in Ref. 1.

We consider the time Fourier transform of L_I which we will denote here by $L_I(\omega)$ for simplicity. If the wave functions describing the center-of-mass motion of the impurity in the cavity corresponded to truly stationary states, then $L_I(\omega)$ would be a sum of δ functions at the frequencies $n\omega_I$[5] ($n = 0, \pm 1, \pm 2, \ldots$), where ω_I is the characteristic frequency of the center-of-mass oscillation of the impurity. In reality, one expects a series of peaks of finite width near these frequencies. The contributions to the absorption spectrum for $n \neq 0$ correspond to absorption accompanied by a change in the state of motion of the impurity. Since ω_I is much greater than the characteristic collective frequencies of the host liquid,[6] these contributions will give rise to distinct peaks in the absorption spectrum. Rather than trying to form a detailed model for the motion of the impurity and hence for the shape of the peaks in $L_I(\omega)$, we shall not consider absorption accompanied by a change in the state of impurity center-of-mass motion. We will keep only the $\delta(\omega)$ contribution from L_I:

$$(L_I'/2\pi)\, \delta(\omega) ,$$

where

$$\begin{aligned} L_I' &\equiv \lim_{t\to\infty} \langle \rho_I(\vec{r}_I, t),\ \rho_I(\vec{r}_I\,', 0)\rangle\rangle \\ &\equiv g_I(r_I)\, g_I(r_I') . \end{aligned}$$

We are then assuming that the contributions in the absorption spectrum arising from the finite width of the peak at $\omega = 0$ in $L_I(\omega)$ are negligible. *This will be a limiting factor in our calculation.* Considering a peak of finite width would have the effect of adding a second frequency convolution in Eq. (5) and hence broadening the line further. The peaks in $L_I(\omega)$ at $n\omega_I$, $n \neq 0$ are much broader than the zero-frequency peak.[6] Thus, the details of $S(\vec{q}, \omega)$ will be further masked in the portion of the spectrum corresponding to absorption accompanied by a change in the center-of-mass motion. Since our interest is in $S(\vec{q}, \omega)$, this provides further motivation for studying only the frequency region $\omega \ll \omega_I$.[7]

Equation (2) now becomes

$$\begin{aligned} \Phi(t) = K \sum_{\mu\nu} \int & d\vec{r}\, d\vec{r}\,'\, d\vec{r}_I\, d\vec{r}_I\,'\, d\vec{R}\, d\vec{R}' \\ & \times T^{\mu\nu}(\vec{r} - \vec{r}_I)\, T^{\mu\nu}(\vec{r}\,' - \vec{r}_I\,')\, \bar{g}(r)\, \bar{g}(r')\, g_I(r_I)\, g_I(r_I') \\ & \times S(\vec{r} - \vec{r}\,' - (\vec{R} - \vec{R}'), t)\, S_c(\vec{R} - \vec{R}', t) , \qquad (4) \end{aligned}$$

where $S(\vec{r}, t) = G(\vec{r}, t) - \rho_0^2$ is the Van Hove correlation function.

We define a quantity $t^{\mu\nu}$ as

$$t^{\mu\nu}(\vec{r}) = \bar{g}(r) \int d\vec{r}_I\, g_I(r_I)\, T^{\mu\nu}(\vec{r} - \vec{r}_I) .$$

Using this in Eq. (4) and introducing the Fourier

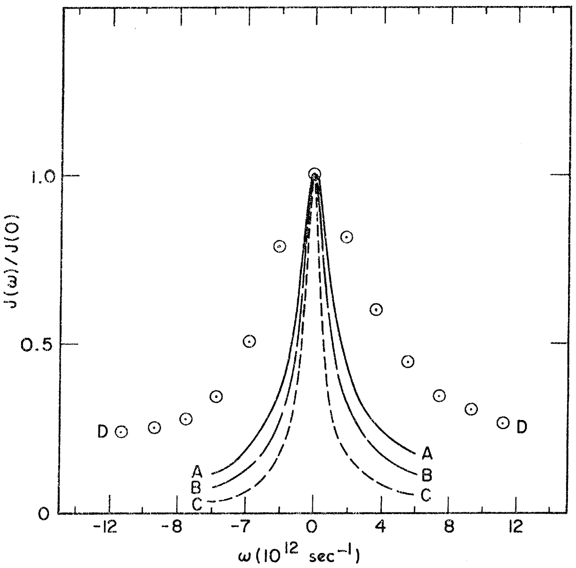

FIG. 1. Calculated line shapes without diffusive effects for various values of the cavity radius R_0: Curve (A) $R_0 = 2.9$ Å, curve (B) $R_0 = 3.7$ Å, curve (C) $R_0 = 4.7$ Å, curve (D) experimental points.

transforms of the various quantities we can write

$$J(\omega) = K' \int d\vec{q}\, d\omega' \left|\tau(q)\right|^2 S(q,\omega') \times S_c(-q, \omega - \omega') , \qquad (5)$$

where τ has been defined by

$$t^{\mu\nu}(\vec{q}) = \sum_m (12\mu\nu | 3m)\, Y_m^3(\hat{q})\, \tau(q) .$$

Equation (5) is the basic form we shall use in calculating the absorption spectrum.

It is shown in the Appendix that

$$|\tau(q)| = \left|(\sigma^4/2\pi^2)\sqrt{\tfrac{3}{7}} \int_0^\infty dr\, j_3(qr)\, \bar{g}(r)\, r^{-2}\right| , \qquad (6)$$

where j_n is the spherical Bessel function of index n. We further simplify by choosing the simplest possible form for the function $\bar{g}$ which describes the exclusion of the host from the cavity. That is, we take $\bar{g}$ to be a step function[8];

$$\begin{aligned} \bar{g}(r) &= 1, \quad r \geq R_0 \\ &= 0, \quad r \leq R_0 . \end{aligned}$$

We shall think of R_0 as a parameter of the calculation. With this form for $\bar{g}$ Eq. (6) becomes

$$|\tau(q)| = (\sigma^4/2\pi^2)\sqrt{\tfrac{3}{7}}\,(qR_0^2)^{-1}\, |j_2(qR_0)| .$$

The integral in Eq. (5) was done numerically using various functional forms for the cavity correlation function $S_c(q,\omega)$ which is discussed in Sec. III, and an approximate form for the Van Hove correlation function worked out by Chung and Yip.[9,10] The moments required in this expression were computed numerically using the pair-correlation function of Verlet.[11]

The agreement found by Chung and Yip between their expression and neutron scattering data and the computer experiments of Rahman[12] is quite good. The accuracy of the calculation presented here is probably more limited by the other approximations involved than by the accuracy of the Van Hove correlation function we use.

III. RESULTS

We first consider the case where the cavity is fixed during the absorption process. This does not correspond to the impurity being motionless, but requires that the center of its center-of-mass motion be fixed. In this case

$$\begin{aligned} S_c(q,\omega) &\propto \int dt\, e^{i\omega t} \int dR\, e^{-i\vec{q}\cdot\vec{R}}\, \delta(R) \\ &\propto \int dt\, e^{i\omega t} \\ &= \delta(\omega) , \end{aligned}$$

and hence Eq. (5) becomes

$$J(\omega) = K' \int d\vec{q}\, |\tau(q)|^2 S(q,\omega) \qquad (7)$$

as in Ref. 1.

Some curves for the absorption coefficient computed from this expression for typical values of the parameter R_0 are shown in Fig. 1. The asymmetry of this line is due to the Boltzmann factor $e^{-\beta\hbar\omega/2}$ of the correlation function. In Fig. 2 there is a plot of the half-width of the symmetric line, that is without this Boltzmann factor, obtained from Eq. (7) versus the cavity radius R_0. In all cases considered here the width of the line is narrower than the experimental width, even though the shape of the calculated line seems in qualitative agreement.

We can make an estimate of R_0 as follows: We consider a hard sphere with the mass of hydrogen molecule and of diameter ~3 Å (hard-sphere radius of H_2). We think of this sphere as being in a spherical well and minimize its kinetic energy plus the cavity energy (PV) with respect to the radius of the well. Here the radius of the cavity is equal to the radius of the well plus the hard-sphere radius of the H_2. The value R_0 is equal to this cavity radius plus the hard-sphere radius of an argon atom. This leads to a value $R_0 \sim 3.7$ Å. We note here that this value is relatively insensitive to pressure since it is already large enough to force the atoms down to their hard-sphere separation. This value of R_0 corresponds to a (symmetrized) width in this diffusionless model of $6.8 \times 10^{11}\ \text{sec}^{-1}$ compared with an experimental width of $\sim 3.9 \times 10^{12}\ \text{sec}^{-1}$. The maximum width in Fig. 2 is still about three times too small and corresponds to a value of R_0 (2.9 Å) that seems physically too small, since $R_0 < \rho_{\text{Ar}}^{-1/3} = 3.5$ Å, whereas one expects the zero-point motions to lead to cavity that has more volume than that occupied by a host atom.

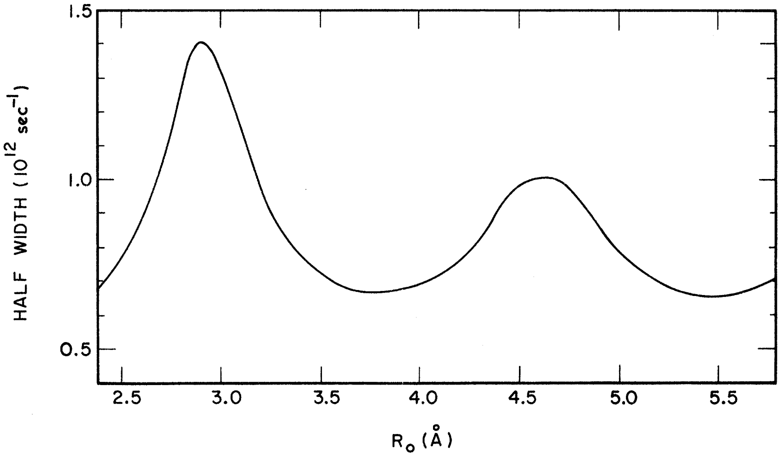

FIG. 2. Plot of the half-width of calculated line versus the cavity radius R_0. The half-width is that of the symmetrical line, that is, of the line calculated excluding the Boltzmann asymmetry of $S(q, \omega)$.

The structure in the curve in Fig. 2 can be understood as follows: The function $q^2|\tau(q)|^2$ determines the relative size of the contributions of $S(q,\omega)$ to the integral in Eq. 7. We recall that

$$q^2|\tau(q)|^2 \propto (R_0^{-2})[j_2(qR_0)]^2 .$$

There is a large peak in $S(q,\omega)$ at about $q = 2$ Å^{-1}, $\omega = 0$ with frequency width 1.0×10^{12} sec^{-1}. We note that this peak just corresponds to the largest peak in the static structure factor, that is, to nearest-neighbor correlation. This peak tends to give the largest contribution to the integral (peak marked C in Fig. 3). This peak is narrower (in ω) than the central ($\omega = 0$) peak of $S(\vec{q},\omega)$ for neighboring q values. Thus, when a maximum of $|\tau(q)|^2$ falls exactly on this peak (B in Fig. 3), the integral $J(\omega)$ tends to be narrower, whereas, when a zero of $|\tau(q)|^2$ falls on this peak (A in Fig. 3), $J(\omega)$ tends to be wider.

We make the following other observations about the contributions to $J(\omega)$: The largest contributions tend to come from q values corresponding to $2\pi/$(nearest-neighbor distance). This is just the location of the largest peak in the static structure factor $S(\vec{q}) = \int d\omega\, S(\vec{q},\omega)$. Significant but smaller contributions do occur for smaller q, the contribution coming from the peak which for fixed q is centered at $\omega = 0$. The "rotonlike" dynamic modes are not giving a significant contribution. This last effect was what we hoped to find, as pointed out earlier.

The fact that distinct sidebands can be seen in some solids but not here can be understood by considering the difference between $S(\vec{q},\omega)$ for solids and liquids. There are three important differences here. First, in the solid all modes are propagating

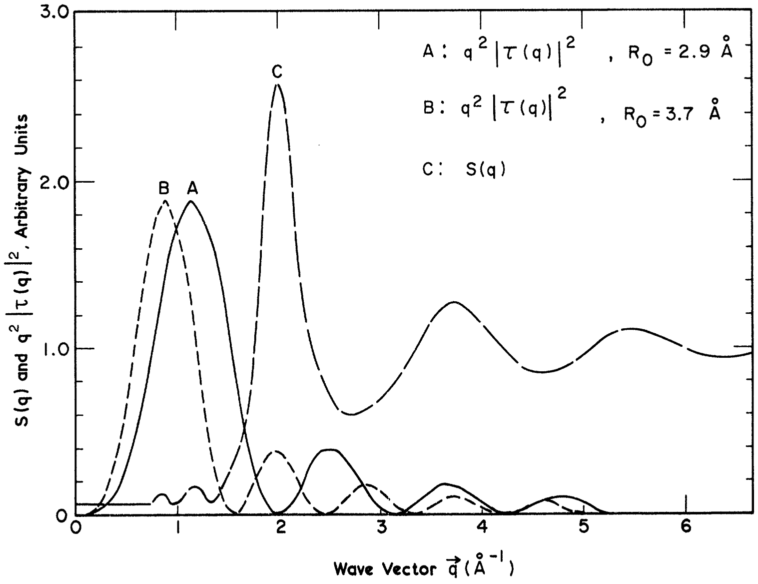

FIG. 3. Curves (A) and (B) are plots of $q^2|\tau(q)|^2$ for $R_0 = 2.9$ Å and 3.7 Å, respectively (in arbitrary units). Curve (C) is the static structure factor $S(q) = \int d\omega\, S(q, \omega)$.

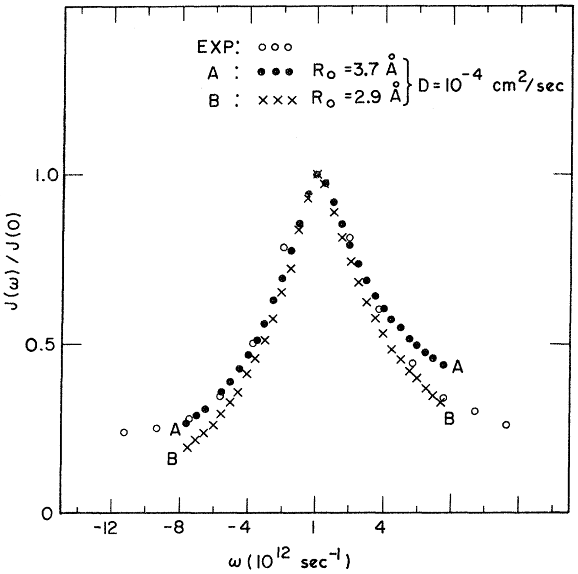

FIG. 4. Calculated curve including diffusive effects. (A) $R_0 = 2.9$ Å, $D = 10^{-4}$cm^2/sec, (B) $R_0 = 3.7$ Å, $D = 10^{-4}$ cm^2/sec.

and are well defined out to the zone boundary. That is, for fixed q there are sharp peaks (away from $\omega = 0$). In the liquid there is a peak near $\omega = 0$ for all q corresponding to a nonpropagating mode. The peaks, for fixed q, in the liquid correlation function corresponding to propagating modes are less sharp than in the solid and tend to be comparable or smaller than $\omega \cong 0$ peaks in intensity. Second, in the solid there may be optical modes giving a relatively large contribution to the absorption spectrum in a narrow band of frequencies. Third, in the liquid there is a large peak at $q \sim 2\pi/$(nearest-neighbor distance) which is large and relatively wide as a function of ω. The contribution of this peak to the absorption spectrum masks the contributions from smaller q's where the collective modes are well defined. In the solid the corresponding peak is very narrow both as a function of q and of ω, and does not lead to this masking effect.

In order to understand the discrepancy between calculated and experimental absorption lines, we next remove the restriction that the cavity be fixed. We then calculate the line shape using Eq. 6. We use the same functions $\tau(q)$ and $S(q,\omega)$, and for the cavity correlation function we use

$$S_c(q,\omega) = \pi^{-1} q^2 D/(\omega^2 + (q^2 D)^2) \quad ,$$

which is the correct form for diffusive motion (at small q) with D being the diffusion constant. We shall treat D as a parameter of the calculation. In Figs. 4 and 5 are a few curves calculated in this manner. In Fig. 4, curve A, tne value of R_0 is that estimated earlier. The value of D is chosen to achieve approximate agreement with experiment. Curve B uses the same value of D but different R_0. The value of D obtained in this way is smaller by a factor of about $\frac{1}{4}$ than estimates made from kinetic-type theories. Such estimates give values $4-5\times10^{-4}$ cm^2/sec. Figure 5 shows a curve with such a value for D and an R_0 chosen to bring approximate agreement with experiments. The shape here does not seem to agree quite as well as with the curves in Fig. 4. The estimate of R_0 is probably more dependable than the kinetic-theory estimate of D, as this estimate does not properly take into account interactions other than the hard cores. In a dense system, especially a liquid, these are important, and one expects they tend to lower D.[13] In no cases has an attempt to do a detailed fitting to the experimental curve been made, as the theory here is not sufficiently accurate for such a fitting to be meaningful.

In Fig. 6 we have plotted the linewidth of the curves not containing the Boltzmann factor versus D for several values of R_0. We noted earlier that the value of R_0 tends to vary little with pressure. We see here that the linewidth depends linearly on D ($D \geqslant 1\times10^{-4}$ cm^2/sec) for fixed R_0. Since we expect D to vary approximately as the inverse of the density, we expect that same behavior for the linewidth will occur, in agreement with experiment.

IV. CONCLUDING REMARKS

The first point to be learned from this study is that the dynamic collective modes of the host liquid

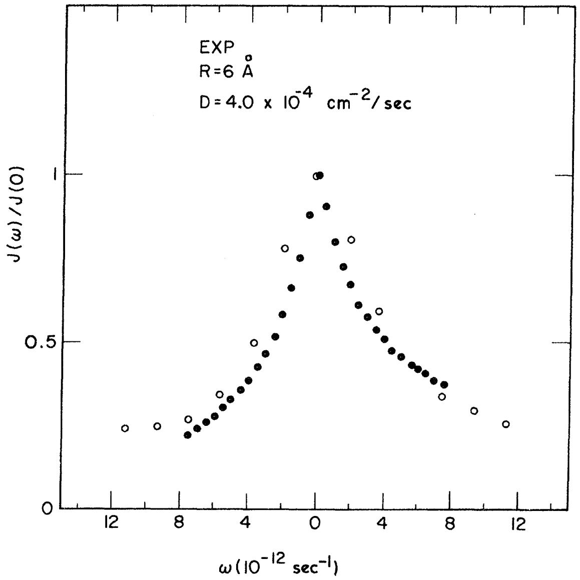

FIG. 5. Calculated curve including diffusive effects. $R_0 = 6$ Å, $D = 4\times10^{-4}$ cm^2/sec.

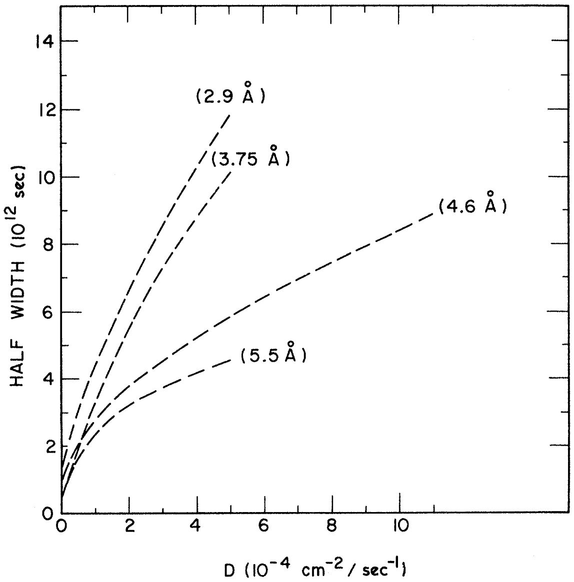

FIG. 6. Dependence of linewidth (symmetrical line) on the diffusion constant D for fixed cavity radius R_0.

do not give a significant contribution to the absorption line shape. It is interesting to note that even in our model calculation, which excluded diffusive motion of the impurity, no sidebands can be seen. In terms of the formalism used in the calculation, this occurs because the portion of $S(\vec{q},\omega)$ corresponding to dynamic modes is small relative to the $\omega \simeq 0$ nonpropagating modes and because the peak corresponding to nearest neighbors is large and wide as a function of ω. The differences between this case and that of a solid are that in the solid (a) the nearest-neighbor peak is very narrow, (b) all modes propagate and remain well defined to large q, and (c) there may be optical modes.

The second main point is that the density dependence of the linewidth does in fact come from the diffusive motion of the impurity which broadens the basic line discussed above. This is in agreement with the work of Zaidi and Van Kranendonk.[3] The inverse-density dependence arises as follows: The function $|\tau(q)|^2$ selects a few values of the wave vector $\vec{q}$ which give dominant contributions to the integral in Eq. (5). The one or two of these values near the nearest-neighbor value ($q \sim 2$ Å^{-1}), that is, the main peak in $S(q)$, give by far the largest contribution. At each of these wave vectors the frequency convolution has the approximate effect of adding the frequency widths of S and S_c. For fixed q the frequency width of S_c depends linearly on the diffusion constant D. Hence the line shape tends to have a width approximately linear in D, and we expect D to be inversely proportional to density. Here we have assumed that the effects of the density dependence of quantities, other than the D which are involved, are small. Thus, we find qualitative agreement with experiment. We note that although this density dependence arises through the dependence on a diffusion constant, as does the proposed explanation of Zaidi and Van Kranendonk, our picture of the motions involved is considerably different in that we envision the impurity oscillating within a cavity formed by the host liquid. This motion is present even in that form of our model that we describe as not including diffusion. When we speak of diffusion we are referring to the cavity as a whole and are assuming that the motion of the impurity within the cavity is faster than the motion of the cavity itself. (The characteristic frequency of oscillation of the impurity within the cavity is[6] about five times the half-width of the observed absorption line.)

Finally, we consider the relationship between the absorption process studied in this paper and the two-roton Raman scattering process in liquid helium. In the latter, incident light polarizes a helium atom. The field of this atom polarizes another atom. The field of the second atom gives rise to the observed scattered light. The spectrum of the scattered light can then be written as[14]

$$H(\omega) \propto \omega^4 \int d\vec{q}\, d\omega' \, S(-\vec{q}, \Omega-\omega') S(\vec{q},\omega') g^2(\vec{q}) \, ,$$

where Ω is the frequency shift of the scattered light, $S(q,\omega)$ is the Van Hove correlation function for liquid helium, and $g(\vec{q})$ is a cutoff function that arises because an atom does not polarize itself. This description is basically the same as for the H_2-liquid argon absorption process, but here the incident light must polarize an argon atom, and the oscillating dipolar field of this atom excites the quadrupole moment of the H_2 impurity. The function τ is analogous to g.

The spectrum for the two processes is different because the correlation functions are different: In liquid helium the correlation function $S(\vec{q},\omega)$ has peaks for fixed wave vector $\vec{q}$ centered at the frequencies $\pm\,\omega(q)$, where $\omega(q)$ is the angular frequency of the phonon roton at wave vector $\vec{q}$ in liquid helium. Unlike argon, these peaks are distinct even for large values of $\vec{q}$. In argon, both for large and small q, there is a nonpropagating mode giving rise to a wide peak centered at $\omega = 0$ for fixed $\vec{q}$. It is this peak around $\omega = 0$ with $q = 2\pi/$(nearest-neighbor distance) which dominates the absorption spectrum that we have found. In helium, on the other hand, the peak centered at $\omega = 0$ gives rise only to a smooth background at large q since the width of this peak is much greater than the frequencies of the collective modes. Thus, the absorption spectrum in Ar-H_2 is dominated by the peak around $\omega = 0$ at large q, while the Raman scattering spectrum in helium is dominated by the peaks in $S(\vec{q},\omega)$ at the collective mode frequencies

$\omega(\vec{q})$ at large q. The physical reason for the difference is that the effective thermal conductivity in liquid helium is very large and makes the width of the Raleigh peak about $\omega = 0$ enormous. We can expect on the basis of these results that the Raman scattering in argon probably will not show effects of propagating collective modes either.

APPENDIX

The quadrupole-dipole interaction is

$$T^{\mu\nu}(\vec{r}) = B\left(\frac{\sigma}{r}\right)\sqrt{\tfrac{3}{7}}\sum_m (12\mu\nu|3m)\,Y_m^3(\hat{r}) \ .$$

We have an integral of the form

$$I = \int d\vec{r}_1 d\vec{r}_2\, e^{-i\vec{q}\cdot\vec{r}_1}\bar{g}(r_1)g_I(r_2)|\vec{r}_1 - \vec{r}_2|^{-4}Y_m^3(\hat{\eta}),$$

where

$$\hat{\eta} = (\vec{r}_1 - \vec{r}_2)/|\vec{r}_1 - \vec{r}_2| \ .$$

Define two vectors $\vec{S}_1$ and $\vec{S}_2$ such that $\vec{S}_1$ lies along the x axis and $\vec{S}_2$ is in the first or second quadrant of the x-y plane with

$$|\vec{S}_1| = |\vec{r}_1|; \quad |\vec{S}_2| = |\vec{r}_2|; \quad \vec{S}_1\cdot\vec{S}_2 = \vec{r}_1\cdot\vec{r}_2 \ .$$

Further, let α, β, and γ be the Eulerion angles of the rotation that carry $\vec{S}_1$ and $\vec{S}_2$ into $\vec{r}_1$ and $\vec{r}_2$ and let θ be the angle between $\vec{S}_1$ and $\vec{S}_2$ (or $\vec{r}_1$ and $\vec{r}_2$). We change variables

$$\vec{r}_1,\ \vec{r}_2 \rightarrow S_1,\ S_2,\ \theta,\ \alpha,\ \beta,\ \gamma \ .$$

We have

$$Y_m^3(\hat{\eta}) = \sum_K D_{Km}^3(\alpha,\beta,\gamma)\,Y_K^3(\hat{\eta}') \ ,$$

$$e^{-i\vec{q}\cdot\vec{r}_1} = \sum_{lmm'} 4\pi(-i)^l j_l(qS_1)\,Y_{m'}^l(\hat{q}) \times D_{Km}^{l*}(\alpha,\beta,\gamma)\,Y_K^{l*}(\hat{S}_1) \ ,$$

with

$$\hat{\eta}' = (\vec{S}_1 - \vec{S}_2)/|\vec{S}_1 - \vec{S}_2|$$

and

$$d\vec{r}_1 d\vec{r}_2 \rightarrow S_1^2 S_2^2 \sin\beta \sin\theta\, dS_1 dS_2 d\theta\, d\alpha\, d\beta\, d\gamma \ ,$$

where the D's are the usual rotation matrices. Using the orthogonality

$$\int d\beta\, d\gamma\, d\alpha \sin\beta\, D_{K'm'}^{l'*}(\alpha,\beta,\gamma)\,D_{Km}^l(\alpha,\beta,\gamma) = [8\pi^2/(2l+1)]\,\delta_{l'l}\,\delta_{m'm}\,\delta_{KK'} \ ,$$

we have

$$I = Y_m^3(\hat{q})8\pi^2 i \int dS_1 dS_2\, d(\cos\theta) j_3(qS_1) \times \bar{g}(S_1)g_I(S_2)|\vec{S}_1 - \vec{S}_2|^{-4}S_1^2 S_2^2 P_3(\cos\mu) \ ,$$

where μ is the angle between $\vec{S}_1$ and $\vec{S}_1 - \vec{S}_2$. Doing the remaining integration we find

$$I = Y_m^3(\hat{q})16\pi^2 i \int_0^\infty dS_1 \int_0^\infty dS_2 \times (S_2^2/S_1^2) j_3(S_1 q)\bar{g}(S_1)g_I(S_2)$$

$$= Y_m^3(\hat{q})16\pi^2 i \int_0^\infty dS_1 j_3(qS_1)\bar{g}(S_1)(1/S_1^2) \ .$$

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[5] We are thinking, for simplicity, of a harmonic-oscillator-type potential. For a more general potential, we should say ω_n with $\omega_n - \omega_{n-1} \neq$ constant. This does not affect the arguments since only ω_1 will be important.

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[7] $W_I \sim 158$ cm^{-1} while the experimental absorption linewidth is ~ 21 cm^{-1}.

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