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Estimate of integrated s-wave Raman scattering intensity from the $2\,^1P_1$ ultraviolet absorption line shape in liquid helium*

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We show in a unified model that the shift and width of the ultraviolet absorption line shapes in liquid helium are related to the integrated Raman-scattering cross sections. This relation is used to estimate the magnitude of the integrated s-wave scattering by use of the observed ultraviolet spectrum. We find $0.25 \lesssim \mathcal{I}_s/\mathcal{I}_d \lesssim 3.4$ The model gives standard results for d-wave scattering. We discuss some other possible uses of the model.

I. INTRODUCTION

The only observed optical properties of liquid helium are light scattering, which has recently attracted a great deal of experimental and theoretical attention,[1] and ultraviolet light absorption on which, to our knowledge, one theoretical[2] and one experimental[3] paper have appeared. We direct attention here to a unified model which describes both phenomena in a single framework. This framework leads to certain connections between the intensity of integrated second-order (Raman) scattering and the width of ultraviolet absorption lines.

Physically, this connection exists because the possibility of Raman scattering and the shift and width of the uv absorption line both arise from the fact that the excited electronic state of a given helium atom can be transferred to another atom in the liquid via a hopping process. (A more detailed physical picture of this hopping in the case of Raman scattering appears in Appendix A.) The mechanism of this hopping process is either the classical dipole-dipole interaction or a quantum-mechanical effect such as the overlap of the atomic wave functions of the helium atoms.

Our interest in studying the relation between the Raman scattering and absorption arose partly because the dipole-dipole interaction cannot account theoretically for the observed uv absorption linewidth or peak position, whereas the dipole-dipole interaction is used exclusively in existing theories of Raman scattering. The present theory is partly an attempt to account for this apparent contradiction. We find that the uv absorption shift and width can in fact be used to estimate the expected s-wave Raman scattering intensity. Our model gives a range of values several times larger than the observed upper limit on the s-wave intensity at the two-roton peak. We argue that this implies that the s scattering at higher frequencies is considerably larger than in the two-roton region. A large part of the numerical uncertainty in our prediction arises from uncertainties in the exact uv shift, width, and line shape. These may be overcome by a more complete analysis of the available uv data. Our prediction is useful because the s-wave scattering intensity is very difficult to calculate from first principles and the present study provides a means of estimating it by use of data from ultraviolet absorption measurements.

Our results account for the apparent contradiction discussed above in the following way. We argue that only the first excited electronic state contributes to the s-wave Raman intensity. Since the Raman scattering is proportional to α_0^4, where α_0 is the polarizability, and the first excited state is responsible for about $\frac{1}{3}$ of α_0, the s-wave intensity includes a factor of $(\frac{1}{3})^4 = \frac{1}{81}$ with respect to the d-wave (dipole-dipole) intensity. This accounts for part of the difference between the s- and d-wave intensities, while allowing the s-wave effects on the first excited electronic state in uv absorption to be large. Another useful feature of our result is that the explicit connection between the Raman scattering intensity and uv line shape is independent of the difficulties recently encountered[4] in properly calculating the Raman intensity.

In the following sections we first describe the model and then compare its predictions with published experiments on uv absorption. In Sec. IV we derive an expression for the Raman scattering intensity and in Sec. V we estimate the integrated s-state scattering intensity. Section VI is a discussion. Calculational details appear in appendices.

II. MODEL

The model is an extension of one used in reference 2 to study ultraviolet absorption. The Hamiltonian is

$$\mathcal{H} = \sum_{i,p} E_p \vec{c}^{\,\dagger}_{ip} \cdot \vec{c}_{ip} - \frac{1}{2} \sum_{\substack{i,j \\ p,p'}} \vec{d}_{ip} \cdot \overleftrightarrow{T}^{pp'}_{ij} \cdot \vec{d}_{jp'} + \mathcal{H}_0 , \tag{1}$$

where

$$\vec{d}_{ip} = X_p \vec{c}_{ip} + X_p^* \vec{c}^{\,\dagger}_{ip} .$$

Here $\mathcal{H}_0$ describes the motion of the helium atoms in the ground state and E_p is the energy of the pth excited atomic p state of an isolated atom. The operators $\vec{c}^{\,\dagger}_{ip} = (c^{x\dagger}_{ip}, c^{y\dagger}_{ip}, c^{z\dagger}_{ip})$ produce a p-state excitation transforming like x, y, or z on the ith atom when they operate on any state of the system in which all the helium atoms are in their ground states. X_p is the matrix element of the dipole operator between the ground and excited p state. We will take the c's to be boson operators, as is possible if only a few atoms in excited electronic states are present.[2,5] The matrix $\overleftrightarrow{T}^{pp'}_{ij}$ describes the hopping rate. Because the c's transform as vectors, $\overleftrightarrow{T}^{pp'}_{ij}$ has the general form[1]

$$\overleftrightarrow{T}^{pp'}_{ij} = t^{pp'}_d(R_{ij})\left(3\frac{\overleftarrow{R}_{ij}\overrightarrow{R}_{ij}}{R^2_{ij}} - \overleftrightarrow{1}\right) + t^{pp'}_s(R_{ij})\overleftrightarrow{1}. \quad (2)$$

In Ref. 2 we kept only the d apart of this and used the approximation valid for large r

$$t^{pp'}_d(r) = 1/r^3. \quad (2a)$$

We demonstrate below that previous treatments of Raman scattering are special cases of our model [Eq. (1)]. In these special cases,

$$t^{pp'}_s = 0, \quad t^{pp'}_d(r) = c(r)/r^3, \quad (2b)$$

where $c(r)$ is independent of p and p', approaches 1 for large r, and is cut off in some phenomenological way at small r. We also discuss in a qualitative way the expected exact forms of $t^{pp'}_d$ and $t^{pp'}_s$. Generally it is a very difficult problem in molecular quantum mechanics to calculate these functions from first principles.[6]

The following comments need to be made about the validity of the model:

(a) The $\vec{c}_{ip}$ can only be regarded as boson operators if the occupancy of excited electronic states is much smaller than the total number of helium atoms N. This condition is well satisfied in the experiments to be discussed.

(b) The form of (1) implicitly assumes that the excited electronic states are well localized and can be meaningfully associated with sites i. This is certainly true for the first excited p state of the helium atom but requires further justification for the higher electronic states. We discuss this point further in Sec. VI.

(c) The Hamiltonian manifests the Born-Oppenheimer approximation in that the first two terms, describing electron dynamics, contain the nuclear coordinates only through $\overleftrightarrow{T}^{pp'}_{ij}$. The van der Waals interaction between helium atoms in their ground states is contained in $\mathcal{H}_0$. If a large number of atoms were electronically excited by a radiation field, the van der Waals interaction would be modified. We neglect this effect for the reason mentioned in (a).

(d) For highly excited p states, even if they can be associated with a site i or j, $\overleftrightarrow{T}^{pp'}_{ij}$ may depend on the positions of atoms other than i and j in the liquid. We ignore this effect and present an argument justifying this in Sec. VI.

(e) We restrict attention in (1) to p states because states of other symmetry are not involved in optical processes to the order to which we are working.

III. MOMENTS OF THE ULTRAVIOLET ABSORPTION LINES

Here we cite the results of Ref. 2 with minor extensions. A new feature is the inclusion of both s- and d-type hopping terms [cf. Eq. (2)]. We have directly from Ref. 2 that the nth moment M^p_n of the pth absorption line defined as

$$M^p_n = \frac{\int_{-\hbar\omega^p_L+E_p}^{\hbar\omega^p_L+E_p} (E-E_p)^n A(E)\,dE}{\int_{-\hbar\omega^p_L+E_p}^{\hbar\omega^p_L+E_p} A(E)\,dE}, \quad (3)$$

where

$$(M^p_n)^{1/n} \ll \hbar\omega^p_L \ll |E_p - E_{p-1}|, |E_p - E_{p+1}| \quad (3a)$$

is

$$M^p_n = |X_p|^{2n}\langle (F^p_n)^{xx}\rangle_c,$$

in which

$$\overleftrightarrow{F}^p_{n-1} = \frac{1}{N}\sum_{i_1,\cdots,i_n} \overleftrightarrow{T}^{pp}_{i_1 i_2}\bullet\cdots\bullet\overleftrightarrow{T}^{pp}_{i_{n-1}i_n} e^{i\vec{k}\cdot(\vec{R}_{i_1}-\vec{R}_{i_n})}$$

and $\langle\cdots\rangle_c$ is the cumulant average over atom positions. In particular

$$M^p_1 = |X_p|^2\rho\int d^3r\, g(r)[\overleftrightarrow{T}^{pp}(\vec{r})]^{xx}e^{ikz}, \quad (4)$$

where $g(r)$ is the pair correlation function for helium atoms in thermal equilibrium, k is the wave vector of the light, and z is in the direction of propagation of the light. $A(E)\,dE$ is the absorption rate in the energy range E to $E+dE$. As was shown in Ref. 2, the limit in (4) must be treated carefully when the d part of (2) is inserted for $[\overleftrightarrow{T}^{pp}(\vec{r})]^{xx}$. In general we have by inserting (2) in (4) that

$$M^p_1 = (M^p_1)_d + (M^p_1)_s, \quad (5)$$

where

$$(M^p_1)_d = |X_p|^2\rho\int d^3r\,(3x^2/r^2 - 1)t^{pp}_d(r)e^{ikz}g(r), \quad (6a)$$

$$(M^p_1)_s = |X_p|^2\rho\int d^3r\, t^{pp}_s(r)g(r), \quad (6b)$$

where we can take the limit $k\to 0$ in $(M^p_1)_s$ because $t^{pp}_s(r)$ is not expected to have long-range parts. In Ref. 2, Eq. (6a) was evaluated using the form (2a) for $t^{pp}_d(r)$ with the general result

$$(M^p_1)_d = -\tfrac{4}{3}\pi\rho|X_p|^2, \quad (7)$$

where ρ is the liquid-helium number density.

The derivation of (7) given in Ref. 2 is independent of the behavior of $t^{pp}_d(\vec{r})$ at small r. For the

$2\,^1P_1$ state[7] of helium, we estimate $|X_p|^2$ from the atomic oscillator strength[8]

$$f = |X_p|^2 \frac{2mE_p}{e^2\hbar^2} = 0.28,$$

using $E_p = E - E_0 = 21.4$ eV and find (taking $p = 1$ for the $2\,^1P_1$ state)

$$(M_1^1)_d \simeq -0.066 \text{ eV}, \tag{8}$$

whereas the experimental shift estimated from published data is[3]

$$\delta E_1 \equiv (M_1^1)_{\text{exp}} \simeq 0.212 \text{ eV}. \tag{9}$$

We conclude that

$$(M_1^1)_s \simeq 0.278 \text{ eV}. \tag{10}$$

The result (10) indicates that, even for the lowest-lying p state, $t_s(r)$ makes substantial contributions to the line shift. This provides part of the motivation mentioned in the Introduction for investigating and estimating the contributions of $t_s(r)$ to the Raman scattering.

We next review the expression from Ref. 2 for the second moment of the absorption line and compare it with the experiments. One has from Ref. 2 that

$$M_2^p = |X_p|^4(\rho^3/N)\int d^3r_1\int d^3r_2\int d^3r_3[g_3(\vec{r}_1,\vec{r}_2,\vec{r}_3) - g_2(\vec{r}_1,\vec{r}_2)g_2(\vec{r}_2,\vec{r}_3)]e^{i\vec{k}_0\cdot(\vec{r}_1-\vec{r}_3)}[\overleftrightarrow{T}^{pp}(\vec{r}_{12})\cdot\overleftrightarrow{T}^{pp}(\vec{r}_{23})]^{xx}$$
$$+|X_p|^4(\rho^2/N)\int d^3r_1\int d^3r_2[\overleftrightarrow{T}^{pp}(\vec{r}_{12})\cdot\overleftrightarrow{T}^{pp}(\vec{r}_{12})]^{xx}g_2(r_{12}). \tag{11}$$

In (11) the correlation functions are defined by

$$\sum_{i_1,\ldots,i_n}{}' \langle f(\vec{R}_{i_1},\ldots,\vec{R}_{i_n})\rangle = \rho^n\int\cdots\int f(\vec{r}_1,\ldots,\vec{r}_n)g_n(\vec{r}_1,\ldots,\vec{r}_n)\,d^3r_1\ldots d^3r_n, \tag{12}$$

where the prime on the sum on the left-hand side of (12) means that terms with any pair of i's equal are to be omitted and f is an arbitrary function. The definition (12) is equivalent to that of Ref. 2 except for the factor ρ^n on the right-hand side. The $g_n(\vec{r}_1,\ldots,\vec{r}_n)$ used here are dimensionless, and $g_2(r) = g(r)$.

Inserting Eq. (2) in Eq. (11) we have

$$M_2^p = (M_2^p)_{dd} + 2(M_2^p)_{sd} + (M_2^p)_{ss}. \tag{13}$$

Here

$$(M_2^p)_{\mu\nu} = |X_p|^4(\rho^3/N)\int d^3r_1\int d^3r_2\int d^3r_2[g_3(\vec{r}_1,\vec{r}_2,\vec{r}_3) - g_2(\vec{r}_1,\vec{r}_2)g_2(\vec{r}_2,\vec{r}_3)]e^{i\vec{k}\cdot(\vec{r}_1-\vec{r}_3)}[\overleftrightarrow{T}^{pp}_{\mu}(r_{12})\cdot\overleftrightarrow{T}^{pp}_{\nu}(r_{23})]^{xx}$$
$$+|X_p|^4(\rho^2/N)\int d^3r_1\int d^3r_2[\overleftrightarrow{T}^{pp}_{\mu}(\vec{r}_{12})\cdot\overleftrightarrow{T}^{pp}_{\nu}(\vec{r}_{12})]^{xx}g_2(\vec{r}_{12}), \tag{14}$$

where μ, ν take the value s, d. $\overleftrightarrow{T}^{pp}_s$ is the first term in Eq. (2) and $\overleftrightarrow{T}^{ss}_d$ is the second term in Eq. (2). The first term in Eq. (13) was evaluated in Ref. 2 using Eq. (2a) for $t_d(r)$ with a step-function cutoff and using the Kirkwood superposition approximation for $g_3(\vec{r}_1,\vec{r}_2,\vec{r}_3)$. The result was

$$(M_2^1)_{dd} = 11.3\rho|X_p|^4. \tag{15}$$

To compare this with the experiments on $2\,^1P_1$ line, one must determine the experimental second moment with respect to the unshifted atomic frequency E_p. Since the experimental data[3] have not been fully analyzed, we cannot compute this moment directly. We relate it instead to the line width W^p by

$$\left(\frac{W^p}{\chi^p}\right)^2 = \frac{\int(E - E_p - \delta E_p)^2 A(E)\,dE}{\int A(E)\,dE}. \tag{16}$$

The factor χ^p reflects the fact that the ratio between the width and second moment depend on the exact line shape. Simple models for the line shape give $2 \lesssim (\chi^p)^2 \lesssim 20$ as reasonable bounds for this factor. Note also that the values of W^1 and the line shift δE_1 used below are somewhat uncertain since they are based on an analysis of the data using a Lorentzian ansatz for the absorption line.[3]

It is easy to show using (13) and (16) that

$$(M_2^p) = (W^p/\chi^p)^2 + (M_1^p)^2. \tag{17}$$

Using the measured values $W^1 = 0.43$ eV and $M_1^1 = 0.212$ eV for the $2\,^1P_1$ state and $2 \lesssim (\chi^1)^2 \lesssim 20$ gives

$$0.232 \lesssim (M_2^1)^{1/2} \lesssim 0.376 \text{ eV}. \tag{18}$$

On the other hand, again using the atomic oscillator strength for the $2\,^1P_1$ state, we have from (15) that

$$[(M_2^1)_{dd}]^{1/2} = 0.053 \text{ eV}. \tag{19}$$

Comparing (18) and (19) one sees that the inadequacy of the dipole-dipole part of $\overleftrightarrow{T}^{pp}$ in accounting for the second moment is quite marked. This

might have been anticipated from the form of Eq. (11) and the analysis of Ref. 2 because it turns out that the long-range part of the dipole-dipole interaction does not contribute to (11), while it does contribute to (4). Thus the second moment is determined largely by short-range interactions between an excited and a ground-state atom. These short-range interactions, arising partly from wavefunction overlap can be expected to have a substantial s-like part.

The total intensity of the second-order inelastic (Raman) light scattering in liquid helium will be shown in Sec. IV to be bilinear in $\overleftrightarrow{T}$ and of a form similar to (14). If the uv width has substantial s-like contributions, we might then expect the Raman intensity to have s-like contributions. This conclusion is verified in Sec. V.

IV. RAMAN SCATTERING INTENSITY

Here we derive an expression for the Raman-scattering extinction coefficient $h_{\hat{\epsilon}_n}(\hat{R}, \omega_n)$ defined by

$$h_{\hat{\epsilon}_n}(\hat{R}, \omega_n) = I_{\hat{\epsilon}_n}(\hat{R}, \omega_n)/I_0, \tag{20}$$

where $I_{\hat{\epsilon}_n}(\hat{R}, \omega_n)$ is the light-scattering intensity per unit volume of sample, per unit solid angle, per unit of light frequency emitted in the direction $\hat{R}$ at frequency ω_n and with polarization $\hat{\epsilon}_n$. I_0 is the intensity of incident light. This quantity has been calculated many times before[9–14] for Raman scattering in liquid helium. The difference between earlier treatments and the present one is that we use the Hamiltonian (1) and thus treat the electronic excitations explicitly within our model.

In the treatments of Refs. 10 and 12–14, the electronic excitations are taken into account implicitly through the polarizability in a semiclassical model. As we will show, this approach, in general, gives complete results only when $\overleftrightarrow{T}$ is of form (2b). We have argued in Sec. III, however, that there are experimental grounds for believing that $\overleftrightarrow{T}$ contains substantial parts of an explicitly quantum-mechanical nature which are not of this form.

In Refs. 9 and 11 the electronic excitations were treated explicitly. In the first[9] of these, the dynamics of the liquid was treated in an unrealistic approximation. In the second previous work treating the electronic excitations explicitly, [11] an approximation equivalent to that of Refs. 10, 13, and 14 was made, so that the consequences we find were not pointed out. In this section we treat the electromagnetic field *outside* the sample of liquid helium semiclassically (this is entirely adequate for the experiments in question[15]) but we give a fully quantum-mechanical treatment of the polarizability of the liquid helium in contrast to Refs. 10, 11, 13, and 14. In Appendix A we obtain the same results by quantizing the electromagnetic field inside and outside the sample and using the Fermi golden rule in third order. The latter approach[16] is in some respects simpler, but it obscures the question of which effects are really quantum mechanical.

To calculate $h_{\hat{\epsilon}_n}(\hat{R}, \omega_n)$ we use the fact that the intensity $I_{\hat{\epsilon}_n}(\hat{R}, \omega_n)$ of scattered light at the point $\vec{R}$ is[14,17]

$$I_{\hat{\epsilon}_n}(\hat{R}, \omega_n) = \frac{R^2 c}{\Omega(4\pi)^2 2\tau} \langle | E'_{\hat{\epsilon}_n}(\vec{R}, \omega_n)|^2 \rangle, \tag{21}$$

where $E'_{\hat{\epsilon}_n}(\vec{R}, \omega_n)$ is the time Fourier transform of the component of the electric field of the scattered light in the direction of the unit vector $\hat{\epsilon}_n$. 2τ is the duration in time of an incoming pulse of light and Ω is the volume of the sample scattering the light. The average $\langle \cdots \rangle$ is a statistical average to be taken over the states of the sample. Solution[10,14,17] of Maxwell's equation gives the following result for the time Fourier transform $\vec{E}(\vec{R}, \omega_n)$ of the total electromagnetic field at a point $\vec{R}$ far from the sample:

$$\vec{E}(\vec{R}, \omega_n) = \vec{E}_0(\vec{R}, \omega_n) + \vec{E}'(\vec{R}, \omega_n), \tag{22}$$

where

$$\vec{E}'(\vec{R}, \omega_n) = \frac{\omega_n^2}{c^2 R} e^{i\omega_n R/c}(\overleftrightarrow{1} - \hat{R}\hat{R}) \times \int dt' \, e^{i\omega_n t'} \int d^3r' e^{-i(\omega_n/c)\hat{R}\cdot\vec{r}'} \vec{P}(\vec{r}', t'). \tag{23}$$

Here $\vec{E}_0(\vec{R}, \omega_n)$ is the time Fourier transform of the electric field of the incident pulse of light. In (23) the integral on $\vec{r}'$ is over the sample volume, so $\vec{P}(\vec{r}', t')$, the polarization at point $\vec{r}'$ and time t', should be treated as an operator. Taking the dot product

$$E'_{\hat{\epsilon}_n}(\vec{R}, \omega_n) = \hat{\epsilon}_n \cdot \vec{E}'(\vec{R}, \omega_n)$$

we have for the important factor in (21) the expression

$$\langle | E'_{\hat{\epsilon}_n}(\vec{R}, \omega_n)|^2 \rangle = \frac{2\omega_n^4 \tau}{c^4 R^2} \int_{-\infty}^{+\infty} dt' e^{i\omega_n t'} \int d^3r' \int d^3r'' e^{-i\vec{k}_n\cdot(\vec{r}'-\vec{r}'')} \langle P_{\hat{\epsilon}_n}(\vec{r}', t') P^\dagger_{\hat{\epsilon}_n}(\vec{r}'', 0) \rangle, \tag{24}$$

where we have assumed that τ is much larger than any correlation times involved in the expectation value. We have written $\vec{k}_n = (\omega_n/c)\hat{R}$, which is the wave vector of the scattered light. In (24),

$$P_{\hat{\epsilon}_n}(\vec{r},\ t)=\hat{\epsilon}_n\cdot\vec{P}(\vec{r},\ t),$$

where we take $\vec{P}$ to be an operator since it refers to processes inside the scattering volume. We have used $\hat{\epsilon}_n\cdot(\overleftrightarrow{1}-\hat{R}\hat{R})=\hat{\epsilon}_n$. To complete the derivation we must find $\vec{P}(\vec{r},\ t)$ in the presence of an external field $\vec{E}_0(\vec{R},\ t)$. Within the model described by Eq. (1), the operator $\vec{P}(\vec{r},\ t)$ is

$$\vec{P}(\vec{r},\ t)=\sum_{i,p}(X_p^*\vec{c}_{ip}^{\,\dagger}+X_p\vec{c}_{ip})\delta(\vec{r}-\vec{r}_i(t)). \tag{25}$$

In the presence of an external field $\vec{E}_0(\vec{r},\ t)$, Eq. (1) becomes

$$\mathcal{H}=\sum_{i,p}E_p\vec{c}_{ip}^{\,\dagger}\cdot\vec{c}_{ip}-\sum_{p,p'}\sum_{i<j}\vec{d}_{ip}\cdot\overleftrightarrow{T}_{ij}^{pp'}\cdot\vec{d}_{jp'}$$
$$-\sum_{i,p}\vec{E}_0(\vec{r}_i,\ t)\cdot(X_p^*\vec{c}_{ip}^{\,\dagger}+X_p\vec{c}_{ip})+\mathcal{H}_0, \tag{26}$$

where

$$\vec{E}_0(\vec{r},\ t)=\vec{E}_0\cos(\vec{k}_0\cdot\vec{r}-\omega_0 t).$$

The equation of motion of $\vec{c}_{ip}$ is

$$\frac{d\vec{c}_{ip}}{dt}=-i\omega_p\vec{c}_{ip}+(iX_p^*/\hbar)\vec{E}_0(\vec{r}_i,\ t)$$
$$+\frac{iX_p^*}{\hbar}\sum_{p'}\sum_{j}\overleftrightarrow{T}_{ij}^{pp'}\cdot\vec{d}_{jp'}+\frac{[\vec{c}_{ip},\ \mathcal{H}_0]}{i\hbar}, \tag{27}$$

where $\omega_p=E_p/\hbar$. We now take into account the fact that $\omega_p\gg|T_{ij}|/\hbar\gg$ (frequencies of atomic motion) to approximately solve this equation. ($\hbar\omega_p\gtrsim 20$ eV, $T\sim 0.1$ eV while the energies of nuclear motion are 10^{-2} eV.) The solution of (27) is given in Appendix B. This result, inserted in the expression (25) for the polarizability gives

$$\vec{P}(\vec{r},\ t)=\vec{P}^{(0)}(\vec{r},\ t)+\vec{P}^{(1)}(\vec{r},\ t)+\cdots, \tag{28}$$

where

$$\vec{P}^{(0)}(\vec{r},\ t)=\alpha_0(\omega_0)\sum_i\vec{E}_0(\vec{r}_i,\ t)\delta(\vec{r}-\vec{r}_i(t)), \tag{29}$$

$$\alpha_0(\omega_0)=2\sum_p\frac{E_p|X_p|^2}{E_p^2-E_0^2}, \tag{30}$$

where

$$E_0=\hbar\omega_0 \tag{31}$$

and

$$\vec{P}^{(1)}(\vec{r},\ t)=\sum_{\substack{i,j\\p,p'}}\alpha_p(\omega_0)$$
$$\times\overleftrightarrow{T}_{ij}^{pp'}\alpha_{p'}(\omega_0)\cdot\vec{E}_0(\vec{r}_j,\ t)\delta(\vec{r}-\vec{r}_i(t)) \tag{32}$$

where

$$\alpha_p(\omega_0)=2\frac{|X_p|^2E_p}{E_p^2-E_0^2}. \tag{33}$$

The successive terms in (28) represent increasing powers of $|T_{ij}^{pp'}|/E_p$. $\alpha_0(\omega_0)$ given by (30) is the dispersive form of the polarizability.

Inserting $\vec{P}^{(0)}(\vec{r},\ t)$ in (24) gives the usual result for Brillouin scattering:

$$h_{\hat{\epsilon}_n}^{(0)}=\rho(\omega_n/c)^4\alpha_0^2(\omega_0)(\hat{\epsilon}_0\cdot\hat{\epsilon}_n)^2S(\vec{k}_0-\vec{k}_n,\ \omega_n-\omega_0). \tag{34}$$

The only interesting feature emerging for Brillouin scattering in this treatment is that the frequency-dependent polarizability appears. In practice this is not important for liquid helium because $E_p\sim 20$ eV and $\hbar\omega_0\sim 1$ eV, so that (34) reduces to the usual expression. Putting (32) in (24) we find an expression for the Raman-scattering extinction coefficient[18]:

$$h_{\hat{\epsilon}_n}^{(1)}(\hat{R},\ \omega_n)=(\rho^3/2\pi)(\omega_n/c)^4\sum_{\vec{q},\vec{q}'}F(\vec{q})F(\vec{q}')$$
$$\times S_4(\vec{q}-\vec{k}_n,\ \vec{k}_0-\vec{q},\ \vec{k}_n-\vec{q}',\ \omega_n-\omega_0), \tag{35}$$

where

$$F(\vec{q})=\sum_{p,p'}\alpha_p(\omega_0)\alpha_{p'}(\omega_0)\hat{\epsilon}_n\cdot\overleftrightarrow{T}^{pp'}(\vec{q})\cdot\hat{\epsilon}_0. \tag{36}$$

Here the spatial Fourier transform of $\overleftrightarrow{T}^{pp'}(\vec{r})$ has been defined as

$$\overleftrightarrow{T}^{pp'}(\vec{q})=\int d^3r\,e^{-i\vec{q}\cdot\vec{r}}\overleftrightarrow{T}^{pp'}(\vec{r}) \tag{37}$$

and

$$S_4(\vec{k}_1,\ \vec{k}_2,\ \vec{k}_3,\ \omega)$$
$$=\frac{1}{N^3}\int_{-\infty}^{+\infty}dt\,e^{i\omega t}\langle\rho_{\vec{k}_1}(t)\rho_{\vec{k}_2}(t)\rho_{\vec{k}_3}\rho_{-(\vec{k}_1+\vec{k}_2+\vec{k}_3)}\rangle.$$

Equation (35) is the same as the expression obtained by other authors[13,14] for the scattering intensity. In these treatments $F(\vec{q})$ is replaced by

$$F'(\vec{q})=\alpha_0^2[\hat{\epsilon}_n\cdot\overleftrightarrow{G}_{dd}(\vec{q})\cdot\hat{\epsilon}_0], \tag{38}$$

where $\overleftrightarrow{G}_d(\vec{q})$ is the spatial Fourier transform of $[c(r)/r^3](3\hat{r}\hat{r}-\overleftrightarrow{1})$, where $c(r)$ is a short-distance cutoff function such as $\Theta(|r-a|)$ [cf. Eq. (2b)].

If we insert the following expression for T,

$$\overleftrightarrow{T}^{pp'}(\vec{r})=[c(r)/r^3](3\hat{r}\hat{r}-\overleftrightarrow{1}), \tag{38a}$$

in Eqs. (33), (36), and (37) we obtain

$$F(\vec{q})=\sum_{pp'}\alpha_p(\omega_0)\alpha_{p'}(\omega_0)\hat{\epsilon}_n\cdot\overleftrightarrow{G}_d(\vec{q})\cdot\hat{\epsilon}_0$$
$$=\alpha_0(\omega_0)^2\hat{\epsilon}_n\cdot\overleftrightarrow{G}_d(\vec{q})\cdot\hat{\epsilon}_0; \tag{39}$$

so (39) is the same as (38) with α_0 replaced by $\alpha_0(\omega_0)$. The appearance of the factor $\alpha_0^2(\omega_0)$ is due to the assumption in (38a) that $\overleftrightarrow{T}^{pp'}(\vec{r})$ is independent of p and p'. While this is certainly true for large distances, there is no reason for it to be so when r is small.

We now investigate the contribution $\overleftrightarrow{T}_s^{pp'}(\vec{q})$ to the form factor (36). The possibility of an s-like contribution to the scattering has been discussed on symmetry grounds by Iwamoto[19] and by Cowley and Woods.[13] To express our result in the language of reference 13 we write (taking $k_0\to 0$, $k\to 0$ and as-

suming that $E_p \gg E_0$)

$$H(\vec{q}_1, \vec{q}_2, \omega) = (N^3/2\pi) S_4(-\vec{q}_1, \vec{q}_1, \vec{q}_2, \omega), \tag{40}$$

$$f_{\alpha\beta}(\vec{q}) = \frac{1}{\alpha_0^2} \sum_{p,p'} \alpha_p(\omega_0)\alpha_{p'}(\omega_0)[\overleftrightarrow{T}^{pp'}(\vec{q})]^{\alpha\beta}, \tag{41}$$

and have

$$h_{\hat{\epsilon}_n}^{(1)}(\hat{R},\omega_n) = \frac{\rho^3}{N^2}\left(\frac{\omega_n}{c}\right)^4 \sum_{\alpha\beta\gamma\delta} I_{\alpha\beta\gamma\delta}\epsilon_0^\alpha \epsilon_n^\beta \epsilon_0^\gamma \epsilon_n^\delta, \tag{42}$$

where

$$I_{\alpha\beta\gamma\delta}(\omega) = \frac{\alpha_0^4}{N}\sum_{\vec{q},\vec{q}'} f_{\alpha\beta}(\vec{q}) f_{\gamma\delta}(\vec{q}\,')H(\vec{q}, \vec{q}\,', \omega), \quad \omega = \omega_n - \omega_0. \tag{43}$$

(43) is identical to (5.7) of Ref. 13. (41) gives an explicit expression for $f_{\alpha\beta}(\vec{q})$ within the model used here. Using the fact that the fluid is isotropic in the absence of an electromagnetic field one then has in general that[20]

$$I_{\alpha\beta\gamma\delta}(\omega) = \lambda\delta_{\alpha\beta}\delta_{\gamma\delta} + \mu(\delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma}), \tag{44}$$

which permits $h_{\hat{\epsilon}_n}^{(1)}(\omega_n)$ to be written as

$$h_{\hat{\epsilon}_n}^{(1)}(\omega_n) = (\rho^3/N^2)(\omega_n/c)^4 \times \{(\lambda + \tfrac{2}{3}\mu)(\hat{\epsilon}_0\cdot\hat{\epsilon}_n)^2 + \mu[1 + \tfrac{1}{3}(\hat{\epsilon}_0\cdot\hat{\epsilon}_n)^2]\}, \tag{45}$$

while using (43) and (44) gives

$$\begin{aligned} h_{\hat{\epsilon}_n}^{(1)}(\omega_n) &= \rho^3(\omega_n/c)^4(1/N^2) \times \{I_s(\omega)(\hat{\epsilon}_0\cdot\hat{\epsilon}_n)^2 + I_d(\omega)[1 + \tfrac{1}{3}(\hat{\epsilon}_0\cdot\hat{\epsilon}_n)^2]\} \\ &\equiv h_s^{(1)}(\omega)(\hat{\epsilon}_0\cdot\hat{\epsilon}_n)^2 + h_d^{(1)}(\omega)[1 + \tfrac{1}{3}(\hat{\epsilon}_0\cdot\hat{\epsilon}_n)^2], \end{aligned} \tag{46}$$

where

$$I_{s,d}(\omega) = \frac{\alpha_0^4}{N}\sum_{\vec{q},\vec{q}'} \mathfrak{F}_{s,d}(\vec{q})\mathfrak{F}_{s,d}(\vec{q}\,')H(\vec{q}, \vec{q}\,', \omega), \tag{47}$$

$$\mathfrak{F}_s(\vec{q}) \equiv \tfrac{1}{3}\,\mathrm{Tr}\,\overleftrightarrow{f}(\vec{q}), \tag{48}$$

$$\mathfrak{F}_d(\vec{q}) \equiv f_{xy}(\vec{q}). \tag{49}$$

Finally, (47) is expressed in terms of scalar functions characterizing the light-fluid coupling by writing

$$\overleftrightarrow{f}(\vec{q}) = f_s(q)\overleftrightarrow{1} + (3\hat{q}\hat{q} - \overleftrightarrow{1})f_d(q), \tag{50}$$

where

$$f_{s,d}(q) = \frac{1}{\alpha_0^2}\sum_{p,p'} \alpha_p(\omega_0)\alpha_{p'}(\omega_0) t_{s,d}^{pp'}(q), \tag{51}$$

$$\mathfrak{F}_s(\vec{q}) = f_s(q),$$

$$\mathfrak{F}_d(\vec{q}) = 3\frac{q_x q_y}{q^2} f_d(q),$$

and

$$\begin{aligned} t_s^{pp'}(q) &= 4\pi\int r^2 t_s^{pp'}(r) j_0(qr)\,dr, \\ t_d^{pp'}(q) &= 4\pi\int r^2 t_d^{pp'}(r) j_2(qr)\,dr. \end{aligned} \tag{52}$$

In Eqs. (52) $t_s(r)$, $t_d(r)$ are defined by Eq. (2).

Equation (47) then becomes

$$I_s = \frac{\alpha_0^4}{4\pi N}\sum_{\vec{q},\vec{q}'} f_s(q) f_s(q') H_s(q, q', \omega), \tag{53}$$

$$I_d = \frac{6}{5}\frac{\alpha_0^4}{4\pi N}\sum_{\vec{q},\vec{q}'} f_d(q) f_d(q') H_d(q, q', \omega), \tag{54}$$

in which $H_{s,d}(q, q', \omega)$ are defined through the relations

$$\begin{aligned} H(\vec{q}, \vec{q}\,', \omega) &= \sum_{\substack{l,m \\ l',m'}} Y_m^l(\hat{q}) Y_{m'}^{l'}(\hat{q}\,') H_{lm}^{l'm'}(q, q', \omega), \\ H_s(q, q', \omega) &= H_{0,0}^{0,0}(q, q', \omega), \\ H_d(q, q', \omega) &= -H_{2,2}^{2,2}(q, q', \omega) + 2H_{2,2}^{2,-2}(q, q', \omega) - H_{2,-2}^{2,-2}(q, q', \omega). \end{aligned} \tag{55}$$

V. INTEGRATED s-WAVE SCATTERING INTENSITY ESTIMATES FROM uv ABSORPTION

To illustrate the usefulness of the unified picture outlined here, we use the results of Secs. III and IV to establish a connection between the integrated s-wave scattering intensity and the shift and width of the uv absorption.

To obtain a prediction for the s-wave scattering intensity, we integrate the first of the Eqs. (53) on frequency to give for the s-wave part of the extinction coefficient:

$$\begin{aligned} g_s &= \int h_s^{(1)}(\hat{R}, \omega)\,d\omega \\ &= \frac{\rho}{4\pi N}\left(\frac{\omega_0}{c}\right)^4 \sum_{\substack{p,p' \\ p'',p'''}} \sum_{ijkl}{}' \alpha_p\alpha_{p''}\alpha_{p'}\alpha_{p'''} \\ &\quad \times \langle t_s^{pp''}(r_{ij}) t_s^{p'p'''}(r_{kl}) e^{i\vec{k}\cdot\vec{r}_{ik}} e^{-i\vec{k}_0\cdot\vec{r}_{jl}}\rangle, \end{aligned} \tag{56}$$

where by (2)

$$t_s^{pp''}(r) = \tfrac{1}{3}\,\mathrm{Tr}\,\overleftrightarrow{T}^{pp''}(\vec{r})$$

and

$$\alpha_p = 2\frac{|X_p|^2}{E_p}\frac{E_p^2}{E_p^2 - E_0^2}. \tag{57}$$

[The general form for the integrated intensity may also be obtained by integrating (35) with respect to ω_n or summing the square of (A14) over intermediate states.]

$t_s^p(r)$ has the dimensions of density (inverse volume) and α_p has the dimensions of polarizability (length cubed). The prime on the sum on sites means that we take only $i \neq j$ and $k \neq l$. We now argue that we can limit the sums on p, p', p'', p''' to the first excited p state, as long as the integral on the left-hand side of (56) is cut off for frequencies smaller than those of experimental interest in Raman scattering. To make this argument we return to the Fourier-transformed form of (56) [Eqs. (46), (51), and (53)] which is (omitting factors de-

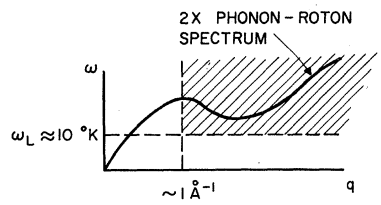

FIG. 1. Sketch of twice phonon-roton spectrum illustrating the argument for limiting sums in Eq. (58) to the term with $p=p'=p''=p'''=1$. The shaded area indicates the region of the $\omega-q$ plane in which both the factors involving t_s and the factors involving H are expected to be substantial.

pending on $\vec{k}$, $\vec{k}_0$)

$$\int h_s^{(1)}(\omega)\,d\omega=\rho\left(\frac{\omega_0}{c}\right)^4\frac{1}{4\pi N}\sum_{\substack{p,p'\\p'',p'''}}\alpha_p\alpha_{p''}\alpha_{p'}\alpha_{p'''}\times\sum_{\vec{q},\vec{q}'}t_s^{pp''}(q)t_s^{p'p'''}(q')\int H_s(q,\,q',\,\omega)\,d\omega\,. \qquad (58)$$

Now the existing approximations for $H(\vec{q},\vec{q}\,',\omega)$ indicate that the dominant contributions for $\hbar\omega/k_B \gtrsim 10\,^\circ\mathrm{K}$ come from values of q and q' which are greater than or of the order of 1 Å^{-1}. On the other hand, $t_s^{pp'}(r)$ is expected to be of range $R^s_{pp'}$ which increases with p and p'. Thus $t_s^{pp'}(q)$ can be expected to have substantial weight for $q>1$ Å^{-1} only when $R^s_{p,p'}\lesssim 1$ Å (Fig. 1). A rough measure for $R^s_{p,p'}$ is the sum of the radii of the ground state and excited electronic state p or p'. For the first ($n=2$) singly excited state this sum is already about 2.3 Å and will increase roughly as n^2 for the higher states. The other excited states are also large. Hence we assume in the rest of this section that the sums on p, p', p'', p''' in (56) can be truncated at the first term. With this assumption (56) becomes

$$\mathcal{S}_s=\frac{\rho\alpha_1^4}{4\pi N}\left(\frac{\omega_0}{c}\right)^4\sum_{ijkl}{}'\langle t_s^{11}(r_{ij})t_s^{11}(r_{kl})e^{i(\vec{k}\cdot\vec{r}_{ik}-\vec{k}_0\cdot\vec{r}_{jl})}\rangle\,, \qquad (59)$$

where α_1 is that part of the polarizability arising from the first p state. Note that this argument limiting the sums to the first p state cannot be made for the d part of the scattering because $t_d^{pp'}(r)$ has a long-range part (2a) which is important for $g>1$ Å^{-1} and is not state dependent.

In the same notation, the s-wave contribution to the second moment of the uv absorption line around the excited state $2\,^1P_1$ is [using Ref. 2—this is equivalent to equation (14) of the present paper]

$$(M_2^p)_{ss}=\tfrac{1}{4}\alpha_p^2E_p^2\left[\frac{1}{N}\sum_{ijk}{}'\langle t_s^{pp}(r_{ij})t_s^{pp}(r_{jk})\rangle-\left(\frac{1}{N}\sum_{ij}{}'\langle t_s^{pp}(r_{ij})\rangle\right)^2\right], \qquad (60)$$

where we have neglected the frequency dependence of the α_p and the prime on the first term means that $i\neq j$ and $j\neq k$ (though i can be equal to k). The s-wave part of the first moment of the uv absorption line in this notation is

$$(M_1^p)_s=\frac{\alpha_pE_p}{2N}\sum_{ij}{}'\langle t_s^{pp}(r_{ij})\rangle\,, \qquad (61)$$

so (60) can be written (specializing to $p=1$) as

$$(M_2^1)_{ss}+[(M_1^1)_s]^2=\frac{(\alpha_1E_1)^2}{4N}\sum_{ijk}{}'\langle t_s^{11}(r_{ij})t_s^{11}(r_{jk})\rangle\,. \qquad (62)$$

Comparing (62) with (59) one sees that the s-like Raman scattering intensity involves the sum

$$S_R=\frac{1}{N}\sum_{ijkl}{}'\langle t_s^{11}(r_{ij})t_s^{11}(r_{kl})e^{i(\vec{k}-\vec{k}_0)\cdot\vec{r}_{ik}}\rangle\,, \qquad (63)$$

while the moments of the absorption line involve the sum

$$S_A=\frac{1}{N}\sum_{ijk}\langle t_s^{11}(r_{ij})t_s^{11}(r_{jk})\rangle\,. \qquad (64)$$

The exponential factors have been dropped in (60)–(62) and (64) since the range of t_s^{11} is much less than $2\pi/k_0$ or $2\pi/k$. In (63) they need only be retained in the terms for which all four indices are distinct. To compare these two sums we write them in terms of the static correlation functions defined in Eq. (13).

$$S_R=2S_2+4S_3+S_4\,, \qquad (65a)$$

$$S_A=S_2+S_3\,, \qquad (65b)$$

in which

$$S_2=\rho\int g_2(r_{12})[t_s^{11}(r_{12})]^2\,d^3r_{12}\,,\quad g_2(r)=g(r)\,, \qquad (66a)$$

$$S_3=(\rho^3/N)\int g_3(\vec{r}_1,\,\vec{r}_2,\,\vec{r}_3)t_s^{11}(r_{12})t_s^{11}(r_{23})\,d^3r_1\,d^3r_2\,d^3r_3\,, \qquad (66b)$$

$$S_4=(\rho^4/N)\int g_4(\vec{r}_1,\,\vec{r}_2,\,\vec{r}_3,\,\vec{r}_4)t_s^{11}(r_{12})t_s^{11}(r_{34})e^{i(\vec{k}-\vec{k}_0)\cdot\vec{r}_{13}}\,d^3r_1\,d^3r_2\,d^3r_3\,d^3r_4\,. \qquad (66c)$$

Combining (65a) and (65b)

$$S_R=2S_A+2S_3+S_4\,. \qquad (67)$$

Equation (62) will be used to get a number for S_A from the data on ultraviolet absorption. No such strategem is available for S_4 which we estimate in the following way:

$$S_4=(\rho^4/N)\Big[\int[g_4(1,2,3,4)-f(R)g_2(1,2)g_2(3,4)]e^{i(\vec{k}-\vec{k}_0)\cdot\vec{R}}t_s^{11}(12)t_s^{11}(34)\,d(1)\,d(2)\,d(3)\,d(4)$$
$$+\int g_2(12)g_2(34)f(R)e^{i(\vec{k}-\vec{k}_0)\cdot\vec{R}}t_s^{11}(12)t_s^{11}(34)\,d(1)\,d(2)\,d(3)\,d(4)\Big]. \tag{68a}$$

Here we may take $\vec{R}=\frac{1}{2}(\vec{r}_1+\vec{r}_2)-\frac{1}{2}(\vec{r}_3+\vec{r}_4)$, because $t_s^{11}(r)$ is of short range and $f(R)$ is an arbitrary function to be chosen so that the first term in (68a) is small. In Appendix C we argue that this can be accomplished if $f(R)$ is taken to be a step function that is 0 for $R\le R_1$ and 1 for $R>R_1$, where $R_1\ge 3.17$ Å. Our estimate for S_4 is then

$$S_4\cong\rho^3\int g_2(12)g_2(34)[f(R)-1]\,t_s^{11}(12)t_s^{11}(34)\,d^3r_{12}\,d^3r_{34}\,d^3R$$
$$-\rho^3\int e^{i(\vec{k}-\vec{k}_0)\cdot\vec{R}}\,d^3R\int g_2(12)g_2(34)t_s^{11}(12)t_s^{11}(34)\,d^3r_{12}\,d^3r_{34},$$
$$=-\rho\frac{4\pi R_1^3}{3}\Big[\rho\int g_2(r)t_s^{11}(r)\,d^3r\Big]^2, \tag{68b}$$

because $\vec{k}\ne\vec{k}_0$.

Thus (67) becomes

$$S_R\cong 2S_A+2S_3-\rho\Big(\frac{4\pi R_1^3}{3}\Big)\Big[\rho\int g_2(r)t_s^{11}(r)\,d^3r\Big]^2. \tag{69}$$

To estimate S_R from (69) we must have information about S_3. To get this we use the Kirkwood superposition approximation $g_3(123)=g_2(12)g_2(23)g_2(31)$ in (66b). Owing to the short range of the function $t_s^{11}(r)$ and the rapid fall off of $g(r)$ at small r, the range of values of r_{12} and r_{23} that contribute to (66b) are limited between about 2 and 2.5 Å (cf. Appendix C). Let θ be the angle between $\vec{r}_{12}$ and $\vec{r}_{23}$. For $\theta\gtrsim\frac{1}{2}\pi$ it follows that 2.8 Å $\lesssim r_{13}\lesssim$ 5 Å. For this range of values, $g_2(13)$ is about equal to 1 or larger and does not vary rapidly. As θ decreases, the factor $g_2(13)$ will rapidly become much smaller in the effective region of integration owing to the decrease to zero at small r_{13}. Hence the contribution to S_3 for $\theta<\frac{1}{2}\pi$ will be considerably smaller than for $\theta\ge\frac{1}{2}\pi$. It may even be negative if $t_s^{11}(r)$ changes sign but the magnitude must be less. Thus to estimate S_3 we replace $g_2(13)$ by a constant and use (6b) getting

$$S_3\doteq K[(M_1^1)_s]^2/|X_1|^4,\quad K\cong\tfrac{1}{2}. \tag{69a}$$

By use of equations (59), (61)–(64), and (69a), we may now obtain an estimate for the s-wave scattering intensity from (69) in terms of known quantities:

$$\mathcal{I}_s\cong\frac{\rho\alpha_1^2}{\pi E_1^2}\Big(\frac{\omega_0}{c}\Big)^4\{2(M_2^1)_s+(2+2K-\rho\overline{V}_1)[(M_1^1)_s]^2\}, \tag{70}$$

where from Appendix C

$$\overline{V}_1=\tfrac{4}{3}\pi R_1^3,\quad R_1\cong 3.17\text{ Å}.$$

Here we have used the fact that $(M_2^1)_{sd}=0$ which is proved in Appendix D. The right-hand side of (70) is expressed entirely in terms of known quantities:

$$0.0514\lesssim(M_2^1)_{ss}\lesssim 0.134\text{ eV}^2,$$

from equations (13), (18), (19) using $2\le(\chi^1)^2\le 20$ and $(M_1^1)_s=0.278$ eV [Eq. (10)], $E_1=21.4$, $\rho=0.0218$ Å^{-3}, $\frac{1}{2}\le K\le 1$, $\alpha_1=6.68\times10^{-2}$ Å^3 (from oscillator strength 0.28), $2\pi c/\omega_0=5145$ Å (for Greytak experiments). We find

$$0.164\times10^{-11}\lesssim\mathcal{I}_s\lesssim 0.534\times10^{-11}\text{ cm}^{-1}. \tag{71}$$

If we compare this to the experiments, we need to know an absolute value for the experimental extinction coefficient. There is some dispute about the right value for this. We use Baeriswyl's value[14] of

$$\int h^{(1)}(\omega)\,d\omega=1.3\pm0.4\times10^{-11}\text{ cm}^{-1}, \tag{72}$$

where $h^{(1)}(\omega)$ is $h_{\hat{\epsilon}_n}^{(1)}(\omega_n)$ summed over $\hat{\epsilon}_n$. This is related to the d-state scattering by

$$\mathcal{I}_d=\int h_d^{(1)}(\omega)\,d\omega=\frac{3}{7}\int h^{(1)}(\omega)\,d\omega-\tfrac{3}{7}\mathcal{I}_s. \tag{73}$$

Equations (71)–(73) give

$$0.25\lesssim\mathcal{I}_s/\mathcal{I}_d\lesssim 3.4. \tag{74}$$

A precise measurement of the polarization dependence of the Raman scattering is available only for a region of ω about 5 °K wide at twice the roton frequency.[15] Over this restricted frequency range one finds that

$$\frac{\int_{\text{two-roton}}h_s^{(1)}(\omega)\,d\omega}{\int_{\text{two-roton}}h_d^{(1)}(\omega)\,d\omega}=0.03\pm0.04. \tag{75}$$

(The two-roton peak accounts for about $\frac{1}{3}$ of the observed integrated scattering intensity.) Since (75) is considerably less than the prediction of $\mathcal{I}_s/\mathcal{I}_d$ in (74), we conclude that the s scattering must be considerably larger at higher ω than in the two-roton region. This is reasonable since the short range

of $t_s^{11}(r)$ means that the associated $f_s(q)$ [cf. Eq. (51)] may be large at high q and hence make $I_s(\omega)$ [Eq. (47)] relatively large at high ω. An experimental test of this possibility would be of great interest.

We now consider the reasons for the uncertainty in (74) within the context of our model for the s scattering. (Discussion of the assumptions of the model itself is contained in Sec. VI.) The most important of these is the connection between $(M_1^1)_s$, $(M_2^1)_s$ and the uv experiments.[3] Since a full analysis computing the absorption line from the reflectance data has yet to be performed, the shift and width values for the absorption used above are only approximate and the adjustable factor χ^1 relating the width to the second moment had to be introduced. Some further uncertainty is introduced by the experimental error in g_d; the fact that α_1 in the liquid is not known precisely (analysis of the uv data should resolve this); and the assumptions made in estimating $(M_2^1)_{dd}$, S_3, and S_4. The contribution of $(M_2^1)_{dd}$ to (74) is quite small so the error in it should be unimportant. More careful estimates of S_3 and S_4 can be made once the uncertainties in the experimental data have been resolved.

VI. DISCUSSION

The most serious approximation we have made is the assumption that the sums on p in the s-wave scattering can be limited to $p=1$. We believe that our argument for this approximation is a good one but it is difficult to make it quantitative.

It would be particularly desirable to discover the spectral shape of the s-wave scattering to aid experimentalists in looking for it. This would be possible from Eqs. (46), (47), and (52) if a form for $t_s^{pp'}(r)$ were known. Unfortunately $t_s^{pp'}(r)$ is precisely what we don't know. One could look at models of $t_s^{pp'}(r)$ but the results are not likely to be meaningful until a completely convincing calculation of the detailed structure of $H(\vec{q}, \vec{q}\,', \omega)$ is available. We emphasize that our order of magnitude estimate of the s-state scattering intensity can be improved by more detailed analysis of the uv experiments. Nevertheless, a more detailed experimental study of the polarization of the Raman scattering at high frequencies is warranted by this study.

Another interesting feature which can be further pursued is that the line shape of the d-wave Raman scattering (unlike the uv shifts) depends in a detailed way on the *short*-range behavior of $t_d^{pp'}(r)$ which is approximated in the existing models by a θ function or other ansatz. It will be interesting to see what the experiments tell us about this, once a reliable calculation of $H(\vec{q}, \vec{q}\,', \omega)$ has been performed. In any case, the possibility that $t_d^{pp'}(r)$ has peculiar short-range behavior should be borne in mind in discussing the experimental light-scattering evidence concerning the right form of $H(\vec{q}, \vec{q}\,', \omega)$.

We note that we qualitatively predict a substantial s-wave scattering matrix element owing to electronic states with $p>1$ when Raman scattering energy transfer is below about 10 °K. It would be interesting to see if this is borne out experimentally, though the density of states [or $H(\vec{q}, \vec{q}\,', \omega)$] is small in this frequency region.

In deriving our general expression for the Raman scattering (including d scattering), we have assumed that the excited electronic p states can be associated with a single (central) atomic site. This is certainly reasonable for the first ($n=2$) excited p state, since its radius is less than the average interatomic spacing. One must consider all the higher p states as well, however. In fact only about one-fourth of the polarizability α_0 is due to the singly excited states, the continuum states giving the largest contribution.[21] Since most of these are quite large (the $n=4$ singly excited state will already have a radius of about 8 Å), they will feel the effects of an average over many atoms. The dielectric constant of helium is very close to 1, so these states can be expected to be very similar to the corresponding free atom states. This argument is bolstered by the fact that α_0 for the low-density gas is only about 3% larger than for He II.[21] By the same reasoning, one expects that the "hopping" function $\overleftrightarrow{T}$ should depend on two atomic sites only, as we have assumed. These arguments about the excited states and $\overleftrightarrow{T}$ are probably weakest for the smaller singly excited states (especially the $n=3$ state), as is also indicated by the absence of a peak corresponding to a $3\,^1P_1$ final state in uv absorption.[3] Finally, we note that the theory can be applied to light scattering and light absorption in other rare-gas liquids.

ACKNOWLEDGMENTS

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APPENDIX A: DERIVATION OF RAMAN SCATTERING RATES USING PERTURBATION THEORY AND QUANTIZED ELECTROMAGNETIC FIELD

In this appendix we obtain an expression for the Raman scattering rate and extinction coefficient in a fully quantum-mechanical treatment.

We are dealing with third-order processes like the one illustrated in Fig. 2. (1) The incoming photon excites a p state (p) on site i. (2) A second excited p state (p') is created at j while the one at i is destroyed through the hopping term. (3) The p state at j decays to the ground state with emission of the outgoing photon. We refer to the excited electronic p states as "excitons" below, since they

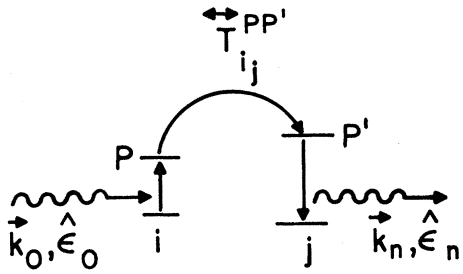

FIG. 2. Typical third-order scattering process calculated in Appendix A. The incoming photon $\vec{k}_0\,\hat{\epsilon}_0$ excites a virtual state p at site i which is transferred by the hopping term t to a virtual state p' at site j that emits the outgoing photon $\vec{k}_n\,\hat{\epsilon}_n$.

are similar to Frenkel excitons in solids. The amplitude for scattering by these processes is calculated in third-order perturbation theory and its square is taken to find the scattering rate. Several terms arise in calculating the amplitude since we must consider all possible orders in which the photons and excitons may be created or destroyed. Our treatment is similar to the calculation of Nakajima,[11] the main difference being that we allow the possibility of more than one excited p state and do not restrict the form of the hopping term.

The Hamiltonian [see Eq. (1)] is the sum of $\mathcal{H}_1$ and a perturbing term $\mathcal{H}'$ describing the coupling to radiation and the exciton "hopping"

$$\begin{aligned}
&\mathcal{H}=\mathcal{H}_1+\mathcal{H}',\\
&\mathcal{H}_1=\sum_{ip}E_p\vec{c}^{\,\dagger}_{ip}\cdot\vec{c}_{ip}+\mathcal{H}_0,\\
&\mathcal{H}'=\mathcal{H}'_{\rm ph}+\mathcal{H}'_{\rm ex},\\
&\mathcal{H}'_{\rm ph}=\sum_{k,\lambda,n}\frac{e_n}{m_n}\left(\frac{2\pi\hbar}{kVc}\right)^{1/2}(a_{\vec{k}\lambda}\vec{p}_n\cdot\hat{\epsilon}_\lambda e^{i\vec{k}\cdot\vec{r}_n}+\text{H. c.}),\\
&\mathcal{H}'_{\rm ex}=-\frac{1}{2}\sum_{\substack{ij\\pp'}}\vec{d}_{ip}\cdot\overleftrightarrow{T}^{pp'}_{ij}\vec{d}_{jp'},
\end{aligned}\tag{A1}$$

where $\vec{p}_n$, e_n, and m_n are, respectively, the momentum, charge, and mass of the nth particle (helium nucleus or electron) in the system. $a_{\vec{k}\lambda}$ is a photon annihilation operator, $\vec{k}$ is the photon wave vector, λ is a polarization index, and V is the normalization volume. $\mathcal{H}_0$ is the Hamiltonian of the liquid with no excitons present (the "ordinary" liquid). We express $\mathcal{H}'_{\rm ph}$ terms of the $\vec{c}_{ip}$ by use of the dipole approximation

$$\mathcal{H}'_{\rm ph}=\sum_{\vec{k},\lambda}\left(\frac{2\pi\hbar}{kVc}\right)^{1/2}\left(\sum_{i\beta}-e\dot{\vec{r}}_{i\beta}e^{i\vec{k}\cdot\vec{R}_i}\cdot\hat{\epsilon}_\lambda a_{\vec{k}\lambda}+\text{H. c.}\right),\tag{A2}$$

where $\vec{r}_{i\beta}$ is the coordinate of the βth electron associated with the nucleus located at $\vec{R}_i$. In the dipole approximation we have

$$\sum_\beta -e\vec{r}_{i\beta}=\vec{d}_i=\sum_p\vec{d}_{ip},\tag{A3}$$

where

$$\vec{d}_{ip}=X_p^*\vec{c}^{\,\dagger}_{ip}+X_p\vec{c}_{ip}.\tag{A4}$$

X_p is the matrix element of the dipole operator between the ground and excited state p. The time derivative of $\vec{d}_{ip}$ is then

$$\begin{aligned}\dot{\vec{d}}_{ip}&=(i/\hbar)[\vec{d}_{ip},\mathcal{H}]\\&\cong-(i/\hbar)E_p(X_p\vec{c}_{ip}-X_p^*\vec{c}^{\,\dagger}_{ip}).\end{aligned}\tag{A5}$$

We now do time-dependent perturbation theory on the system $\mathcal{H}_1+\mathcal{H}'$ with $\mathcal{H}'$ as a perturbation to find the transition rate from an initial state (of the total unperturbed system) $|0_T\rangle$ with no excitons and n_0 photons of wave vector $\vec{k}_0$ and polarization $\hat{\epsilon}_0$ to a final state $|n_T\rangle$ with no excitons and n_0-1 photons $\vec{k}_0$, $\hat{\epsilon}_0$ and one photon $\vec{k}_n$, $\hat{\epsilon}_n$. The states $|m_T\rangle$ are taken to be products of eigenstates $|m\rangle$ of $\mathcal{H}_0$ and unperturbed exciton states and free photon states, consistent with the Born-Oppenheimer approximation. In the same spirit we neglect $\mathcal{H}_0$ in computing $\dot{\vec{d}}$ in (A5) since the $\vec{R}_i$ may be considered stationary during the scattering process (the times associated with thermal motions are very long compared to $\hbar/E_p$ or $\hbar/T$).

In computing the amplitude for the transition from $|0_T\rangle$ to $|n_T\rangle$, we must keep only those terms linear in T, since Raman scattering corresponds to a single exciton "hop." Thus a second-order perturbation term like $\mathcal{H}'_{\rm ph}\mathcal{H}'_{\rm ph}$ cannot contribute since it is independent of T. The photon-matter coupling term proportional to $\vec{A}^2$ (which we have not explicitly included in $\mathcal{H}'_{\rm ph}$) does not contribute for the same reason although it must be kept to get the complete Brillouin amplitude.[11]

Thus we must compute all third-order terms of the type $\mathcal{H}'_{\rm ph}\mathcal{H}'_{\rm ph}\mathcal{H}'_{\rm ex}$. Since we consider the case of low incoming light intensity only, we may neglect terms of higher order in $\mathcal{H}'_{\rm ph}$. This corresponds to keeping only the lowest-order terms in an expansion in powers of $\rho\alpha_0$. In calculating these terms we may replace $\mathcal{H}'_{\rm ph}$ by

$$\mathcal{H}'_d=-i\left(\frac{2\pi n_0}{k_0V\hbar c}\right)^{1/2}\sum_{ip}E_p(X_p\vec{c}_{ip}-X_p^*\vec{c}^{\,\dagger}_{ip})\cdot\hat{\epsilon}_0a_{\vec{k}_0}e^{i\vec{k}_0\cdot\vec{R}_i},\tag{A6}$$

or

$$\mathcal{H}'_c = -i\left(\frac{2\pi}{k_n V\hbar c}\right)^{1/2} \sum_{ip} E_p(X_p \vec{c}_{ip} - X_p^* \vec{c}^{\,\dagger}_{ip}) \cdot \hat{\epsilon}_n a^\dagger_{\vec{k}_n} e^{-i\vec{k}_n\cdot\vec{R}_i}, \tag{A7}$$

depending on whether a photon is destroyed or created. We have for the transition rate in general

$$\Gamma_{0,n} = \frac{2\pi}{\hbar} \sum_{m_1, m_2} \left| \frac{\langle n_T|\mathcal{H}'|m_{2T}\rangle\langle m_{2T}|\mathcal{H}'|m_{1T}\rangle\langle m_{1T}|\mathcal{H}'|0_T\rangle}{(\epsilon_{m_2} - \epsilon_0 + i\eta)(\epsilon_{m_1} - \epsilon_0 + i\eta)} \right|^2 \delta(\epsilon_0 - \epsilon_n), \tag{A8}$$

where ϵ_0, ϵ_{m_1}, ϵ_{m_2} are energies of the total unperturbed system (eigenvalue of $\mathcal{H}_1$ plus photon energies). Note that the full expression for the scattering rate is actually the square of an amplitude which is the sum of a Brillouin term (independent of T) and a Raman term. However Baeriswyl has shown[14] that the cross term gives a negligible contribution at Raman energy transfers. Now define the transition amplitude

$$\begin{aligned}\lambda_{0,n} &= \frac{\langle n_T|\mathcal{H}'|m_{2T}\rangle\langle m_{2T}|\mathcal{H}'|m_{1T}\rangle\langle m_{1T}|\mathcal{H}'|0_T\rangle}{(\epsilon_{m_i} - \epsilon_0 + i\eta)(\epsilon_{m_1} - \epsilon_0 + i\eta)} \\ &\equiv -\frac{1}{2\hbar c}\frac{2\pi}{V}\left(\frac{n_0}{k_0 k_n}\right)^{1/2} \gamma_{0,n}\end{aligned} \tag{A9}$$

There are six terms contributing to $\gamma_{0,n}$ corresponding to the permutations of $\mathcal{H}'_d$, $\mathcal{H}'_c$, $\mathcal{H}'_{ex}$. The term d-c-ex is

$$\gamma^{(1)}_{0,n} = -\frac{1}{2}\sum_{ij} \langle n|e^{i(\vec{k}_0\cdot\vec{R}_i - \vec{k}_n\cdot R_j)}\hat{\epsilon}_0 \cdot \overleftrightarrow{T}^{pp'}_{ij} \cdot \hat{\epsilon}_n|0\rangle \alpha_p\alpha_{p'} \frac{(E_p E_{p'})^2}{(E_p + E_{p'})(E_p + E_0)}. \tag{A10}$$

In (A10) the states $|n\rangle$ and $|0\rangle$ are eigenstates of the "ordinary" liquid Hamiltonian $\mathcal{H}_0$—the photon and exciton coordinates have been integrated out. The polarization due to the state p is

$$\alpha_p(\omega_0) = 2\frac{|X_p|^2}{E_p}\frac{\omega_p^2}{\omega_p^2 - \omega_0^2} \equiv \alpha_p \frac{\omega_p^2}{\omega_p^2 - \omega_0^2}; \quad E_p = \hbar\omega_p, \quad E_0 = \hbar\omega_0 \tag{A11}$$

and we have used $\hat{\epsilon}_n \cdot \overleftrightarrow{T}^{p'p}_{ji} \cdot \hat{\epsilon}_0 = \hat{\epsilon}_0 \cdot \overleftrightarrow{T}^{pp'}_{ij} \cdot \hat{\epsilon}_n$ which follows by time reversal invariance. Since none of the energy denominators are small, we have neglected contributions of the change in the eigenvalue of $\mathcal{H}_0$ to them. Further we have replaced the final photon energy E_n by the initial photon energy E_0 since their difference is of the order of thermal energies. Adding the terms arising from c-d-ex, ex-d-c, and ex-c-d to $\gamma^{(1)}_{0,n}$ gives

$$\gamma^{(a)}_{0,n} = -\frac{1}{2}\sum_{\substack{ij\\pp'}} \langle n|e^{i(\vec{k}_0\cdot\vec{R}_i - \vec{k}_n\cdot\vec{R}_j)}\hat{\epsilon}_0 \cdot \overleftrightarrow{T}^{pp'}_{ij} \cdot \hat{\epsilon}_n|0\rangle \alpha_p\alpha_{p'} \frac{(E_p E_{p'})^2}{E_p + E_{p'}}\left(2\frac{E_p}{E_p^2 - E_0^2} + 2\frac{E_{p'}}{E_{p'}^2 - E_0^2}\right). \tag{A12}$$

The only terms remaining are d-ex-c and c-ex-d. They tend to cancel $\gamma^{(a)}_{0,n}$ since, in the former for instance, $\mathcal{H}'_c$ creates an exciton while $\mathcal{H}'_d$ destroys one which brings in an extra minus sign. Furthermore, the part of $\mathcal{H}'_{ex}$ that contributes is

$$\sum_{\substack{ij\\pp'}} \vec{c}_{ip} \cdot \overleftrightarrow{T}^{pp'}_{ij} \cdot \vec{c}^{\,\dagger}_{jp'} + \sum \vec{c}^{\,\dagger}_{ip} \cdot \overleftrightarrow{T}^{pp'}_{ij} \cdot \vec{c}_{jp'} = 2\sum \vec{c}^{\,\dagger}_{jp} \cdot \overleftrightarrow{T}^{pp'}_{ij} \cdot \vec{c}_{jp'},$$

so an extra factor of 2 arises. Evaluating these terms gives

$$\gamma^{(b)}_{0,n} = +\frac{1}{2}\sum_{\substack{ij\\pp'}} \langle n|e^{i(\vec{k}_0\cdot\vec{R}_i - \vec{k}_n\cdot\vec{R}_j)}\hat{\epsilon}_0 \cdot \overleftrightarrow{T}^{pp'}_{ij} \cdot \hat{\epsilon}_n|0\rangle \alpha_p\alpha_{p'}(E_p E_{p'})^2\left(\frac{1}{(E_p + E_0)(E'_p + E_0)} + \frac{1}{(E_p - E_0)(E_{p'} - E_0)}\right). \tag{A13}$$

Combining (A9), (A12), and (A13) then gives

$$\lambda_{0,n} = -\frac{E_0^2}{\hbar c}\frac{2\pi}{V}\left(\frac{n_0}{k_0 k_f}\right)^{1/2} \sum_{\substack{ij\\pp'}} \alpha_p(\omega_0)\alpha_{p'}(\omega_0)\langle n|e^{i(\vec{k}_0\cdot\vec{R}_i - \vec{k}_n\cdot\vec{R}_j)}\hat{\epsilon}_0 \cdot \overleftrightarrow{T}^{pp'}_{ij} \cdot \hat{\epsilon}_n|0\rangle, \tag{A14}$$

where the frequency-dependent polarizability of each p state appears

$$\begin{aligned}\alpha_p(\omega_0) &= \alpha_p \frac{\omega_p^2}{\omega_p^2 - \omega_0^2} \\ &= 2\frac{|X_p|^2}{E_p}\frac{E_p^2}{E_p^2 - E_0^2}.\end{aligned} \tag{A15}$$

Note that if T is independent of p and p' and we set $\alpha_p(\omega_0) = \alpha_p$ then $\lambda_{0,n}$ is proportional to α_0^2 as in phenomenological treatments of Raman scattering. (A14) is to be compared with Eq. (32), the expression for the polarization operator found in the text.

Note that the photon and exciton coordinates have been summed out of (A14). Hence the scattering

rate may be computed using the method applied by van Hove to thermal neutron scattering, and the result will contain a time-displaced correlation function referring to the liquid in thermal equilibrium. The final result is more complicated than the corresponding formula for neutron scattering for two reasons. First, the amplitude $\lambda_{0,n}$ refers to two liquid sites so four density operators appear in the dynamic correlation function. Second, this function is integrated with two hopping functions $\overleftrightarrow{T}_{ij}^{pp'}$ which (aside from constants and polarization factors) account for the light-helium coupling.

Now the scattering rate of energy transfer $\hbar\omega$ is

$$R(\omega)=\sum_n \frac{2\pi}{\hbar}|\lambda_{0,n}|^2\delta(\hbar\omega-e_n+e_0), \tag{A16}$$

where e_n and e_0 are the eigenvalues of $\mathcal{H}_0$. Since $\lambda_{0,n}$ can be considered the matrix element $\langle n|A|0\rangle$ of some operator A, we have

$$R(\omega)=\frac{1}{\hbar^2}\int e^{i\omega t}\langle 0|A^*(t)A(0)|0\rangle\, dt, \tag{A17}$$

where $A(t)$ propagates according to $\mathcal{H}_0$. Combining (A14) and (A17) gives

$$R(\omega)=\left(\frac{2\pi}{V}\right)^2 n_0\omega_0^2\sum_{\substack{ij\\lm}}\int\langle F(\vec{R}_{ij}(t))F(\vec{R}_{lm}(0))\, e^{-i[\vec{k}_0\cdot\vec{R}_i(t)-\vec{k}_n\cdot\vec{R}_j(t)]}e^{i[\vec{k}_0\cdot\vec{R}_l(0)-\vec{k}_n\cdot\vec{R}_m(0)]}\rangle e^{i\omega t}\, dt, \tag{A18}$$

where consistent with Eq. (36)

$$F(\vec{R}_{ij})\equiv\sum_{pp'}\alpha_p(\omega_0)\alpha_{p'}(\omega_0)\hat{\epsilon}_0\cdot\overleftrightarrow{T}_{ij}^{pp'}\cdot\hat{\epsilon}_n,$$

ω_0 is the frequency of the incident photons, and we have summed (A17) over a thermal ensemble of initial states. Now (A18) may be written

$$R(\omega)=\left(\frac{2\pi}{V}\right)^2 n_0\omega_0^2 N\rho^2\sum_{qq'}F(\vec{q})F(\vec{q}\,')\times S_4(\vec{q}-\vec{k}_n,\ \vec{k}_0-\vec{q},\ \vec{k}_n-\vec{q}\,',\ \omega), \tag{A19}$$

where Ω is the volume of the liquid and

$$F(\vec{q})=\int e^{-i\vec{q}\cdot\vec{r}}F(\vec{r})\, d^3r,$$

$$S_4(\vec{k}_1,\ \vec{k}_2,\ \vec{k}_3,\ \omega)=\frac{1}{N^3}\int e^{i\omega t}\langle\rho_{\vec{k}_1}(t)\rho_{\vec{k}_2}(t)\rho_{\vec{k}_3}\rho_{-(\vec{k}_1+\vec{k}_2+\vec{k}_3)}\rangle\, dt, \tag{A20}$$

$$\rho_{\vec{k}}=\sum_i e^{i\vec{k}\cdot\vec{R}_i}.$$

[See Eqs. (36) and (37).]

Now we calculate the Raman scattering extinction coefficient defined (cf. Sec. IV) by

$$h_{\hat{\epsilon}_n}(\hat{R},\ \omega_n)=I_{\hat{\epsilon}_n}(\hat{R},\ \omega_n)/I_0, \tag{A21}$$

where $I_{\hat{\epsilon}_n}(\hat{R},\ \omega_n)$ is the light scattering intensity per unit volume of sample, per unit solid angle per unit of light frequency emitted in the direction $\hat{R}$ at frequency ω_n and with polarization $\hat{\epsilon}_n$. I_0 is the incident light intensity. Since there are n_0 incident photons of frequency ω_0 in a normalization volume V we have

$$I_0=n_0\hbar\omega_0(c/V). \tag{A22}$$

On the other hand, after a time τ the energy of emitted photons in state $\vec{k}_n$, $\hat{\epsilon}_n$ is

$$R(\omega)\hbar\omega_n\tau[V/(2\pi)^3]d^3k_n=R(\omega)\hbar\omega_n\tau[V/(2\pi)^3]d^2\Omega_{\vec{k}_n}k_n^2(d\omega_n/c), \tag{A23}$$

where we have multiplied by the number of photon states in d^3k_n. Dividing by the sample volume and time, solid angle, and frequency intervals gives

$$I_{\hat{\epsilon}_n}(\hat{R},\ \omega_n)=\frac{1}{\Omega}\frac{V}{(2\pi)^3}\hbar\left(\frac{\omega_n}{c}\right)^3 R(\omega)$$

and so

$$h_{\hat{\epsilon}_n}(\hat{R},\ \omega_n)=\frac{\omega_0^2}{c^4}\frac{1}{\Omega}\frac{V^2}{(2\pi)^3}\frac{1}{n_0}R(\omega), \tag{A24}$$

where we have neglected the difference between ω_0 and ω_n. Combining (A19) and (A24) we have

$$h_{\hat{\epsilon}_n}(\hat{R},\ \omega_n)=\frac{1}{2\pi}\left(\frac{\omega_0}{c}\right)^4\rho^3\sum_{q,q'}F(\vec{q})F(\vec{q}\,')\times S_4(\vec{q}-\vec{k}_n,\ \vec{k}_0-\vec{q},\ \vec{k}_n-\vec{q}\,',\ \omega). \tag{A25}$$

This is the same as the expression (35) obtained by treating the field outside the liquid classically.

APPENDIX B: BEHAVIOR OF $\vec{d}_i$

In this appendix we find the behavior of the dipole moments $\vec{d}_i$ of the helium atoms in the presence of an external electric field and a hopping term. To do this consider the semi-classical equation of motion (27) neglecting atomic motions.

$$\dot{\vec{c}}_{ip}=-i\omega_p\vec{c}_{ip}+(i/\hbar)X_p^*\vec{E}_0(\vec{r}_i,\ t)+\frac{i}{\hbar}X_p^*\sum_{p',j}\overleftrightarrow{T}_{ij}^{pp'}\cdot\vec{d}_{jp'}. \tag{B1}$$

Now the dipole moment operator associated with each excited electronic state is

$$\vec{d}_{ip}=X_p^*\vec{c}_{ip}^{\,\dagger}+X_p\vec{c}_{ip}. \tag{B2}$$

Combining (B2), (B1), and the adjoint of (B1) gives

$$\dot{\vec{d}}_{ip} = i\omega_p(X_p^* \vec{c}_{ip}^{\,\dagger} - X_p \vec{c}_{ip}) \tag{B3}$$

and

$$\ddot{\vec{d}}_{ip} = -\omega_p^2 \vec{d}_{ip} + 2\frac{\omega_p}{\hbar}|X_p|^2 \sum_{j,p'} \overleftrightarrow{T}_{ij}^{pp'} \cdot \vec{d}_{jp'} + 2(\omega_p/\hbar)|X_p|^2 \vec{E}_0(\vec{r}_i, t). \tag{B4}$$

Now we want to solve (B4) in successive powers of X^2T/ω_p. Let

$$\vec{E}_0(\vec{r}_i, t) = \vec{E}_0 \cos(\vec{k}_0 \cdot \vec{r}_i - \omega_0 t). \tag{B5}$$

This external field is applied over a time long compared to $1/\omega_p$. Hence we find the steady-state solution of (B4) which is easily seen to be

$$\vec{d}_{ip}^{\,(0)} = \alpha_p(\omega_0)\vec{E}_0(\vec{r}_i, t), \tag{B6}$$

where

$$\alpha_p(\omega_0) = 2\frac{|X_p|^2}{E_p}\frac{\omega_p^2}{\omega_p^2 - \omega_0^2} \tag{B7}$$

is the contribution to the frequency-dependent polarizability due to the p state in question and we have kept the zeroth order in the hopping term. The equation for the polarization of $O(X^2T/\omega_p)$ is then from (B4)

$$\ddot{\vec{d}}_{ip}^{\,(1)} = -\omega_p^2 \vec{d}_{ip}^{\,(1)} + 2\frac{\omega_p}{\hbar}|X_p|^2 \sum_{jp'} \overleftrightarrow{T}_{ij}^{pp'} \cdot \vec{d}_{jp'}^{\,(0)}. \tag{B8}$$

The steady-state solution is

$$\vec{d}_{ip}^{\,(1)} = \alpha_p(\omega_0) \sum_{jp'} \overleftrightarrow{T}_{ij}^{pp'} \cdot \alpha_{p'}(\omega_0)\vec{E}_0(\vec{r}_j, t). \tag{B9}$$

Hence for the polarization we have

$$\vec{P}(\vec{r}, t) = \sum_{ip} \vec{d}_{ip}\delta(\vec{r} - \vec{r}_i(t)) = \vec{P}^{(0)} + \vec{P}^{(1)} + \cdots,$$

where

$$\vec{P}^{(0)}(\vec{r}, t) = \alpha_0(\omega_0)\sum_i \vec{E}_0(\vec{r}_i, t)\delta(\vec{r} - \vec{r}_i(t)),$$

$$\vec{P}^{(1)}(\vec{r}, t) = \sum_{\substack{ij \\ pp'}} \alpha_p(\omega_0)\overleftrightarrow{T}_{ij}^{pp'} \alpha_{p'}(\omega_0) \cdot \vec{E}_0(\vec{r}_j, t)\delta(\vec{r} - \vec{r}_i(t)), \tag{B10}$$

and we have used

$$\alpha_0(\omega_0) = \sum_p \alpha_p(\omega_0).$$

APPENDIX C: ESTIMATE OF S_4

In this appendix we estimate the magnitude of the quantity S_4 given in (68a). The function $t_s^{11}(r)$ drops sharply to zero at some radius R_t while $g_2(r)$ vanishes for $r \le R_0$. The value of R_0 is about 2 Å while R_t estimated from the radii of electronic wave functions is about 2.3 Å. Hence the factor $g_2(r)t_s^{11}(r)$ is nonzero for only a relatively small range of r. This means that in the effective region of integration particle 1 is near particle 2 and particle 3 is near particle 4. If we imagine these two distances being fixed (Fig. 3), the remaining independent variables can be taken to be $\vec{R}$ and a center of mass variable for all four particles. For large R, we have $g_4(1234) = g_2(12)g_2(34)$. This occurs for $R \ll 1/|\vec{k} - \vec{k}_0|$ (since $1/|\vec{k} - \vec{k}_0| \ll 100$ Å). Hence if we let $f(R) = 1$ for large R, we may neglect the exponential in the first term of (68a) and the second term becomes

$$\left[\frac{(M_1^1)_s}{|X_1|^2}\right]^2 \left(\rho \int [f(R) - 1]d^3R + \rho \int e^{i(\vec{k}-\vec{k}_0)\cdot\vec{R}} d^3R\right). \tag{C1}$$

The second term of (C1) does not contribute since $\vec{k} - \vec{k}_0 \neq 0$.

Now we let

$$f(R) = \Theta(R_1 - R). \tag{C2}$$

Then

$$S_4 = \frac{\rho^4}{N}\int [g_4(1234) - \Theta(R_1 - R)g(12)g(34)] \times t_s^{11}(12)t_s^{11}(34)\,d1\,d2\,d3\,d4 - \tfrac{4}{3}\pi\rho R_1^3(M_1^1)_s^2. \tag{C3}$$

By properly choosing R_1 we may make the first term in (C3) small so that the main contribution is due to the second term which we can evaluate exactly. Regarding $\vec{r}_1$, $\vec{r}_2$ and $|\vec{r}_3 - \vec{r}_4|$ as fixed, we are left with a five-dimensional integral in the first term of (C3). Now g_4 will vanish when the distances between any pair is equal or less than R_0. On the other hand, $\Theta(R_1 - R)g(12)g(34)$ vanishes in a different region. We choose R_1 so the volumes of the regions are the same. Since one expects $t_s^{11}(r)$ to be growing for $r \le R_0$ and $g_4(1234) = g_2(12)g_2(34)$ to give numerically reasonable results for the integral over the outer region, this condition should be sufficient.

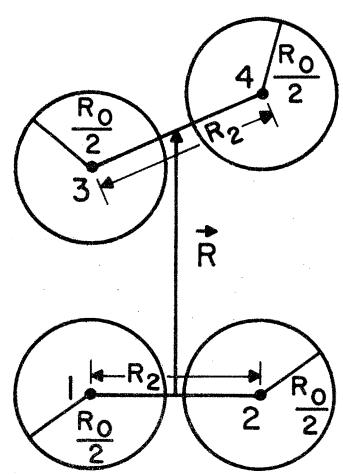

FIG. 3. Illustration of variables discussed in Appendix C. The centers 1234 do not lie in the same plane.

The volume V_1 where the $\Theta(R_1 - R)t_s^{11}(12)t_s^{11}(34)$ term vanishes is just the overlap volume of two spheres of radius $\frac{1}{2}R_1$:

$$V_1 = (\tfrac{4}{3}\pi R_1^3)4\pi(R_2)^2 . \tag{C4}$$

The factor $4\pi R_2^2$ comes from an integration over the angle between particles three and four (we hold one and two fixed in the integration). The volume V_2 where g_4 vanishes can be computed by imagining each particle to be surrounded by a sphere of radius $\frac{1}{2}R_0$ and finding the volume for which at least two spheres overlap. When the sphere around 3 overlaps with that around 2 we have a contribution

$$V_2^{(a)} = \tfrac{4}{3}\pi R_0^3 4\pi R_2^2 . \tag{C5}$$

When the sphere around 3 overlaps with that around 1 we find

$$V_2^{(b)} = V_2^{(a)} . \tag{C6}$$

Now the total volume is

$$V_2 = 2(V_2^{(a)} + V_2^{(b)} - V_2^{(c)}) . \tag{C7}$$

Here the factor of 2 accounts for the configurations in which we exchange 3 with 4 and $V_2^{(c)}$ must be subtracted to correct for the configurations for which two pairs of spheres overlap, which have been counted twice. R_1 is obtained by equating the volumes

$$\begin{aligned} &V_1 = V_2 , \\ &\tfrac{4}{3}\pi R_1^3[4\pi(R_2)^2] = 4(\tfrac{4}{3}\pi R_0^3)(4\pi R_2^2) , \\ &\tfrac{4}{3}\pi R_1^3 = 4(\tfrac{4}{3}\pi R_0^3) , \\ &R_1 = 4^{1/3}R_0 \simeq 3.17\ \text{Å} \end{aligned} \tag{C8}$$

In calculating (C8) we have neglected the correction due to $V_2^{(c)}$. This overestimates R_1 slightly, thereby making S_4 more negative [cf. (C3)].

Putting (C8) in (C3) we obtain finally

$$\begin{aligned} &S_4 \simeq -\rho(\tfrac{4}{3}\pi R_1^3)((M_1^1)_s/|X_1|^2)^2 , \\ &R_1 \simeq 3.17\ \text{Å} . \end{aligned}$$

APPENDIX D: PROOF THAT $(M_2^1)_{sd}=0$

In this appendix we consider $(M_2^1)_{sd}$ which arises in the expression for the second moment of the uv absorption line associated with the first excited p state. This quantity is defined in (14) when one lets $\mu = s$ and $\nu = d$ and hence involves both $\overleftrightarrow{T}_d^{11}$ and $\overleftrightarrow{T}_s^{11}$. We show below that it vanishes.

From (14) and (2) we have

$$\begin{aligned} (M_2^1)_{sd} = &(|X_1|^4 \rho^3/N)\int [g_3(123) - g_2(12)g_2(23)]e^{i\mathbf{k}\cdot(\mathbf{r}_1-\mathbf{r}_3)}t_s^{11}(12)[\overleftrightarrow{T}_d^{11}(23)]^{xx} d^3r_1 d^3r_2 d^3r_3 d^3r_4 \\ &+(|X_1|^4 \rho^2/N)\int g_2(12)t_s^{11}(12)[\overleftrightarrow{T}_d^{11}(12)]^{xx} d^3r_1 d^3r_2 . \end{aligned} \tag{D1}$$

Consider the second term in (D1). Since the range of T_s^{11} is much less than $1/k$ we may ignore the exponential. Since the liquid is isotropic the remaining factors are spherically symmetric except T_d^{11}. By rotating coordinates and using the fact that $\sum_\gamma [\overleftrightarrow{T}_d^{11}]^{\gamma\gamma} = 0$ we find that this term is zero.

Now the factor $t_s^{11}(12)$ keeps the distance between 1 and 2 small in the integrand of the first term of (D1). When 3 is far from 1 and 2 we have

$$g_3(123) = g_2(12)g_2(23) = g_2(12) \tag{D2}$$

and the integrand vanishes. This happens at distances considerably smaller than $1/k$. For 3 near 1 and 2 we may replace the exponential by one. In this region if we rotate all coordinates equally all factors are invariant except $[\overleftrightarrow{T}_d^{11}(23)]^{\gamma\gamma}$. Hence the argument demonstrating that the second term vanishes applies here as well.

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