

Rayleigh scattering of light by a polar gas

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(Submitted February 6, 1974)

ZhETF Pis. Red. 19, 376-378 (March 20, 1974)

An additional mechanism of Rayleigh scattering of light by polar gases is indicated at frequencies ω lower than the vibrational frequencies ω_{vib} of the molecules. This mechanism is connected with stimulated rotational motion of the dipoles, caused by the incident wave.

It is known that scattering of light is due to the fact that the alternating periodic field imparts to the particles of the medium dipole moments that oscillate at the field frequency ω . The scattered wave can be described as a result of radiation by these alternating dipoles. Usually one takes into account only the induced dipole $d^{(1)}$, which is proportional to the polarizability of the molecule. This mechanism was considered already by Rayleigh (see e.g., [1]), and is the predominant one at sufficiently high frequency. Its characteristic contribution to the scattering cross section is proportional to the fourth power of the frequency. If the scattering gas is polar, however, an additional alternating electric moment $d^{(2)}$ is produced by the rotation of the constant dipoles. The cross section due to the induced rotation of the dipoles, as can be easily verified, does not depend on the frequency at all. It is therefore clear that to describe scattering of electromagnetic waves of sufficiently low frequency in polar media it is necessary to take both mechanisms into account. We shall show below that the corresponding region begins with frequencies lower than the vibrational frequencies of the molecule.

We consider the scattering of electromagnetic waves by one molecule with a dipole moment d and a moment-of-inertia tensor J_{ik} . In the case of a spherical top this problem was solved, for example, in [2]. The solution for an asymmetrical top is obtained analogously and consists in the following. If the frequency ω of the incident wave is much higher than the frequency Ω_0 of the thermal rotation of the molecule, then the natural rotation can be neglected and we can consider only the forced rotation. The equation of this motion is $d(J_{ki}\Omega_i)/$

$dt = [d \times E]_k$, where Ω is the angular velocity. The change of the dipole-moment vector upon rotation is given by $d(d)/dt = \Omega \times d$. From these two equations we get

$$\ddot{d}_i = f_{ij} E_j, \quad f_{ij} = e_{ikl} d_l N_{kq} e_{qnj} d_n, \quad (1)$$

where N_{kq} is the inverse of the inertia tensor and e_{ikl} is a unit antisymmetric tensor. In the derivation of (1) we have left out small terms quadratic in Ω . The alternating moment $d^{(2)}$ is thus equal to

$$d_i^{(2)} = -\frac{1}{\omega^2} f_{ij} E_j. \quad (2)$$

We note that from expression (1) we can obtain all the characteristics of the light scattered by the molecule. If we assume all the molecule orientations to be on a par and average over them, then the answer will contain only the values of the principal moments of inertia and of the dipole moment.

We consider now Rayleigh scattering by a polar gas. Let the radiation wavelength λ be much larger than the mean free path l . It is known that in this case the Rayleigh scattering in the gas is connected with fluctuations of the density and the anisotropy, and the latter lead to a relatively smeared out line with a maximum at $\omega' = \omega$. We consider therefore the density fluctuations, i.e., we average the polarization over the molecule orientations.

As noted in the introduction, the polarization of a gas by an alternating field consists of the induced dipole $4\pi\alpha_{ij}(\omega)nE_j$ (α_{ij} is the polarizability tensor of the molecule) and of a dipole connected with the forced rotation

of the molecule $(-1)4\pi\overline{f_{ij}n}E_j/\omega^2$. Here n is the density of the gas molecules, and the bar denotes averaging over the orientations. Thus, to describe scalar scattering it suffices to substitute for $\delta\epsilon$ in the formula for the extinction coefficient^[1]

$$h = \frac{\omega^4}{6\pi c^4} V \overline{(\delta\epsilon)^2}$$

the expression

$$\delta\epsilon = \frac{4\pi}{3} \left[\alpha_{ii}(\omega) - \frac{B}{\omega^2} \right] \delta n, \quad (3)$$

where $b = d^2 N_{ii} - d_i N_{ij} d_j$ and account is taken of the fact that $\overline{f_{ij}} = \delta_{ij} B/3$.

The ratio of the first term of (3) to the second can be easily estimated by noting that the molecule polarizability α is proportional to the molecule volume V . This ratio is of the form $V\omega^2 J/d^2$ and is approximately equal to $(\omega/\omega_{vib})^2$, where ω_{vib} is of the order of magnitude of the frequencies of the intramolecular vibrations.

The condition $\omega \gg \Omega_0$, which is important for the derivation of formula (1), yields $\omega \gg 2.5 \times 10^{13}$ Hz at $\Omega \sim \sqrt{kT/J}$, $J \sim 10^{-40}$ g-cm², and $T \sim 500^\circ\text{K}$.

The condition $\omega < \omega_{vib}$, which is needed to be able to calculate $d^{(2)}$ in accord with the rigid dipole model, is

not a strong limitation, since the amplitude of the oscillation of d is small in comparison with the average value of the dipole moment. We have disregarded throughout the molecule-molecule interaction, which leads to orientational relaxation. In the low-frequency limit $\omega\tau_D \ll 1$ (τ_D is the Debye relaxation time) we can neglect the inertia of the molecule rotation, and then the frequency dependence of the polarizability is described by the well known Debye formula. In the considered case of high frequencies $\omega\tau_D \gg 1$, we retain the inertia term in the equation of motion of the molecule and neglect the relaxation.

In connection with the development of CO₂ lasers, it has become possible recently to study Rayleigh scattering in the infrared band. In this region, both terms in (3) are generally speaking of one order of magnitude.

The author is indebted to E. I. Rashba for valuable remarks.

¹L. D. Landau and E. M. Lifshitz, *Elektrodinamika sploshnykh sred* (Electrodynamics of Continuous Media), Fizmatgiz, 1959 [Pergamon, 1959].

²L. D. Landau and E. M. Lifshitz, *Teoriya polya* (Field Theory), Nauka 1967.