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The Lorentz internal field model has been widely used in order to correct the observed infrared spectra for the effect of the internal electric field. In all previous papers, the total polarization required in the Lorentz model has been considered to have only one component. In this paper, however, another component was introduced, and the total polarization was given by the sum of the two components. Such a change in the Lorentz model led to a new equation for the absolute band intensity corrected for the internal field effect.

I. INTRODUCTION

It has long been recognized that when the infrared absorption spectra are measured in condensed phases, the observed spectra must be corrected for the effect of the so-called internal electric field. The spectra thus corrected provide information on a molecular level correctly. For such a correction, it is necessary to employ some model for the internal field. The Lorentz model[1] has been widely used for this purpose, and several equations which make a correction based on this model have already been presented.[2–4]

The Lorentz internal field is derived by calculating the field within a spherical cavity in the dielectric medium, and it requires the total polarization of the dielectric medium. In all attempts previously made,[2–5] this polarization has been considered to have only one component whose resonance frequencies are in the infrared region. However, there exists another polarization which resonates with frequencies in the visible or ultraviolet region, and has the same phase as the applied electric field. Therefore, we must take the total polarization of the dielectric medium as the sum of these two components. In the present paper, such a change in the Lorentz model led to a new equation which corrects the observed band intensity in condensed phases for the effect of the internal field. The new equation thus obtained is the generalization of the equation derived for solution phases,[6] and it seems to be applicable to dielectrics (liquid, solution, and so on) which satisfy the Lorentz internal field.

II. DERIVATION

If the infrared radiation of frequency ν travels in dielectrics, two kinds of polarization will be excited; P_0 and P_1. The polarization P_0 is resonant with the infrared radiation, and shows a phase shift from the microscopic electric field or the internal electric field, E_i. This phase shift gives rise to the absorption of radiant energy. For this polarization, Clifford and Crawford[4] defined the local susceptibility, $\hat{C}_0 (= C_0' + iC_0'')$, which is written as

$$P_0 = \hat{C}_0 \cdot E_i . \tag{1}$$

Another polarization P_1 has resonance frequencies in the visible or ultraviolet region, and is in phase with the macroscopic electric field, E. These two polarizations superpose linearly without perturbing each other,[7] and then the total polarization of dielectrics, P, is given by

$$P = P_0 + P_1 . \tag{2}$$

When the Lorentz model is chosen for the internal field, it requires the total polarization of the dielectric medium. Using Eq. (2), the result is

$$E_i = E + [(4\pi)/3] \cdot (P_0 + P_1) . \tag{3}$$

In previous studies,[2–5] P_1 in Eq. (3) has not been taken into consideration. Thus, Eq. (3) leads to a new equation for the internal field correction as follows.

Substituting Eq. (3) into Eq. (1) yields

$$\hat{C}_0 = \frac{3 \cdot (\hat{\chi} - \hat{\chi}_1)}{4\pi\hat{\chi} + 3} . \tag{4}$$

Here, the relations of $P = \hat{\chi} \cdot E$, $\hat{\chi} (= \chi' + i\chi'')$ and $P_1 = \hat{\chi}_1 \cdot E$, $\hat{\chi}_1 (= \chi_1' + i\chi_1'')$ are used. Equation (4) corresponds to Eq. (3) of the paper of Clifford and Crawford,[4] but χ_1 does not appear in their equation because of the neglect of P_1. According to electromagnetic theory, the real and imaginary parts of $\hat{\chi}$ are expressed as follows, respectively:

$$\chi' = (n^2 - k^2 - 1)/(4\pi) ,$$
$$\chi'' = (n \cdot k)/(2\pi) , \tag{5}$$

where n and k are the refractive index and the extinction coefficient of dielectrics, respectively. Similar relations hold for $\hat{\chi}_1$, but the imaginary part χ_1'' equals zero, because P_1 is in phase with E. On the other hand, considering P_1 is entirely due to the displacement of electrons and corresponds to the optical polarization, it will be very nearly true that

$$\chi_1' \doteqdot (n_D^2 - 1)/(4\pi) . \tag{6}$$

Here n_D is the refractive index of dielectrics at the frequency of Na–D line. Hence, using Eqs. (5) and (6), separation of Eq. (4) into the real and imaginary parts yields

$$C_0' = \frac{3}{4\pi} \cdot \frac{(n^2 - n_D^2 - k^2) \cdot (n^2 - k^2 + 2) + 4n^2k^2}{(n^2 - k^2 + 2)^2 + 4n^2k^2} , \tag{7}$$

$$C_0'' = \frac{3c}{8\pi^2 \nu} \cdot \frac{n \cdot \kappa (n_D^2 + 2)}{(n^2 - k^2 + 2)^2 + 4n^2k^2} , \tag{8}$$

where c is the light velocity *in vacuo*, and κ is the absorption coefficient of dielectrics; $\kappa = 4\pi\nu k/c$.

When the integration of C_0'' is carried out over the entire absorption band, one finds

$$\frac{8\pi^2}{Nc}\int C_0'' \cdot v \cdot dv = \frac{\pi}{3c}\left(\frac{\partial\mu}{\partial Q}\right)_0^2 , \tag{9}$$

where N is the number of absorbing molecules per unit volume of dielectrics, and $(\partial\mu/\partial Q)_0$ is the dipole moment derivative of an absorbing molecule. Equation (9) is derived[6] from the probability of a fundamental transition by the harmonic oscillator in a bath of radiant energy. Thus, by inserting Eq. (8) into Eq. (9), we obtain a new equation for the absolute band intensity corrected for the internal field effect, A_{cor}; namely

$$A_{cor} = \frac{1}{N}\int \frac{3n \cdot \kappa(n_D^2 + 2)}{(n^2 - k^2 + 2)^2 + 4n^2k^2}\, dv = \frac{\pi}{3c}\left(\frac{\partial\mu}{\partial Q}\right)_0^2 . \tag{10}$$

If P_1 is neglected, n_D is unity from Eq. (6), and then the numerator of Eq. (10) becomes $9n\kappa$, which is identical to the previous equation.[3,4]

When an absorbing molecule is supposed to be a classical single resonance damped oscillator whose charge and mass are e and m respectively, such a model gives the result that

$$C_0' = \frac{N \cdot e^2}{m} \cdot \frac{\omega_0^2 - \omega^2}{(\omega_0^2 - \omega^2)^2 + 4\gamma^2\omega^2} , \tag{11}$$

$$C_0'' = \frac{N \cdot e^2}{m} \cdot \frac{2\gamma\omega}{(\omega_0^2 - \omega^2)^2 + 4\gamma^2\omega^2} , \tag{12}$$

where $\omega = 2\pi v$, ω_0 is the molecular resonance angular frequency, and γ is the damping constant. These equations are derived by solving the equation of the motion of the oscillator.[6] Connecting Eqs. (7) and (8) with Eqs. (11) and (12), respectively, one can relate the molecular quantities, e^2/m, ω_0, and γ, to the measurable quantities of dielectrics n, k, and κ.

III. DISCUSSION

Fröhlich[7] has already concluded that the total polarization can be divided into two independent components; the infrared polarization P_{IR} and the optical polarization P_o. The polarizations P_0 and P_1 introduced in this paper correspond to these two components, respectively. Therefore, to take the total polarization as the sum of P_0 and P_1 is in accordance with Fröhlich's theory.

The necessity of taking into account of P_1 is shown by calculating the refractive index of dielectrics in the infrared region. Connecting Eq. (7) with Eq. (11), the damped oscillator model gives the refractive index, which is approximately expressed as

$$n^2 - n_D^2 \doteqdot \frac{4\pi N \cdot e^2}{m} \cdot \frac{1}{\omega_0^2 - \omega^2} . \tag{13}$$

Equation (13) indicates that for the refractive index in the infrared region, there exists a background contribution from the visible region. This finding is consistent with the experimental data, and also shows that Eq. (6) is a good approximation. However, if P_1 is omitted, the left-hand side of Eq. (13) becomes $n^2 - 1$, which is contrary to the observed results.

In order to explain the background contribution, Clifford and Crawford[4] actually introduced a constant real quantity in the local susceptibility. Warner and Wolfsberg[5] also included a constant real term in the molecular polarizability. Therefore, it is certain that they recognized the two components of the polarization. However, they took only one component P_0 as the total polarization required in the Lorentz model. Such treatments seem to be conflicting.

Further work is required to confirm fully the present results, and we are now attempting to test them experimentally.

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