The Oscillator Strength of a Dipole Transition in a Lorentz-Lorenz Field

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Quantum theory has allowed the correlation of numerous aspects of chemistry. Of great importance is the interaction of light with matter. Upon this rests spectroscopy, diffraction and photoactivation.

In connection with a study on the effect of solvents upon the ultra-violet spectrum of sulfur[2], a relationship was needed to correlate the change in spectrum with the changing internal field of the solvent. It is the purpose of the present note to expand upon the derivation given only as an appendix in a former paper.[2] The present discussion, which had its origin in the interaction of a non-bonded pair of electrons of a basic nitrogen atom with a sulfur atom, is preliminary to the discussion of the interaction between the nitrogen and sulfur atom within an aminothiol. Such a study is of great importance due to the ability of some aminothiols to serve as radiation protectors. In a future paper from this laboratory, we will discuss the nature of the interaction in the simplest aminothiol, aminoethanethiol, and several of its N-alkyl derivatives.

Consider a molecule with steady state wave functions:

$$\phi_0, \ \phi_1, \ \phi_2 \ \cdots \tag{1}$$

in the absence of external perturbation with energy levels:

$$\epsilon_0, \ \epsilon_1, \ \epsilon_2, \ \cdots \tag{2}$$

Placing the molecule in a beam of light, the electric field on the molecule will be given by

$$E = E_0 \cos \omega t \tag{3}$$

The perturbation Hamiltonion operator will be

$$H^1 = - \Sigma \ e_m \ x_m \ |E| \tag{4}$$

$$= - m_x \ |E_0| \cos \omega t \tag{5}$$

where m is a charged particle of charge e_m in an x-coordinate of x_m and m_x is the x-component operator of the dipole moment summed over all particles, m:

$$m_x = \Sigma \ e_m \ x_m \tag{6}$$

The time-dependant wave function of the molecule now becomes

$$\Psi = \Sigma_j \ a_j \ (t) \ \phi_j \tag{7}$$

where

$$a_j \ (t) = \frac{|E_0| \ m_{x_{jo}} \ e^{-i \ E_j t/\hbar}}{2\hbar} \left[\frac{e^{i(\omega_{jo} + \omega)t} - 1}{\omega_{jo} + \omega} + \frac{e^{i(\omega_{jo} - \omega)t} - 1}{\omega_{jo} - \omega} \right] \ j \neq 0 \tag{8}$$

where

$$\omega_{jo} = (E_j - E_0)/\hbar \tag{9}$$

$$m_{x_{jo}} = \int \phi_j^* \ (\Sigma \ e_m \ x_m) \ \phi_0 \ d \ \tau \tag{10}$$

The value of $/a_j(t)/^2$ is then the probability that the molecule has been excited to state ϕ_j at time t. The x-component of the dipole moment in the direction of the field will be

$$\overline{m_x} = \frac{\int \Psi^* \ m_x \ \Psi \ d \ \tau}{\int \Psi^* \ \Psi \ d \ \tau} \tag{11}$$

Substitution of (7) into (11) and neglecting cross product terms of a_j (except of a_o) gives:

$$\overline{m_x} = \int \phi_o^* \ m_x \ \phi_o \ d \ \tau + a_o \ \Sigma \ a_j^* \int \phi_j^* \ m_x \ \phi_o \ d \ \tau \tag{12}$$
$$+ \ a_o^* \ \Sigma \ a_j \int \phi_o^* \ m_x \ \phi_j \ d \ \tau$$

$$\overline{m_x} = m_{x_{oo}} + \frac{2 \ |E_o|}{\hbar} \ \cos \ \omega \ t \ \sum \frac{|m_{x_{jo}}|^2 \ \omega_{jo}}{\omega_{jo}^2 - \omega^2} - \varphi \tag{13}$$

$$\varphi = \frac{2 \ |E_o|}{\hbar} \ \sum \frac{|m_{x_{jo}}|^2 \ \omega_{jo} \ \cos \ \omega_{jo} \ t}{\omega_{oj}^2 - \omega^2}$$

The first term, $m_{x_{oo}}$, is time-independent and represents the x-component of the permanent dipole moment of the molecule. The second term oscillates in phase with the light while the third term (φ) represents oscillating dipole moments with frequencies independent of the light. Generalization to a three coordinate space (x, y, z) involves replacement of the $/m_{x_{jo}}/^2$ term by the average of the squares of the three components, $/m_{jo}/^2$. Thus the polarizability, a, becomes

$$a = \frac{2}{3 \ \hbar} \ \sum \frac{\omega_{jo} \ |\overrightarrow{m_{jo}}|^2}{\omega_{jo}^2 - \omega^2} \tag{14}$$

The oscillator strength, f_J, is now

$$f_J = \frac{8 \ \pi^2 \ m_e \ \nu_{jo} \ |\overrightarrow{m_{jo}}|^2}{3 \ h \ e^2} \tag{15}$$

where

$$\nu_{jo} = (E_j - E_o)/h$$

Expression (15) represents a normal electronic dipole transition between states j and o of the molecule with wave functions, ϕ_j and ϕ_o.

Placing the molecule in a solvent medium of refractive index, n, introduces several new effects. Chako[1] considered these problems and the following discussion is from his paper. Dispersion and damping will occur and the absorption bonds will be continuous and broader. The plane wave will experience the effect of a complex refractive index: $n' = n(1 - ik)$, k, a constant. The theory of dispersion now predicts that

$$n'^2 - 1 = n^2 \ (1 - k^2) - 1 - 2 \ n^2 \ ik$$
$$= \frac{e^2}{\pi \ m} \ N^1 \ \sum \frac{f_i}{\nu_{jo}^2 - \nu^2 + i\gamma_j \ \nu} \tag{16}$$

where N is the number of absorbing molecules per cc, γ_j measures the damping in $\sec^{-1}$. and band width, and γ is some other frequency. If a Lorentz-Lorenz force is now applied due to the internal field effect and polarization of the surrounding molecules, the force on each molecule is

$$F + \frac{4r}{3} \ P = F \ [1 + \frac{4r}{3}(n^2 - 1)] \tag{17}$$

where F is the field and P is the polarization/cc. Equation (16) must now be modified by replacement of $n^2 - 1$ by $\dfrac{3 \ (n^2 - 1)}{n + 2}$.

The molar extinction coefficient, e, is now related to the oscillator strength (in vacuo), f_J, of equation (15) by

$$\int \epsilon \, d \, \gamma = \frac{\pi \, e^2}{c \, m \, \gamma_{jo}^2} \, \overline{N} \frac{(n_o^2 + 2)^2}{9 \, n_o} \tag{18}$$

where

$$\overline{N} = \frac{6.02 \times 10^{23}}{1000} = \frac{N}{1000}$$

As all of the quantities in (18) are constants, we now have a relationship between e and n. Solution gives

$$\epsilon = k \, (n_o^3 + 4n_o + \frac{4}{n_o}) \tag{19}$$

with k a constant:

$$k = \frac{f_j \, \pi \, Ne^2}{9 \, \delta \, 2303 \, m_e c} \tag{20}$$

where δ is the half-band width in cm^{-1} when $\epsilon = \epsilon$ max.

The derivation of equation (18) by Chako[1] has been discussed by Kauzmann[4] and Mulliken.[5] While equation (15) is exact and depends only upon the proper choice of a basic set of wave functions, equation (18) contains several assumptions. The only perturbation by solvent is assumed to be due only to the operation of a Lorentz-Lorenz force. Such a force is classical and cannot express chemical effects due to hydrogen bonding, association or chemical reaction. Mulliken[5] when faced with these problems dropped the internal field correction term:

$$\frac{(n^{o2} + 2)^2}{9n_o} \tag{21}$$

which is unity *in vacuo* as $n_o = 1$ and only 0.75 at $n_o = 1.5$. Chako[1] observed that the expressions for the oscillator strengths, f_j, $\overline{f_j}$ and $\overline{\overline{f_j}}$, were

$$\overline{f_j} = n_o f_j \tag{22}$$

$$\overline{\overline{f_j}} = \frac{9n_o}{(n^{o2} + 2)^2} \tag{23}$$

These terms were not strictly constant for the ultraviolet absorption bands of numerous organic compounds include aromatics, carboxylic acids, ketones, azo compounds, and alkyl halides.

Reexamination of the derivation of equation (18) and the basic fundamentals of the interaction leads to several new conclusions. Therefore the limitations of the applicability are more readily apparent. Molecules whose extinction coefficients would most closely correlate with equations (18) and (19) would have several properties. The oscillator strengths should be between 1 and 0.001 effective electrons and thus represent an allowed transition. Further the term:

$$\int \phi_o^* \, \overrightarrow{m} \, \phi_o \, d \, \tau \equiv 0 \tag{24}$$

for the ground state should be zero. This represents the first term of equations (12) and (13). Thus the permanent dipole moment of the molecule should be zero. The average time derivative of (24):

$$\frac{d}{dt} \int \phi_o^* \, \overrightarrow{m} \, \phi_o \, d \, \tau \equiv 0 \tag{25}$$

would be zero. Thus no polarization of the surrounding solvent would occur.

In the present investigation, octatomic sulfur has been found to obey the relationship (19) (Fig. 1). Thus we conclude that the nature of the
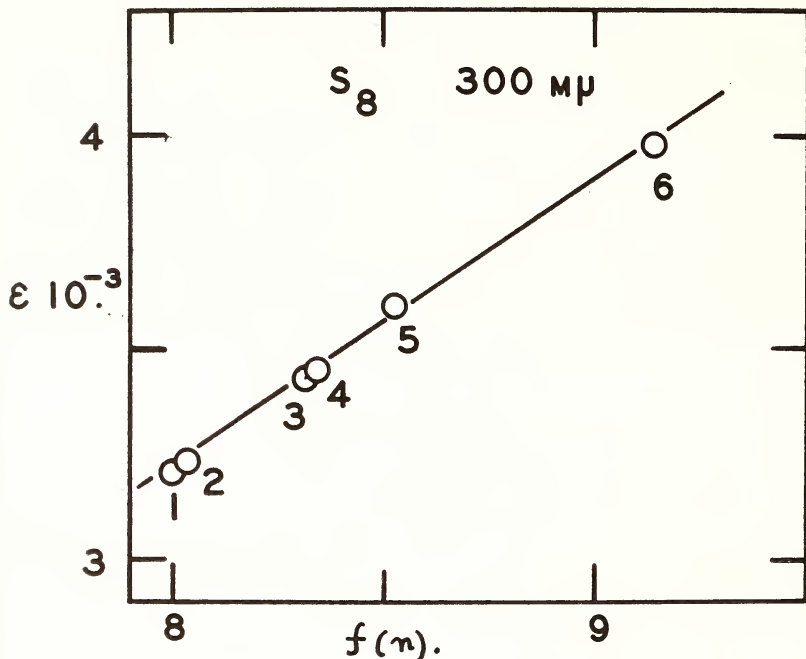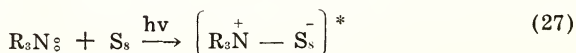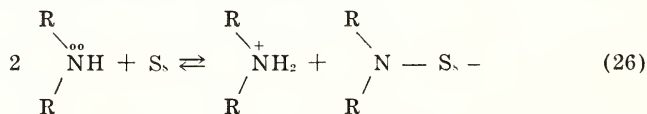
Fig. 1. Extinction coefficient of Sulfur[3] at 300 mμ versus n^3 + 4n + $\dfrac{4}{n}$ where n is the refractive index. 1. Methanol, 2. Water, 3. Ethanol, 4. 90% Ethanol—10% Water, 5. n-Hexane, 6. Chloroform.
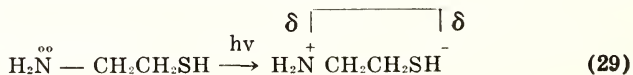
interaction between a sulfur molecule and the solvent is very small in magnitude.

The classical Lorentz-Lorenz force due to the internal field of the solvent also correctly predicts the dependance of the spectrum upon solvent refractive index for inert solvents.

In another paper we will discuss the abnormal spectrum of sulfur in amine solvents. In such cases strong chemical interactions have been shown to occur.

$$2 \quad \overset{R}{\underset{R}{\diagdown}} \overset{oo}{NH} + S_x \rightleftarrows \overset{R}{\underset{R}{\diagdown}} \overset{+}{NH_2} + \overset{R}{\underset{R}{\diagdown}} N - S_x - \qquad (26)$$

$$R_3\overset{oo}{N} + S_8 \xrightarrow{hv} \left[R_3\overset{+}{N} - \overset{-}{S_x} \right]^* \qquad (27)$$

The problem of the aminothiols will be discussed.

$$H_2\overset{oo}{N} - CH_2CH_2SH \rightleftarrows H_3\overset{+}{N} \, CH_2CH_2\overset{-}{S} \qquad (28)$$

$$H_2\overset{oo}{N} - CH_2CH_2SH \xrightarrow{hv} H_2\overset{+}{N} \, CH_2CH_2\overset{-}{SH} \qquad (29)$$

Acknowledgement

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