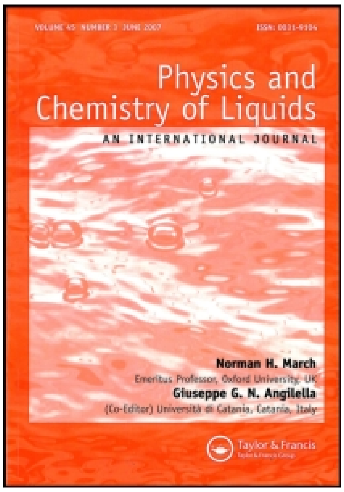

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A THEORETICAL MODEL FOR DETERMINING OSCILLATOR STRENGTH USING A NON-SPHERICAL MOLECULAR CAVITY AND MEASUREMENT OF THE He–Ne LASER LIGHT ABSORPTION COEFFICIENT IN SOLUTIONS*

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An alternative theoretical formulation for determining oscillator strength using a non-spherical molecular cavity is developed and this model correlated with experimental measurements made using non-resonant scattering of a He–Ne laser beam incident upon select aqueous ionic concentrations of NaCl. The light beam was transmitted through each sample and measurements made, at room temperature, on the transmitted light to determine the shape factor. The shape factor was estimated to be 0.30 from the results of this experiment. The nature of the ion–solvent interaction was obtained from the dielectric decrement.

KEY WORDS: Light absorption, ion–solvent interaction.

I INTRODUCTION

The coupling of electromagnetic radiation with systems whose molecules interact strongly with one another, e.g., aqueous electrolytic solutions, can differ markedly from interactions arising in low pressure gaseous systems wherein intermolecular distances are large. In such low pressure systems these interactions are observed via taking the low pressure gas spectrum for the system. Important information about intermolecular forces can be obtained for systems through a knowledge of the oscillator strengths and their relation to the nature of the absorption of the incident radiation. It is difficult to calculate oscillator strengths. *Ab initio* calculations are found[1] to differ from experimental values by factors of two to four. For large molecules, the quantum mechanical calculations are predicted only in a semi-empirical way. A correlation between oscillator strengths with the co-efficients of light absorption may be fruitful in making better predictions for oscillator strengths.

The purpose of this investigation was to formulate an alternative model based on dielectric polarization for oscillator strengths using a non-spherical molecular cavity geometry and Buckingham's formula.[2] Experimental measurements of the He–Ne

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laser light absorption coefficient for aqueous solutions of sodium chloride (NaCl) for various concentrations and at room temperature were correlated with the model proposed and the shape factor was estimated. The ion–solvent interactions were analyzed and an internal field correction was applied through analysis of the non-resonant scattered laser light.

II THEORETICAL FORMULATION

Consider an electric dipole moment operator $\hat{d}$ which can be separated into a sum over electrons and a sum over nuclei. The electronic wave functions Ψ'_{el} and Ψ''_{el} are eigen functions of the Hermitian operator H_{el} with different eigen values and therefore they are orthonormal. If we consider that the initial nuclear wave functions are normalized, it is possible to eliminate the nuclear wave function. Under these conditions we can define[1] the oscillator strength (f) of an electronic absorption transition in the gas phase as

$$f_g = [8\pi^2 vm/3he^2]|\langle\Psi'_{el}|d_{el}|\Psi''_{el}\rangle|^2, \tag{1}$$

where v is an absorption transition frequency, m is the mass of the electron, e is the electronic charge and h is Planck's constant.

Yamada and Person[3] have defined an apparent oscillator strength for an oscillator imbedded in a solution which we can write as

$$Ml(f_s) = \int \ln(I_0/I)dv, \tag{2}$$

where M represents the molar concentration, l is the path length of light propagation. I and I_0 are the intensity of light after and before the interaction with the absorbing sample. For a solvent, other than gas, the absolute oscillator strength can be obtained from Eq. (2) by letting $Ml \rightarrow 0$.

Buckingham[2] has formulated a relation for the ratio (f_s/f_g) based on the dielectric polarization which can be expressed by the following equation

$$(f_s/f_g)^{1/2} = \{n_{12}^2(1 - g_p\alpha_p)^{-1}\}/\{(n)^{1/2}[n_{12}^2 - (n_{12}^2 - 1)S_p]\}, \tag{3}$$

where a monochromatic source of light, e.g., He–Ne laser light, is used for interaction with the solution, one can then ignore the contribution of orientational polarizability because, for frequencies in the visible part of the spectrum, the electronic and atomic polarizability become dominant mechanisms. Therefore, we can write

$$(f_s/f_g)^{1/2} = \{\varepsilon_{\infty 12}(1 - g_p\alpha_p)^{-1}\}/\{(\varepsilon_{\infty 1})^{\frac{1}{4}}[\varepsilon_{\infty 12} - (\varepsilon_{\infty 12} - 1)S_p]\}. \tag{4}$$

where S_p is the shape factor for a non-spherical molecular cavity model and α_p is the polarizability of the ellipsoid taken out of the solution medium for the principal axis system. The quantity g_p is the reaction field factor, $\varepsilon_{\infty 12}$ is the high frequency permittivity of the solution and $\varepsilon_{\infty 1}$ is that of the solvent.

Scholte[4] has derived an expression for α_p and g_p which is given below (in SI units) as

$$a_p = (abc/3)\Sigma_j N_j \alpha_j \tag{5}$$

and

$$g_p = [3/abc](\varepsilon_{\infty 12}^2 - 1)S_p(1 - S_p)/[\varepsilon_{\infty 12} - (\varepsilon_{\infty 12} - 1)S_p], \tag{6}$$

where α_j is the polarizability of the molecule of the jth component and N_j is the number of molecules per unit volume. Therefore, from Eq. (5) and Eq. (6) we get

$$1 - \alpha_p g_p = 1 - \{(\varepsilon_{\infty 12} - 1)S_p(1 - S_p)/[\varepsilon_{\infty 12} - (\varepsilon_{\infty 12} - 1)S_p]\}\Sigma_j N_j \alpha_j. \tag{17}$$

To determine the summation $\Sigma N_j \alpha_j$ over j we need to consider the internal field E_s that acts at the site of the molecule (or ion) which is significantly different from the value of the macroscopic electric field E and is written[5] as (in SI units)

$$E_s = E_0 + \Sigma_i\{3(\boldsymbol{\mu}_i \cdot \mathbf{r}_i)\mathbf{r}_i - \mathbf{r}_i^2 \cdot \boldsymbol{\mu}_i\}/[4\pi\varepsilon_0 r_i^5] \tag{8}$$

where ε_0 is the permittivity of the vacuum (8.8542×10^{-12} F/m) and E_0 is the electric field produced by the field charges external to the body. The second term in the right hand side of Eq. (8) includes the polarization electric field E_1 from a surface charge density on the outer surface of the specimen and the field E_2 arises from polarization charges on the inside of a cavity "cut out" of the specimen and the field E_3 is due to the molecules inside of the hypothetical sphere concentric with the reference molecule, which vanishes at the reference site under cubic symmetry.

Defining $E \equiv E_0 + E_1$ as the macroscopic field, we can relate the dielectric constant to the polarizability through E_2 as given below

$$E_2 = S_p P/\varepsilon_0. \tag{9}$$

Therefore, the internal field is represented as

$$E_s = E + S_p P/\varepsilon_0. \tag{10}$$

The polarization of the solution (P) may be expressed (8) approximately as the product of the polarizabilities of the molecules times the internal (or local) electric field i.e.,

$$P \approx \varepsilon_0 \Sigma_j N_j \mu_j = \varepsilon_0 \Sigma_j N_j \alpha_j (E_j(j)), \tag{11}$$

where α_j is the polarizability of the molecules, μ_j is the dipole moment and $E_j(j)$ is the local electric field. The suffix j designates the molecular site.

From Eq. (10) and (11) we can write

$$P \approx \varepsilon_0 \Sigma_j N_j \alpha_j (E + S_p P/\varepsilon_0). \tag{12}$$

Using Maxwell's equations, the ratio of P and E obtained from Eq. (12) may be related to Drude's expression as given below

$$P/E = [\varepsilon_0 \Sigma_j N_j \alpha_j]/[1 - S_p \Sigma_j N_j \alpha_j] = \varepsilon_0(\varepsilon_{\infty 12} - 1). \tag{13}$$

Equation (13) may be solved for the summation $\Sigma_j N_j \alpha_j$ to give the result

$$\Sigma_j N_j \alpha_j = (\varepsilon_{\infty 12} - 1)/[1 + S_p(\varepsilon_{\infty 12} - 1)]. \tag{14}$$

If we substitute Eq. (14) into Eq. (7), the following equation is produced

$$(1 - \alpha_p g_p)^{-1} = [\varepsilon_{\infty 12} - (\varepsilon_{\infty 12} - 1)S_p][1 + (\varepsilon_{\infty 12} - 1)S_p]/\varepsilon_{\infty 12}. \tag{15}$$

Then, by combining Eq. (15) with Eq. (4) the ratio of the apparent oscillator strength in solution to that of the oscillator strength in the gas phase is given by the equation

$$(f_s/f_g) = \{[1 + S_p(\varepsilon_{\infty 12} - 1)]/(\varepsilon_{\infty 1})^{1/4}\}^2. \tag{16}$$

Equation (16) is applicable when the surrounding medium of the solute molecule is non-polar (or the medium is in the gas phase). When aqueous electrolytic solution systems are to be studied, Eq. (16) needs to be modified to take the following form

$$(f_s/f_g)^{1/2} = [\varepsilon_{\infty 1} + (\varepsilon_{\infty 12} - \varepsilon_{\infty 1})S_p]/(\varepsilon_{\infty 1})^{5/4}. \tag{17}$$

The atomic polarizability, in general. does not contribute significantly in comparison to the electronic polarizability. Under this assumption, Eq. (17) can be rewritten, with $\varepsilon_{\infty 12} \approx n_{12}^2$ and $\varepsilon_{\infty 1} = n_1^2$, as

$$(f_s/f_g)^{1/2} = [n_1^2 + (n_{12}^2 - n_1^2)S_p]/(n_1)^{5/2}. \tag{18}$$

Therefore,

$$f_s^{1/2} = (f_g/n_1)^{1/2}[(n_{12}^2 - n_1^2)S_p]/(n_1)^2 + (f_g/n_1)^{1/2} \tag{19}$$

In Eq. (19), n_1 is the refractive index of the solvent (for water $n = 1.3333$) and n_{12} is that for the solution. The derivation of Eq. (19) represents an alternate method which is useful to determine the shape factor S_p from the experimental data. Moreover, the equation has general application into the visible part of the electromagnetic spectrum where orientational polarizability may be neglected.

III EXPERIMENTAL DESIGN

The experimental arrangement used[5] to conduct the present experiment is outlined in Figure 1. The amount of light scattered perpendicular to the laser beam was shielded by means of an opaque cylinder surrounding the laser beam over the path length. The source of laser light was a He-Ne laser (model 125 by Spectra Physics) lasing at 6328 Å and with a power output of 60 mW. The laser beam was directed normal to the surface of the optically ground cell. The optically ground parallel faces were separated by 10 mm for the path length of the laser beam within the sample contained in the cell. The cells were sealed with polyethylene caps to reduce contamination and to lower the evaporation rate of the solvent. The focal zone of the laser beam was confined to a cross-sectional area of about 1 mm^2. The emergent beam passed through the monochromator (Model 0200, Jarrell-Ash, Division of Fisher Scientific Co.) and into the photo-multiplier tube for analysis and detection. The output signals were monitored both by display onto an oscilloscope and recorded on a single pen constant rate chart recorder for a permanent record.

The amplitude of the signal profile obtained in the neighborhood of 6328 Å wavelength was determined in the absence of the sample in the absorption cell and then with the samples in place in the optical cells. Thus, the difference between the absorbing sample and the background could be established.

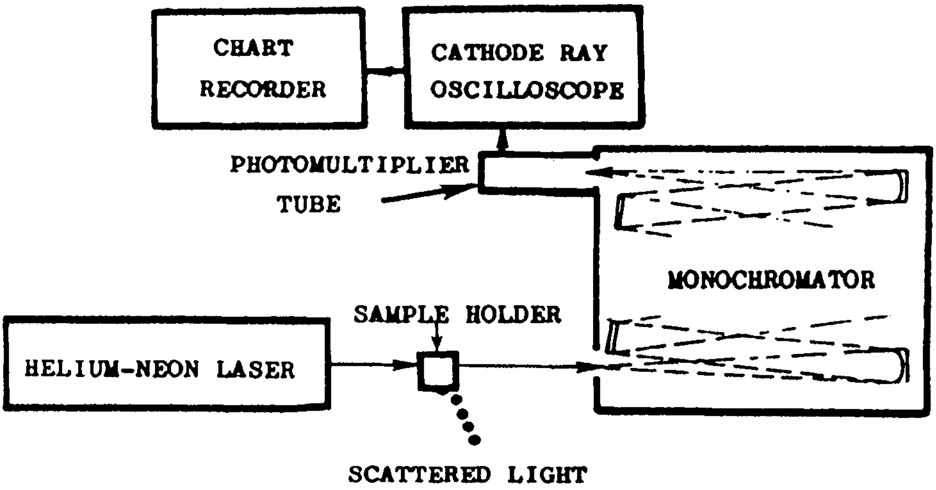

Figure 1 A schematic diagram of the basic experimental apparatus used to make the measurements reported in this work.

A simple model can be developed for the intensity behavior of the laser beam as it passes through the absorbing medium in the absorption cell as follows.

Consider an electromagnetic wave of frequency ω propagating in the z-direction through a medium whose refractive index is n_{12}. The electric field of the wave is given by

$$E = E_0 \exp[i\omega(t - n_{12}^{*} z/c)], \tag{20}$$

where c is the speed of light in vacuum. The refractive index is complex and is given by

$$n_{12}^{*\prime} = n'_{12} - jn''_{12}, \tag{21}$$

where n'_{12} and n''_{12} are the real and imaginary parts of the index of refraction, respectively.

If both sides of Eq. (20) are squared and the replacements $I = |E|^2$ and $I_0 = |E_0|^2$ are made, the intensity relationship for absorption is

$$I = I_0 \exp[-2n''_{12}\omega z/c] \tag{22}$$

or

$$I = I_0 \exp[-\beta_{12}^{\neq} z], \text{ with } \beta_{12}^{\neq} \equiv 2n''_{12}\omega/c. \tag{23}$$

Equation (23) shows that $\beta_{12}^{\neq}$, the absorption coefficient per unit length of propagation, is directly proportional to n''_{12}. Thus, the absorption at a given wavelength can be calculated[6,7] using the following relation

$$\beta(\lambda) = \beta_{12}^{\neq}\lambda = (\lambda/d) \ln(I_0/I), \tag{24}$$

where λ is the wavelength of the incident radiation, d is the thickness of the sample, I_0 is the undiminished light intensity and I is the intensity of the light after it has passed through the absorbing material.

IV DISCUSSION OF CORRELATIONS BETWEEN THEORETICAL AND EXPERIMENTAL RESULTS

From Eq. (2), the oscillator strength can be obtained from the integrated absorption coefficient per unit concentration (gm-mole/cm^3) over a unit path length of propagation. For infinitely sharp absorption lines which we can assume for monochromatic sources of light, e.g., He–Ne lasers, the ratio of the molar integrated absorption coefficient in solution of that in the gas phase may be approximated as equal to the ratio of β_{12} of the solution to β_1 of the solvent. Therefore, we can write from Eq. (19) and Eq. (24) the following relationship

$$(\beta_{12})^{1/2} \approx (\beta_1/n_1)^{1/2}[(n_{12}^2 - n_1^2)/n_1^2]S_p + (\beta_1/n_1)^{1/2}. \tag{25}$$

Inspection of Eq. (25) shows that if the two variables $(\beta_{12})^{1/2}$ and $(n_{12}^2 - n_1^2)/n_1^2$ are defined, in the standard way, and the plot of $(\beta_{12})^{1/2}$ vs. $(n_{12}^2 - n_1^2)/n_1^2$ is fitted to a linear least-squares regression, the shape factor S_p, if the slope is taken as $(\beta_{12})^{1/2}S_p$, is given by the following ratio

$$S_p = [\text{line Slope/Line Intercept}] \tag{26}$$

It is worth noting that the molecular polarizability is not a scalar quantity but is a tensor quantity when the molelcule is not completely spherical. For practical purposes, however, the effect of this so-called anisotropy of the polarizability is small and the tensor $\hat{\alpha}$ may be replaced by a scalar polarizability $\alpha = [\ (1/3)\mathrm{Tr}(\hat{\alpha})]$ as was also pointed out by Böttcher[8]. When an ellipsoid has a spherical form, $S_p = 1/3$ for any axis. If the final form is a thin slab (normal), $S_p = 1$, a thin slab (in plane), $S_p = 0$, a long circular cylinder (longitudinal), $S_p = 0$ and for a long circular cylinder (transverse), $S_p = 1/2$. These values are given in S.I. units and $0 \leq S_p \leq 1$[5]. For the perfect sphere, $S_p = 1/3$, Eq. (25) reduces to

$$(\beta_{12})^{1/2} = (\beta_1/n_1)^{1/2}[(n_{12}^2/n_1^2) + 2]/3. \tag{27}$$

The model has been applied to aqueous solutions of NaCl at various concentrations. The coefficients of light absorption β_{12} for various concentrations of NaCl are given in Table 1. The value of the refractive index at each of these concentrations given in Table 1 have been obtained by interpolation of those from the literature[9] for aqueous solutions of NaCl. The least-squares regression of $(\beta_{12})^{1/2}$ versus $(n_{12}^2 - n_1^2)/n_1^2$ yields a slope of -0.3585 and an intercept of 1.174 with a 98% correlation factor. The ratio of the slope to intercept gives a value for S_p of 0.30. The negative sign before the slope indicates a decrement in the dielectric value with increasing concentrations of ions. This effect was expected and has already been reported by Winsor and Cole[10] at microwave frequencies and Hubbard *et al.*[11] at radio frequencies.

Table 1 A list of coefficients for He-Ne laser light absorption in aqueous solutions of NaCl and refractive index at various ionic concentrations. The temperature was kept at room temperature during measurement of the light absorption coefficients at each concentration.

Concentration (gm-mole/cm^3) × 10^4	$\beta_{12} \times 10^4$	$(\beta_{12})^{1/2} \times 10^2$	n_{12}[9]	$\{n_{12}^2 - n_1^2\} \times 10^4/n_1^2$
0.0170	1.3491	1.1615	1.3332	−1.6876
0.4278	1.7052	1.3058	1.3334	1.6876
0.6845	1.3847	1.1767	1.3344	6.1878
1.3689	1.2100	1.1000	1.3337	16.3133
7.7002	0.4081	0.6388	1.3407	111.3806
11.9781	0.2494	0.4994	1.3446	169.8835
21.3895	0.0250	0.1581	1.3537	308.2654

V CONCLUSIONS

Although the formulation presented is not highly rigorous, it does provide a good correlation with experimentally obtained absorption coefficients. From such experiments one should be able to extract information about ion-solvent interaction through the dielectric decrement. Moreover, the extrapolated value of the absorption coefficient (1.8452×10^{-4}) in water for zero ion concentration is different from that measured (2.0425×10^{-4}) in pure water. Therefore, it appears that water molecules in the neighborhood of ions has an appreciably different behavior than that of the bulk solvent.

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