

ON THE DISTRIBUTION OF ENERGY IN THE CONTINUOUS SPECTRUM OF RAYLEIGH SCATTERING OF LIGHT IN ORGANIC LIQUIDS FAR FROM THE MELTING POINT

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Abstract

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PHYSICS

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ON THE DISTRIBUTION OF ENERGY IN THE CONTINUOUS SPECTRUM OF RAYLEIGH SCATTERING OF LIGHT IN ORGANIC LIQUIDS FAR FROM THE MELT- ING POINT

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A considerable number of theoretical works have been devoted to the continuous spectrum of the Rayleigh line in a liquid*. However, in none of them is there a unified description of the entire spectrum, including its near (up to $\sim 40 \text{ cm}^{-1}$) and far (up to $\sim 150 \text{ cm}^{-1}$) parts—the so-called background and wing. Moreover, most works are based on phenomenological concepts. In the existing attempt at a molecular approach ⁽²⁾, the picture is coarsened by the introduction of a viscosity coefficient into the equation of motion of the molecule.

The investigation undertaken by us is based on the following assumptions. Each molecule of a liquid, during the settled lifetime τ ⁽³⁾, performs quasi-elastic rotational oscillations in a potential well (mean frequency ω_0 , half-period $\tau_0 = \pi/\omega_0$). The oscillations are perturbed by Brownian reorientations and by irregular intermolecular interactions of the impact type (with frequency z). The first of these processes may be regarded as strong; it leads to loss of the oscillation phase; the second as weak: after it the molecule retains information about the phase. In this case $\tau > \tau_0 > 1/z$. Taking into account the slowness of the motion ($\tau_0 \sim 10^{-12} \text{ s}$ ⁽⁴⁾), the discussion is carried out in the classical approximation.

Far from the melting point, the rotational oscillations of the molecules of a liquid are practically incoherent. In this case the intensity of the scattered light $J(\omega)$ is determined, as is known, by the square of the amplitude of the spectrum of the natural (thermal) oscillations of the molecules $G(\omega)$. To find the latter, we used the method of the frequency characteristic. It gives the dependence of the amplitude $Q(\omega)$ of the forced oscillation on the frequency ω of the generalized driving force $f = F \cos \omega t$ ($F = \text{const}$). If $\hbar\omega \ll kT$, then $G^2(\omega)$ is proportional to $Q^2(\omega)$, and therefore

$$J(\omega) \sim Q^2(\omega). \quad (1)$$

The general solution of the differential equation for the rotational oscillations of a molecule in the presence of the force f has the form

$$q = C_1 \cos \omega_0 t + C_2 \sin \omega_0 t + \frac{F}{I(\omega_0^2 - \omega^2)} \cos \omega t; \quad p = I\dot{q}, \quad (2)$$

where q is the oscillatory coordinate, I is the moment of inertia of the molecule, and p is the generalized momentum^{**}. The values of C_1 and C_2 are determined by the initial conditions. They change after each strong or weak interaction and can be determined by the methods of statistics.

Let a weak interaction have occurred at the instant $t_1 = t - \theta$, separated from the current instant t by the interval θ . The weakness of the interactions means that, as a result of them, the distribution of molecules over orientations does not

* See, for example, the monograph ⁽¹⁾.

** To avoid an infinite discontinuity at $\omega = \omega_0$, damping or anharmonicity is usually introduced. This, however, is not necessary here, since during the time τ the oscillation amplitude remains a quantity bounded by $\leq F\tau/2I\omega_0$ ⁽⁵⁾.

will be random. Using Boltzmann statistics, we obtain

$$\bar{q}(t_1) = g \int_{-\infty}^{\infty} q \exp \left[-\frac{E(q, p, t_1)}{kT} \right] dq dp = \frac{F}{I\omega_0^2} \cos \omega t_1 \quad (3)$$

$$\bar{p}(t_1) = \int_{-\infty}^{\infty} p \exp \left[-\frac{E(q, p, t_1)}{kT} \right] dp dq = 0;$$

here

$$E = E_0 + \frac{1}{2} I \omega_0^2 q^2 + \frac{1}{2I} p^2 - Fq \cos \omega t$$

is the vibrational energy, and g is a normalizing factor. The quantities (3) could be taken as the mean values of q and p only in the absence of Brownian reorientations. The latter are so strong a factor that, as a result of them, the oscillatory process begins again from the beginning. If the reorientation is referred to the instant $t_1 - \eta$, then the probability of reorientation in the interval $d\eta$ is determined as

$$\frac{1}{\tau} \exp \left(-\frac{\eta}{\tau} \right) d\eta,$$

whence

$$q(t_1) = \frac{1}{\tau} \int_0^\infty \bar{q}(t_1 - \eta) \exp\left(-\frac{\eta}{\tau}\right) d\eta = \frac{F}{I\omega_0^2} \frac{\cos \omega t_1 + \omega \tau \sin \omega t_1}{1 + \tau^2 \omega^2}; \quad \bar{p}(t_1) = 0^*. \quad (4)$$

Replacing in the left-hand side of expressions (2) q and p by their mean values (4) and solving the system with respect to C_1 and C_2 , we find the values $C_1(t_1)$ and $C_2(t_1)$ for the instant t_1 . The expressions obtained (because of their cumbersome form we do not give them) determine one of the particular solutions of the oscillatory problem:

$$q_1 = C_1(t_1) \cos \omega_0 t + C_2(t_1) \sin \omega_0 t + \frac{F}{I(\omega_0^2 - \omega^2)} \cos \omega t.$$

Finally, let us take into account that a weak interaction can occur at an arbitrary instant of time ($0 \leq \theta < \infty$) and randomly (gas approximation—liquid far from the melting point). Averaging q_1 over θ , we obtain the equation of motion for a certain mean molecule of the liquid in the form

$$q(t) = z \int_0^\infty q_1 \exp(-z\theta) d\theta = A(\omega) \cos \omega t + B(\omega) \sin \omega t;$$

here it is denoted that

$$A(\omega) = \frac{F}{2I\omega_0^2} \left\{ \left(S_p - \frac{\omega}{\omega_0} S_n \right) + \frac{1}{1 + \tau^2 \omega^2} \left[\xi^2 S_p - \omega \tau \xi \left(\frac{\omega}{\omega_0} S_p - S_n \right) \right] \right\},$$

$$B(\omega) = \frac{F}{2I\omega_0^2} \left\{ \xi S_n + \frac{1}{1 + \tau^2 \omega^2} \left[\omega \tau \xi^2 S_p + \xi \left(\frac{\omega}{\omega_0} S_p - S_n \right) \right] \right\},$$

$$S_{p,n} = \frac{\omega_0^2}{z^2 + (\omega_0 - \omega)^2} \pm \frac{\omega_0^2}{z^2 + (\omega_0 + \omega)^2}; \quad \xi = \frac{z}{\omega_0}.$$

The quantity $Q^2(\omega)$, entering into (1), has the expression $A^2 + B^2$, which is easily transformed to such a form that $J(\omega)$ splits into two terms $J(\omega) = J_\phi + J_\kappa$. After neglecting the small term

$$\left(\frac{\omega}{\omega_0} S_p - S_n \right)^2,$$

the latter take the form

$$J_\phi = \frac{1}{4} \frac{J_\phi^0 (\xi^2 + 1)^2}{1 + \tau^2 \omega^2} (S_p^2 - S_n^2) \simeq_{(\xi > 1)} \frac{J_\phi^0}{1 + \tau^2 \omega^2}; \quad (5)$$

Fig. 1. Experimental dependence of the wing intensity on frequency for various substances at 20°. 1 –chlorobenzene, 2 –benzene, 3 –toluene, 4 –o-xylene, 5 –anisole, 6 –pyridine, 7 –acetophenone

Figure 1: Fig. 1. Experimental dependence of the wing intensity on frequency for various substances at 20°. 1 –chlorobenzene, 2 –benzene, 3 –toluene, 4 –o-xylene, 5 –anisole, 6 –pyridine, 7 –acetophenone

*

Here the first averaging is denoted by one bar over the variable symbol, the second by two bars.

$$J_k = \frac{1}{4} J_k^0 (\xi^2 + 1)^2 (S_p^2 - S_n^2) \underset{(\xi \gg 1)}{\sim} \frac{J_k^0}{[1 + \omega^2 / \omega_0^2 (1 + \xi^2)]^2} \quad (6)$$

and may be interpreted as the intensities of the background and the wing of the Rayleigh line as functions of frequency; J_ϕ^0 and J_k^0 are the corresponding intensities at zero:

$$J_\phi^0 \sim \xi^2 (\xi^2 + 2) / (\xi^2 + 1)^2; \quad J_k^0 \sim \left(1 + \frac{2\xi}{\pi} \frac{\tau_0}{\tau} \right) / (\xi^2 + 1)^2. \quad (7)$$

Term (5) is due mainly to Brownian reorientations of the molecules. Term (6) represents the spectrum, modified by weak interactions, of the natural rotational vibrations of liquid molecules in a potential well.

Fig. 1. Experimental dependence of the wing intensity on frequency for various substances at 20°. 1 –chlorobenzene, 2 –benzene, 3 –toluene, 4 –o-xylene, 5 –anisole, 6 –pyridine, 7 –acetophenone.

Expressions (5) and (6) (and the relative intensity J_ϕ^0 / J_k^0) depend substantially on the parameter ξ . For $\xi \ll 1$ * the difference $S_p^2 - S_n^2$ entering them has a maximum near ω_0 . As ξ increases, the maximum shifts toward lower frequencies and, beginning with $\xi = 1$, falls to zero. For $\xi > 1$ (and for $\tau_0 / \tau \sim 10^{-1}$ ⁽⁴⁾) the functions J_ϕ and J_k are well approximated by the expressions shown in (5) and (6) on the right. The first of these (for J_ϕ) is the well-known Leontovich formula ⁽⁷⁾. The second (J_k) requires experimental verification.

It should be noted that in Leontovich' s theory the parameter τ is treated macroscopically and has the meaning of the relaxation time of fluctuations of the anisotropy of the liquid. In experimental studies ⁽⁴⁾, however, this parameter is identified with the mean time between Brownian reorientations of the

molecules. The results of the present work, in the sense indicated, may be regarded as an argument in favor of the legitimacy of such an identification. In this case the Leontovich formula appears as a special case of the dependence $J(\omega)$, which we have now obtained not from phenomenological but from molecular considerations.

The experimental study of the wing of the Rayleigh line was carried out by us for a number of organic liquids (Fig. 1). The scattering spectra were excited by low-pressure mercury lamps from the Hg 4358 Å line. Representation of the observed contour as a superposition of the background and the wing caused no difficulty, since in intensity the background predominates in the near part of the spectrum and has been studied in detail in the literature—

Table 1*

Liquid, 20° C	ν_1 , cm ⁻¹	τ , 10 ¹² sec	ξ
Benzene	41	1.8	3.7
Pyridine	30	2.9	4.0
Toluene	27	3.0	3.9

* Measurement error 5–10%.

* Such values of ξ occur in the gas phase and enter into the theory of broadening and shifting of spectral lines produced by foreign gases (⁶). The magnitude of the impact broadening is determined by the function S_p .

re (4). If, however, one uses dependences (5) and (6), then it is obtained quite unambiguously. From Fig. 1 it is seen that between the quantities $J_k^{-1/2}$ and ω^2 , at least in the frequency region up to ~ 100 cm⁻¹, there is a linear dependence. This may be regarded as an experimental confirmation of formula (6)*.

From the experimental data it proved possible to estimate the parameter ξ . (For this purpose such a frequency ω_1 was found at which $J_\phi = J_k$. Then formulas (5)–(7) give $\xi \simeq \omega_1 \tau$.) It was found that for nonassociated substances ξ has close values ~ 3.8 (Table 1). This means that the liquid molecule experiences on average about 12 weak interactions during a half-period of vibration ($z\tau_0 = \pi\xi$). It is possible that this reflects a connection with the mean coordination number of organic liquids, which, as is known, is close to 12. At the indicated value of ξ , the coefficient at ν^2 ($\nu = \omega/2\pi$) entering formula (6) practically coincides with $(\tau_0/2)^2$.

In conclusion we note a substantial experimental fact which, in our opinion, speaks in favor of the idea of the Rayleigh wing as a broadened low-frequency spectrum of a crystal (8). Our investigations show that in a number of cases near the melting point the Rayleigh wing of the line exhibits maxima. (From Fig. 2 one can see the correspondence between these maxima and low frequencies for *n*-dichlorobenzene.***) This phenomenon can be understood on the basis of

Fig. 2. Scattering spectrum of *n*-dichlorobenzene in the liquid (l) and polycrystalline (s) states at different temperatures. 1—53.2° l; 2— $\geq 53^\circ$ l; 3— $< 53^\circ$ s; 4—52.8°; 5—52°; 6—51°; 7—20°

Figure 2: Fig. 2. Scattering spectrum of *n*-dichlorobenzene in the liquid (l) and polycrystalline (s) states at different temperatures. 1—53.2° l; 2— $\geq 53^\circ$ l; 3— $< 53^\circ$ s; 4—52.8°; 5—52°; 6—51°; 7—20°

the data of the present work. Indeed, if it is assumed that, in the liquid, on approaching crystallization, molecular complexes arise, then the disordered weak interactions of the molecules should gradually give way to coupled vibrations of molecules in the complexes. In this case ξ , as a random function of weak interactions, should decrease in magnitude, and formula (6) will give a maximum ($0 < \omega_{\max} < \omega_0$). One may expect that, owing to the interaction of vibrations, not one but several maxima arise, related in nature to the low frequencies of a crystal.

Fig. 2. Scattering spectrum of *n*-dichlorobenzene in the liquid (l) and polycrystalline (s) states at different temperatures. 1—53.2° l; 2— $\geq 53^\circ$ l; 3— $< 53^\circ$ s; 4—52.8°; 5—52°; 6—51°; 7—20°.

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* In the more distant region, the experimental error does not permit such definite conclusions to be drawn. It is possible that there the intensity of the spectrum falls with frequency somewhat faster than given by (6).

** The study of the spectra of *n*-dichlorobenzene was carried out by A. A. Artamonov and B. P. Nevzorov on a DFS-12 spectrometer.

Note: Figure translations are in progress. See original paper for figures.

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