

Internal field correction on infrared spectra of condensed phases

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Internal field correction on infrared spectra of condensed phases

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Infrared spectra observed in condensed phases must be corrected for the effect of the internal electric field. A new equation for such correction was derived by employing the Lorentz internal field model. The previous equation which has been widely used was also derived in order to make clear why the difference occurs, and the validity of the present derivation was pointed out.

Moreover, the new equation was applied to the 678 cm^{-1} band of liquid benzene, and the results were found to be quite reasonable.

I. INTRODUCTION

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. This correction results from the fact that the microscopic or the internal field acting directly on molecules is different from the applied macroscopic electric field. For such a correction, it is necessary to employ some model for the internal field. Bakhshiev *et al.*¹ and Crawford *et al.*² used the Lorentz model,³ and presented the same equation for the internal field correction. Their equation becomes the well-known Polo-Wilson equation⁴ under some approximations.

In our previous paper,⁵ however, we also used the Lorentz model and derived a different equation. In the present study, we made clear why such a difference occurs, and pointed out the validity of our derivation. Then, we applied our new equation to the 678 cm^{-1} band of liquid benzene, and found the results to be quite reasonable.

II. DERIVATION OF THE NEW EQUATION

If the infrared radiation of frequency ν travels in dielectrics, two kinds of polarization will be excited; that is, \mathbf{P}_0 and \mathbf{P}_1 . The polarization \mathbf{P}_0 is resonant with the infrared radiation, and shows a lag in phase from the microscopic electric field or the internal electric field, \mathbf{E}_i . This phase shift gives rise to the absorption of radiant energy. For this polarization, the local susceptibility, $\hat{C}_0 (= C'_0 + iC''_0)$, is defined by

$$\mathbf{P}_0 = \hat{C}_0 \cdot \mathbf{E}_i. \quad (1)$$

Another polarization \mathbf{P}_1 has resonance frequencies in the visible or ultraviolet region, and is in phase with the macroscopic electric field of the infrared frequency, \mathbf{E} . These two polarizations superpose linearly without perturbing each other,⁶ and then the total polarization of dielectrics, \mathbf{P} , is given by

$$\mathbf{P} = \mathbf{P}_0 + \mathbf{P}_1. \quad (2)$$

When the Lorentz model is employed as in previous works^{1,2} the internal field is described as

$$\mathbf{E}_i = \mathbf{E} + (4\pi/3) \cdot \mathbf{P}. \quad (3)$$

Substituting Eqs. (2) and (3) into Eq. (1) yields

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

where, the relations of $\mathbf{P} = \hat{\chi} \cdot \mathbf{E}$, $\hat{\chi} (= \chi' + i\chi'')$, and $\mathbf{P}_1 = \hat{\chi}_1 \cdot \mathbf{E}$, $\hat{\chi}_1 (= \chi'_1 + i\chi''_1)$ are used. According to electromagnetic theory, the real and imaginary parts of $\hat{\chi}$ of dielectrics are expressed as follows, respectively:

$$\begin{aligned} \chi' &= (n^2 - k^2 - 1)/4\pi, \\ \chi'' &= (n \cdot k / 2\pi), \end{aligned} \quad (5)$$

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 \mathbf{P}_1 is in phase with \mathbf{E} . On the other hand, considering \mathbf{P}_1 is entirely due to the displacement of electrons and corresponds to the optical polarization, it will be very nearly true that

$$\chi'_1 \doteq (n_D^2 - 1)/4\pi. \quad (6)$$

Here n_D is the refractive index of dielectrics at the frequency of Na-D line. Hence, $\hat{\chi}_1$ is a constant real quantity. Using Eqs. (5) and (6), separation of Eq. (4) into the real and imaginary parts gives

$$C'_0 = \frac{3}{4\pi} \cdot \frac{(n^2 - n_D^2 - k^2) \cdot (n^2 - k^2 + 2) + 4n^2k^2}{(n^2 - k^2 + 2)^2 + 4n^2k^2}, \quad (7)$$

$$C''_0 = \frac{3c}{8\pi^2\nu} \cdot \frac{n \cdot \kappa (n_D^2 + 2)}{(n^2 - k^2 + 2)^2 + 4n^2k^2}, \quad (8)$$

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

In order to express \hat{C}_0 in terms of molecular quantities, let us suppose \mathbf{P}_0 to be due to the displacement of a classical forced-damped oscillator whose charge and mass are e and m , respectively. The equation of motion is

$$\ddot{\mathbf{P}}_0 + 2\gamma\dot{\mathbf{P}}_0 + 4\pi^2\nu_0^2\mathbf{P}_0 = \frac{N \cdot e^2}{m} \cdot \mathbf{E}_i, \quad (9)$$

where γ is the damping constant, ν_0 is the oscillator's resonance frequency, and N is the number of absorbing molecules per unit volume of dielectrics. The solution of Eq. (9) gives

$$C'_0 = \frac{N \cdot e^2}{4m} \cdot \frac{\nu_0^2 - \nu^2}{\pi^2(\nu_0^2 - \nu^2)^2 + (\gamma\nu)^2}, \quad (10)$$

$$C''_0 = \frac{N \cdot e^2}{4\pi m} \cdot \frac{\gamma\nu}{\pi^2(\nu_0^2 - \nu^2)^2 + (\gamma\nu)^2}. \quad (11)$$

Moreover, the integration of Eq. (11) is

$$\int C_0'' \cdot \nu \cdot d\nu = \frac{N}{24\pi} \left(\frac{\partial \mu}{\partial Q} \right)_0^2, \quad (12)$$

where $(\partial \mu / \partial Q)_0$ is the dipole moment derivative, and e^2/m is replaced by $1/3 \cdot (\partial \mu / \partial Q)_0^2$. Thus, by inserting Eq. (8) into Eq. (12), we obtain a new equation for the absolute band intensity corrected for the internal field effect, A_{cor} ; namely,

$$A_{\text{cor}} = \frac{1}{N} \int \frac{3n\kappa(n_D^2 + 2)}{(n^2 - k^2 + 2)^2 + 4n^2k^2} \cdot d\nu = \frac{\pi}{3c} \cdot \left(\frac{\partial \mu}{\partial Q} \right)_0^2, \quad (13)$$

where the integrand gives the corrected absorption coefficient: κ_{cor} . When $n \doteq n_D$ and $k \doteq 0$, Eq. (13) becomes

$$A_{\text{cor}} = \frac{3 \cdot n_D}{n_D^2 + 2} \cdot A_{\text{obs}}$$

with

$$A_{\text{obs}} = \frac{1}{N} \int \kappa \cdot d\nu. \quad (14)$$

This equation corresponds to the Polo-Wilson equation.

III. COMPARISON WITH THE PREVIOUS EQUATION

In order to compare the new equation with that of Bakshiev *et al.*¹ and Crawford *et al.*² the derivation due to Clifford and Crawford² will be briefly described below. They define \hat{C} by

$$\mathbf{P} = \hat{C} \cdot \mathbf{E}_i. \quad (15)$$

Substituting Eq. (3) (the Lorentz model) into Eq. (15) yields

$$\hat{C} = \frac{3\hat{\chi}}{4\pi\hat{\chi} + 3}. \quad (16)$$

Here they make an approximation of

$$\hat{C} = \hat{C}_0 + K, \quad (17)$$

where K is a constant real quantity. Thus, the real and imaginary parts of \hat{C}_0 are given by

$$C'_0 = \frac{3}{4\pi} \cdot \frac{(n^2 - k^2 - 1)(n^2 - k^2 + 2) + 4n^2k^2}{(n^2 - k^2 + 2)^2 + 4n^2k^2} - K, \quad (18)$$

$$C''_0 = \frac{3c}{8\pi^2\nu} \cdot \frac{3 \cdot n \cdot \kappa}{(n^2 - k^2 + 2)^2 + 4n^2k^2}, \quad (19)$$

where the relations of Eq. (5) are used. Integrating Eq. (19), they obtain

$$A_{\text{cor}} = \frac{1}{N} \int \frac{9 \cdot n \cdot \kappa}{(n^2 - k^2 + 2)^2 + 4n^2k^2} \cdot d\nu. \quad (20)$$

Under the approximations of $n \doteq n_D$ and $k \doteq 0$, Eq. (20) becomes the Polo-Wilson equation.

Equation (17) in this derivation indicates that Clifford and Crawford approximate the ratio of $\mathbf{P}_1/\mathbf{E}_i$ to be a real quantity K . In our derivation, on the other hand, we take the ratio of \mathbf{P}_1/\mathbf{E} to be a real quantity χ'_1 , as shown by Eq. (6).

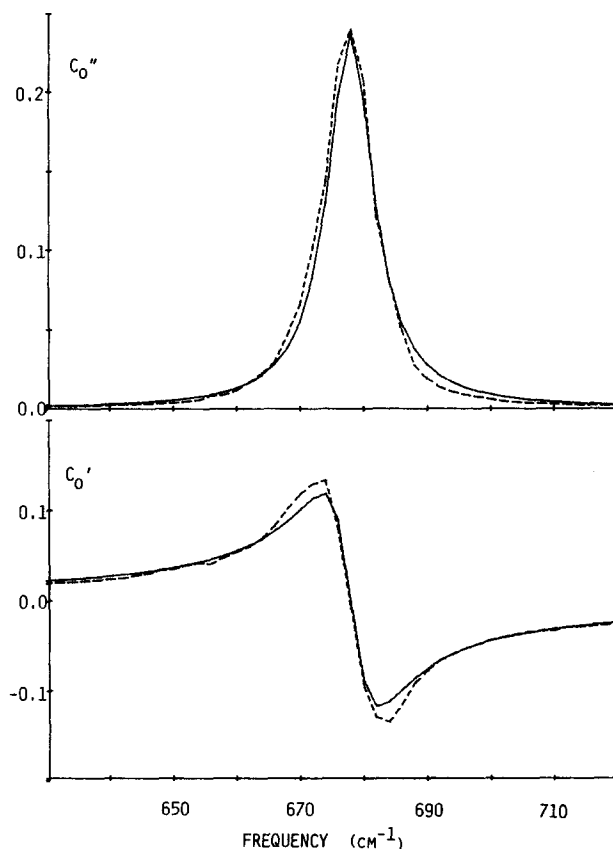


FIG. 1. Local susceptibility for the benzene 678 cm^{-1} band. The dashed lines due to experimental data and the solid lines calculated by using the damped oscillator model.

This difference finally results in the two different equations for A_{cor} .

Now, we must discuss which approximation is more reasonable. On introducing Eq. (3) and dividing through by \mathbf{E} , it is found that

$$\frac{\mathbf{P}_1}{\mathbf{E}_i} = \frac{\mathbf{P}_1}{\mathbf{E} + (4\pi/3)\mathbf{P}} = \frac{\hat{\chi}_1}{1 + (4\pi/3)\hat{\chi}}. \quad (21)$$

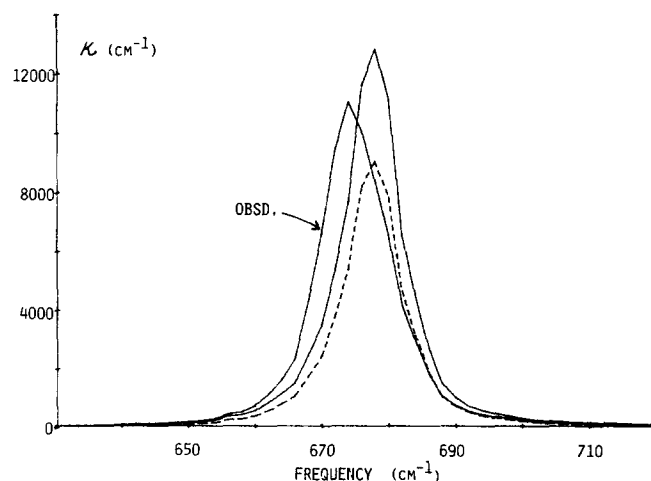


FIG. 2. Absorption coefficients for the benzene 678 cm^{-1} band. The solid lines calculated by the new equation, Eq. (13), and the dashed lines by the previous one, Eq. (20).

Here $\hat{\chi}_1$ is considered to be a real quantity as discussed below, while $\hat{\chi}$ is evidently a complex one. Therefore, it seems unsuitable to make an approximation of $\mathbf{P}_1/\mathbf{E}_i$ being a real quantity. On the other hand, the damped oscillator model mentioned above suggests that $\hat{\chi}_1$ is a real quantity as follows. Inserting Eq. (3) into Eq. (9) and taking into account other oscillators, one finds

$$\hat{\chi} = \sum_j \frac{N_j \cdot e_j^2}{4\pi m_j} \cdot \frac{1}{\pi(\nu_{0j}'^2 - \nu^2) - i\gamma_j \cdot \nu}$$

with

$$\nu_{0j}'^2 = \nu_{0j}^2 - (N_j e_j^2 / 3\pi m_j). \quad (22)$$

Here the apparent resonance frequency ν_{0j}' for off-resonant polarization \mathbf{P}_1 is sufficiently remote from ν . Therefore, $\hat{\chi}_1$ can be approximated by a real quantity. According to these discussions, it seems to be preferable to approximate $\mathbf{P}_1/\mathbf{E}_i$, not $\mathbf{P}_1/\mathbf{E}_t$, to be a constant real quantity.

IV. APPLICATION OF THE NEW EQUATION

Clifford and Crawford² have already measured accurately both of the refractive index n , and the extinction coefficient k of the 678 cm^{-1} band of liquid benzene by the method of ATR. Using their data and taking $n_D = 1.5$, C'_0 , and C''_0 were obtained from Eqs. (7) and (8), respectively, and they are shown as dashed curves in Fig. 1. Next, the molecular quantities appearing in Eq. (11) were determined so that

C''_0 values calculated by Eq. (11) lie on the C''_0 -dashed curve. The results are as follows: $e^2/m = 7.4 \times 10^3 \text{ cm}^3/\text{s}^2$, $\gamma = 27.5 \text{ cm}^{-1}$, and $\nu_0 = 678 \text{ cm}^{-1}$. These values made it possible to calculate C'_0 and C''_0 by using the damped oscillator model, Eqs. (10) and (11), respectively, and the results are plotted as solid curves in Fig. 1. The dashed and solid curves almost overlap one another, and this good overlapping shows that our derivation, including the approximation of Eq. (6), is quite reasonable.

The observed absolute band intensity, A_{obs} , was corrected by both Eqs. (13) and (20); that is, the new equation and the previous one. The κ_{cor} values calculated are illustrated in Fig. 2. The corrected intensities are as follows: A_{cor} [Eq. (13)] = 146, A_{cor} [Eq. (20)] = 103, while $A_{\text{obs}} = 142 \text{ km/mol}$. It should be noted that the new equation results in $A_{\text{cor}} \neq A_{\text{obs}}$. At the present time, it is difficult to decide conclusively which value is preferable. Further investigation, of course, is necessary to confirm fully the validity of the new equation.

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