



Absorption and emission spectral studies of two vinylogous series of cyanine dyes  
by Nancy Jane Land Roth

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree  
DOCTOR OF PHILOSOPHY in Chemistry  
Montana State University  
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Abstract:

The absorption and emission spectra in methanol of the dyes of the 3,3'-diethylthiacyanine iodide series and of the 3,3'-diethyloxacyanine iodide series (except for the first member which was the triiodide) were determined. The integrated intensities and oscillator strengths were calculated. In each series these quantities increase as the methylene chain length increases. From the absorption and emission spectra, the radiative lifetimes were calculated by the formula derived by Strickler and Berg as modified by Birks and Dyson: The lifetimes were of the order of three nanoseconds for the thiacyanine series and of the order of two nanoseconds for the oxacyanine series. The fluorescence efficiencies were determined. They increase by a factor of ten as the chain length, increases except for the first member of the sulfur series which is lower by a factor of 100 from the next member. The observable lifetimes were calculate from the radiative lifetimes and the fluorescence efficiencies. Since the rate of all decay processes is the inverse of the observable lifetime, a minimum may be placed on the rate of energy transfer from the first excited state for these dyes when energy transfer processes take place.

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ABSORPTION AND EMISSION SPECTRAL STUDIES OF TWO  
VINYLOGOUS SERIES OF CYANINE DYES

by

NANCY JANE LAND ROTH

A thesis submitted to the Graduate Faculty in partial  
fulfillment of the requirements for the degree

of

DOCTOR OF PHILOSOPHY

in

Chemistry

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## ABSTRACT

The absorption and emission spectra in methanol of the dyes of the 3,3'-diethylthiacyanine iodide series and of the 3,3'-diethyloxacyanine iodide series (except for the first member which was the triiodide) were determined. The integrated intensities and oscillator strengths were calculated. In each series these quantities increase as the methylene chain length increases. From the absorption and emission spectra, the radiative lifetimes were calculated by the formula derived by Strickler and Berg as modified by Birks and Dyson:

$$\frac{1}{\tau_0} = 2.880 \times 10^{-9} \frac{n_{u \rightarrow l}^3}{n_{l \rightarrow u}} \left\langle \frac{\bar{\nu}_f - 3}{\bar{\nu}_{av}} \right\rangle^{-1} \frac{g_l}{g_u}$$

$$\int \epsilon(\bar{\nu}_{l \rightarrow u}) d \ln \bar{\nu}_{l \rightarrow u}$$

The lifetimes were of the order of three nanoseconds for the thiacyanine series and of the order of two nanoseconds for the oxacyanine series. The fluorescence efficiencies were determined. They increase by a factor of ten as the chain length increases except for the first member of the sulfur series which is lower by a factor of 100 from the next member. The observable lifetimes were calculated from the radiative lifetimes and the fluorescence efficiencies. Since the rate of all decay processes is the inverse of the observable lifetime, a minimum may be placed on the rate of energy transfer from the first excited state for these dyes when energy transfer processes take place.

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## INTRODUCTION

A colorful, bright purple dye formed in small yield when A. W. Hofmann<sup>1</sup> in 1887 reacted 3-pentylbenzothiazolium iodide and 2-methyl-3-pentylbenzothiazolium iodide in the presence of ammonia. Like other dyes of the cyanine class, this compound was not stable enough for dyeing textiles. Previously in 1873, H. W. Vogel<sup>2</sup> had found that photographic emulsions could be made sensitive to colors other than blue by bathing the photographic plates in a dilute solution of dyes such as the cyanines. Since the cyanine dyes including that one first prepared by Hofmann were found to be useful for sensitizing photographic films, members of this family of dyes were synthesized and characterized.

Hofmann's dye was found by W. H. Mills<sup>3</sup> to have the structure shown in Figure 1 where  $Y = S$  and  $n = 1$ . The common name for this dye is 3,3'-diethylthiacarbocyanine iodide (Dye II) while the dye with  $Y = S$  and  $n = 0$  is 3,3'-diethylthiacyanine iodide (Dye I) and the dye with  $Y = S$  and  $n = 2$  is 3,3'-diethylthiadibenzocarbocyanine iodide (Dye III).

There is a similar vinylogous series of dyes where  $Y = O$ . The first member where  $n = 0$  is 3,3'-diethylox-

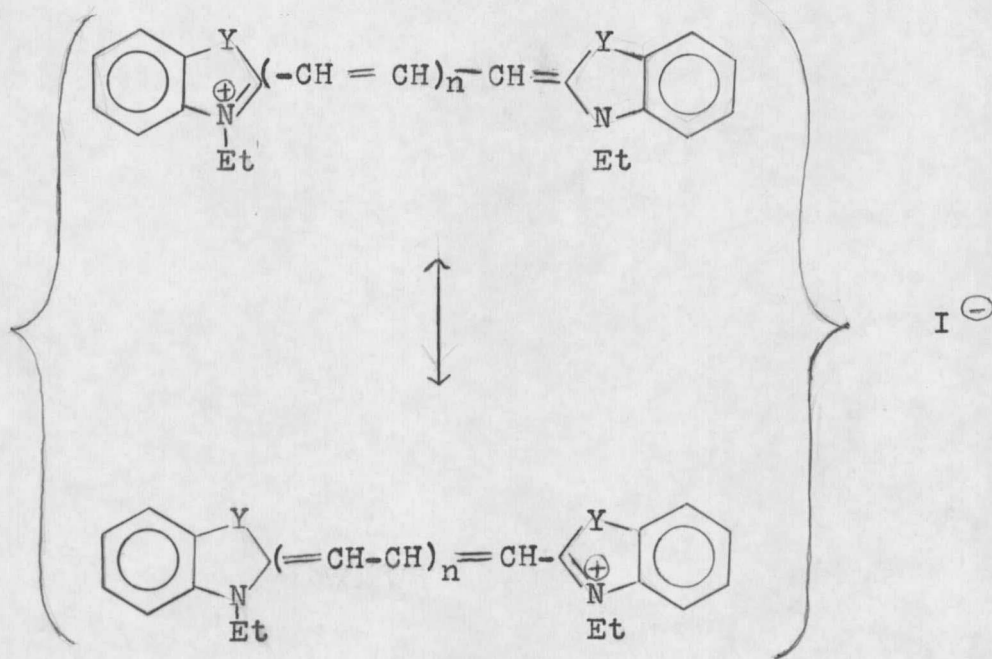


Figure 1

cyanine iodide (Dye IV when iodide is replaced by triiodide ion); the second where  $n = 1$  is 3,3'-diethyloxacarbocyanine iodide (Dye V); and the third where  $n = 2$  is 3,3'-diethyloxadicarbocyanine iodide (Dye VI).

A cyanine, such as that shown in Figure 1, is a mono-acid salt in which the nitrogen atoms of two heterocyclic rings are linked by a chain of alternating double and single bonds. Since this chain consists of an odd number of carbon atoms, the two structures



are resonance hybrids. Thus each nitrogen atom is probably best represented as something between tertiary and quaternary, and each bond as something between single and double.

A molecule with a conjugated system of this type might be expected to have a relatively small energy difference between the ground state and the first electronic excited state. This has been found to be true. Fisher and Hamer<sup>4</sup> reported wavelengths for the absorption maxima of the six dyes: Dye I, 422 m $\mu$ ; Dye II, 557 m $\mu$ ; Dye III, 650 m $\mu$ ; Dye IV, 372 m $\mu$ ; Dye V, 485 m $\mu$ ; Dye VI, 580 m $\mu$ . They also gave the qualitative visual colors of the fluorescence for these dyes. Hofer, et al.<sup>5</sup> in 1950 studied the monomeric fluorescence of some of these dyes at room temperature in glycerol. The positions of the fluorescent maxima were determined visually from photographic plates. The maxima quoted were the following: Dye I, no observable fluorescence; Dye II, 586 m $\mu$ ; Dye III, 691 m $\mu$ ; Dye V, 512 m $\mu$ . Some work was done in a rigid medium of E.P.A. (ethanol-ether-isopentane 2 : 5 : 5) at 77° K. by Mazzucato, et al.<sup>6</sup> in 1964. Their results were 575 m $\mu$  for the fluorescence of Dye II under these conditions and 498 m $\mu$  for Dye V.

To measure the absorption spectrum of a molecule in solution, the sample is contained in a cell of path length  $l$  (in cm.), at a concentration  $C$  (in g. moles per liter), and the ratio of the transmitted light intensity  $I$  to the incident light intensity  $I_0$  is determined. This ratio is given also by

$$\log \frac{I}{I_0} = \epsilon C l$$

where  $\epsilon$  is called the extinction coefficient (units of liter moles<sup>-1</sup> cm.<sup>-1</sup>). The maximum value of  $\epsilon$  ( $\epsilon_{\max}$ ) for an absorption band is a rough measure of the intensity of the band. However, absorption bands for most molecules are broad and different in shape. Thus a better measure of intensity is the area under the absorption curve, that is, the integrated intensity. Since the oscillator strength  $f$  is proportional to the integrated intensity, the oscillator strength is generally calculated to compare the intensities of absorption bands.<sup>7</sup>

The intensity of absorption for a transition from a state of energy  $E_n$  to a state  $E_m$  (where  $E_m > E_n$ ) may be defined as the energy absorbed from the incident beam of 1 cm.<sup>2</sup> cross-section per unit time. If  $\bar{\nu}$  is

the wave number in  $\text{cm.}^{-1}$  of the incident radiation, and

$\rho(\bar{\nu})$  is its radiation density, then

$$I_{\text{abs.}} = \rho(\bar{\nu}) N_n B_{nm} h c \bar{\nu} dl \quad (1)$$

where  $N_n$  is the number of molecules per  $\text{cm.}^3$  in the initial state,  $B_{nm}$  is Einstein's coefficient of absorption, which is a characteristic of the molecule, and  $dl$  is the thickness of the layer in cm. The quantity  $h$  is Planck's constant while  $c$  is the speed of light.

The intensity of the incident light,  $I$ , which is the energy falling on  $1 \text{ cm.}^2$  per second, can be given by

$$I = c \rho(\bar{\nu}) d\bar{\nu} \quad (2)$$

If equation (1) is multiplied on both sides by  $d\bar{\nu}$ , and equation (2) is substituted into equation (1) then the following equation is obtained:

$$I_{\text{abs.}} d\bar{\nu} = I N_n B_{nm} h \bar{\nu} dl \quad (3)$$

When  $I$  passes through an absorbing layer of thickness  $dl$ , the part of  $I$  absorbed will be proportional to both  $I$  and  $dl$  such that

$$I_{\text{abs.}} = -\alpha I dl \quad (4)$$

where  $\alpha$  is the absorption coefficient. The absorption coefficient is related to the molar extinction coefficient in the following way:

$$\ln \frac{I_0}{I} = \alpha l = \log \frac{I_0}{I} \left( \ln 10 \right) \left( \frac{1}{22.41} \right) \epsilon l$$

so that  $\alpha = 0.1028 \epsilon$  . . . (5)

Substitution of the value of  $\epsilon$  into equation (4) gives

$$I_{\text{abs.}} = -0.1028 \epsilon I d l . \quad (6)$$

If equation (6) is multiplied on both sides by  $d\bar{\nu}$  and subtracted from equation (3), the following will result

$$0.1028 \epsilon (\bar{\nu}) d\bar{\nu} = N_n B_{nm} h \bar{\nu} . \quad (7)$$

Since the absorption band of a molecule is broad, the strength of a molecular electronic transition can be defined by the integral of the intensity over the whole band of the particular electronic transition. Then equation (7) can be written as

$$0.1028 \int \epsilon (\bar{\nu}) d\bar{\nu} = N_n B_{nm} h \bar{\nu} \quad (8)$$

for molecular absorptions.

If an electron were considered to be a three-dimensional harmonic oscillator then the intensity of absorption would be

$$I_{\text{abs.}} = f_{nm} N_n \pi \frac{e^2}{m_e c} \rho(\bar{\nu}) d l \quad (9)$$

where  $f_{nm}$ , the oscillator strength, is equal to one. In this equation  $m_e$  is the mass of the electron and  $e$  is the charge of an electron.

Then equation (9) can be equated to equation (1) to give

$$f_{nm} = \frac{h c^2 m_e}{\pi e^2} \bar{\nu} B_{nm} \quad (10)$$

When equation (10) is substituted into equation (8), the oscillator strength is given as

$$f_{nm} = \frac{0.1028 c^2 m_e}{N_n \pi e^2} \int \epsilon(\bar{\nu}) d \bar{\nu}$$

$$4.319 \times 10^{-9} \int \epsilon(\bar{\nu}) d \bar{\nu} \quad (11)$$

Thus the oscillator strength is proportional to the integrated absorption intensity.<sup>8</sup>

The mean lifetime for spontaneous emission from an excited state of a molecule is the inverse of  $A$ , the Einstein transition probability coefficient for spontaneous emission. The spontaneous emission probability was shown by Einstein to be directly proportional to the corresponding absorption probability and to the third power of the frequency of the transition.

If the molecule has two electronic states, a ground state  $\underline{l}$  and an excited state  $\underline{u}$ , the corresponding electronic wave functions may be called  $\Theta_{\underline{l}}$  and  $\Theta_{\underline{u}}$ . A series of vibrational states are associated with each electronic level. In the Born-Oppenheimer approximation, each vibronic state has a wave function  $\Psi$  which can be written as a product of an electronic function  $\Theta$  and a vibrational function  $\phi$ , such that  $\Psi_{\underline{l}a} = \Theta_{\underline{l}} \phi_{\underline{l}a}$  and  $\Psi_{\underline{u}b} = \Theta_{\underline{u}} \phi_{\underline{u}b}$  where  $\underline{a}$  and  $\underline{b}$  are the quantum numbers describing the state of nuclear motion.

If a large number of these molecules, immersed in a nonabsorbing medium of refractive index  $\underline{n}$ , are in thermal equilibrium within a cavity in some material at a temperature  $\underline{T}$ , the radiation density within the medium is given by Planck's blackbody radiation law

$$\rho(\underline{\nu}) = (8 \pi h \underline{\nu}^3 n^3 / c^3) [\exp(h \underline{\nu} / kT) - 1]^{-1} \quad (12)$$

where  $\nu$  is the frequency in cycles/sec.

These molecules can be excited from state la to state ub by transitions induced by the radiation in the cavity. The rate of molecules undergoing this transition by absorption of radiation is

$$N_{1a} B_{1a \rightarrow ub} \rho(\nu_{1a \rightarrow ub}) \quad (13)$$

where  $N_{1a}$  is the number of molecules in state la. Molecules in state ub can go to state la by spontaneous emission with probability  $A_{ub \rightarrow la}$  or by induced emission with probability  $B_{ub \rightarrow la} \rho(\nu_{ub \rightarrow la})$ . The rate at which molecules undergo this transition downward is

$$N_{ub} [A_{ub \rightarrow la} + B_{ub \rightarrow la} \rho(\nu_{ub \rightarrow la})] \quad (14)$$

where  $B_{ub \rightarrow la} = B_{1a \rightarrow ub}$  and  $\nu_{ub \rightarrow la} = \nu_{1a \rightarrow ub}$ . At equilibrium the two opposing rates must be equal, so if expressions (13) and (14) are equated, the resultant equation is

$$A_{ub \rightarrow la} / B_{ub \rightarrow la} = [(N_{1a} / N_{ub}) - 1] \rho(\nu_{ub \rightarrow la}) \quad (15)$$

According to the Boltzmann distribution law, the number of molecules in each of the two states at equilibrium is related by

$$N_{ub}/N_{la} = \exp \left[ - (h \nu_{ub \rightarrow la} / k T) \right]. \quad (16)$$

If equations (12) and (16) are substituted into equation (15), the resultant is Einstein's relation

$$A_{ub \rightarrow la} = 8 \pi h \nu_{ub \rightarrow la}^3 n_{ub \rightarrow la}^3 c^{-3} B_{ub \rightarrow la}. \quad (17)$$

In the usual absorption experiment the molar extinction coefficient  $\epsilon$  can also be defined by

$$\rho(\nu, l) / \rho(\nu, 0) = 10^{-\epsilon(\nu)cl} = e^{-2.303 \epsilon(\nu)cl} \quad (18)$$

if  $\rho(\nu, l)$  is the radiation density in the light beam after it has passed a distance  $l$  through the sample and  $\rho(\nu, 0)$  is the initial radiation density. If a short distance  $dl$  is considered, the change in radiation density may be written as

$$-d\rho(\nu) = 2.303 \epsilon(\nu) \rho(\nu, 0) c dl \quad (19)$$

All the molecules will be assumed to be in the ground vibronic state,  $\psi_{10}$ , for ease of derivation since the result will not be materially different than if the true distribution of molecules in the vibronic states were used. When  $N_{10}$  is the number of molecules in the lowest vibrational level per  $\text{cm.}^2$  cross-section and  $\mathcal{N}$  is Avogadro's number, the following equality



can be made:

$$c \, d l = 1000 \, N_{10} \, \eta^{-1}. \quad (20)$$

Furthermore  $\Delta N(\nu)$ , the number of molecules excited per second with energy  $h\nu$ , is given by

$$\Delta N(\nu) = -c \, d \, \rho(\nu) / (h \, \nu \, n). \quad (21)$$

The combination of equations (19), (20) and (21) gives

$$\Delta N(\nu) / N_{10} = \left[ 2303 \, c \, \epsilon(\nu) / h \, \nu \, n \, \eta \right] \rho(\nu, 0). \quad (22)$$

Equation (22) gives the probability that a molecule in state lo will absorb a quantum of energy  $h\nu$  and go to some excited state. To obtain the probability of going to state ub, equation (22) must be integrated over the finite range of frequencies for this occurrence. Then  $\rho(\nu, 0)$  can be assumed constant over this range and equal to  $\rho(\nu_{lo \rightarrow ub})$ . Thus the integrated equation is

$$\frac{\Delta N_{lo \rightarrow ub}}{N_{10}} = \left[ \frac{2303 \, c}{h \, \eta \, n_{lo \rightarrow ub}} \int \frac{\epsilon(\nu_{lo \rightarrow ub}) \, d\nu_{lo \rightarrow ub}}{\nu_{lo \rightarrow ub}} \right] \rho(\nu_{lo \rightarrow ub})$$

$$= \left[ \frac{2303 c}{h \eta n_{10 \rightarrow ub}} \int \epsilon(\nu_{10 \rightarrow ub}) d \ln \nu_{10 \rightarrow ub} \right] \rho(\nu_{10 \rightarrow ub}) \quad (23)$$

This equation shows for a molecule in state l<sub>0</sub> that the probability of undergoing a transition to state ub is proportional to  $\rho(\nu_{10 \rightarrow ub})$ , the constant of proportionality being the term in brackets. Expression (13) gave a similar relation for a molecule in state l<sub>0</sub> with the proportionality constant being given as  $B_{10 \rightarrow ub}$ . Therefore, identifying the constant  $B_{10 \rightarrow ub}$  with the bracketed expression of equation (23) gives

$$B_{10 \rightarrow ub} = \frac{2303 c}{h \eta n_{10 \rightarrow ub}} \int \epsilon(\nu_{10 \rightarrow ub}) d \ln \nu_{10 \rightarrow ub} \quad (24)$$

Still assuming that all the molecules originate in the state l<sub>0</sub>, it is possible to sum expression (24) over all the vibrational levels of the excited electronic state to obtain a probability coefficient for all transitions to the electronic state u. This is given by

$$B_{10 \rightarrow u} = \sum_b B_{10 \rightarrow ub}$$

$$= \frac{2303 c}{h \pi n_{10 \rightarrow u}} \int \epsilon(\nu_{10 \rightarrow u}) d \ln \nu_{10 \rightarrow u} \quad (25)$$

where  $n_{10 \rightarrow u}$  is the mean refractive index of the non-absorbing medium over the absorption band which is an approximation.

When a molecule goes from a lower electronic state to an upper one by absorption, it will often be to an excited vibrational level of the upper electronic state. However, if the molecule is in a condensed medium, it will usually lose energy by collision until it is in the lowest vibrational level of the state. In fluorescing, the molecule may then go to various vibrational levels of the ground electronic state. Thus in absorption the transitions observed are the  $l_0 \rightarrow \sum_b u_b$ , while in fluorescence they are the  $u_0 \rightarrow \sum_a l_a$ . It is necessary, therefore, to find a relationship between

$$B_{l_0 \rightarrow u} = \sum_b B_{l_0 \rightarrow u_b} \text{ and } A_{u_0 \rightarrow l} = \sum_a A_{u_0 \rightarrow l_a}$$

The wave functions of vibronic states,  $\psi$ , are functions of both the electronic coordinates  $\underline{x}$  and the nuclear coordinates, which may be taken as the normal coordinates  $\underline{Q}$ . If  $\underline{M}(\underline{x})$  is the electric dipole operator for the electrons, then the probability for induced absorption or emission between two states is

proportional to the square of the matrix element of  $\underline{M(x)}$  between the two states; that is

$$B_{1a \rightarrow ub} = B_{ub \rightarrow 1a} \\ = K \left| \iint \psi_{1a}^*(x, Q) M(x) \psi_{ub}(x, Q) dx dQ \right|^2 \quad (26)$$

where  $K$  is the proportionality constant.

The wave functions can be written as products of the electronic and vibrational parts, for example,

$$\psi_{1a}(x, Q) = \theta_{1l}(x, Q) \phi_{1a}(Q). \quad (27)$$

So the integral in equation (26) may be expressed as

$$\iint \psi_{1a}^*(x, Q) M(x) \psi_{ub}(x, Q) dx dQ \\ = \int \phi_{1a}^*(Q) M_{lu}(Q) \phi_{ub}(Q) dQ \quad (28)$$

where

$$M_{lu}(Q) = \int \theta_{1l}^*(x, Q) M(x) \theta_u(x, Q) dx$$

is an electronic transition moment integral for the transition, assuming the nuclei to be fixed in a position  $Q$ . It can be expanded in a power series in the normal coordinates of the molecule:

$$M_{lu}(Q) = M_{lu}(0) + \sum_r \left( \partial M_{lu} / \partial Q_r \right)_0 Q_r \dots \quad (29)$$

For strongly allowed transitions in a molecule, and for reasonably small displacements from the equilibrium nuclear configuration, the zeroth-order term in this expansion should be the dominant one. With the assumption that this is the case, equation (26) reduces to

$$\begin{aligned} B_{la \rightarrow ub} &= B_{ub \rightarrow la} \\ &= K \left| M_{lu}(0) \right|^2 \left| \int \phi_{la}^* \phi_{ub} dQ \right|^2 \end{aligned} \quad (30)$$

The quantity necessary for the calculation of the lifetime is  $A_{uo \rightarrow l}$ , the rate constant for emission from the lowest vibrational level of the excited electronic state to all the vibrational levels of the ground electronic state. From equations (17) and (30) this can be written as

$$\begin{aligned} A_{uo \rightarrow l} &= \sum_a A_{uo \rightarrow la} \\ &= (8 \pi h n_{uo \rightarrow l}^3 / c^3) K \left| M_{lu}(0) \right|^2 \sum_a \nu_{uo \rightarrow la}^3 \\ &\quad \cdot \left| \int \phi_{la}^* \phi_{ub} dQ \right|^2 \end{aligned} \quad (31)$$

where  $n_{u_0 \rightarrow l_1}$  is the mean refractive index of the non-absorbing medium over the fluorescence band, an approximation.

It is desirable to be able to evaluate the term  $\sum_a \nu_{u_0 \rightarrow l_1}^3 \left| \int \phi_{l_1}^* \phi_{u_0} dQ \right|^2$  experimentally. Since the fluorescence band is not narrow, a possible procedure can be derived by dividing the term by  $\sum_a \left| \int \phi_{l_1}^* \phi_{u_0} dQ \right|^2 = 1$ . This sum is equal to unity since the  $\phi_{l_1}$  comprise a complete orthonormal set in  $Q$  space. This gives the following expression:

$$\frac{\sum_a \nu_{u_0 \rightarrow l_1}^3 \left| \int \phi_{l_1}^* \phi_{u_0} dQ \right|^2}{\sum_a \left| \int \phi_{l_1}^* \phi_{u_0} dQ \right|^2}$$

Each term in the numerator of this expression is proportional to the intensity of one vibronic band in the fluorescence spectrum. Each term in the denominator is proportional to  $\nu^{-3}$  times the intensity of one vibronic band. The sums over all the vibronic bands can be replaced by integrals over the fluorescence spectrum, so that the expression reduces to

$$\frac{\int I(\nu) d\nu}{\int \nu^{-3} I(\nu) d\nu} = \left\langle \nu^{-3} \right\rangle_{av}^{-1} \quad (33)$$

the reciprocal of the mean value of  $\nu^{-3}$  in the fluorescence spectrum, where  $I(\nu)$ , the intensity in the spectrum, is measured in terms of relative numbers of quanta at each frequency.

From equation (30) when  $B_{10 \rightarrow ub}$  is summed over  $b$ , the result is

$$\begin{aligned}
 B_{10 \rightarrow u} &= \sum_b B_{10 \rightarrow ub} \\
 &= K \left| M_{1u}(0) \right|^2 \sum_b \left| \int \phi_{1a}^* \phi_{ub} dQ \right|^2, \\
 B_{10 \rightarrow u} &= K \left| M_{1u}(0) \right|^2, \tag{34}
 \end{aligned}$$

since the  $\phi_{ub}$  comprise a complete orthonormal set in  $Q$  space. Thus from equations (34) and (25), the expressions for  $B_{10 \rightarrow u}$  can be equated:

$$\begin{aligned}
 &K \left| M_{1u}(0) \right|^2 \\
 &= \frac{2303 e}{h \pi \tilde{n}_{10 \rightarrow u}} \int \epsilon(\nu_{10 \rightarrow u}) d \ln \nu_{10 \rightarrow u}. \tag{35}
 \end{aligned}$$

If equations (33) and (35) are substituted into equation (31), the result is:

$$A_{uo \rightarrow l} = \frac{8 \times 2303 \cdot \pi \cdot n_{uo \rightarrow l}^3}{c^2 \mathcal{N} \cdot n_{lo \rightarrow u}} \left\langle \nu_f^{-3} \right\rangle_{av}^{-1} \int \epsilon(\nu_{lo \rightarrow u}) d \ln \nu_{lo \rightarrow u} \quad (36)$$

If either or both of the electronic states are degenerate, a factor of  $g_l/g_u$  is multiplied times the right-hand side of equation (36) to sum over these states.

It is more convenient to use this equation in terms of  $\bar{\nu}$  instead of  $\nu$ . The result of this conversion is

$$\begin{aligned} \frac{1}{\tau_o} = A_{uo \rightarrow l} &= \frac{8 \times 2303 \cdot \pi \cdot c \cdot n_{uo \rightarrow l}^3}{\mathcal{N} \cdot n_{lo \rightarrow u}} \left\langle \bar{\nu}_f^{-3} \right\rangle_{av}^{-1} \\ &\cdot \frac{g_l}{g_u} \int \epsilon(\bar{\nu}_{lo \rightarrow u}) d \ln \bar{\nu}_{lo \rightarrow u} \\ &= 2.880 \times 10^{-9} \frac{n_{uo \rightarrow l}^3}{n_{lo \rightarrow u}} \left\langle \bar{\nu}_f^{-3} \right\rangle_{av}^{-1} \frac{g_l}{g_u} \\ &\cdot \int \epsilon(\bar{\nu}_{lo \rightarrow u}) d \ln \bar{\nu}_{lo \rightarrow u} \quad (37) \end{aligned}$$

This equation is applicable to strongly allowed transitions and to only reasonably small displacements of the atoms from the equilibrium nuclear configuration in both electronic states.<sup>9</sup>



Another quantity of interest which may be determined from the emission spectrum is the quantum efficiency of the fluorescence. To determine fluorescence efficiency directly it is necessary to compare the rate of absorption of exciting light with the total rate of emission of fluorescence of all wavelengths and in all directions. In principle this is simple but in practice it is a difficult experiment to perform with precision. An easier method by which fluorescence efficiency may be determined is comparison between a known "standard" substance and the material of interest.<sup>10</sup>

If a solution of the compound of interest is dilute enough that errors due to excessive absorption of exciting light or to self-absorption of the fluorescence are negligible, the total rate of emission of fluorescence is proportional to the product  $I_0 \epsilon C l \phi_f$  where  $\phi_f$  is the quantum efficiency. Now the integrated area under the corrected fluorescence spectrum is also proportional to the total rate of emission of fluorescence. Thus, if the fluorescence emission spectra of two solutions are measured with the same instrumental geometry and at the same intensity of exciting light, the ratio of the two observed fluorescence intensities is given by















































































































