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# Internal field correction for infrared band intensity measured in solutions

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The Polo and Wilson equation has been widely used to eliminate the effect of the internal electric field from the observed infrared absorption intensities in the condensed phase. However, the validity of this equation for solution states has not been confirmed yet. This paper gives a new equation for the internal electric field correction in solution states according to the two kinds of molecular models. The equation obtained is identical to that of Polo and Wilson to the limit of pure liquid.

## I. INTRODUCTION

When the absolute intensities of the infrared absorption bands are measured in condensed phases such as liquid and solution, the observed values must be corrected for the effect of the so-called internal electric field. The intensities thus corrected yield the usual effective bond moments and their derivatives in dense media. Several workers have previously proposed various equations which make such correction. Among them, the equation of Polo and Wilson (PW)<sup>1</sup> has been widely used, and its validity for pure liquids has already been confirmed.<sup>2</sup> However, it seems to be doubtful whether the PW equation is also applicable to solutions.

In this study, we present a new equation for the internal field correction in solutions according to the two kinds of molecular models. The new equation obtained is identical to that of PW to the limit of pure liquid. The derivation of the PW equation was also carried out, and a questionable point in applying it to solutions was pointed out.

## II. DERIVATION

### A. Quantum mechanical model

Let us suppose that the incident light of the frequency  $\nu$  travels in a solution, and that only solute molecules absorb the radiant energy. This radiant energy  $dW$  absorbed in a volume  $dV$  for a time  $dt$  is given quantum mechanically by

$$dW = \frac{N\pi}{3} \cdot \left( \frac{\partial \mu}{\partial Q} \right)_0^2 \cdot \rho(E_i) \cdot dV \cdot dt, \quad (1)$$

with

$$\rho(E_i) = \frac{1}{4\pi} \cdot \langle |E_i|^2 \rangle,$$

where  $N$  is the number of solute molecules per unit volume,  $(\partial \mu / \partial Q)_0$  is the dipole moment derivative of the solute molecule,  $\rho$  is the density of energy of radiation, and  $\langle |E_i|^2 \rangle$  represents the time-average value of the square of the internal electric field strength. We derived Eq. (1) from the probability of a fundamental transition by the harmonic oscillator in a bath of radiation of density  $\rho(E_i)$ .<sup>3</sup> The energy absorbed, on the other hand, is equal to the work done by the electric field, and according to electromagnetic theory this work can be expressed by the product of the electric field and the polarization. In the present case, the electric field applied to the harmonic oscillator is the internal field  $E_i$ , and the polarization must be the polarization of the solute  $P_0$ , because  $dW$  in

Eq. (1) arises from the resonance of solute molecules with  $E_i$ . Thus  $dW$  can be written as

$$dW = E_i \cdot dP_0 \cdot dV \cdot d\nu. \quad (2)$$

By using  $E_i = E_i^0 \exp(-i\omega t)$ , where  $\omega = 2\pi\nu$ , and the relation of  $P_0 = \hat{C}_0 \cdot E_i$ , where  $\hat{C}_0 (= C_0' + iC_0'')$  is the local susceptibility<sup>2</sup> of the solute, Eq. (2) becomes

$$dW = \omega \langle |E_i|^2 \rangle \cdot C_0'' \cdot dt \cdot dV \cdot d\nu. \quad (3)$$

By introducing some suitable model for the internal field,  $C_0''$  can be expressed in terms of the measurable quantities of the solution; the refractive index  $n$ , and the absorption coefficient  $\kappa$ . We chose the Lorentz model<sup>4</sup> which is described as

$$E_i = E + \frac{4\pi P}{3}, \quad (4)$$

with

$$P = P_v + P_0,$$

where  $E$  is the external field and  $P_v$  is the polarization of the solvent. Equation (4) is derived by calculating the field within a microscopic spherical cavity in the dielectric medium of the solution. Therefore,  $P$  in Eq. (4) should be the polarization of the solution, and then  $P = \hat{\chi} \cdot E$ , where  $\hat{\chi} (= \chi' + i\chi'')$  is the complex susceptibility of the solution. If Eq. (4) is employed,  $\hat{C}_0$  becomes

$$\hat{C}_0 = \frac{\hat{\chi} - \hat{\chi}_v}{1 + (4\pi/3) \cdot \hat{\chi}}, \quad (5)$$

where  $\hat{\chi}_v = P_v/E$ . The real and imaginary parts of  $\hat{\chi}$  are expressed in terms of  $n$  and  $\kappa$  as follows, respectively:

$$\chi' = \frac{1}{4\pi} \cdot (n^2 - k^2 - 1), \quad (6)$$

$$\chi'' = \frac{c\kappa}{4\pi\omega},$$

where  $k = c\kappa/2\omega$ , and  $c$  is the light velocity *in vacuo*. Similar relations hold for  $\hat{\chi}_v$ . Since the energy absorbed by the solvent is neglected,  $\chi_v''$  becomes zero, while  $\chi_v' = (n_v^2 - 1)/4\pi$ , where  $n_v$  is the refractive index arising from the solvent molecules. Then, substituting Eq. (6) into Eq. (5) yields

$$C_0'' = \frac{3c}{4\pi\omega} \cdot \frac{n \cdot \kappa(n_v^2 + 2)}{(n^2 - k^2 + 2)^2 + 4n^2k^2}. \quad (7)$$

On substituting Eq. (7) into Eq. (3), and by comparison with Eq. (1), the following expression can be drawn:

$$\frac{1}{N} \int \frac{3\kappa n_v^2 + 2}{(n^2 - k^2 + 2)^2 + 4n^2 k^2} \cdot d\nu = \frac{\pi}{3c} \cdot \left( \frac{\partial \mu}{\partial Q} \right)_0^2, \quad (8)$$

where the integration is carried out over the entire band. The left-hand side of Eq. (8) gives the new corrected integrated absorption coefficient, and it can be written as follows for dilute solutions, since  $n \doteq n_v$  and  $k \doteq 0$ :

$$A_{\text{cor}}(\text{Present}) = \frac{3n_v}{n_v^2 + 2} \cdot A_{\text{obs}},$$

with (9)

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

### B. Classical damped oscillator model

Let us suppose a solute molecule to be a classical single-resonance damped oscillator whose charge and mass are  $e$  and  $m$ , respectively. The equation of motion is

$$\ddot{\mathbf{x}} + 2\gamma\dot{\mathbf{x}} + \omega_0^2\mathbf{x} = \frac{e}{m} \mathbf{E}_i, \quad (10)$$

where  $\gamma$  is the damping constant, and  $\omega_0$  is the molecular resonance angular frequency. The polarization arising from the displacement  $\mathbf{x}$  is that of the solute  $\mathbf{P}_0$ . Then

$$\mathbf{P}_0 = N \cdot e \cdot \mathbf{x}. \quad (11)$$

Substituting Eq. (11) into Eq. (10) yields

$$\ddot{\mathbf{P}}_0 + 2\gamma\dot{\mathbf{P}}_0 + \omega_0^2 \cdot \mathbf{P}_0 = \frac{Ne^2}{m} \mathbf{E}_i. \quad (12)$$

The solution of Eq. (12) is  $\mathbf{P}_0 = \hat{C}_0 \cdot \mathbf{E}_i$ , where

$$\hat{C}_0 = \frac{Ne^2}{m} \cdot \frac{1}{\omega_0^2 - \omega^2 - i2\gamma\omega}. \quad (13)$$

If the Lorentz internal field is employed, the imaginary part of  $\hat{C}_0$  is given by Eq. (7). Comparison of the imaginary part of Eq. (13) with Eq. (7) indicates that

$$\frac{3\kappa n(n_v^2 + 2)}{(n^2 - k^2 + 2)^2 + 4n^2 k^2} = \frac{Ne^2}{mc} \cdot \frac{8\pi\gamma\omega^2}{(\omega_0^2 - \omega^2)^2 + (2\gamma\omega)^2}, \quad (14)$$

where  $e^2/m$  can be replaced by  $1/3 \cdot (\partial \mu / \partial Q)_0^2$ .<sup>5</sup> The integration of Eq. (14) over the entire band under the approximation of  $\omega \doteq \omega_0$  leads to the new equations, Eqs. (8) and (9).

### III. DISCUSSION

According to Warner and Wolfsberg,<sup>6</sup>  $n_v^2$  in Eq. (8) can be expressed as

$$n_v^2 = 1 + \frac{4\pi N_v \cdot \alpha_b}{1 - 4\pi N_v \cdot \alpha_b / 3}, \quad (15)$$

where  $N_v$  is the number of solvent molecules per unit volume, and  $\alpha_b$  is a constant background contribution to the polarizability of the solvent molecule arising from off-resonance terms. Thus when  $N_v = 0$  (the pure liquid solute), Eq. (8) becomes

$$\frac{1}{N} \int \frac{9\kappa n}{(n^2 - k^2 + 2)^2 + 4n^2 k^2} \cdot d\nu = \frac{\pi}{3c} \cdot \left( \frac{\partial \mu}{\partial Q} \right)_0^2. \quad (16)$$

The left-hand side is identical to the PW equation.

When Eq. (16) is applied to dilute solutions, the result is

$$A_{\text{cor}}(\text{PW}) = \frac{9n_v}{(n_v^2 + 2)^2} A_{\text{obs}}. \quad (17)$$

It is interesting to clarify why the difference between Eqs. (9) and (17) occurs. Equation (17) can be derived by using  $\mathbf{P}$  (solution) instead of  $\mathbf{P}_0$  (solute) as the polarization. Then,  $dW$  is given by

$$dW = \mathbf{E}_i \cdot d\mathbf{P} \cdot dV \cdot d\nu. \quad (18)$$

Similar derivation as before is possible by the use of  $\mathbf{P} = \hat{C} \cdot \mathbf{E}_i$ , where  $\hat{C}$  is the local susceptibility of the solution, and Eq. (3) is changed to

$$dW = \omega \langle |\mathbf{E}_i|^2 \rangle C'' \cdot dt \cdot dV \cdot d\nu. \quad (19)$$

If the Lorentz internal field is used, the imaginary part of  $\hat{C}$  is written as follows:

$$C'' = \frac{9c}{4\pi\omega} \cdot \frac{n\kappa}{(n^2 - k^2 + 2)^2 + 4n^2 k^2}. \quad (20)$$

On substituting Eq. (20) into Eq. (19), and by comparison with Eq. (1), one obtains the PW equation. In the case of the damped oscillator model, one has in place of Eq. (12):

$$\ddot{\mathbf{P}} + 2\gamma\dot{\mathbf{P}} + \omega_0^2 \cdot \mathbf{P} = \frac{Ne^2}{m} \cdot \mathbf{E}_i. \quad (21)$$

Correspondingly, Eq. (13) is changed to

$$\hat{C} = \frac{Ne^2}{m} \cdot \frac{1}{\omega_0^2 - \omega^2 - i2\gamma\omega}. \quad (22)$$

The imaginary part of Eq. (22) is combined with Eq. (20) to yield the PW equation.

Therefore, it can be concluded that the difference between  $A_{\text{cor}}(\text{Present})$  and  $A_{\text{cor}}(\text{PW})$  comes from whether  $\mathbf{P}$  or  $\mathbf{P}_0$  is employed as the polarization. It is reasonable to use  $\mathbf{P}_0$  instead of  $\mathbf{P}$ , because the energy concerned is that absorbed by the solute molecules. On the other hand, in the case of Eqs. (18) and (21), the solution must be supposed to be made up of certain imaginary "solution molecules" whose number per unit volume is  $N$ . These results indicate that the new equation presented is preferable to the PW equation for solutions. However, experimental tests are necessary to confirm fully this interesting conclusion.

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