

The experimental and theoretical expressions for the molecular electronic oscillator strength in solution

Takehiro Abe and Idowu Iweibo

Citation: *The Journal of Chemical Physics* **83**, 1546 (1985); doi: 10.1063/1.449390

View online: <http://dx.doi.org/10.1063/1.449390>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/83/4?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Experimental and theoretical study on generalized oscillator strengths of the valence-shell electronic excitations in CF₄](#)

J. Chem. Phys. **134**, 064307 (2011); 10.1063/1.3549135

[Comments on "The effect of solvent environment on molecular electronic oscillator strengths"](#)

J. Chem. Phys. **77**, 1074 (1982); 10.1063/1.443911

[The effect of solvent environment on molecular electronic oscillator strengths](#)

J. Chem. Phys. **73**, 5314 (1980); 10.1063/1.439961

[Determination of Generalized Oscillator Strengths for Molecular Hydrogen by Electron Impact](#)

J. Chem. Phys. **40**, 1222 (1964); 10.1063/1.1725301

[Solution Spectra and Oscillator Strengths of Electronic Transitions of Pyridine and Some Monosubstituted Derivatives](#)

J. Chem. Phys. **22**, 1077 (1954); 10.1063/1.1740268



The experimental and theoretical expressions for the molecular electronic oscillator strength in solution

Takehiro Abe and Idowu Iweibo^{a)}

College of General Education, Tohoku University, Kawauchi, Sendai 980, Japan

(Received 1 October 1984; accepted 6 May 1985)

In this paper we propose the appropriate fundamental definition of the oscillator strength in solution and clearly show that both the experimental and theoretical expressions of the oscillator strength should contain refractive index correction factors of α and β , respectively. Therefore, in the discussion of the solvent effects on the oscillator strength the experimental and theoretical expressions containing the correction factors should be used instead of the usual expressions of $\alpha = 1$ and $\beta = 1$.

I. INTRODUCTION

In many published pieces of research work in the literature there appears to be no uniformity in the application of a refractive index correction factor in the calculation of the oscillator strengths of electronic transitions from the experimentally determined molar absorption coefficient integrals of a solute in solution. Nor is there a definitive picture as to the form that the refractive index correction factor should assume in the theoretical expression for the oscillator strength.

Recently, Abe¹ and Birge² in their comments have argued on different aspects of the experimental and theoretical expressions for the solvent effects on molecular electronic oscillator strengths. For the transition from the ground state to the i th excited state in a solute molecule, the following equations have been proposed for the experimental and theoretical oscillator strengths in solution:

$$f^{\text{exp}}(\text{soln}) = \alpha \times \frac{10^3(\ln 10)m_e c^2}{\pi e^2 N_A} \int \epsilon(\tilde{\nu}) d\tilde{\nu} \quad (1)$$

and

$$f^{\text{theor}}(\text{soln}) = \beta \times \frac{8\pi^2 m_e c}{3\hbar e^2} \times \tilde{\nu}_{oi} |\mu_{oi}(\text{soln})|^2, \quad (2)$$

where α and β are the refractive index correction factors, c is the speed of light in vacuum, \hbar the Planck constant, e the charge of proton, m_e the mass of electron, and N_A the Avogadro constant. Here $\tilde{\nu}_{oi}$ is the wave number of the transition energy $\epsilon(\tilde{\nu})$, the molar absorption coefficient at wave number $\tilde{\nu}$, and $\mu_{oi}(\text{soln})$ the transition moment of the solute in a solution. We denote the refractive index of solvent by n . Abe^{1,3} has proposed $\alpha = 1/n^2$ and $\beta = (1/n^2)[3n^2/(2n^2 + 1)]^2$, while Myers and Birge^{2,4} have proposed $\alpha = 1$. Their β value corresponds to a complicated expression of the term in brackets involving a vector sum of individual molecule transition moments in Eq. (17) of Ref. 4, which comes from the transition moment for the composite system in the direction of the original solute transition moment. Apparently, the difference between their α values lies in whether or not the experimental expression contains the refractive index correction factor. Of course, Eq. (1) with $\alpha = 1$ is usually used as the experimental expression for the oscillator strength in solu-

tion, although Eq. (1) with $\alpha = 1/n$ has recently been used.^{5,6}

Hitherto, many theories have been presented for the solvent effects on the oscillator strength in solution.⁷⁻¹² However, no experimental and theoretical expressions, based on the fundamental definition of the oscillator strength in solution, have been derived and discussed. The argument between Abe and Birge seems to originate from the absence of such a complete discussion. In view of the well-known importance of the oscillator strength as a measure of the intensity of an electronic absorption transition, we attempt in this paper to provide conclusive argument that the experimental and theoretical expressions for the oscillator strength in solution should contain correction factors involving solvent macroscopic parameters on the basis of the fundamental definition of the oscillator strength.

II. DISCUSSION

A. Definition

According to Birge,² Myers and Birge⁴ have chosen to define the experimental oscillator strength by Eq. (1) with $\alpha = 1$ for the following two reasons: (i) Introducing solvent corrections directly into the experimental data is contrary to common practice and can lead to considerable confusion. (ii) It would be more logical to use the refractive index of the solute to adjust the velocity of the photon inside the cavity. Equation (1) is, however, clearly not a fundamental definition, because even Eq. (1) with $\alpha = 1$ for the vapor is derived from a definition as described below. As is well known, the amount of energy (W_{oi}) absorbed in unit time by the transition from the ground state to the i th excited state in the absorbing molecule is given by $B_{oi} \rho(\nu) h\nu$, where B_{oi} is the Einstein transition probability coefficient of the absorbing molecule and $\rho(\nu)$ is the radiation energy density of the exciting light of frequency ν in the solution. Here ν is the transition energy in the unit of frequency. We write the corresponding amount of energy (W_h) absorbed as $[B_h \rho(\nu)]_{\text{harm}} h\nu$ for a transition of a three-dimensional isotropic harmonic oscillator, in which the vibrational quantum changes from 0 to 1 owing to the transition. Then the oscillator strength is most fundamentally defined by the ratio of the amounts of energies absorbed as

^{a)} Permanent address: Department of Chemistry, University of Ibadan, Ibadan, Nigeria.

$$f \equiv \frac{W_{oi}}{W_h} = \frac{B_{oi} \rho(\nu)}{[B_h \rho(\nu)]_{\text{harm}}} \quad (3)$$

According to Eq. (3), the oscillator strength of the gaseous absorbing system is directly obtained as

$$f(\text{vap}) = \frac{B_{oi}(\text{vap})}{B_h(\text{vap})}, \quad (4)$$

because the energy density of $\rho_0(\nu)$ in vapor, i.e., approximately in vacuum is common to the denominator and numerator of Eq. (3) in this case. In Eq. (4) $B_{oi}(\text{vap})$ and $B_h(\text{vap})$ are the Einstein coefficients of the absorbing molecule and the harmonic oscillator, respectively, in vapor. Here, $B_h(\text{vap})$ is given by $\pi e^2 / h c m_e \tilde{\nu}_{oi}$ for the $0 \rightarrow 1$ harmonic oscillator transition, because the harmonic oscillator is defined to have the vibrational frequency equal to the frequency of the electronic transition in question.¹³ Either Eqs. (3) or (4) is written as the definition of the oscillator strength in recent books.

In the case of the oscillator strength for solution, there are two ways of choosing $[B_h \rho(\nu)]_{\text{harm}}$ in Eq. (3). If one assumes that the harmonic oscillator is always in vapor, one may define the oscillator strength for solution by

$$f(\text{soln}) = \frac{B_{oi}(\text{soln}) \rho(\nu)}{B_h(\text{vap}) \rho_0(\nu)}. \quad (5)$$

If one assumes that the harmonic oscillator is immersed in the same solvent as the solute molecule is, one may define the oscillator strength by

$$f(\text{soln}) = \frac{B_{oi}(\text{soln})}{B_h(\text{soln})}, \quad (6)$$

because $\rho(\nu)$ is common to the denominator and numerator of Eq. (3) in the latter case. Of course, $B_h(\text{soln})$ is the probability coefficient of the harmonic oscillator in the solvent. In this case one must reasonably assume that both the solute and the harmonic oscillator experience the same effective field in solution and hence that $B_h(\text{soln})$ contains the same refractive index correction factor as does $B_{oi}(\text{soln})$. Accordingly, the oscillator strength defined by Eq. (6) will always lack an electric field-dependent refractive index correction factor. According to Eq. (6), therefore, the definition of oscillator strength may differ with the solvent, because, by definition, $B_h(\text{soln})$ is solvent dependent. In this case, therefore, the comparison of the oscillator strengths measured in various solvents will be meaningless. On the other hand, Eq. (5) shows that the ratio of the oscillator strength in, e.g., two solvents corresponds to that of the $B_{oi}(\text{soln}) \rho(\nu) \tilde{\nu}_{oi}$ values for these solvents, because $B_h(\text{vap})$ is equal to $\pi e^2 / h c m_e \tilde{\nu}_{oi}$ and $\rho_0(\nu)$ may be regarded as being approximately constant in the optical region. The transition energy of frequency ν does not differ so remarkably with the solvent. This is the reason for the nearly constant $\rho_0(\nu)$ value. Then, if the values of $\tilde{\nu}_{oi}$ are replaced by those of $\nu_{oi} = c \tilde{\nu}_{oi}$, the ratio of the oscillator strengths [$B_{oi}(\text{soln}) \rho(\nu) \tilde{\nu}_{oi}$ values] will give the ratio of the amounts of energies absorbed in unit time by the transitions. Thus, we propose to choose Eq. (5) as the fundamental definition of the oscillator strength in solution.

Here $\rho(\nu)$ is given by

$$\rho(\nu) = \frac{\epsilon_r(\nu)}{8\pi} E^2, \quad (7)$$

where E is the electric field of the light of frequency ν in the solution and $\epsilon_r(\nu)$ equal to n^2 is the relative permittivity of the solvent at ν . We denote the corresponding field in vacuum by E_0 . Then one obtains $\rho_0(\nu) = E_0^2 / 8\pi$. In order to obtain the ratio of $\rho(\nu) / \rho_0(\nu)$ in Eq. (5), it is now necessary to relate E to E_0 . For the light moving in a transparent solvent we, for convenience, assume a plane-polarized electromagnetic wave consisting of an x component (E_x) of the electric field and a y component (H_y) of the magnetic field. For the wave moving in air, i.e., approximately in vacuum we denote the corresponding components by E_{0x} and H_{0y} . We assume that the wave travels in the direction of z increasing from air to the solvent, where the two media are separated by a plane boundary taken parallel to the xy plane. Considering the reflection and refraction of the incident wave at the boundary, one obtains at normal incidence the relation¹⁴ given by

$$\gamma = \frac{E_x}{E_{0x}} = \frac{2}{1+n}. \quad (8)$$

In this case, the intensity of the reflected wave is generally much smaller than that of the incident wave.¹⁴ In order to obtain an expression simpler than Eq. (8), therefore, we approximately neglect the reflected wave. The neglect of the reflected wave independently gives two relations; one is

$$\frac{E_x}{E_{0x}} = \frac{1}{n}, \quad (9)$$

with $H_y = H_{0y}$ and the other is $E_x / E_{0x} = 1$ with $H_y = (1/n) H_{0y}$. Here we choose only Eq. (9), because the exact expression of Eq. (8) contains the refractive index factor. From the conservation of the energy fluxes for only the incident and refracted waves, another approximate relation is obtained as

$$\frac{E_x}{E_{0x}} = \frac{1}{n^{1/2}}. \quad (10)$$

In a few papers,^{8,15} Eq. (10) is used in the discussion of the solvent effects on the oscillator strength. Substitution of numerical values for n into the approximate expressions of Eqs. (9) and (10) and the exact expression of Eq. (8) shows that Eq. (10) is a better approximation than Eq. (9). Using Eqs. (7) and (8), one may write Eq. (5) as

$$f(\text{soln}) = n^2 \gamma^2 \times \frac{B_{oi}(\text{soln})}{B_h(\text{vap})}, \quad (11)$$

where $\gamma = 2/(1+n)$. When one uses the approximate expressions of Eqs. (9) and (10) instead of Eq. (8), one must use $\gamma = 1/n$ and $\gamma = n^{-1/2}$, respectively. Using Eq. (11), we will discuss further under the following subsections.

B. Experimental expression

When $B_{oi}(\text{vap})$ is obtained by the use of the Lambert-Beer law on the assumption of $n = 1$, Eq. (1) with $\alpha = 1$ is derived, as is well known, as the experimental oscillator strength in vapor from Eq. (4). When $B_{oi}(\text{soln})$ is obtained by using the Lambert-Beer law in the same way as $B_{oi}(\text{vap})$ is, one obtains the following same equation that Strickler and Berg¹⁶ have already obtained:

$$B_{oi}^{\text{exp}}(\text{soln}) = \frac{10^3(\ln 10)}{hN_A} \times \frac{c}{n} \int \frac{\varepsilon(\nu)}{\nu} d\nu. \quad (12)$$

The factor of c/n in Eq. (12) comes from obtaining the number of solute molecules excited per unit time with energy $h\nu$. Here $\varepsilon(\nu)$ is the molar absorption coefficient in solution at frequency ν . By putting Eq. (12) into Eq. (11), one may obtain the experimental expression of the oscillator strength in solution. Here we consider spectral linewidths for $B_{oi}^{\text{exp}}(\text{soln})$ as is done for the experimental Einstein coefficient in vapor. From Eq. (12) one obtains

$$\frac{dB_{oi}^{\text{exp}}(\text{soln})}{d\nu} = \frac{10^3(\ln 10)}{hN_A} \times \frac{c}{n} \times \frac{\varepsilon(\nu)}{\nu}. \quad (13)$$

Then, considering the spectral linewidths for Eq. (11) into which Eq. (12) is inserted, one may write the experimental expression of the oscillator strength in solution with the use of Eq. (13) as follows:

$$\begin{aligned} f^{\text{exp}}(\text{soln}) &= \int \left(\frac{df}{d\nu} \right) d\nu \\ &= \int \frac{n^2 \gamma^2}{B_h(\text{vap})} \left(\frac{dB_{oi}^{\text{exp}}(\text{soln})}{d\nu} \right) d\nu \\ &= (n\gamma^2) \frac{10^3(\ln 10)m_e c}{\pi e^2 N_A} \int \varepsilon(\nu) d\nu. \end{aligned} \quad (14)$$

After passing through the solution, the emergent light of frequency ν is detected as the wave number of $\tilde{\nu}$ by a spectrophotometer in air. The molar absorption coefficient of $\varepsilon(\tilde{\nu})$ at wave number $\tilde{\nu}$ is usually obtained by measuring the ratio of the intensity of the emergent light from the solution to that of the reference light emerging from the same reference solvent under the same conditions with the spectrophotometer in air. Accordingly, the molar absorption coefficient integral is practically obtained as a value in air. We apply, therefore, the usual conversion of $\int \varepsilon(\nu) d\nu = c \int \varepsilon(\tilde{\nu}) d\tilde{\nu}$ to Eq. (14) instead of Abe's previous conversion of $\int \varepsilon(\nu) d\nu = (c/n) \int \varepsilon(\tilde{\nu}) d\tilde{\nu}$, as is pointed out by Birge² and recently done by Kuboyama and his co-workers.⁶ Thus, from Eq. (14) one finally obtains Eq. (1) with

$$\alpha = n\gamma^2 = 4n/(1+n)^2, \quad (15)$$

as the experimental oscillator strength in solution according to the definition of Eq. (5).

On the assumption of $\gamma = 1$ in Eq. (15), one will obtain Sklar's experimental oscillator strength ($\alpha = n$)¹⁷ for solution. Equation (15) gives an α value slightly smaller than unity. For example, one obtains the α value of 0.960 for $n = 1.5$. The usual experimental expression of Eq. (1) with $\alpha = 1$ is obviously derived on the assumption that the refractive index of the solution is unity. We do not oppose the convenient use of the usual experimental expression for the solution provided the solvent is defined. However, Eq. (1) with $\alpha = 4n/(1+n)^2$ should be used in the discussion of the solvent effects on the oscillator strength. Otherwise, the comparison of the oscillator strength measured in various solvents will be meaningless as described in the preceding subsection.

C. Theoretical expression

Although Birge² states that the refractive index correction made by Abe^{1,3} assumes the same velocities for the photon in both the cavity and the solvent, Abe has really not considered the photon but treated the exciting light, i.e., a stream of photons, as a transverse electromagnetic wave, as is usually done. In this framework, the wavelength of the light is extremely longer than the diameter of the solute molecule. Accordingly, the electric field strength of the light can be expressed only by the vector potential because the gradient of the scalar potential can be neglected for the dimension of the solute. Then, according to Ref. 3, the theoretical expression for the Einstein transition probability coefficient of the absorbing molecule is given by

$$B_{oi}^{\text{theor}}(\text{soln}) = \frac{8\pi^3}{3h^2} \times \frac{\delta^2}{n^2} |\mu_{oi}(\text{soln})|^2, \quad (16)$$

where $\delta = 3n^2/(2n^2 + 1)$. Abe^{1,3} treated the theoretical problem by double-perturbation theory; time dependent in the interaction with the electromagnetic field and time independent in the intermolecular interaction.¹⁰ The parameters of $1/n^2$ and δ^2 in Eq. (16) come from the radiation energy density of Eq. (7) and the Onsager cavity field, respectively. The Onsager cavity field can be replaced with the Lorentz field as was done in a previous paper.³ The refractive index correction factor of δ^2/n^2 comes from the time-dependent perturbation approach and the solute-solvent interaction is considered for $\mu_{oi}(\text{soln})$ as described in previous papers.^{1,3} Therefore, $\mu_{oi}(\text{soln})$ is, of course, solvent dependent. In the case where the interactions between nonpolar solvents and a solute are weak, the values of $\mu_{oi}(\text{soln})$ for these solvents may be approximately constant.^{3,6}

In Eq. (1) of Ref. 3, the expression of frequency-dependent field $E(\nu)$ in terms of change of the vector potential with time contains a solvent correction factor of $\varepsilon_r(\nu)^{-1/2}n(\nu)$ which does not give any information concerning an expression of the corresponding field in vacuum, because the vector potential for solution is different from that for vacuum and is not explicitly expressed by being connected with the potential for vacuum. In any case, insofar as the expression of the radiation energy density of the exciting light moving in the solution is reasonable, whatever is selected as the solvent correction factor in the expression relating $E(\nu)$ to the vector potential will in no way alter the finally derived expression for B_{oi} , because such a correction factor is absorbed into the expression for the radiation energy density which is eliminated in the derivation process.

Only by analogy with the expression of $B_{oi}(\text{vap}) = (8\pi^3/3h^2) |\mu_{oi}^\circ|^2$ (where μ_{oi}° is the transition moment of the free molecule), did Bakhshiev *et al.*¹⁸ assume that

$$B_{oi}^{\text{theor}}(\text{soln}) = \frac{8\pi^3}{3h^2} |\mu_{oi}(\text{soln})|^2. \quad (17)$$

Such an analogy evidently lacks the refractive index correction factor resulting from the time-dependent perturbation approach, because the factor is unity for $B_{oi}(\text{vap})$.

By putting Eq. (16) into Eq. (11), one obtains Eq. (2) with

$$\beta = \gamma^2 \delta^2 = \frac{36n^4}{(1+n)^2(2n^2+1)^2} \quad (18)$$

for the theoretical oscillator strength in solution. Equation (18) also gives a β value slightly smaller than unity. For example, for $n = 1.5$ one obtains the β value of 0.964 close to the α value of 0.960. Thus, under the condition that the values of $\mu_{oi}(\text{soln})$ for various solvents may be regarded as being approximately constant, the correlation of the present theoretical oscillator strength [Eq. (2) with $\beta = \gamma^2 \delta^2$] with the present experimental one [Eq. (1) with $\alpha = n\gamma^2$] is expected to be as good as that obtained by Kuboyama and his co-workers⁶ for 2,5-di-*t*-butyl-*p*-benzoquinone [where they have used Eq. (1) with $\alpha = 1/n$ and Eq. (2) with $\beta = \delta^2/n^2$], because the correction ratio ($\beta/\alpha = \delta^2/n$) of the present theoretical oscillator strength to the present experimental one is the same as that of Kuboyama and his co-workers.

The refractive index correction factor of Eq. (18) differs from that (δ^2/n^2) of the equation previously presented by Abe.^{1,3} The previous theoretical expression of Abe^{1,3} for the oscillator strength in solution will be obtained only by approximating γ by Eq. (9). This weak point in Abe's previous expression originates in his previous definition of the oscillator strength in solution, i.e., $f(\text{soln}) = B_{oi}(\text{soln})/B_h(\text{vap})$ obtained from the expansion of Eq. (4).

Birge² states that their theoretical expression for the oscillator strength⁴ would violate the Thomas–Kuhn sum rule if the refractive index were introduced. The sum rule is, however, rigorously verified to hold for only the gaseous system¹⁹ on the assumption of $\mathbf{E}_0 = \mathbf{E} = \mathbf{D}$.²⁰ Here \mathbf{E}_0 , \mathbf{E} , and \mathbf{D} are the external field, the local field, and the electric displacement, respectively. Chako²¹ already indicated that the oscillator strength cannot be interpreted as “electron number” for $n \neq 1$. Chako's treatment, as well as Abe's, assumes that the solute molecule is embedded in an isotropic continuous medium of the solvent. On the other hand, Myers and Birge⁴ write the total wave functions of the ground and excited states for the entire ensemble of the composite system. According to Birge,² the sum rule should hold for the entire ensemble and it is possible to prove that the theoretical expression derived by Myers and Birge obeys the sum rule.

Finally we state that the whole discussion described above is not completely rigorous for the following reason: In the spectral measurements of solutes in solutions, one usually chooses solvents that absorb at much shorter wavelengths than the solutes do. Therefore, the velocity ($u = c/n$) of the electromagnetic wave in solution, the energy density expression [Eq. (7) for $\rho(\nu)$] and the ratio [Eq. (8) for γ] between the electric fields in the vapor and in solution strictly hold for the transparent solvent in which the exciting light is not absorbed in the optical region. The absorption of light, however, occurs in the solution consisting of the solute and solvent, because the solute molecule absorbs the light in this case. Accordingly, all the expressions used above for u , $\rho(\nu)$, and γ do not strictly hold for the solution. Thus, the experimental and theoretical expressions derived using these expressions for u , $\rho(\nu)$, and γ are not rigorous. The complex refractive index (\bar{n}) of the solution and the complex electric and magnetic fields ($\bar{\mathbf{E}}$ and $\bar{\mathbf{H}}$, respectively) must be used for the absorbing solution. According to Landau and Lifshitz,²²

the velocity u in the absorbing solution is given by

$$u = \bar{S}/\bar{\rho}, \quad (19)$$

where \bar{S} and $\bar{\rho}$ are average values of the Poynting vector \mathbf{S} and energy density ρ . Here \mathbf{S} and ρ are given by

$$\mathbf{S} = \frac{c}{8\pi} \left(\frac{\bar{\mathbf{E}}_r}{\mu} \right)^{1/2} \bar{\mathbf{E}} \bar{\mathbf{E}}^* \quad (20)$$

and

$$\rho = \frac{1}{16\pi} \left\{ \frac{d(\omega \bar{\mathbf{E}}_r)}{d\omega} \bar{\mathbf{E}} \bar{\mathbf{E}}^* + \frac{d(\omega \mu)}{d\omega} \bar{\mathbf{H}} \bar{\mathbf{H}}^* \right\}, \quad (21)$$

respectively,²² where μ is a permeability of the solution, ω is an angular frequency, and $\varepsilon_r(\omega)$ is abbreviated to $\bar{\mathbf{E}}_r$. In Eqs. (20) and (21), $\bar{\mathbf{E}}_r$ is, of course, complex. Moreover, the ratio of γ is not so simple as one given by Eq. (8) in this case.²³ Accordingly, one may be confronted with the difficulty that the expressions of the oscillator strength for the solution will be complicated, because \mathbf{S} , ρ and γ will be complex and contain distance-dependent factors. To avoid such a complicated treatment, for convenience, the refractive index of the absorbing solution and the electric field of the exciting light in the solution are usually assumed to be regarded as the refractive index of the transparent solvent and the field in the solvent, respectively, on the assumption that the concentration of the solute is very low. Here we write the complex refractive index and relative permittivity for the absorbing solution as $\bar{n} = n' - in''$ and $\bar{\varepsilon}_r = \varepsilon' - i\varepsilon''$, respectively, where n' and ε' are real parts and i denotes $\sqrt{-1}$. Then one easily obtains the relation of $\varepsilon' = (n')^2 - (n'')^2$ and $\varepsilon'' = 2n'n''$ from $\bar{\varepsilon}_r = \bar{n}^2$. According to Linder and Abdulnur,¹⁰ one may obtain

$$n'' = \frac{2.303cc_s\varepsilon(\nu)}{4\pi\nu}, \quad (22)$$

where c_s is the concentration of the solute. When one assumes, e.g., $c_s = 10^{-5} \text{ mol dm}^{-3}$ and $\varepsilon(\nu) = 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ at the wavelength of 400 nm, one obtains the n'' value smaller than 10^{-7} according to Eq. (22). As described in Ref. 22, this very small n'' value means that n'' and ε'' may be approximately neglected in the expressions of $\bar{n} = n' - in''$ and $\bar{\varepsilon}_r = \varepsilon' - i\varepsilon''$, respectively, according to $\varepsilon' = (n')^2 - (n'')^2$ and $\varepsilon'' = 2n'n''$. Thus, Eqs. (7) and (8) and $u = c/n$ may approximately hold for the solution under investigation although they are not rigorous.

III. CONCLUSION

Equation (5) is proposed for the appropriate fundamental definition of the oscillator strength in solution. As a result of the definition, the experimental oscillator strength is expressed as Eq. (1) with $\alpha = 4n/(1+n)^2$. The theoretical oscillator strength is given by Eq. (2) with $\beta = 4\delta^2/(1+n)^2$, where $\delta = 3n^2/(2n^2+1)$ is the correction factor due to the Onsager cavity field.

¹T. Abe, J. Chem. Phys. **77**, 1074 (1982).

²R. R. Birge, J. Chem. Phys. **77**, 1075 (1982).

³T. Abe, Bull. Chem. Soc. Jpn. **43**, 625 (1970).

- ⁴A. B. Myers and R. R. Birge, *J. Chem. Phys.* **73**, 5314 (1980).
- ⁵I. Iweibo, R. A. Oderinde, and J. A. Faniran, *Spectrochem. Acta Part A* **38**, 1 (1982).
- ⁶Y. Jinnouchi, M. Kohno, and A. Kuboyama, *Bull. Chem. Soc. Jpn.* **57**, 1147 (1984).
- ⁷Almost all references concerning the theoretical treatments of the solvent effects on the oscillator strength in solution are cited in the recent paper of Ref. 8 except Refs. 7–12. See Ref. 8.
- ⁸T. Shibuya, *J. Chem. Phys.* **78**, 5175 (1983). His proposed theory has recently been applied in the following paper: T. Shibuya, *Bull. Chem. Soc. Jpn.* **57**, 2991 (1984).
- ⁹M. Koyanagi, *J. Mol. Spectrosc.* **25**, 273 (1968).
- ¹⁰B. Linder and S. Abdunur, *J. Chem. Phys.* **54**, 1807 (1971).
- ¹¹S. F. Abdunur, *J. Chem. Phys.* **58**, 4175 (1973).
- ¹²K. Nakashima, K. Uchida-Kai, M. Koyanagi, and Y. Kanda, *Bull. Chem. Soc. Jpn.* **55**, 415 (1982).
- ¹³See, for example, I. N. Levine, *Molecular Spectroscopy* (Wiley, New York, 1975), p. 307.
- ¹⁴J. C. Slater and N. H. Frank, *Introduction of Theoretical Physics* (McGraw-Hill, New York, 1933), Chap. 23.
- ¹⁵D. E. Sullivan and J. M. Deutch, *J. Chem. Phys.* **65**, 5315 (1976).
- ¹⁶S. J. Strickler and R. A. Berg, *J. Chem. Phys.* **37**, 814 (1962).
- ¹⁷A. L. Sklar, *Rev. Mod. Phys.* **14**, 232 (1942).
- ¹⁸N. G. Bakhshiev, O. P. Girin, and V. S. Libov, *Opt. Spektrosk.* **14**, 255 (1963).
- ¹⁹See, for example, A. S. Davydov, *Quantum Mechanics*, translated by D. T. Haar (Pergamon, Oxford, 1969), p. 316.
- ²⁰J. O. Hirschfelder, C. F. Curtiss, and R. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1967), p. 880.
- ²¹N. Q. Chako, *J. Chem. Phys.* **2**, 644 (1934).
- ²²L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media* (Pergamon, Oxford, 1960), Secs. 61 and 63.
- ²³See, for example, J. C. Slater and N. H. Frank, *Electromagnetism* (McGraw-Hill, New York, 1947), Chap. X.