

POLYATOMIC MOLECULE IN GASEOUS ASSEMBLY WITH VIEW TO QUANTUM MECHANICAL WAY

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Abstract: In this paper, the absorption and dispersion of light have been explained using the hypothesis that the molecules of ponderable bodies contain small bodies that are set in vibration by the periodic forces existing in a beam of light or radiant heat. In the Quantum theory, however, the actual mechanism of the dynamical system does not come into the picture except its transition frequencies. Hence the theory is of quite general application to resonant systems. In the first part, we deal with the problem classically and make a transition to the quantum theory by replacing the strength of the oscillator with the quantum mechanical expression for it. In the second part, we shall deal with quantum mechanical theory and point out the significant differences between the two theories and also have derived an expression in another formula like Van Vleck-Weisskopf formulae and so on.

KEY WORDS: Polyatomic molecule, Quantum mechanical theory.

I. INTRODUCTION

In contradiction to Michelson's approach, Lorentz attached the problem from the point of view of the mechanics of the absorption of radiation by molecules. He explained the absorption and dispersion of light employing the hypothesis that the molecules of ponderable bodies contain small bodies that are set in vibration by the periodic forces existing in a beam of light or radiant heat. If a molecule does not undergo a collision its vibrating electron will follow the electric force associated with the incident radiation. If the frequency of the incident radiation is the same as the natural vibrational frequency of the electron, a classical resonance condition may be expected to prevail and but for a regulating factor, the increase of the vibrational amplitude with limit would be expected. The collision of the molecule with another will serve to limit this amplitude increase, for Lorentz, supposed that by the encounter the molecular vibration would be changed into a vibration of a different kind. The electron will carry out this new vibration until another collision essentially stops this vibration and starts still another one and so on. Thus in this way, in analogy to a resistance proportional to the velocity, the amplitude of the vibrations will be limited.

Thus if the collisions are both strong and adiabatic the molecules, after impact, can be regarded as distributed by the Boltzmann law appropriate to the instantaneous value of the field at collision. Weak collisions, on the other hand, leave the molecule with a hangover. Here the assumption is made that any individual collision has but little effect in disturbing the original orientation or polarization of the molecule so that an appropriate change in distribution is obtained only as of the result of a large number of impacts. The well-known theory of Debye on the relaxation behavior of electric liquids may be regarded as the embodiment of the weak collision-mechanism for the non-resonant case. It is therefore of interest to obtain precise information on the relaxation times of polyatomic molecules in a gaseous assembly for an understanding of the mechanism of energy transfer. In this connection, the study of the absorption coefficients and the refractive indices of the infra-red active polyatomic gases offer an alternative method of determining relaxation times with a fair degree of accuracy over a wide range of temperatures.

II. THEORY

A strict theory of dispersion would, of course, require us to consider the complete Hamiltonian of the molecule taking account of the various interactions in the molecule, and to treat the problem in a strictly quantum mechanical way.

(a) Absorption Coefficient and Refractive index:

The present section considers the gas to be isotropic and to be polarized only in the direction of the applied field. Let X', Y', Z' be the space fixed axes (Σ') and X, Y, Z the axes fixed in the molecule (Σ). Let the direction of the applied field be along Z' axis. In terms of the displacements of atoms k , of charge e_k , constituting the molecule, the effective polarization of a single molecule is given by

$$P_{z'} = \sum_k e_k z_k \vec{k}' = \sum_k e_k (X_k \vec{i} + Y_k \vec{j} + Z_k \vec{k}) \quad (1.1)$$

where X_k, Y_k , and Z_k are the components of z_k' . ($\vec{i}, \vec{j}, \vec{k}$ are the vectors in Σ , \vec{k}' is unit vector along z' axis.). Because of the isotropy of the gas, we may regard X_k, Y_k, Z_k as the displacements of the atoms averaged overall orientation of the molecules along the δ body fixed axes, under the influence of the external field $E_{z'}$. Indicating the averaging process relevant to random orientations by a single bar and introducing the normal co-ordinates αE_j , corresponding to the frequency ω_j of the j^{th} normal modes, we write for the magnitude of the polarization:

$$|P_{z'}| = \sum_j \sqrt{\left(\frac{\delta P_x}{\delta E_j}\right)_0^2 + \left(\frac{\delta P_y}{\delta E_j}\right)_0^2 + \left(\frac{\delta P_z}{\delta E_j}\right)_0^2} \bar{E}_j = \sum_j A_j E_j \quad (1.2)$$

where P_x, P_y, P_z are the polarizations along the x, y , and z directions. If there are N_j molecules in the j^{th} mode distributed over the amplitudes \bar{E}_j (or the energy levels of the j^{th} mode). We shall indicate the average value of \bar{E}_j by $\bar{\bar{E}}_j$, the additional bar indicating the average over all the amplitudes in the j^{th} mode. The total polarization of the gas can then be written as;

$$|P_{z'}| = \sum_j A_j N_j \bar{\bar{E}}_j \quad (1.3a)$$

We may regard

$$P_j = A_j \bar{E}_j \tag{1.3b}$$

as the mean polarization associated with each mode j. We shall see later that this quantity provides a convenient transition from classical to quantum mechanical theory. The problem is to determine \bar{E}_j . Using the equation of motion for \bar{E}_j , we find that \bar{E}_j is given by

$$\ddot{\bar{E}}_j(t) = E_z^0 e^{i\omega t} A_j (f_j' - f_j'') \tag{1.4}$$

where $E_z^0 e^{i\omega t}$ is the applied field of angular frequency ω and f_j' , f_j'' are quantities depending only on the properties of the gas (resonance frequency, relaxation time). Depending on the complex susceptibility by

$$|P_{z'}| = (X' + iX'') |E_{z'}| \tag{1.5}$$

We obtain the real and imaginary parts of the susceptibility.

$$X' = \sum_j A_j^2 N_j f_j'$$

$$X'' = -\sum_j A_j^2 N_j f_j''$$

The absorption coefficient γ and the refractive index n are given by Maxwell's theory:

$$\gamma = -\frac{4\pi\omega}{c} X''$$

$$n^2 - 1 = 4\pi X' \tag{1.6}$$

Hence,

$$\gamma = \frac{4\pi\omega}{c} \sum_j A_j^2 N_j f_j''$$

$$n^2 - 1 = 4\pi \sum_j A_j^2 N_j f_j' \tag{1.7}$$

(b) Forced Oscillation of a Polyatomic Molecule:

In term of the normal coordinates, the motion of the polyatomic molecule under the action of the periodic field is given by:

$$\ddot{\bar{E}}_j + \omega_j^2 \bar{E}_j = \bar{Q}_j$$

Where \bar{Q}_j is defined in terms of the applied field by:

$$\sum_j \bar{Q}_j \bar{E}_j = E_{z'} \sum_j A_j \bar{E}_j$$

(The single bar indicates that we are considering the vibrational motion averaged over all the orientations of the molecules.) From the definition of polarization (1.2), we get

$$\bar{Q}_j = E_{z'} A_j$$

Writing $\bar{Q}_j = Q_j^0 e^{i\omega t}$ and $E_{z'} = E_{z'}^0 e^{i\omega t}$ we have

$$\bar{Q}_j^0 = E_{z'}^0 A_j$$

The complete solution of the differential equation is given by

$$\bar{E}_j = \frac{\bar{Q}_j^0 e^{i\omega t}}{\omega_j^2 - \omega^2} + C_j' e^{i\omega_j t} + C_j'' e^{-i\omega_j t} \tag{1.8}$$

To determine C_j' and C_j'' we assume the following initial condition as in the theory of collision broadening due to Van-Vleck and Weisskopf. At any time $t = t_0$ the class of molecules coming into mutual collisions is restored to the thermal equilibrium state appropriate to the instantaneous value of the field at t_0 .

This assumption yields the value of \bar{E}_j and $\dot{\bar{E}}_j$ at t_0 from which C_j' and C_j'' can be evaluated. These averages are given by :

$$\bar{E}_j(t_0) = \frac{\int_{-\infty}^{+\infty} E_j e^{-\frac{H(t_0)}{kT}} dE_j dE_j}{\int_{-\infty}^{+\infty} e^{-\frac{H(t_0)}{kT}} dE_j dE_j}$$

$$\dot{\bar{E}}_j(t_0) = \frac{\int_{-\infty}^{+\infty} \dot{E}_j e^{-\frac{H(t_0)}{kT}} dE_j dE_j}{\int_{-\infty}^{+\infty} e^{-\frac{H(t_0)}{kT}} dE_j dE_j}$$

The Hamiltonian H(t) is the sum of the unperturbed Hamiltonian

$$H_0 = \frac{1}{2} \sum_j (\omega_j^2 E_j^2 + \dot{E}_j^2)$$

and the perturbation energy due to the interaction of the molecule with the applied field:

$$dH = -E_{z'}^0 e^{i\omega t} \sum_j A_j E_j$$

These averages are easily evaluated, and we find

$$\bar{E}_j(t_0) = \frac{(A_j E_{z'}^0)}{\omega_j^2} \text{ and } \dot{\bar{E}}_j(t_0) = 0 \tag{1.9}$$

the complete solution with the constants evaluated is then

$$\bar{E}_j(t) = \frac{E_{z'}^0 A_j e^{i\omega t}}{\omega_j^2 - \omega^2} \left[1 - \frac{1}{2} \frac{\omega_j - \omega}{\omega_j} e^{i(\omega_j - \omega)\theta} - \frac{1}{2} \frac{\omega_j - \omega}{\omega_j} e^{i(\omega_j - \omega)\theta} \right] + \frac{E_{z'}^0 A_j e^{i\omega t}}{2\omega_j^2} \left[e^{i(\omega_j - \omega)\theta} + e^{-i(\omega_j - \omega)\theta} \right] \tag{1.10}$$

Where $\theta = (t - t_0)$. This gives the normal coordinates at any time t, of a class of molecules which have all suffered collisions θ seconds before t.

III. THE DENSITY MATRIX REGARDING QUANTUM THEORY OF DISPERSION:

The present section briefly indicates the out-line of the statistical quantum theory where the average polarization is formed from the density matrix P(t) of the whole gas at time t under the influence of the external field

$$\bar{P}_z(t) = \sum_{mt} (\mu_z)_{mt} P_{mt}(t) \tag{1.11}$$

The double bar indicates the two-folds averaging process giving the quantum mechanical average or the expectation value of the dipole moment operator μ_z and the statistical average. The density matrix of the gas in thermal equilibrium, free from the external radiation field, is given by the Boltzmann distribution

$$(P_0)_{mn} = \frac{e^{-E_m/KT}}{\sum e^{-E_m/KT}} \sigma_{mn} = P_m \sigma_{mn} \tag{1.12}$$

where E_m are the Eigen values of the unperturbed Hamiltonian H_0 of the molecules. The density operator of a class of molecules that suffer collisions at $t=t_0$ and which are under the influence of the external field is denoted by $P(t_0, t_0)$. At the time of collision t_0 , the thermal equilibrium states appropriate to the value of the field at t_0 is assumed to be valid for the class of molecules in question and is given by:

$$P(t_0, t_0) = \frac{e^{-H(t_0)/KT}}{\sum e^{-H(t_0)/KT}} \tag{1.13}$$

where $H(t)$ is the Hamiltonian of the molecule perturbed by the field:

$$H(t) = H_0 - \mu_z E_z^0 \cos\theta \tag{1.14}$$

Thereafter under the influence of the field as the class of the molecules is colliding at t_0 absorb energy, the system deviates from the thermal equilibrium state and the density matrix develop from $P(t_0, t_0)$ to $P(t, t_0)$ according to the equation of motion

$$\frac{P(t, t_0)}{t} = -\frac{i}{\hbar} [H(t)P(t, t_0) - P(t, t_0)H(t)] \tag{1.14}$$

The density operator for the whole gas is obtained by averaging over all classes of molecules at time t

$$P(t) = \frac{1}{\tau} \int_0^\infty P(t, t_0) e^{-(t-t_0)} d(t - t_0) \tag{1.15}$$

The main result of the theory is that the time development of the density matrix for the whole gas under the influence of the external field $E_z^0 e^{i\omega t}$ is given by:

$$P_{lm}(t) = P_l \sigma_{lm} + E_z^0 (\mu_z)_{lm} (B_{lm} e^{i\omega t} + B_{lm}^* e^{-i\omega t}) \tag{1.16}$$

Where B_{lm} are complex constant.

Noting that

$$\sum_{lm} (\mu_z)_{lm} P_l \sigma_{lm} = \sum_m (\mu_z)_{mm} P_m \sigma_{mm}$$

Since, $(\mu_z)_{mm} = 0$, we get on pairing terms involving the same indices l, m ,

$$\bar{P}_z(t) = E_z^0 \sum_{ml} (\mu_z)_{ml}^2 [(B_{lm} + B_{ml}) e^{i\omega t} + (B_{lm}^* + B_{ml}^*) e^{-i\omega t}] \tag{1.17}$$

For the susceptibility we get,

$$X = X' + X'' = 2 \sum_{ml} (\mu_z)_{ml}^2 (B_{lm} + B_{ml})$$

where X is defined by

$$\bar{P}_z(t) = \frac{1}{2} E_z^0 (X' e^{i\omega t} + X'' e^{-i\omega t})$$

writing

$$B_{lm} = B'_{lm} + i B''_{ml}$$

and using (1.6) we get the following expression for the absorption coefficient and the refractive index:

$$\gamma = -\frac{\sigma\pi\omega}{c} \sum_{ml} (\mu_z)_{ml}^2 (B''_{lm} + B''_{ml}) \tag{1.18}$$

$$n^2 - 1 = \sigma\pi \sum_{ml} (\mu_z)_{ml}^2 (B'_{lm} + B'_{ml}) \tag{1.19}$$

With the approximation that $\frac{\mu_z E_z^0}{KT}$ is small compared with unity and neglecting quantities of the second order $E_z^0 (\mu D - D\mu)$, where D is the operator representing the deviation from the thermal equilibrium state, assumed to be very small compared with the equilibrium operator $P(t, t_0)$, we get for the time development of $P(t)$, through equations (1.11), (1.12), (1.13), (1.14) and (1.15):

$$P_{mn}(t) = P_m \sigma_{mn} + \frac{(\mu_z)_{mn}}{4\pi KT} E_z^0 (P_m + P_n) \left[\left(1 - \frac{\omega}{\omega + \omega_{mn} + i\tau_{mn}^{-1}}\right) e^{i\omega t} \left(1 - \frac{\omega}{\omega - \omega_{mn} + i\tau_{mn}^{-1}}\right) e^{-i\omega t} \right] \tag{1.20}$$

On comparing with (4.26) we get:

$$B'_{mn} = \frac{1}{4\pi KT} (P_m + P_n) \left(1 - \frac{\omega(\omega + \omega_{mn})}{(\omega + \omega_{mn})^2 + \tau_{mn}^{-2}}\right) \tag{1.21}$$

$$B''_{mn} = -\frac{\omega}{4KT} (P_m + P_n) \left(\frac{\tau_{mn}^{-1}}{(\omega + \omega_{mn})^2 + \tau_{mn}^{-2}}\right) \tag{1.22}$$

Hence the absorption coefficient and the refractive index of gas is

$$\gamma = \frac{\sigma\pi^2 v^2 N}{CKT} \sum_{mn} (\mu_z)_{nm}^2 (P_m + P_n) \left[\frac{1}{(v + v_{mn})^2 + \left(\frac{1}{2\pi\tau_{mn}}\right)^2} + \frac{1}{(v - v_{mn})^2 + \left(\frac{1}{2\pi\tau_{mn}}\right)^2} \right] \tag{1.23}$$

$$n^2 - 1 = \frac{4\pi N}{KT} \sum_{mn} (\mu_z)_{nm}^2 (P_m + P_n)$$

$\left[1 - \frac{\frac{1}{2}\left(\frac{v}{v_{mn}}\right) + \frac{1}{2}\left(\frac{v}{v_{mn}}\right)^2}{(v + v_{mn})^2 + \left(\frac{1}{2\pi\tau_{mn}}\right)^2} + \frac{\frac{1}{2}\left(\frac{v}{v_{mn}}\right) - \frac{1}{2}\left(\frac{v}{v_{mn}}\right)^2}{(v - v_{mn})^2 + \left(\frac{1}{2\pi\tau_{mn}}\right)^2} \right]$ is placed in an external magnetic field. So, some components lines are observed

corresponding to different energies due to the splitting of degeneracy.

IV. COMPARISON WITH VAN VLECK-WEISSKOPF FORMULA:

The formulae (1.23) and (1.24) derived from the quantum theory of this section and the formulae (1.8) and (1.9) derived from the classical theory and translated into quantum theory by the correspondence (1.7) are seen to be different. The absolute temperature T makes its appearance in the quantum mechanical formulae of this section, whereas it does not figure at all in the formula of the previous section (Nevertheless the half-width measured from in both the cases and hence the relaxation times would be the same). We briefly recall that in the quantum theory of this section only the approximation $\mu_z E_z \ll KT$ is so far involved whereas in the theory outlined in the previous section no approximation of any kind has been made and in the previous section transition to quantum mechanics is made through (1.7). If instead of the prescription (1.7) for the transition from classical to the quantum theory we consider the dipole moment P_j for this transition in the following manner, the classical theory is seen to lead to the factor involving the temperature as in (1.23). We have for the average value of ξ_j at t_0 the expression

$$\bar{\xi}_j(t_0) = \frac{A_j E}{\omega_j^2} = \frac{A_j^2 \xi_j^2 E}{A_j \omega_j^2 \xi_j^2} = \frac{P_j P_j^* E}{A_j \omega_j^2 \xi_j^2} \tag{1.25}$$

where P_j is the dipole moment associated with the j^{th} mode. In statistical equilibrium, we may associate each of the two degrees of freedom in vibrational motion with the energy $\frac{1}{2} kT$. Hence the average value of $\bar{\xi}_j(t_0)$ is:

$$\bar{\xi}_j(t_0) = \frac{|\mu_{ij}|^2}{A_j kT} \tag{1.25}$$

By using the initial value of $\bar{\xi}_j(t_0)$ given by (1.25) which imply means replacing $N_j \left(\frac{A_j^2}{\omega_j^2}\right)$ in the classical formula (1.5) {refer definition of A_j in (1.2)} by $\frac{|\mu_{ij}|^2}{kT} (N_i + N_j)$. We recover the formula (1.13) for γ . However, we note that while there is perfect agreement between the two theories so far as γ as concerned, there is a difference between them with the refractive index. Further points of comparison are detailed below:

(a) At low frequency:

At microwave and radiofrequency the approximate condition $\frac{h\nu_{mn}}{kT} \ll 1$ is valid. Then

$$P_m + P_n \sim 2 \cdot \frac{e^{-(E_m+E_n)/2kT}}{\sum_i e^{E_i/kT}}$$

$$\text{or, } P_m - P_n \sim \frac{h\nu_{mn}}{2kT} P_m + P_n,$$

The absorption coefficient and refractive index are given by :

$$\gamma = \frac{\sigma \pi^2 \nu^2 N}{hc} \sum_{mn} |(\mu_z)_{mn}|^2 \left(\frac{P_m - P_n}{\nu_{mn}}\right) \left[\frac{1}{(\nu + \nu_{mn})^2 + \left(\frac{1}{2\pi\tau_{mn}}\right)^2} + \frac{1}{(\nu - \nu_{mn})^2 + \left(\frac{1}{2\pi\tau_{mn}}\right)^2} \right] \tag{1.26}$$

$$n^2 - 1 = \frac{4\pi N}{h} \sum_{mn} |(\mu_z)_{mn}|^2 \left(\frac{P_m - P_n}{\nu_{mn}}\right) \left[1 - \nu_{mn}^2 \frac{\frac{1}{2}\left(\frac{\nu}{\nu_{mn}}\right) + \frac{1}{2}\left(\frac{\nu}{\nu_{mn}}\right)^2}{(\nu + \nu_{mn})^2 + \left(\frac{1}{2\pi\tau_{mn}}\right)^2} + \nu_{mn}^2 \frac{\frac{1}{2}\left(\frac{\nu}{\nu_{mn}}\right) - \frac{1}{2}\left(\frac{\nu}{\nu_{mn}}\right)^2}{(\nu - \nu_{mn})^2 + \left(\frac{1}{2\pi\tau_{mn}}\right)^2} \right] \tag{1.27}$$

Making use of the line shape function

$$\phi(\nu_{ij}, \nu) = -f(\nu_{ij}, \nu) = \frac{1}{\pi} \frac{\nu}{\nu_{ij}} \left[\frac{\frac{1}{2\pi\tau_{ij}}}{(\nu_{ij} + \nu)^2 + \left(\frac{1}{2\pi\tau_{ij}}\right)^2} + \frac{\frac{1}{2\pi\tau_{ij}}}{(\nu_{ij} - \nu)^2 + \left(\frac{1}{2\pi\tau_{ij}}\right)^2} \right]$$

We may write for γ :

$$\gamma = \frac{\sigma \pi^3 N}{hc} \sum_{mn} |(\mu_z)_{mn}|^2 (P_m - P_n) f(\nu_{mn}, \nu) \tag{1.28}$$

This is Van Vleck-Weisskopf formula (1.8). it seems fortuitous that the two formulae for γ (1.8) and (1.23), the former derived classically and then transformed through (1.7) and the latter derived in a strictly quantum mechanical way using the density matrix, agree only in the limiting case $\frac{h\nu_{mn}}{kT} \ll 1$.

(b) Other limiting cases:

(i) We recover the special case of the static susceptibility, $X = \frac{n^2 - 1}{4}$ by putting $\left(\frac{\nu}{\nu_{mn}}\right) = \frac{1}{2\pi\tau_{mn}} = 0$. From (1.23) and (1.24):

$$\gamma = 0, \quad X = \frac{N}{kT} \sum_{mn} (\mu_z)_{nm}^2 (P_m + P_n) \tag{1.29}$$

This is essentially the Langevin formula $X = \frac{NP^2}{3kT}$.

The factor $\frac{1}{3}$ can be accounted for by taking the angle effect in the polarization energy.

(ii) For extremely long relaxation times, which can be mathematically approximated by $1 \rightarrow \infty, \gamma = 0$.

However, if radiation damping were considered even in this limiting case there will be attenuation. The refractive index is given by the following expression having the significant resonance factor which accounts for anomalous dispersion,

$$\frac{4\pi N}{kT} \sum_{mn} |(\mu_z)_{mn}|^2 (P_m + P_n) \frac{\nu_{mn}^2}{\nu_{mn}^2 - \nu^2} \tag{1.30}$$

The formula for n of the previous section leads to the same result even though the general formula for the refractive index of the two sections (1.2) and (1.3) are different. (iii). When the relaxation times are extremely short the susceptibility and the refractive index become independent of the frequency of the applied field and attain the static value (1.28). But this case is very likely not of much physical interest since, at high pressures under which this limiting case arises, it would be necessary to consider multiple collisions.

V. CONCLUSION:

The main result of the theory is that the time development of the density matrix for the whole gas under the influence of the external field $E_z^0 e^{i\omega t}$. We shall find that these formulae are not at variance with those developed in section 3 using the density matrix and a strict quantum mechanical approach. The standard procedure of going from the classical to the quantum mechanical theory is used. The present section now brings in the main idea of this discussion that the time of collision t_0 is relevant to the mode in the question since the energetic changes of the modes of vibration will occur at different times. The time of energy transfer to the lowest mode is different from that to the other modes in general since energy requires a finite time to go into the higher modes especially if the frequency gap is large.

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