$$Z_1 = \zeta_{12} + \zeta_{13} - \tfrac{1}{2}(\zeta_{12} + \zeta_{13})\zeta_{23} - \zeta_{12}\zeta_{13} + \tfrac{2}{3}\zeta_{12}\zeta_{13}\zeta_{23} \,. \qquad (9)$$

This is the correct result, and it has been obtained here much more easily than in previous work.[11,12,14]

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I am grateful to B. H. Brandow for his suggestion of a simple derivation of such results as Eq. (9). This idea led directly to the results of this note.

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Collective Effects in the Optical Absorption of Diatomic Molecules in Simple Liquids*

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We develop a theory of optical absorption of a diatomic molecule in a simple monatomic liquid. Using approximations appropriate to the case of a light molecule like H_2, we show that the absorption spectrum near an infrared-inactive vibrational transition of the molecule can be interpreted to give information about collective effects in the fluid. We show that some features of existing experimental results on H_2-Ar mixtures are consistent with the theory, although no direct evidence of collective effects is seen in these experiments.

I. INTRODUCTION

A primary motivation for the study of optical properties of liquids is the possibility that collective properties of the liquid may be studied optically. This possibility has recently been realized in Raman scattering experiments,[1] but no collective effects have yet been identified in optical absorption spectra in liquids. In an earlier study[2] we showed that sidebands analogous to those seen in intrinsic optical absorption in solids would not be observed in optical absorption in pure liquids, and hence that phonons in liquids could not be studied by this method as they are in solids. The physical reason for this result is the following: In an insulating solid, when the electron-phonon coupling is weak, the one-exciton no-phonon peak is narrow because absorption takes place only into the $k = 0$ exciton mode. In a liquid, even if the coupling is weak, the one-exciton peak will be greatly broadened because in the weak-coupling limit the excitons cannot be characterized by a k vector. The absorption corresponding to the one-exciton peak in a solid is then broadened in a liquid because absorption takes place into many exciton modes corresponding to various solutions of the exciton problem in a system of amorphously distributed fixed sites. The bandwidth of this spectrum of solutions is of the order of the transfer rate of excitations from site to site through the Coulomb interactions between electronic states on different sites. In liquid helium both theory and experiment[3] indicate that this width is of the order of a few tenths of an electron volt. Thus, the one-exciton peak is broadened to swamp the phonon sidebands in a liquid.

In our previous work we suggested that this problem of broadening of the one-exciton peak would not exist in impurity spectra in liquids where the transfer of the excitation from the impurity to neighboring sites could not take place because the atomic excitations on the host atoms would not have the same energy as the excitation on the impurity. In the present paper we study the consequences of this idea. We choose to study the vibrational transitions of a diatomic molecule in weakly polarizable liquid. In particular, we have in mind the H_2 molecule in rare-gas liquids including helium. The reasons for this choice of system include the following:

(a) The H_2 molecule is light and small, making it more likely that the weak-coupling approximation between the molecule and the liquid will apply.

(b) A vibrational mode is selected because the size of the molecule does not greatly change on exciton of a vibrational mode (though it does for exciton of an excited electronic state). This also improves the weak-coupling approximation.

(c) Rare-gas liquids are considered for their simplicity and because some information on collective effects already exists.[4]

(d) There are already some studies of hydrogen-molecule spectra in rare gases in the vapor phase as well as some partially analyzed data of H_2 molecules in liquid argon.[5]

We study the absorption spectrum of the molecule in the neighborhood of a forbidden vibrational transition, making a series of simple decoupling approximations which seem physically justified at least for the H_2–rare-gas-liquid system. Comparing our results with some accessible features of the experiments gives good agreement. A more detailed comparison of the theory with experiments requires a numerical line-shape calculation which will be reported later.

The microscopic mechanisms of absorption of light by an infrared forbidden vibrational level in a molecule are described in perturbation theory as follows: The light couples to the host atoms of the liquid, virtually exciting them through the dipole interaction to high-lying odd-parity states (or equivalently, causing a fluctuating dipole moment on these host atoms). The virtually excited host atoms couple to the excited vibrational levels of the molecule either through the quadrupole-dipole part of the direct Coulomb interaction between molecule and host atom or through effects arising from the overlap of host-atom and molecular wave functions.

In Secs. II–VI we derive formulas for the absorption line shape of a forbidden vibrational transition in a homonuclear diatomic impurity dissolved in a simple liquid on the basis of these ideas. We assume the impurity concentration to be small enough to justify neglect of any interaction between impurities. The translational motions enter the line shape through a four-point dynamical density correlation function. In order to make the formulas of practical use, we assume the impurity and liquid motions to be independent in a certain sense which implies the factorization of the correlation function. The motion of the liquid then enters the spectrum through the van Hove correlation function.

In Sec. VII we illustrate some of the uses of these formulas by estimating two of the dimensionless quantities which characterize the spectrum for the case of hydrogen in liquid argon. We compare these with experiment and find qualitative agreement. From this comparison it appears that single-particle motions in the liquid and local-mode motions of the impurity affect the line shape, but we find no direct evidence for collective-motion effects in the reported experiments.

Finally we discuss how the experimental data can be analyzed more extensively and what results are to be expected from studies of other impurity-liquid system, in particular regarding the observation of collective effects. An alternative interpretation of the absorption line shapes in Ar-H_2 is discussed.

II. ABSORPTION SPECTRUM

Confining attention to electric dipole transitions, the optical absorption coefficient of a many-body system is

$$A(\omega)=\mathcal{K}\sum_{i,j}(p_i-p_j)\left|\langle j|\vec{\mathrm{M}}|i\rangle\right|^2\delta(\omega-\omega_j+\omega_i), \quad (1)$$

where ω_i are the energies of the exact eigenstates $|i\rangle$ of the system; p_i are the associated Boltzmann factors; $\vec{\mathrm{M}}$ is the electric dipole moment operator; and $\mathcal{K}=8\pi^3/3\hbar V\lambda n$, n being the refractive index and λ the wavelength at frequency ω.

It is easier to calculate the related function $J(\omega)$,

$$J(\omega)=\mathcal{K}\sum_{i,j}p_i\left|\langle j|M|i\rangle\right|^2\delta(\omega-\omega_j+\omega_i), \quad (2)$$

which is connected with $A(\omega)$, thus

$$A(\omega)=(1-e^{-\beta\hbar\omega})J(\omega). \quad (3)$$

The function J is the Fourier transform of the electric dipole moment autocorrelation function:

$$J(\omega)=(\mathcal{K}/2\pi)\int_{-\infty}^{\infty}dt\,e^{i\omega t}\,\Phi(t), \quad (4a)$$

where

$$\Phi(t)=\sum_\nu\Phi^{\nu\nu}(t)\;, \quad (4b)$$

$$\Phi^{\nu\nu'}(t)=\langle M^\nu(t)M^{\nu'}(0)\rangle\,. \quad (4c)$$

For the purpose of calculation, we describe the physical mechanism of absorption near the vibrational frequency already mentioned in the introduction as follows: For a free homonuclear diatomic molecule there is no electric dipole moment associated with vibrations, and therefore, no vibrational absorption. When such a molecule is perturbed by the presence of atoms of a host solute, electric dipole moments fluctuating at the vibrational frequency are induced on the host atoms and the restriction is lifted.

We assume that the concentration of the impurity molecules in the liquid is so small that the interaction between them is negligible. Then the moments induced in the host by different impurity molecules are independent and we have

$$\Phi^{\nu\nu'}(t)=\sum_n \langle M_n^\nu(t)M_n^\nu(0)\rangle, \tag{5}$$

where M_n is the electric dipole moment operator arising from the nth impurity molecule. If there are N impurities in the volume V and we call $\phi=\Phi/N$, then

$$\phi^{\nu\nu'}(t)=\langle m^\nu(t)\, m^{\nu'}(0)\rangle, \tag{6}$$

where m is the electric dipole moment operator associated with any one impurity. By calculating ϕ and using Eqs. (4a), (4b), and (3), we obtain the absorption coefficient. $\phi^{\nu\nu'}(t)$ is equal to $\Phi^{\nu\nu'}(t)$ for a one-impurity system. We calculate $\phi^{\nu\nu'}(t)$ for a one-impurity system in Sec. III.

III. INDUCED ELECTRIC DIPOLE MOMENT OPERATORS

Let x be the vibrational coordinate of the impurity molecule. The electric moment of the impurity-liquid system can be expanded in x:

$$\vec{\mathrm{m}}=\vec{\mathrm{m}}^0+x\vec{\mathrm{m}}'=\ldots \, . \tag{7}$$

Since we are interested only in vibrational transitions, $\vec{\mathrm{m}}^0$ is of no interest, and we assume the vibrational amplitude to be small enough to justify neglect of all but the second term.

We write the dependence of $\vec{\mathrm{m}}'$ on the positions of the host atoms and the orientation of the impurity molecule as

$$\vec{\mathrm{m}}'=\sum_j \vec{\mu}\,(\vec{\mathrm{R}}_j,\Psi), \tag{8a}$$

where $\vec{\mathrm{R}}_j$ is the position of the jth host atom relative to the impurity and Ψ is the pair of angles specifying the orientation of the molecular axis relative to fixed axes. Here we have assumed that the interaction between the impurity and a host atom at j is independent of the presence of other host atoms.

It is convenient to have $\vec{\mu}$ expressed as a function of dummy variables; to this end we introduce densities $\rho(\vec{\mathrm{r}})$ and $\rho_I(\xi)$ defined as

$$\rho(\vec{\mathrm{r}})=\sum_i \delta(\vec{\mathrm{r}}-\vec{\mathrm{r}}_i), \quad \rho_I(\xi)=\delta(\xi-\vec{\mathrm{r}}_I),$$

where $\vec{\mathrm{r}}_i$ and $\vec{\mathrm{r}}_I$ are the positions of the ith host atom and of the impurity. Then we have

$$\vec{\mathrm{m}}'=\int d^3\vec{\mathrm{r}}\, d^3\vec{\xi}\, \vec{\mu}(\vec{\mathrm{r}}-\xi,\Psi)\, \rho(\vec{\mathrm{r}})\, \rho_I(\xi). \tag{8b}$$

Following van Kranendonk[6] we represent $\vec{\mu}$ as the sum of its longest- and shortest-range parts. The first part arises from the interaction of the quadrupole moment of the impurity molecule with the dipole moment of the host atom. It falls off as $1/R^4$ and depends on the orientation of the molecule. The second short-range part comes from the distortion of the atomic and molecular charge clouds due to their overlap. It is found that this part of $\vec{\mu}$ is almost independent of Ψ and to that approximation is parallel to the line joining the impurity to the host atom. It falls off approximately exponentially with distance. We express these facts as follows:

$$\vec{\mu}=\vec{\mu}_q+\vec{\mu}_d\,, \tag{9a}$$

$$\vec{\mu}_q^{\,\nu}=B_q\sum_\sigma Y_2^\sigma(\Psi)T_q^{\sigma\nu}(\vec{\mathrm{R}}), \tag{9b}$$

$$\vec{\mu}_q^{\,\nu}=B_d T_d^\nu(\vec{\mathrm{R}}). \tag{9c}$$

The B's have the dimensions of charge and characterize the strengths of the induced moments. We can write B_q explicitly as

$$B_q=2\pi\alpha\, \frac{dq}{dx}\bigg|_{x=0}\frac{1}{\sigma^4}\,, \tag{10}$$

where $q(x)$ is the quadrupole moment of the impurity, α is the atomic polarizability of the host atoms, and σ is a length which we later identify with the range of the Lennard-Jones potential between impurity and host molecules. The T's are dimensionless function of R which are shown in the Appendix to be

$$T_q^{\sigma\nu}(\vec{\mathrm{R}})=(\sigma/R)^4\sqrt{\tfrac{3}{7}}\sum_m\langle 12\nu\sigma|3m\rangle\, Y_3^m(\hat{R})\,, \tag{11a}$$

$$T_d^\nu(\vec{\mathrm{R}})=e^{-R/\rho}(3/4\pi)^{1/2}\,Y_1^\nu(\hat{R})\,, \tag{11b}$$

where ρ is a length characterizing the range of the overlap moment.

Using Eqs. 9(a)–9(c), (8a), and (8b) in (7) and omitting m^0 we have

$$\begin{aligned} m^\nu &= x\int d^3\vec{\mathrm{r}}\, d^3\xi\, \rho(\vec{\mathrm{r}})\,\rho_I(\xi) \\ &\quad\times\Big[B_q\sum_\sigma Y_2^\sigma(\Psi)\,T_q^{\sigma\nu}(\vec{\mathrm{r}}-\xi)+B_d\,T_d^\nu(\vec{\mathrm{r}}-\xi)\Big] \\ &= m_q^\nu+m_d^\nu\,. \end{aligned} \tag{12}$$

IV. VIBRATION-ROTATION BANDS

In using Eq. (12) in Eq. (6) we assume (a) that the motion of x is independent of both the translational and rotational motions and (b) that the motion of Ψ is independent of the translational motions.

Assumption (a) is expected to be good since the vibrational energy is much greater than (i) the x-dependent part of the interaction between impurity and host molecules and (ii) the vibration-rotation coupling. Assumption (b) is known to be quite good for hydrogen in solution,[5] but is presumably not so good for other impurities.

The thermal average in Eq. (6) can then be factored into averages over the vibrational, rotational, and translational spaces. We notice that cross terms between m_q and m_d must vanish since in Ψ space m_q is a sum of second-rank tensors while m_d is a scalar. Therefore we have

$$\varphi^{\nu\nu'}(t)=\langle m_q^\nu(t)m_q^{\nu'}(0)\rangle+\langle m_d^\nu(t)m_d^{\nu'}(0)\rangle$$

$$=\varphi_q^{\nu\nu'}(t)+\varphi_d^{\nu\nu'}(t)\ . \tag{13}$$

A. Vibration Average

The same vibration average occurs as a factor in both ϕ_q and ϕ_d. Since the vibrational temperature will usually be much greater than the experimental temperature we may take this average in the vibrational ground state:

$$\langle x(t)x(0)\rangle\simeq\langle 0|x(t)x(0)|0\rangle=e^{-i\Omega_0 t}\bar{x}^2\ , \tag{14}$$

where $\bar{x}^2$ is the mean square displacement and Ω_0 is the vibrational frequency.

B. Rotation Averages

By the free rotation assumption we can consider different rotational transitions independently. First, we consider transitions $J\rightarrow J'$, $J\neq J'$. Since m_d is a scalar in Ψ space, ϕ_d vanishes in this case. The rotational averages which occur in ϕ_d are of the type

$$P_J\sum_{M,M'}\langle JM|\,Y_2^\sigma(\Psi(t))^*|J'M'\rangle\langle J'M'|\,Y_2^{\sigma'}(\Psi(0))|JM\rangle=\delta_{\sigma,\sigma'}P_J\sum_{M,M'}|\langle J'M'|\,Y_2^\sigma(\Psi)|JM\rangle|^2e^{i(E_J-E_{J'})t/\hbar}$$

$$=\delta_{\sigma,\sigma'}P_J\sum_{M,M'}\left(\frac{5}{4\pi}\right)(2J'+1)(2J+1)\begin{pmatrix}J & J' & 2\\ 0 & 0 & 0\end{pmatrix}^2\begin{pmatrix}J & J' & 2\\ M & -M' & \sigma\end{pmatrix}e^{i(E_J-E_{J'})t/\hbar}$$

$$=\delta_{\sigma,\sigma'}\frac{P_J}{4\pi}(2J'+1)(2J+1)\begin{pmatrix}J & J' & 2\\ 0 & 0 & 0\end{pmatrix}^2e^{i(E_J-E_{J'})t/\hbar}$$

$$=\delta_{\sigma,\sigma'}C_{JJ'}e^{i(E_J-E_{J'})t/\hbar}\ , \tag{15}$$

where P_J is the Boltzmann factor for a single magnetic state of the J rotational level, which has energy E_J.

Denoting by $\phi_{JJ'}$ the part of ϕ pertaining to the $J\rightarrow J'$ transition, and combining Eqs. (15), (12), and (6), we have for $J\neq J'$

$$\phi_{JJ'}(t)=\phi_{qJJ'}(t)$$

$$=e^{-i(\Omega_0+E_{J'}-E_J)t/\hbar}|B_q|^2C_{JJ'}\bar{X}^2$$

$$\times\sum_{\nu,\sigma}\int d^3\vec{r}\,d^3\vec{r}'\,d^3\vec{y}\,d^3\vec{y}'\ T_q^{\sigma\nu}(\vec{r}-\vec{y})$$

$$\times T_q^{\sigma\nu}(\vec{r}'-\vec{y}')L(\vec{r},\vec{r}',\vec{y},\vec{y}',t)\ , \tag{16}$$

where

$$L(\vec{r},\vec{r}',\vec{y},\vec{y}',t)=\langle\rho(\vec{r},t)\rho_I(\vec{y},t)\rho(\vec{r}',0)\rho_I(\vec{y}',0)\rangle. \tag{17}$$

From the definition of $C_{JJ'}$ we note that if $J\neq J'$ then $J=\pm 2$. From Eq. (16) we deduce the important result that under our assumptions (a) and (b) the line shape of every $J\neq J'$ transition is identical. This follows from the fact that the time dependence responsible for the line shape occurs in a factor which is independent of J, J'.

If $J=J'$, $\phi_{qJJ'}$ does not vanish in general (only in the important case $J=J'=0$), but we must add to it $\phi_{dJJ'}$. The rotational average is trivial in this case and we have $[C_J=P_J(2J+1)]$

$$\phi_{dJJ'}(t)=e^{-i\Omega_0 t}C_J|B_d|^2\bar{X}^2$$

$$\times\sum_\nu\int d^3\vec{r}\,d^3\vec{r}'\,d^3\vec{y}\,d^3\vec{y}'\ T_d^\nu(\vec{r}'-\vec{y})T_d^{\nu'}(\vec{r}'-\vec{y}')$$

$$\times L(\vec{r},\vec{r}',\vec{y},\vec{y}';t)\ . \tag{18}$$

For a general rotational transition we have then

$$\phi_{JJ'}(t)=\phi_{qJJ'}(t)+\delta_{J,J'}\phi_{dJJ'}(t)\ , \tag{19}$$

with $\phi_{qJJ'}$ and $\phi_{dJJ'}$ given by Eqs. (16) and (18).

V. TRANSLATIONAL DYNAMICS

The translational motions of the system insofar as they affect the spectrum, are all contained in the function $L(\vec{r},\vec{r}',\vec{y},\vec{y}';t)$. We assume the impurity to be performing a quasioscillatory motion in the cage of surrounding host atoms, the center of oscillation R being fixed; diffusion of the impurity is ignored. The host liquid density also fluctuates, but we take this motion to be independent of the impurity oscillation in the sense that we can approximate

$$L(\vec{r},\vec{r}',\vec{y},\vec{y}';t)\simeq\langle\rho(\vec{r},t)\rho(\vec{r}',0)\rangle_{\vec{R}}\langle\rho_I(\vec{y},t)\rho_I(\vec{y}',t)\rangle_{\vec{R}}$$

$$\equiv L_H(\vec{r},\vec{r}\,';t)L_I(\vec{y},\vec{y}\,';t)\ . \qquad (20)$$

We regard this assumption as a reasonable approximation for the case of H_2 in heavy rare-gas liquids because the light H_2 molecule will have much higher resonant vibrational frequencies than will the fluid due to the difference in masses. This is borne out in the experiments in H_2-Ar, where the H_2 vibrational frequency is[5] 158 cm^{-1}. The collective excitation frequency in argon on the other hand is about 25 cm^{-1}.

In the Eq. (20), the subscripts R are a reminder that these averages are functions of the relative coordinates $\vec{r}-\vec{R}$, $\vec{y}-\vec{R}$, etc., L_H and L_I describe, respectively, the correlated density fluctuation of the host liquid and local-mode fluctuations of the impurity. In order to separate the characteristic frequencies ω_H, ω_I of these two, we assume the impurity to be light, so that $\omega_I \gg \omega_H$. We separate from L_H and L_I the zero frequency parts L_H' and L_I' defined by

$$L_{H,I}' = \lim L_{H,I}(t) \quad \text{as } t\to\infty \qquad (21)$$

and call

$$\tilde{L}_{H,I}(t) = L_{H,I}(t) - L_{H,I}'\ . \qquad (22)$$

The Fourier transform of L_H has most of its intensity in a region of width $\Delta\omega \simeq 2\omega_H$ around $\omega = 0$; the intensity of the transform of L_I will be concentrated in the regions $\omega \simeq n\omega_I$, with n a positive or negative integer or zero. The widths of these regions will be related to the damping of the oscillatory motion. We expect most of the intensity to occur for $n=\pm 1$, corresponding to emission or absorption of one quantum of oscillation. Now divide L_I into parts L_I^0 and L_I^1, which oscillate in the frequency regions corresponding to $n=0$ and $|n| \simeq 1$, respectively[7]:

$$\tilde{L}_I(t) = L_I^0(t) + L_I^1(t)\ . \qquad (23)$$

This allows us to divide $L(t)$ into zero-, low-, and high-frequency parts:

$$L(t) = L' + L^0(t) + L^1(t)\ , \qquad (24)$$

with

$$L' = L_H' L_I'\ , \qquad (25a)$$

$$L^0 = L_H' L_I^0 + L_I' \tilde{L}_H + L_I^0 \tilde{L}_H\ , \qquad (25b)$$

$$L^1 = L_H' L_I^1 + \tilde{L}_H L_I^1\ . \qquad (25c)$$

A. Zero Frequency

The self-correlation of the motions of both the impurity and the liquid damp to zero at large times:

$$L_H' = \lim_{t\to\infty} \langle \rho(\vec{r},t)\rho(\vec{r}\,',0)\rangle_{\vec{R}} = \langle \rho(\vec{r})\rangle_{\vec{R}} \langle \rho(\vec{r}\,')\rangle_{\vec{R}}$$
$$= g(\vec{r})g(\vec{r}\,')\ , \qquad (26a)$$

$$L_I' = \lim_{t\to\infty} \langle \rho_I(\vec{y},t)\rho_I(\vec{y}\,',0)\rangle = \langle \rho_I(\vec{y})\rangle_{\vec{R}} \langle \rho_I(\vec{y}\,')\rangle_{\vec{R}} \qquad (26b)$$

[These equations define the densities $g(\vec{r})$, $g_I(\vec{y})$.] Therefore we have

$$L'(\vec{r},\vec{r}\,',\vec{y},\vec{y}\,';t) = g(\vec{r})g(\vec{r}\,')g_I(\vec{y})g_I(\vec{y}\,')\ . \qquad (27)$$

B. Low Frequency

In order to write L_H in terms of familiar functions we make the approximate decomposition

$$\langle \rho(\vec{r},t)\rho(\vec{r}\,',0)\rangle_{\vec{R}} \simeq \bar{g}(\vec{r})\bar{g}(\vec{r}\,')\,(S(\vec{r}-\vec{r}\,',t)+\rho_0^2)\ , \qquad (28)$$

where $\bar{g} = g/\rho_0$, ρ_0 being the mean density of the liquid, and S is the Van Hove correlation function for the pure liquid

$$S(\vec{r}-\vec{r}\,',t) = \langle (\rho(\vec{r},t)-\rho_0)(\rho(\vec{r}\,',0)-\rho_0)\rangle\ . \qquad (29)$$

Equations (22), (26a), and (29) give

$$\tilde{L}_H(\vec{r},\vec{r}\,',t) = \bar{g}(\vec{r})\bar{g}(\vec{r}\,')S(\vec{r}-\vec{r}\,',t)\ .$$

We do not treat L_I^0 explicitly, except to note that it would vanish if the oscillations of the impurity were truly undamped [see discussion of Eq. (23)],

$$L^0(\vec{r},\vec{r}\,',\vec{y},\vec{y}\,';t) = g(\vec{r})g(\vec{r}\,')L_I^0(\vec{y},\vec{y}\,',t) + \bar{g}(\vec{r})\bar{g}(\vec{r}\,')$$
$$\times S(\vec{r}-\vec{r}\,',t)\,(g_I(\vec{y})g_I(\vec{y}\,') + L_I^0(\vec{y},\vec{y}\,',t))\ . \qquad (30)$$

C. High Frequency

Using Eq. (28) we have approximately

$$L^1(\vec{r},\vec{r}\,',\vec{y},\vec{y}\,';t) = \bar{g}(\vec{r})\bar{g}(\vec{r}\,')\,(S(\vec{r}-\vec{r}\,',t)+\rho_0^2)L_I^1(\vec{y},\vec{y}\,',t)\ . \qquad (31)$$

By hypothesis $L_I^1(t)$ fluctuates much faster than $S(t)$, so that we can replace the latter by $S(t=0)$. If we call $G(\vec{r}-\vec{r}\,') = \rho_0^2 + S(\vec{r}-\vec{r}\,', t=0)$ we have

$$L^1(\vec{r},\vec{r}\,',\vec{y},\vec{y}\,';t) = \bar{g}(\vec{r})\bar{g}(\vec{r}\,')G(\vec{r}-\vec{r}\,')L_I^1(\vec{y},\vec{y}\,';t)\ .$$

VI. FINAL FORM FOR ABSORPTION SPECTRUM

We now examine the contributions of $L(t)$ in the three frequency regions when integrated with the T functions over the spatial coordinates [cf. Eqs. (16) and (18)]. We define

$$F(t) = \int d^3\vec{r}\,d^3\vec{r}\,'\,d^3\vec{y}\,d^3\vec{y}\,'\;T(\vec{r}-\vec{y})$$
$$\times T(\vec{r}\,'-\vec{y}\,')\,L(\vec{r},\vec{r}\,',\vec{y},\vec{y}\,';t)\ , \qquad (32)$$

where T stands for a component of either T_q or T_d.

A. Zero Frequency

We have

$$F'(t) = \int d^3\vec{r}\,d^3\vec{r}\,'\,d^3\vec{y}\,d^3\vec{y}\,'\;T(\vec{r}-\vec{y})$$

$$\times T(\vec{r}\,'-\vec{y}\,')g(\vec{r})g(\vec{r}\,')g_I(\vec{y})g_I(\vec{y}\,')=0\ ,$$

since T is odd under inversion [Eqs. (11a) and (11b)]. There is, therefore, no zero-frequency part of $F(t)$.

B. Low Frequency

This is the regime in which we expect to find collective effects. If L_I^0 can be neglected, then

$$F^0(t)=\int d^3\vec{r}\,d^3\vec{r}\,'\,d^3\vec{y}\,d^3\vec{y}\,'\,T(\vec{r}-\vec{y})T(\vec{r}\,'-\vec{y}\,')$$

$$\times\bar{g}(\vec{r})\bar{g}(\vec{r}\,')g_I(\vec{y})g_I(\vec{y}\,')S(\vec{r}-\vec{r}\,',t) \tag{33}$$

$$=\int d^3\vec{r}\,d^3\vec{r}\,'\,\tilde{T}(\vec{r})\tilde{T}(\vec{r}\,')\bar{g}(\vec{r})\bar{g}(\vec{r}\,')S(\vec{r}-\vec{r}\,',t)\ , \tag{34}$$

the second equation serving as a definition for $\tilde{T}$. We introduce the spatial transforms, e.g.,

$$S(\vec{r},t)=[1/(2\pi)^3]\int d^3\vec{k}\,S(\vec{k},t)\,e^{i\vec{k}\cdot\vec{r}} \tag{35}$$

to get

$$F^0(t)=[1/(2\pi)^3]\int d^3\vec{k}\,t(\vec{k})t(-\vec{k})S(\vec{k},t)\ , \tag{36}$$

where $t(\vec{k})$ is the transform of $\tilde{T}(r)\bar{g}(r)$. For quadrupole-dipole and distortion parts let us write

$$t_q^{\sigma\nu}(\vec{k})=\textstyle\sum_m\langle 12\sigma\nu\,|\,3m\rangle\,Y_3^m(\hat{k})\tau_q(k)\ ,$$

$$t_d^\nu(\vec{k})=Y_1^\nu(\hat{k})\tau_d(k)\ .$$

Then, the forms for $F^0(t)$ summed over spherical components are

$$\sum_{\sigma\nu}(F_q^0(t))^{\sigma\nu}=\frac{7}{(2\pi)^3}\int_0^\infty|\tau_q(k)|^2k^2\,dk\ , \tag{37a}$$

$$\sum_{\nu}(F_d^0(t))^{\nu}=\frac{3}{(2\pi)^3}\int_0^\infty|\tau_d(k)|^2k^2dk\ , \tag{37b}$$

for quadrupole-dipole and distortion mechanisms, respectively.

Using Eqs. (16)–(19), (37a), and (37b) we find the low-frequency parts of $\phi_{JJ'}(t)$, and thence by Fourier transformations $J_{JJ'}(\omega)$ [the low-frequency part of $J(\omega)$ corresponding to the $J\rightarrow J'$ transition],

$$J^0_{JJ'}(\omega)=\frac{\mathcal{K}N}{(2\pi)^3}\,\overline{X}^2\biggl(7|B_q|^2C_{JJ'}$$

$$\times\int_0^\infty|\tau_q(k)|^2S(k,\omega-\Omega_0+E_J-E_{J'})k^2\,dk$$

$$+3\delta_{J,J'}|B_d|^2C_J\int_0^\infty|\tau_d(k)|^2S(k,\omega-\Omega_0)k^2\,dk\biggr)\ , \tag{38}$$

where $S(k,\omega)$ is the time Fourier transform of $S(k,t)$,

$$S(k,\omega)=(1/2\pi)\int_{-\infty}^{\infty}e^{i\omega t}S(k,t)\,dt\ . \tag{39}$$

C. High Frequency

This part of the absorption corresponds to excitation of a vibrational level plus a local mode. We have

$$F^1(t)=\int\int d^3\vec{r}\,d^3\vec{r}\,'\,d^3\vec{y}\,d^3\vec{y}\,'\,T(\vec{r}-\vec{y})\,T(\vec{r}\,'-\vec{y}\,')$$

$$\times\bar{g}(\vec{r})\bar{g}(\vec{r}\,')G(\vec{r}-\vec{r}\,')\,L_I^1(\vec{y},\vec{y}\,',t)\ . \tag{40}$$

If we define

$$V_q(\vec{y},\vec{y}\,')=\sum_m\int d^3\vec{r}\,d^3\vec{r}\,'\left(\frac{\sigma}{|\vec{r}-\vec{y}|}\right)^4\left(\frac{\sigma}{|\vec{r}\,'-\vec{y}\,'|}\right)^4$$

$$\times Y_3^m(\vec{u}_{\vec{r}-\vec{y}})Y_3^m(\vec{u}_{\vec{r}\,'-\vec{y}\,'})^*\,\bar{g}(r)\bar{g}(r')G(\vec{r}-\vec{r}\,')\ , \tag{41a}$$

$$V_d(\vec{y},\vec{y}\,')=\sum_m\int d^3\vec{r}\,d^3\vec{r}\,'\,e^{-|\vec{r}-\vec{y}|/\rho}\,e^{-|\vec{r}\,'-\vec{y}\,'|/\rho}$$

$$\times Y_1^m(\vec{u}_{\vec{r}-\vec{y}})Y_1^m(\vec{u}_{\vec{r}\,'-\vec{y}\,'})^*\,\bar{g}(r)\bar{g}(r')G(\vec{r}-\vec{r}\,') \tag{41b}$$

(where $\vec{u}_{\vec{r}}\equiv\hat{r}$), we find for the sum over spherical components of F^1

$$\sum_{\sigma,\nu}[F_q^1(t)]^{\sigma\nu}=\tfrac{3}{7}\int d^3\vec{y}\,d^3\vec{y}\,'\,V_q(\vec{y},\vec{y}\,')L_I^1(\vec{y},\vec{y}\,',t)\ , \tag{42a}$$

$$\sum_{\nu}[F_d^1(t)]^{\nu}=\frac{3}{4\pi}\int d^3\vec{y}\,d^3\vec{y}\,'\,V_d(\vec{y},\vec{y}\,')L_I^1(\vec{y},\vec{y}\,',t)\ . \tag{42b}$$

This leads to an expression for the high-frequency part of $J_{JJ'}(\omega)$

$$J^1_{JJ'}(\omega)=\mathcal{K}N\overline{X}^2\biggl(|B_q|^2C_{JJ'}\int d^3\vec{y}\,d^3\vec{y}\,'$$

$$\times V_q(\vec{y},\vec{y}\,')L_I^1(\vec{y},\vec{y}\,',\omega)+|B_d|^2\frac{3}{4\pi}\int d^3\vec{y}\,d^3\vec{y}\,'$$

$$\times V_d(\vec{y},\vec{y}\,')L_I^1(\vec{y},\vec{y}\,',\omega)\biggr)\ , \tag{43}$$

where

$$L_I^1(\vec{y},\vec{y}\,',\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty}dt\,e^{i\omega t}\,L_I^1(\vec{y},\vec{y}\,',t)\ . \tag{44}$$

VII. PREDICTED RELATIVE INTENSITIES

The primary interest of the results of Sec. VI is in Eq. (38). This equation shows that, within our approximation, transitions involving excitation of a forbidden vibrational transition will have a line shape which can be interpreted to give information about the collective properties of the fluid. In Sec. VIII, we will proceed to a discussion of this result. First, it is worthwhile to consider some tests by which the general features of the theory can be checked with experiment. In this section we consider two such simple tests.

A. Rotational Components

The formulas we have derived can be used to calculate the intensity ratios of different rotational components of the spectrum. Indeed, since

$$\int_{-\infty}^{\infty} d\omega \, J_{JJ'}(\omega) = (\mathcal{K}N/2\pi)\, \varphi_{JJ'}(t=0) \;, \tag{45}$$

we need only know the ratios of the $\varphi_{JJ'}$ at $t=0$. According to the discussion of Sec. IV we obtain at the same time a measure of the relative importance of the quadrupole-dipole and distortion mechanisms.

We make a rough estimate of these ratios for hydrogen in liquid argon, using Eqs. (16) and (18), and compare the result with the experimental findings of Ref. 5.

We approximate the $t=0$ value of $L(\vec{r}\vec{r}\,', \vec{y}\vec{y}\,'; t)$ by

$$L(\vec{r}, \vec{r}\,', \vec{y}, \vec{y}\,', t=0) \simeq \delta(\vec{y}-\vec{y}\,')\delta(\vec{r}-\vec{r}\,')\, g_I(y)\, g(r) \;, \tag{46}$$

where g_I and g are defined by Eqs. (26a) and (26b). In fact we should include a $r \neq r'$ part in L for a more accurate estimate. Experiments[5] indicate that the hydrogen spends most of its time in a kind of ground oscillation state within the solute cavity and we therefore represent g_I by the square of a wave function:

$$g_I(y) = |\psi(y)|^2 \;. \tag{47}$$

We take the oscillation frequency from Ref. 5 to be about $2.5 \times 10^{13}\ \mathrm{sec}^{-1}$ and approximate ψ inside the classical turning point by a harmonic oscillator wave function appropriate to this frequency and the mass of a hydrogen molecule. It is known that the substitution of hydrogen in solid argon results in only a small distortion of the lattice.[8] It therefore seems reasonable to assume that the radius of the cavity only depends on the parameters of the host; we take this radius equal to $n_0^{-1/3}$, where n_0 is the density of pure liquid argon. Assuming a uniform distribution of atoms outside the radius and knowing the Lennard-Jones parameters for the hydrogen-argon interaction[9] we calculate the potential felt by the hydrogen molecule inside the cavity and from that we form a WKB approximation to ψ outside the classical turning point. The amplitudes of the WKB and harmonic oscillator functions are matched at the turning point.

From Ref. 9 we also take the parameters contained in B_{d} and B_9. By numerical integration we then find

$$\varphi_{qJ'J''}(t=0)/\varphi_{dJJ} = 0.16 \times 4\pi (C_{J'J''}/C_J) \;. \tag{48}$$

We can now calculate the intensity ratio of the Q and $S(1)$ components of the spectrum (we use the notation of Ref. 5). Supposing that the hydrogen molecules are in the ground orthostate and parastate, the Boltzmann factors are $P_0 = P_1 = \frac{1}{4}$ and the C coefficients are

$$\begin{gathered} C_{11} = \tfrac{3}{10}\,(1/4\pi) \;, \quad C_{13} = \tfrac{9}{20}\,(1/4\pi) \;, \\ C_0 = \tfrac{1}{4} \;, \quad C_1 = \tfrac{3}{4} \;. \end{gathered} \tag{49}$$

The intensity ratio is

$$(\varphi_{q11} + \varphi_{d00} + \varphi_{d11})/\varphi_{q13} \simeq 14 \;, \tag{50}$$

which is in order of magnitude agreement with experiment. It should be noted that since the spatial dependence of the distortion moment is of very short range (about $\frac{1}{10}$ of the intermolecular spacing), an estimate such as we have made is very sensitive to the values chosen for the lengths involved.

B. High and Low Frequency

Another important ratio is the relative intensity of low- and high-frequency contributions. A meaningful estimate is easiest to make for the $J \neq J'$ transitions since only the quadrupole-dipole mechanism then plays a part.

From Eqs. (30) and (31) we see that the relevant ratio is K_1/K_0, where

$$\begin{aligned} K_0 &= \sum_{\sigma,\nu} \int d^3\vec{r}\, d^3\vec{r}\,'\, d^3\vec{y}\, d^3\vec{y}\,'\, T_q^{\sigma\nu}(\vec{r}-\vec{y})\, T_q^{\sigma\nu}(\vec{r}\,'-\vec{y}\,') \\ &\qquad \times \bar{g}(r)\bar{g}(r')S(\vec{r}-\vec{r}\,', t=0)g_I(y)g_I(y') \;, \\ K_1 &= \sum_{\sigma,\nu} \int d^3\vec{r}\, d^3\vec{r}\,'\, d^3\vec{y}\, d^3\vec{y}\,'\, T_q^{\sigma\nu}(\vec{r}-\vec{y})\, T_q^{\sigma\nu}(\vec{r}\,'-\vec{y}\,') \\ &\qquad \times \bar{g}(r)\bar{g}(r')G(\vec{r}-\vec{r}\,')L_I^1(\vec{y}, \vec{y}\,', t=0) \;. \end{aligned} \tag{51}$$

We have taken $L_I^0 = 0$, which implies [using (21), (23), (26b), and (46)]

$$L_I^1(\vec{y}, \vec{y}\,', t=0) = \delta(\vec{y}-\vec{y}\,')g_I(y) - g_I(\vec{y})g_I(\vec{y}\,') \;, \tag{52}$$

so that

$$\begin{aligned} K_1 &= \sum_{\sigma,\nu} \int d^3\vec{r}\, d^3\vec{r}\,'\, d^3\vec{y}\, T_q^{\sigma\nu}(\vec{r}-\vec{y})\, T_q^{\sigma\nu}(\vec{r}\,'-y)\bar{g}(r)\bar{g}(r') \\ &\qquad \times [S(\vec{r}-\vec{r}\,') + n_0^2]g_I(y) - K_0 = K' + K'' - K_0 \;. \end{aligned} \tag{53}$$

Note that K' is very similar to K_0. As we only want an order of magnitude estimate we replace $S(r-r')$ by $n_0\delta(r-r')$, and perform the r, r' integrations, calling

$$S(\vec{y}) = n_0 \sum_{\sigma,\nu} \int d^3\vec{r}\, |T_q^{\sigma\nu}(\vec{r}-\vec{y})|^2 \;. \tag{54}$$

Since we are dealing with entirely Coulomb interactions, and $g_I(y)$ is spherically symmetric, we have

$$\int d^3\vec{y}\, g_I(\vec{y}) T_q^{\sigma\nu}(\vec{r}-\vec{y}) = T_q^{\sigma\nu}(r) \int d^3\vec{y}\, g_I(y) = T_q^{\sigma\nu}(r) \tag{55}$$

for $\vec{r}$ outside the cavity. Therefore we have

$$K_0 = S(y=0)\ ,$$

$$K^1 = \int d^3\vec{y}\, S(y) g_I(y)$$

$$= K_0 + \int d^3\vec{y}\, g_I(y)[\vec{y}\cdot\nabla S(y) + \cdots]\ . \tag{56}$$

This is an expansion in $\delta n_0^{1/3}$ where δ is the range of $g_I(y)$. The parameters we have already used give $\delta n_0^{1/3} = 0.1$, so that the expansion converges rapidly. Only even powers of $\delta n_0^{1/3}$ appear. By numerical integration we find

$$K^1 = K_0(1+0.09)\ . \tag{57}$$

The integral K'' involves the functions

$$t^{\sigma\nu}(y) = n_0 \int d^3\vec{r}\, T_q^{\sigma\nu}(\vec{r}-\vec{y})\bar{g}(r)\ , \tag{58}$$

whose first nonzero terms in an expansion in powers of $\delta n_0^{1/3}$ are cubic, since T_q contains only third-order spherical harmonics. This implies that

$$K_2'' = \sum_{\sigma\nu} \int d^3\vec{y}\, |t^{\sigma\nu}(y)|^2 g(y) \tag{59}$$

is of order $(\delta n_0^{1/3})^6$ and we can therefore neglect it and set $K_1 = K' - K_0$. Equation (57) then shows that

$$K_1/K_0 \simeq 0.09\ , \tag{60}$$

which means that the low-frequency contribution is dominant in the $J \neq J'$ transitions. This is in qualitative agreement with observation, although there is some indication that our prediction for the ratio is somewhat low.

VIII. DISCUSSION

We believe that the most interesting qualitative result of the present work is in Eq. (38) which shows that in a simple liquid, the absorption spectrum of a light diatomic molecule near a forbidden vibrational transition plus a rotational transition ($J \neq J'$) will show features which can be interpreted to give information about the collective excitation spectrum of the liquid. Because the function $\tau_q(k)$ peaks at $k \simeq 1/b$, where b is the size of the cavity containing the molecule, this information will concern the short-wavelength collective excitations in which there is considerable current theoretical and experimental interest.[4]

The results of Sec. VI and an inspection[4] of the known $S(q,\omega)$ for argon indicate that the formula (38) may indeed account for the observed width of the absorption lines observed in Ref. 5. To confirm this more fully requires a numerical calculation of the line shapes based on Eq. (38) which is presently under way. It should be noted that we have omitted diffusive motion of the H_2 molecule from our considerations. Recent work by Zaidi and Van Kranendonk suggests that this motion plays the dominant role in determining the absorption line shape.[10] Application of our results to calculate experimental line shapes together with extensions of our model to include diffusive motion will help to resolve the question of the dominant effects in the line shapes in the future.

APPENDIX: INDUCED MOMENT OPERATORS

We briefly derive the forms Eqs. (11a) and (11b) for the induced moment functions.

The potential produced by the quadrupole moment q of an axially symmetric charge distribution $\rho(r)$:

$$q = (16\pi/5)^{1/2} \int d^3\vec{r}\, Y_2^0(\hat{r}) r^2 \rho(r) \tag{A1}$$

is

$$\varphi(\vec{R}) = Y_2^0(\hat{R})\,(1/R^3)\,(\tfrac{1}{5}\pi)^{1/2} q\ . \tag{A2}$$

This may be equivalently expressed

$$\varphi(\vec{R}) = -\tfrac{1}{4} q (\vec{p}\cdot\nabla)^2 (1/R)\ , \tag{A3}$$

where $\vec{p}$ is a unit vector along the axis of the quadrupole. Therefore the electric field of the quadrupole is

$$\vec{E}(\vec{R}) = \tfrac{1}{4} q (\vec{p}\cdot\nabla)^2 \nabla(1/R). \tag{A4}$$

If we express the angular R dependence of $E(\vec{R})$ in spherical harmonics, then the highest harmonic which enters is of order three. The only other one allowed by parity is of order one; we can verify that the component vanishes by noting that the integral of (A4) with any component of R vanishes. The dependence of $E(r)$ on $|\vec{R}|$ is $|\vec{R}|^{-4}$.

These facts are sufficient to confirm that the functional form of $\mu_q^\nu(\Psi, \vec{R})$ expressed in Eqs. (9b) and (11a) is correct. We now derive the value of the coefficient of Eq. (11a).

Let us write

$$E^\nu(\vec{R}) = \frac{c}{R^4} \sum_{\sigma,m} \langle 12\nu\sigma | 3m \rangle Y_3^m(\hat{R}) Y_2^\sigma(\Psi). \tag{A5}$$

If $\vec{R}$ and Ψ both point along the z axis we have

$$E^0(\vec{R}) = (c/R^4)\langle 1200 | 30 \rangle Y_3^0(0)\, Y_2^0(\omega)\ , \tag{A6}$$

but from Eq. (A2) we see

$$E^0(R) = 3Y_2^0(0)(1/R^4)(\tfrac{1}{5}\pi)^{1/2} q. \tag{A7}$$

Inserting the numerical value of $\langle 1200 | 30 \rangle$ we find

$$c = 2\pi(\sqrt{\tfrac{3}{7}})q\ .$$

This confirms the values of the coefficients in Eqs. (10) and (11a).

The $|R|$ dependence in Eq. (11b) was introduced phenomenologically, and we only have to verify the angular dependence. But if the induced moment lies along the radius vector, then we must have

$$\mu_a^\nu(R) \sim R^\nu$$

for the angular dependence; this is equivalent to Eq. (11b).

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Behavior of He($2\,^3S$) Metastable Atoms in Weakly Ionized Helium Plasmas[*]

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Investigations concerning the behavior of the He($2\,^3S$) population in active-discharge and afterglow helium plasmas are described. Good quantitative agreement is obtained between measured He($2\,^3S$) densities in active discharges and predicted values based on the solution of a nonlinear rate equation. The rate coefficient for ionizing triplet-metastable–metastable collisions is measured in afterglow helium plasmas for the pressure range 10–40 Torr; close agreement is obtained with the value reported by Phelps and Molnar, though consideration of effects due to electrons suggests a downward revision of about 20%. The electron temperature decay in the afterglow is measured and found to agree closely with the decay expected on the basis of calculated energy source and loss processes which affect the electron gas. In this work, measurement of the He($2\,^3S$) metastable density is accomplished by the novel use of a He-Ne laser operating at 1.0798 μ in an interferometer as well as by the conventional optical-absorption method. Advantages and disadvantages of this interferometer technique are discussed.

I. INTRODUCTION

The behavior of atoms excited to the $2\,^3S$ metastable state of helium has been studied in detail by many previous authors.[1-7] In this paper we report further investigations concerning the triplet-metastable populations of weakly ionized active-discharge and afterglow helium plasmas. In our work we attempt to describe accurately the steady-state triplet populations in active discharges in pure helium, the electron temperature decay in helium afterglows, and we perform a remeasurement of the triplet-metastable–metastable collision rate coefficient. Our experimental apparatus includes a laser interferometer operating in the infrared which is used for $2\,^3S$ metastable density measurements, as described in Sec. II. Triplet-metastable concentrations are inferred from plasma refractivity measurements by use of the standard formula for anomalous dispersion.[8] In Sec. III, a continuity equation describing the production and loss of triplet-metastable atoms in active discharges in pure helium is presented. The equation uses cross sections and calculated electron-energy distribution functions which are in the literature. Good quantitative agreement is obtained in the range of pressures and currents studied between the measured triplet-metastable densities and the densities predicted by the solution to the continuity equation. In Sec. IV, the electron temperature decay of an afterglow helium plasma is considered. We show that, with knowledge of triplet-metastable