Dielectric models for solvent effects on electronic spectra[*]

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The effect of solvent dielectric constant on the frequency shifts and intensity of the electronic absorption spectrum of a dissolved molecule is investigated using Wertheim's dielectric model. The results show significant differences from those based on use of the Lorentz–Lorenz and Onsager–Böttcher continuum theories, as well as from the results of a lattice model recently considered by Fulton.

I. INTRODUCTION

In a recent paper[1] we have studied the dependence of light scattering intensities on the dielectric constant of a nonpolar fluid as predicted by several "local-field" models for dielectric properties. It was found that Wertheim's[2] model led to better agreement with experiment than the results obtained with either the Lorentz–Lorenz or Onsager–Böttcher models. It is of interest to compare the predictions of these dielectric models in a related application, namely, the influence of the solvent on the electronic absorption spectrum of an impurity solute molecule.

Most previous investigations[3-7] have examined solvent effects using Onsager's dielectric continuum theory. An exception to this is the recent work of Fulton,[8] which takes account of the microscopic structure of the medium by modeling the solution as a rigid cubic lattice whose sites are occupied by solvent and solute molecules. An analogous microscopic treatment in the case of a real liquid is much more difficult to carry out, owing to the occurrence of fluctuations in the positions of the molecules. Hence we restrict our analysis to a comparison of previous results with those derived using Wertheim's[2] approximate local-field model, which we believe[1] to be more realistic than other continuum theories.

II. THEORY

We consider a system composed of one impurity solute molecule dissolved in a solvent of dielectric constant ϵ_s. Near an isolated resonance the polarizability $\alpha_u(\omega)$ of the solute molecule, assumed isotropic, is of the form[8,9]

$$\alpha_u(\omega) = \alpha_b + \frac{e^2 f_0/m}{\omega_0^2 - \omega^2 - i\gamma\omega} \,, \tag{1}$$

where f_0 is the oscillator strength of the transition having resonance frequency ω_0; e and m are, respectively, the electron charge and mass; γ is a damping factor; and α_b is the background contribution of other transitions.

The various local-field models (Lorentz–Lorenz, Onsager–Böttcher, Wertheim) are based on a continuum approximation of surrounding the solute molecule by a homogeneous medium characterized by the dielectric constant ϵ_s. These models differ in the constraints imposed on the "local electric field" acting on the molecule due to the surrounding continuum.[1] In the presence of an external electric field $\mathbf{E}_0(\omega)$, the average dipole moment $\bar{\mu}(\omega)$ induced in the solute is given according to these models by the general expression

$$\bar{\mu}(\omega) = \alpha_u(\omega)[\mathbf{E}_L(\omega) + b\bar{\mu}(\omega)] \,, \tag{2}$$

which can be written

$$\bar{\mu}(\omega) = \alpha_u'(\omega)\mathbf{E}_L(\omega) \,, \tag{3}$$

where

$$\alpha_u'(\omega) = \frac{\alpha_u(\omega)}{1 - b\alpha_u(\omega)} \,. \tag{4}$$

Apart from a change in the sign of b, we have followed earlier notation.[1] By analogy with the Onsager–Böttcher model, the electric field $\mathbf{E}_L(\omega)$ may be interpreted as the "cavity field," i.e., the field at the position of the solute dipole resulting from modification of the external field $\mathbf{E}_0(\omega)$ by the surrounding solvent medium. The factor $b\bar{\mu}(\omega)$ in Eq. (2) represents the "reaction field," i.e., the field due to polarization of the surroundings by the dipole moment $\bar{\mu}(\omega)$.

Using Eqs. (1) and (4), we obtain

$$\alpha_u'(\omega) = \alpha_b' + \frac{1}{(1+b\alpha_b)^2}\left(\frac{e^2 f_0/m}{\omega_s^2 - \omega^2 - i\gamma\omega}\right) \,, \tag{5}$$

where

$$\omega_s^2 = \omega_0^2 - \frac{be^2 f_0/m}{1 - b\alpha_b} \,, \tag{6}$$

and $\alpha_b' = \alpha_b/(1 - b\alpha_b)$. The "cavity field" $\mathbf{E}_L(\omega)$ does not depend on the properties of the solute dipole. Thus Eqs. (3) and (5) show that ω_s is the effective resonance frequency of the absorbing molecule in solution. Since $\omega_s^2 - \omega_0^2 \approx 2\omega_0(\omega_s - \omega_0) \equiv 2\omega_0\Delta\omega$, the frequency shift may be written

$$\Delta\omega = -\frac{e^2 f_0}{2m\omega_0}\left(\frac{b}{1 - b\alpha_b}\right) \,. \tag{7}$$

The absorption intensity in solution may be determined from the energy transferred to the solute dipole. Since $\mathbf{E}_L(\omega)$ is the field at the dipole due to modification of the external field by the solvent continuum, an elementary calculation[10] gives for the absorption cross section $\sigma(\omega)$

$$\begin{aligned}\sigma(\omega) &= \frac{4\pi\omega}{c}\left|\frac{E_L(\omega)}{E_0(\omega)}\right|^2 \operatorname{Im}\alpha_u'(\omega)\\ &= \frac{4\pi e^2 f_0}{mc}\left|\frac{E_L(\omega)}{E_0(\omega)}\right|^2 \frac{1}{(1-b\alpha_b)^2}\left(\frac{\omega^2\gamma}{(\omega_s^2-\omega_0^2)^2+\omega^2\gamma^2}\right) \,,\end{aligned} \tag{8}$$

where c is the vacuum speed of light. The field $\mathbf{E}_L(\omega)$ may be related to the Maxwell field $\mathbf{E}(\omega)$ in the medium

TABLE I. Solvent effects according to local-field models.

	Lorentz–Lorenz	Onsager–Böttcher[b]	Wertheim[c]
H	$\frac{\epsilon_s+2}{3}$	$\frac{3\epsilon_s}{2\epsilon_s+1}$	$1/q(-\xi)$
b	0	$\frac{2(\epsilon_s-1)}{(2\epsilon_s+1)}\frac{1}{R_u^3}$	$16\xi/R_u^3$
$\Delta\omega/k$[a]	0	$\left(\frac{n_b^2+2}{3}\right)\left(\frac{\epsilon_s-1}{2\epsilon_s+n_b^2}\right)$	$\frac{8\xi}{1-16\xi\alpha_b/R_u^3}$
A_s/A_g	$\frac{1}{n_s}\left(\frac{\epsilon_s+2}{3}\right)^2$	$\frac{1}{n_s}\left(\frac{2+n_b^2}{2+n_b^2/\epsilon_s}\right)$	$\frac{1}{n_s}\{q(-\xi)[1-16\xi\alpha_b/R_u^3]\}^{-2}$

[a] $k=-e^2f_0/m\omega_0R_u^3$.

[b] n_b^2 is defined by Eq. (13).

[c] ϵ_s and ξ are related by Eq. (14).

by the expression

$$\mathbf{E}_L(\omega)=H\mathbf{E}(\omega)\ , \tag{9}$$

where H is a function of the solvent dielectric constant ϵ_s whose form depends on the local-field model being considered. Using the result[1,4]

$$\left|\frac{E(\omega)}{E_0(\omega)}\right|^2=\frac{1}{n_s}\quad , \tag{10}$$

where $n_s=\epsilon_s^{1/2}$ is the solvent refractive index, we obtain for the integrated cross section $A_s\equiv\int_0^\infty d\omega\sigma(\omega)$,

$$A_s=\frac{2\pi^2e^2f_0}{mc}\,\frac{1}{n_s}\left(\frac{H}{1-b\alpha_b}\right)^2\quad . \tag{11}$$

The vapor phase result for the integrated cross section A_g of the solute is found by letting $\epsilon_s\to 1$. In this limit, $b\to 0$ and $H\to 1$; hence the ratio of solution and gas phase cross sections is

$$A_s/A_g=\frac{1}{n_s}\left(\frac{H}{1-b\alpha_b}\right)^2\quad . \tag{12}$$

The expressions for the frequency shift, Eq. (7), and for the intensity ratio, Eq. (12), are the central results of this analysis. These results are in a form that permits comparison of the various local-field models. Explicit expressions for the functions H and b are collected in Table I, along with the resulting expressions for $\Delta\omega$ and A_s/A_g. We draw attention to the following: (1) The parameter b is zero in the Lorentz–Lorenz model, so that this model does not predict a frequency shift. The corresponding expression for the intensity ratio A_s/A_g agrees with the result of Chako[3] and Polo and Wilson.[4] (2) We define the "internal" refractive index n_b of the solute by

$$\frac{n_b^2-1}{n_b^2+2}=\frac{\alpha_b}{R_u^3}\ , \tag{13}$$

where R_u is the solute "cavity radius." The resulting expression for A_s/A_g in the Onsager–Böttcher model agrees with Person's[5] result, while in the case $n_b^2=1$ ($\alpha_b=0$) the result for $\Delta\omega$ agrees with that obtained by Bayliss.[6] (3) The variation of $\Delta\omega$ and A_s/A_g in Wertheim's model with the solvent dielectric constant ϵ_s can be determined by inverting the relations[2]

$$\epsilon_s=q(2\xi)/q(-\xi),\quad q(\xi)=\frac{(1+2\xi)^2}{(1-\xi)^4}\ , \tag{14}$$

to give ξ and $q(-\xi)$ as functions of ϵ_s. These results are discussed in the following section.

III. DISCUSSION

For the case $\alpha_b=0$, Wertheim's model gives $\Delta\omega/k=8\xi$. This is plotted as a function of the "Bayliss parameter" $y\equiv[(\epsilon_s-1)/(2\epsilon_s+1)]$ in Fig. 1, on the curve marked W. The corresponding result in the Onsager–Böttcher model is $\Delta\omega/k=y$, shown by the dashed line in Fig. 1. As y increases, there is an increasing positive deviation of 8ξ from the value y. By inverting Eq. (14), we find for small y

$$8\xi=y+\tfrac{17}{32}y^2+\tfrac{509}{64}y^3+\cdots\quad . \tag{15}$$

As $\epsilon_s\to\infty$, y attains the limiting value of $\frac{1}{2}$, whereas Eq. (14) shows that 8ξ approaches its maximum value of 4 in this limit.

For $\alpha_b>0$, the behavior of $\Delta\omega/k$ in Wertheim's model is similar to that for the case $\alpha_b=0$, with the deviation $(\Delta\omega/k-y)$ at fixed y increasing as α_b increases. For $\alpha_b=0$, the Onsager–Böttcher model also predicts a positive deviation from the Bayliss result $\Delta\omega/k=y$, although showing less dispersion as a function of α_b than does Wertheim's model. One should note that for $(\alpha_b/R_u^3)\gtrsim 1/8$, both $\Delta\omega/k$ and A_s/A_g in Wertheim's model diverge as ξ approaches the value $(16\alpha_b/R_u^3)^{-1}$. Restricting ourselves to values of $\xi\le(16\alpha_b/R_u^3)^{-1}$, for given α_b we find $(\Delta\omega/k)$ (Wertheim) > $(\Delta\omega/k)$ (Onsager).

This behavior of the frequency shift in Wertheim's model differs significantly from the predictions of Fulton's lattice calculation.[8] The present results for $\Delta\omega/k$ may be compared with Eq. (70) in Ref. 8, upon identifying Fulton's parameters d^2 and v (volume of primitive cell) with $e^2f_0/2m\omega_0$ and $4\pi R_u^3/3$, respectively. For given α_b, $(\Delta\omega/k)$ (Fulton) < $(\Delta\omega/k)$ (Onsager), while as a

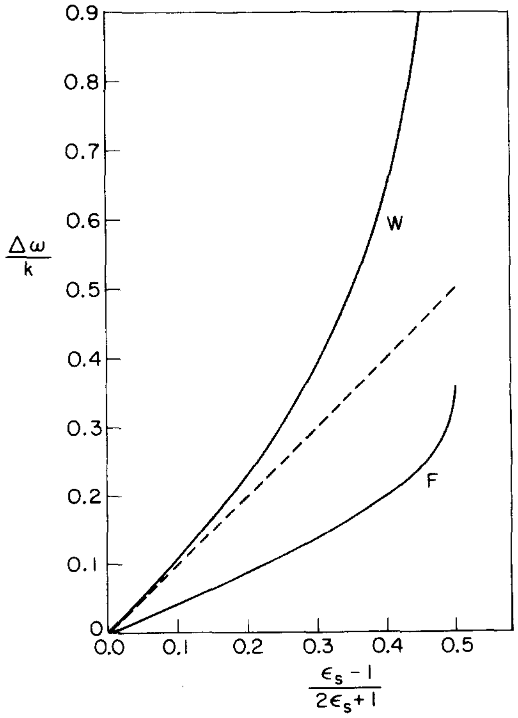

FIG. 1. Frequency shifts according to Wertheim's model (W) and Fulton's model (F), for $\alpha_b=0$, as functions of the Bayliss parameter $(\epsilon_s-1)/(2\epsilon_s+1)$. Straight dashed line of unit slope is the prediction of the Onsager–Böttcher model.

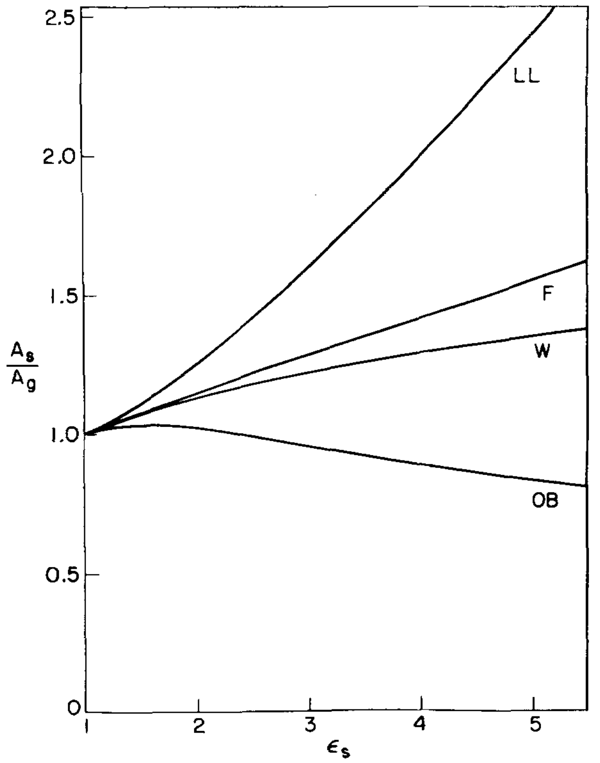

FIG. 2. Ratio of solution to gas phase integrated intensities as functions of solvent dielectric constant, for $\alpha_b = 0$, as given by the models Lorentz–Lorenz (LL), Fulton (F), Wertheim (W), Onsager–Böttcher (OB).

function of α_b Fulton's result for $\Delta\omega/k$ shows less dispersion than does the Onsager–Böttcher approximation.[8] This contrasting behavior of the frequency shift if Fulton's model for the case $\alpha_b = 0$ is shown in Fig. 1, on the curve marked F.

As Fulton[8] has observed concerning his results, for small ranges of ϵ_s the relation between $\Delta\omega$ and y in Wertheim's model is approximately linear, although a linear extrapolation of the curves back to $y = 0$ does not pass through the origin. Such behavior is often observed experimentally.[11,12] However, quantitative comparison between experiment and the theoretical results discussed here hinges on determining the parameters R_u and α_b, which cannot be specified unambiguously.

When $\alpha_b = 0$, the relative behavior of the three local-field model predictions for the absorption intensity ratio A_s/A_g is similar to that found previously[1] for light scattering intensities. For all ϵ_s we find

$$(A_s/A_g)\,(\text{Lorentz}) > (A_s/A_g)\,(\text{Wertheim}) > (A_s/A_g)\,(\text{Onsager}) .$$

Curves of (A_s/A_g) as functions of ϵ_s, with $\alpha_b = 0$, are displayed in Fig. 2. When $\alpha_b > 0$, the trend (A_s/A_g) (Wertheim) > (A_s/A_g) (Onsager) is maintained, although for low values of ϵ_s one or both of these can exceed (A_s/A_g) (Lorentz). As $\epsilon_s \to \infty$, these functions behave asymptotically as

$$(A_s/A_g)\,(\text{Lorentz}) \to n_s^3/q \,, \tag{16a}$$

$$(A_s/A_g)\,(\text{Onsager}) \to \left(\frac{n_b^2+2}{2}\right)^2 \frac{1}{n_s} \,, \tag{16b}$$

while using Eq. (14),

$$(A_s/A_g)\,(\text{Wertheim}) \to \frac{81}{2^{16/3}(1-8\alpha_b/R_u^3)^2} n_s^{1/3} \,. \tag{16c}$$

For $\alpha_b = 0$, these results for (A_s/A_g) are compared in Fig. 2 with those derived by Fulton.[8] The latter agree most closely with the results given by Wertheim's model for the moderate values of ϵ_s considered; however, (A_s/A_g) according to Fulton's evaluation grows as n_s^3 for large n_s, similar to the behavior of the Lorentz–Lorenz model.

The differences between the predictions of the local-field models, in particular Wertheim's model, and Fulton's lattice model may be attributed to the approximate nature of the former and to the different physical situations described. At low to moderate solvent densities we expect that fluid translational fluctuations, which are partially accounted for in Wertheim's model, should lead to differences from a model based on a rigid lattice structure for the solution. At high solvent densities, presumably corresponding to high values of ϵ_s, the fluid structure should more closely resemble that of a close-packed solid and the predicted behavior approach that discussed by Fulton. (In this regard, it should be noted that the numerical results presented in Ref. 8 involve several approximations which affect the high ϵ_s behavior.)[13] In a real fluid, however, the behavior at high density is probably more sensitive to a number of unaccounted effects (e.g., short-range overlap) which diminish the validity of the model considered here and in Ref. 8, employing point dipoles with constant polarizabilities.

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