Relationship between Absorption Intensity and Fluorescence Lifetime of Molecules*

S. J. STRICKLER AND ROBERT A. BERG

Department of Chemistry and Lawrence Radiation Laboratory, University of California, Berkeley, California

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The equations usually given relating fluorescence lifetime to absorption intensity are strictly applicable only to atomic systems, whose transitions are sharp lines. This paper gives the derivation of a modified formula

$$1/\tau_0 = 2.880 \times 10^{-9}\, n^2 \langle \bar{\nu}_f^{-3} \rangle_{\mathrm{Av}}^{-1} (g_l/g_u) \int \epsilon\, d \ln \bar{\nu},$$

which should be valid for broad molecular bands when the transition is strongly allowed.

Lifetimes calculated by this formula have been compared with measured lifetimes for a number of organic molecules in solution. In most cases the values agree within experimental error, indicating that the formula is valid for such systems. The limitations of the formula and the results expected for weak or forbidden transitions are also discussed.

IN 1917, Einstein[1] derived the fundamental relationship between the transition probabilities for induced absorption and emission and that for spontaneous emission. The result showed that the spontaneous-emission probability was directly proportional to the corresponding absorption probability and to the third power of the frequency of the transition. Einstein's equations were soon expressed in terms of more commonly measured quantities by Ladenburg[2] and Tolman.[3] Later a refractive index correction was added by Perrin[4a] and by Lewis and Kasha[4b] for cases where the absorbing systems were in solution. Although the various authors expressed the result in different ways, all their equations may be written in the form

$$1/\tau_0 = A_{u \to l} = 8 \times 2303 \pi c \bar{\nu}_{ul}^2 n^2 \mathfrak{N}^{-1} \frac{g_l}{g_u} \int \epsilon\, d\bar{\nu}. \qquad (1)$$

In this equation, $A_{u \to l}$ is the Einstein transition probability coefficient, or rate constant, for spontaneous emission from an upper state u to the lower state l (usually the ground state); c is the speed of light in a vacuum; $\bar{\nu}_{ul}$ is the frequency of the transition in cm^{-1}; n is the refractive index of the medium; $\mathfrak{N}$ is Avogadro's number; g_l and g_u are the degeneracies of the lower and upper states, respectively; ϵ is the molar extinction coefficient. The integration extends over the absorption band in question. τ_0, the reciprocal of the rate constant, is the maximum possible mean life of state u, i.e., the mean life if the only mechanism of deactivation is spontaneous emission to state l. The actual mean life τ may be shorter than τ_0 if the quantum yield of the luminescence is less than one.

In the derivation of Eq. (1), it is necessary to assume that the absorption band is sharp, and that the fluorescence occurs at the same wavelength as the absorption. This means that, in general, the equation is strictly applicable only to atomic transitions. There are many problems of interest, however, in which it is desirable to calculate the mean life of excited states of molecules, for which Eq. (1) is not accurate. Lewis and Kasha[4b] tried to test the equation approximately for rhodamine B, and concluded that it was probably valid to within a factor of two. Bowen and Metcalf,[5] in discussing the fluorescence of anthracene, gave an equation similar to (1) except for an extra factor of 3 on the right-hand side. They suggested that this factor was necessary for molecules which absorb light only when a component of the electric vector of the light wave is oriented along one particular axis of the molecule. Our work will show that this factor is erroneous. Other authors[6] have pointed out that it is necessary to take account of the frequency difference between absorption and fluorescence. However, they have not given the result in exact form.

It is the purpose of this paper to present a modification of Eq. (1) which is applicable to polyatomic molecules under certain conditions. We shall first derive the equation, and in doing so, for the sake of completeness, we shall repeat the essential points of the derivation of the earlier formulas. We shall then summarize calculations of the fluorescent lifetimes of a number of molecules, and describe the experiments by which we measured these lifetimes. Finally, we shall discuss the limitations of the formula and the cases where it may not be valid.

DERIVATION OF EQUATION FOR MOLECULES

Consider two electronic states of a molecule, a ground state l and an upper state u. The corresponding electronic wave functions may be called Θ_l and Θ_u.

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[1] A. Einstein, Physik. Z. **18**, 121 (1917).
[2] R. Ladenburg, Z. Physik **4**, 451 (1921).
[3] R. C. Tolman, Phys. Rev. **23**, 693 (1924).
[4] (a) F. Perrin, J. phys. radium **7**, 390 (1926); (b) G. N. Lewis and M. Kasha, J. Am. Chem. Soc. **67**, 994 (1945).

[5] E. J. Bowen and W. S. Metcalf, Proc. Roy. Soc. (London) **A206**, 437 (1951).
[6] T. Förster, *Fluoreszenz Organischer Verbindungen* (Vandenhoeck & Ruprecht, Göttingen, 1951), p. 158; F. E. Stafford, Ph.D. dissertation, University of California, Berkeley, 1959, UCRL-8854; V. N. Soshnikov, Soviet Phys.-Uspekhi **4**, 425 (1961).

Associated with each electronic level are a series of states having different wave functions for nuclear motion, vibration, rotation, and translation. For the present purpose it is sufficient to consider only the vibrational states, though the rotational and translational motion might be treated in an analogous manner. In the Born–Oppenheimer approximation, each vibronic state has a wave function Ψ which can be written as a product of an electronic function Θ and a vibrational function Φ. $\Psi_{la} = \Theta_l \Phi_{la}$, $\Psi_{ub} = \Theta_u \Phi_{ub}$. For simplicity in discussion, it will be assumed that each state is single; if degeneracies occur in either the electronic or vibrational part, they can be summed over in the proper manner when necessary.

Relationship Between Einstein A and B Coefficients

Suppose a large number of these molecules, immersed in a nonabsorbing medium of refractive index n, to be in thermal equilibrium within a cavity in some material at temperature T. The radiation density (erg cm^{-3} per unit frequency range) within the medium is given by Planck's blackbody radiation law

$$\rho(\nu) = (8\pi h \nu^3 n^3 / c^3)[\exp(h\nu/kT) - 1]^{-1}. \qquad (2)$$

By the definition of the Einstein transition probability coefficients, the rate of molecules going from state la to state ub by absorption of radiation is

$$N_{la} B_{la \to ub} \rho(\nu_{la \to ub}), \qquad (3)$$

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

$$N_{ub}[A_{ub \to la} + B_{ub \to la} \rho(\nu_{ub \to la})], \qquad (4)$$

where $B_{ub \to la} = B_{la \to ub}$ and $\nu_{ub \to la} = \nu_{la \to ub}$. At equilibrium the two rates must be equal, so by equating expressions (3) and (4), it is found that

$$A_{ub \to la}/B_{ub \to la} = [(N_{la}/N_{ub}) - 1]\rho(\nu_{ub \to la}). \qquad (5)$$

According to the Boltzmann distribution law, the numbers of molecules in the two states at equilibrium are related by

$$N_{ub}/N_{la} = \exp[-(h\nu_{ub \to la}/kT)]. \qquad (6)$$

Substitution of Eqs. (2) and (6) into (5) results in Einstein's relation

$$A_{ub \to la} = 8\pi h \nu_{ub \to la}^3 n^3 c^{-3} B_{ub \to la}. \qquad (7)$$

Relation of B Coefficients to Absorption Intensity

In a common type of absorption meaurement, a beam of essentially parallel light is passed through the sample contained in a cell having planar windows perpendicular to the light beam. It may be assumed for convenience that the light beam has a cross section 1 cm^2 with a uniform intensity over this area. If $\rho(\nu, x)$ is the radiation density in the light beam after it has passed a distance x centimeters through the sample, the molar extinction coefficient ϵ can be defined by

$$\rho(\nu, x)/\rho(\nu, 0) = 10^{-\epsilon(\nu)Cx} = e^{-2.303\epsilon(\nu)Cx},$$

where C is the concentration in moles per liter.

If a short distance dx is considered, the change in radiation density may be written

$$-d\rho(\nu) = 2.303\epsilon(\nu)\rho(\nu, 0)\,Cdx. \qquad (8)$$

For simplicity, all the molecules will be assumed to be in the ground vibronic state, Ψ_{l0}. (This may not be true at normal temperatures, but this will not materially affect the results. It would be possible, but more complicated, to carry through a number of states with appropriate Boltzmann weighting factors.) It is easily seen that

$$Cdx = 1000 N_{l0} \mathfrak{N}^{-1}. \qquad (9)$$

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

$$\Delta N(\nu) = -cd\rho(\nu)/(h\nu n). \qquad (10)$$

Combining Eqs. (8), (9), and (10), it is found that

$$\Delta N(\nu)/N_{l0} = [2303 c\epsilon(\nu)/h\nu n\mathfrak{N}]\rho(\nu, 0). \qquad (11)$$

Equation (11) gives the probability that a molecule in state $l0$ will absorb a quantum of energy $h\nu$ and go to some excited state. To obtain the probability of going to the state ub, it must be realized that this can occur with a finite range of frequencies, and Eq. (11) must be integrated over this range. $\rho(\nu, 0)$ can be assumed constant over this range and equal to $\rho(\nu_{l0 \to ub})$. The value of $\epsilon(\nu)$ must be only that for the one vibronic transition; if the spectrum is well resolved, this would present little difficulty, but it can be done in principle in any case. Then

$$\frac{\Delta N_{l0 \to ub}}{N_{l0}} = \left[\frac{2303 c}{hn\mathfrak{N}}\int \epsilon(\nu)\,d\,\ln\nu\right]\rho(\nu_{l0 \to ub}). \qquad (12)$$

This equation shows that, for a molecule in state $l0$ in a beam of parallel light, the probability of undergoing a transition to state ub is proportional to $\rho(\nu_{l0 \to ub})$, the constant of proportionality being the term in brackets. Expression (3) gave a similar relation for a molecule in an isotropic radiation field, except with proportionality constant $B_{l0 \to ub}$. In the latter case, the photons might be thought of as arriving at a molecule from random directions, whereas in the first case they all arrive from one direction. If, however, the molecules are randomly oriented, the average probability of absorption for a large number of molecules must be the same in either case for the same total radiation density. Therefore,

$$B_{l0 \to ub} = \frac{2303 c}{hn\mathfrak{N}}\int \epsilon d\,\ln\nu, \qquad (13)$$

where the integration is over the $l0 \rightarrow ub$ vibronic absorption band.

Still assuming all the molecules to originate in the state $l0$, it is possible to sum expression (13) over all the vibrational levels of the upper electronic state, to obtain a probability coefficient for all transitions to the electronic state u. This is given by

$$B_{l0 \rightarrow u} = \sum_b B_{l0 \rightarrow ub} = \frac{2303c}{hn\mathfrak{N}} \int \epsilon d \ln \nu, \qquad (14)$$

where the integration is now extended over the whole electronic absorption band of the $l \rightarrow u$ transition.

Lifetime Relationship for Molecules

When a molecule undergoes an electronic absorption process, it will often end up in some excited vibrational level of the upper electronic state. However, if it 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 we observe the transitions $l0 \rightarrow \sum_b ub$, while in fluorescence we observe $u0 \rightarrow \sum_a la$. It is therefore necessary to find a relation between $B_{l0 \rightarrow u} = \sum_b B_{l0 \rightarrow ub}$ and $A_{u0 \rightarrow l} = \sum_a A_{u0 \rightarrow la}$.

The wave functions of vibronic states are functions of both the electronic coordinates x and the nuclear coordinates, which can be taken as normal coordinates Q, since we are neglecting rotations and translations. They can be written as products of electronic and vibrational parts, for example,

$$\Psi_{la}(x, Q) = \Theta_l(x, Q)\Phi_{la}(Q). \qquad (15)$$

The function $\Theta_l(x, Q)$ is an electronic wave function for nuclei fixed in some configuration, so it contains the nuclear coordinates as parameters. If $\mathbf{M}(x)$ is the electric dipole operator for the electrons, it is well known that the probability for induced absorption or emission between two states is proportional to the square of the matrix element of $\mathbf{M}(x)$ between the two states. The constant of proportionality is of no importance here, so it will be designated as K.

$$B_{la \rightarrow ub} = B_{ub \rightarrow la}$$

$$= K \left| \iint \Psi_{la}^*(x, Q)\mathbf{M}(x)\Psi_{ub}(x, Q)dxdQ \right|^2. \qquad (16)$$

Using (15), the integral in this expression can be written

$$\iint \Psi_{la}^*(x, Q)\mathbf{M}(x)\Psi_{ub}(x, Q)dxdQ$$

$$= \int \Phi_{la}^*(Q)\mathbf{M}_{lu}(Q)\Phi_{ub}(Q)dQ,$$

where

$$\mathbf{M}_{lu}(Q) = \int \Theta_l^*(x, Q)\mathbf{M}(x)\Theta_u(x, Q)dx$$

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:

$$\mathbf{M}_{lu}(Q) = \mathbf{M}_{lu}(0) + \sum_r (\partial \mathbf{M}_{lu}/\partial Q_r)_0 Q_r + \cdots. \qquad (17)$$

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. It is only for transitions which are forbidden by symmetry or are weak for other reasons that zeroth-order term is small and higher-order terms become important. Let us make the assumption that we are dealing with a strong, allowed transition, so that only the zeroth-order term in (17) is important. Then Eq. (16) reduces to

$$B_{la \rightarrow ub} = B_{ub \rightarrow la} = K \mid \mathbf{M}_{lu}(0) \mid^2 \left| \int \Phi_{la}^*\Phi_{ub}dQ \right|^2. \qquad (18)$$

Taking the appropriate sums, we find that

$$B_{l0 \rightarrow u} = \sum_b B_{l0 \rightarrow ub} = K \mid \mathbf{M}_{lu}(0) \mid^2 \sum_b \left| \int \Phi_{la}^*\Phi_{ub}dQ \right|^2,$$

$$B_{l0 \rightarrow u} = K \mid \mathbf{M}_{lu}(0) \mid^2, \qquad (19)$$

since the Φ_{ub} comprise a complete orthonormal set in Q space.

The quantity necessary for calculation of the lifetime is $A_{u0 \rightarrow l}$, the rate constant for emission from the lowest vibrational level of electronic state u to all vibrational levels of state l. Using Eqs. (7) and (18) this can be written

$$A_{u0 \rightarrow l} = \sum_a A_{u0 \rightarrow la} = (8\pi hn^3/c^3)K \mid \mathbf{M}_{lu}(0) \mid^2$$

$$\cdot \sum_a \nu_{u0 \rightarrow la}^3 \left| \int \Phi_{la}^*\Phi_{ub}dQ \right|^2. \qquad (20)$$

It is desirable to be able to evaluate the term $\sum_a \nu_{u0 \rightarrow la}^3 \mid \int \Phi_{la}^*\Phi_{ub}dQ \mid^2$ experimentally. If the fluorescence band is narrow, ν^3 can be considered a constant and removed from the summation, the remaining sum being equal to unity. A better procedure can be derived by dividing by $\sum_a \mid \int \Phi_{la}^*\Phi_{u0}dQ \mid^2 = 1$:

$$\frac{\sum_a \nu_{u0 \rightarrow la}^3 \left| \int \Phi_{la}^*\Phi_{u0}dQ \right|^2}{\sum_a \left| \int \Phi_{la}^*\Phi_{u0}dQ \right|^2}.$$

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 ν^{-3} times the intensity of one vibronic band. The sums over all vibronic bands can be replaced by integrals over the fluorescence

spectrum, so that the expression reduces to

$$\frac{\int I(\nu)\,d\nu}{\int \nu^{-3}I(\nu)\,d\nu} = \langle \nu_f^{-3} \rangle_{Av}^{-1},$$

the reciprocal of the mean value of ν^{-3} in the fluorescence spectrum. This can be obtained experimentally. It should be noted that $I(\nu)$, the intensity in the spectrum, must be measured in terms of relative numbers of quanta at each frequency, rather than in the usual energy units.

Now, by combining Eqs. (14), (19), and (20), we obtain

$$A_{u0 \to l} = \frac{8 \times 2303\pi n^2}{c^2 \mathfrak{N}} \langle \nu_f^{-3} \rangle_{Av}^{-1} \int \epsilon d \ln\nu. \quad (21)$$

If either or both of the electronic states are degenerate, it is necessary to sum over the possible transitions. If it is assumed that all the possible transitions between degenerate components are equally allowed (which may or may not be true), or that there is a rapid equilibrium established between molecules in the different component states of each degenerate level (which is probably true under normal conditions), the result is a factor of g_l/g_u on the right-hand side of Eq. (21).

It is convenient to write this equation in terms of the more common units where frequency is measured in cm^{-1} rather than sec^{-1}. The result is

$$1/\tau_0 = A_{u0 \to l} = 8 \times 2303\pi c n^2 \mathfrak{N}^{-1} \langle \bar{\nu}_f^{-3} \rangle_{Av}^{-1} \frac{g_l}{g_u} \int \epsilon d \ln\bar{\nu}$$

$$= 2.880 \times 10^{-9} n^2 \langle \bar{\nu}_f^{-3} \rangle_{Av}^{-1} \frac{g_l}{g_u} \int \epsilon d \ln\bar{\nu}, \quad (22)$$

where the integral is over the whole of the electronic absorption band concerned. This is the desired formula, applicable to strong transitions in molecules.

If, as is the case for most atomic transitions, the band is sharp and the absorption and fluorescence occur at the same wavelength, $\bar{\nu}$ can be considered a constant. A factor of $1/\bar{\nu}$ can be removed from under the integral sign, and $\langle \bar{\nu}_f^{-3} \rangle_{Av}^{-1}$ becomes just $\bar{\nu}^3$. In that case, Eq. (22) reduces to Eq. (1), as must be expected for atomic transitions.

COMPOUNDS FOR TESTING LIFETIME RELATIONS

In choosing molecules for testing Eq. (22), we were guided by several considerations. (a) The lowest energy singlet–singlet electronic absorption band of the molecule must be fairly strong, as this was assumed in the derivation. (b) This first band should be well separated from other absorption bands so that the area under the experimental curve can be measured accurately. (c) Absorption must occur at wavelengths of

3650 Å or longer, as our equipment has glass optics. (d) The quantum yield of fluorescence must be known. In addition, to avoid complicating assumptions about the mechanism of quenching, we used only compounds whose fluorescence yields in solution at room temperature were quite high, preferably nearly equal to one.

On the basis of these criteria, we chose seven compounds for testing the formula derived in the preceding section. The names, structures, and absorption and fluorescence spectra of these compounds are shown in Fig. 1. The absorption intensity scales vary for different molecules. The fluorescence spectra are in units of relative numbers of quanta, except for rhodamine B and rubrene where the scale is plate blackening.

N-methylacridinium chloride was made by reacting acridine with dimethyl sulfate in benzene solution. An aqueous solution of the resulting N-methylacridinium methyl sulfate was treated with saturated NaCl solution to precipitate the chloride. The other compounds were commercially available materials. All compounds were purified by recrystallization.

The absorption spectra were measured on a Cary model 14 spectrophotometer. A few of them require comment. 9-aminoacridine apparently exists as a neutral molecule in ethanol solution. However, in ethanol with HCl, or in water with or without HCl, the spectrum has a somewhat different appearance, probably indicating the presence of a protonated ion. Rhodamine B also exists as an equilibrium mixture of the structure shown and a colorless isomer having a lactone structure.[7] The amount of the colorless form present in ethanol solution is not known, but our final results indicate that it is rather slight. In acid ethanol, rhodamine B forms a protonated ion whose spectrum is similar, but somewhat more intense and shifted to lower energies. As shown in Fig. 1, the first band in N-methylacridinium chloride is overlapped considerably by the strong second transition. This made it necessary to extrapolate the high-energy side of the first band in a rather arbitrary fashion, as indicated by the dotted curve. Because of this, the integrated area under the curve could not be measured with accuracy. The other molecules have much less uncertainty from this source.

The fluorescence spectra of most of the molecules were measured on an American Instrument Company spectrophotofluorometer. It was felt necessary to make some correction for instrument sensitivity, although extreme accuracy was not necessary. For this purpose we used correction factors published by White, Ho, and Weimer,[8] even though these are not strictly applicable to our instrument. To obtain $\langle \bar{\nu}_f^{-3} \rangle_{Av}^{-1}$, two curves were plotted for each spectrum, one of the corrected intensities in units of relative numbers of quanta at each frequency, and the other of $\bar{\nu}^{-3}$ times this value.

[7] S. Wawzonek, *Heterocyclic Compounds*, edited by R. C. Elderfield (John Wiley & Sons, Inc., New York, 1951), Vol. II, Chap. 13.

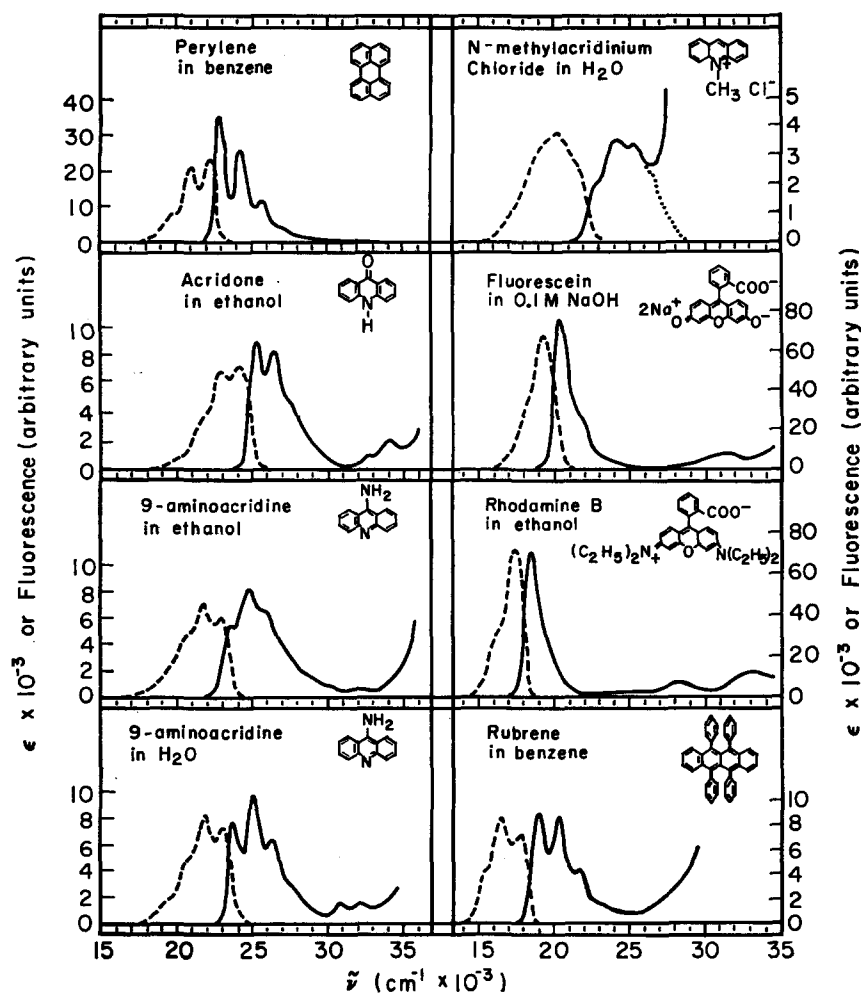[8] C. E. White, M. Ho, and E. Q. Weimer, Anal. Chem. **32**, 438 (1960).

FIG. 1. Absorption spectra (solid lines) and fluorescence spectra (dashed lines) of the compounds used for lifetime studies.

The ratio of the areas under the curves then gives $\langle \bar{\nu}_f^{-3}\rangle_{Av}^{-1}$ with considerable accuracy.

Unfortunately, the fluorescence spectra of rhodamine B and rubrene lie in the red and yellow regions where the photomultiplier in the fluorometer is insensitive. The fluorescence of these molecules was therefore measured on a small Hilger spectrograph, using Eastman plates type III-F. The mean frequency was estimated from a densitometer tracing of the spectra; this value was cubed and taken to be $\langle \bar{\nu}_f^{-3}\rangle_{Av}^{-1}$. This procedure is, of course, less accurate than that used for the other compounds.

It will also be noted in Fig. 1 that in all cases the absorption and fluorescence spectra show a rather good mirror image relationship. This is evidence that at least most of the intensity in the absorption bands is due to a single electronic transition. Some error would be introduced into the calculated lifetimes if there were weaker bands lying in the same region as the observed bands. However, from the appearance of the spectra of these molecules, such other bands could contribute only a small amount to the observed intensity.

In calculating the actual lifetime τ of a compound, the value of τ_0 given by Eq. (22) must be multiplied

by the quantum yield of fluorescence. Quantum yields in room temperature solutions have been measured by a number of workers; the important studies for this paper are those of Melhuish,[9] Weber and Teale,[10] and Bowen and Williams.[11] Fluorescence yields have not been measured for the acid solutions of 9-aminoacridine or rhodamine B. In these cases we have assumed the yield to be unity in calculating the lifetime. This is probably a good assumption for the 9-aminoacridine, since it appears to be mostly in the protonated form in pure water, and the yield is high in that case. There is less reason to suppose it true for rhodamine B in acid, and indeed our final results indicate that the actual quantum yield is considerably less than unity.

For the refractive index term in Eq. (22), we have used the values for the pure solvents at about the mean wavelength of the fluorescence band. The values were taken from *International Critical Tables*.[12]

[9] W. H. Melhuish, J. Phys. Chem. **65**, 229 (1961).
[10] G. Weber and F. W. J. Teale, Trans. Faraday Soc. **53**, 646 (1957).
[11] E. J. Bowen and A. H. Williams, Trans. Faraday Soc. **35**, 765 (1939).
[12] *International Critical Tables*, (McGraw-Hill Book Company Inc., New York, 1926), Vol. VII, pp. 12–15.

TABLE I. Summary of the calculation of lifetimes.

Molecule	Solvent	$\epsilon_{max} \times 10^{-3}$	$\int \epsilon d \ln \bar{\nu} \times 10^{-3}$	$\langle \bar{\nu}_f^{-3} \rangle_{Av}^{-1} \times 10^{-13}$	n^2	Quantum yield	τ_{calc} (nanoseconds)
Perylene	benzene	35.1	3.320	0.948	2.289	0.89[9]	4.29
Acridone	EtOH	8.99	1.041	1.228	1.869	0.83[9]	12.06
9-aminoacridine	EtOH	8.06	1.233	0.968	1.866	0.99[10]	15.43
9-aminoacridine	EtOH-HCl	11.27	1.293	1.014	1.866	⋯	14.19
9-aminoacridine	H_2O	9.29	1.159	1.000	1.790	0.98[10]	16.40
9-aminoacridine	H_2O-HCl	9.59	1.181	0.985	1.790	⋯	16.67
N-methylacridinium chloride	H_2O	3.53	0.587	0.747	1.785	1.00[10]	44.37
Fluorescein	H_2O-NaOH	75.5	6.183	0.670	1.782	0.93[10]	4.37
Rhodamine B	EtOH	71.7	5.937	0.51	1.850	0.97[10]	6.01
Rhodamine B	EtOH-HCl	89.4	7.045	0.48	1.850	⋯	5.55
Rubrene	benzene	9.46	1.438	0.48	2.244	1.00[11]	22.42

Table I gives the pertinent data used in calculating the lifetimes of the molecules. The maximum extinction coefficient of the first band of each substance is included as a check on the purity of the material and the accuracy of the measurements.

LIFETIME MEASUREMENTS

Lifetime measurements were made with a phase fluorometer that had been constructed in the laboratory of L. Brewer. A detailed discussion of the apparatus and its use will be given elsewhere.[13] Figure 2 is a schematic diagram of the optical arrangement. At one end of the water tank a quartz crystal is driven at 2.6 Mc to produce standing waves. The wave pattern diffracts light coming from the source H and a diffraction image of slit S_1 is focused in the plane of slit S_2, through which only the zero order of diffraction passes. Since the standing wave pattern collapses twice during each cycle of excitation of the crystal, light emerging from slit S_2 is sinusoidally modulated at 5.2 Mc. The modulated beam is divided; 3% is reflected to the reference photomultiplier P_1 and the rest is focused at the sample position. A General Electric A-H6 water-cooled mercury lamp was used as light
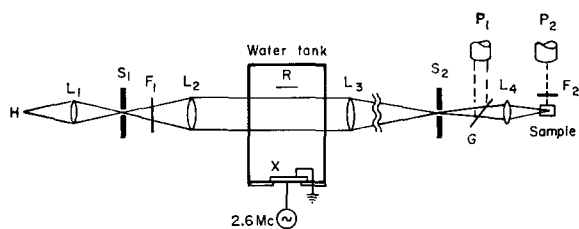

FIG. 2. Schematic diagram of the optical part of the lifetime-measuring apparatus. F, filter; G, glass plate beam-splitter; H, mercury lamp; L, lens; R, reflecting plate; S, slit; P, photomultiplier tube; X, quartz crystal.

[13] See also Robert A. Berg, Ph.D. dissertation, University of California, Berkeley, 1962, UCRL-9954.

source. Filter(s) F_1 isolated the narrow wavelength region used to excite fluorescence.

Each lifetime measurement requires two phase readings: First, a colloidal suspension is placed in the sample position to scatter light to photomultiplier P_2 and the phase relation between the 5.2-Mc signals from the two photomultipliers is measured; then, the scatterer is replaced by a sample and filter F_2 is inserted to block the exciting light. The fluorescent light displays the excitation modulation but is delayed in phase by an angle $\Delta\phi$, which is related to the lifetime of fluorescence τ by the equation $\tan\Delta\phi = 2\pi f\tau$, where f is the frequency of modulation, 5.2 Mc.

In addition to being limited by the precision of the phase meter the accuracy of measurements may be greatly reduced by systematic errors among which the following are particularly important:

(a) Variation of phase along the length of the zeroth-order diffraction beam. This effect was minimized by stopping down the length of slit S_2 so that only the center of the zeroth-order beam is used. Also, the same beam cross section was focused both on the reference photomultiplier and on the sample. The geometries of the scatterer and sample readings were identical.

(b) Variation of phase angle reading with signal size. The intensities of modulated light from the scatterer and from the sample were approximately equalized with neutral-density light filters.

(c) Drift with time of the percent modulation in the modulated beam. Before each set of measurements the water tank reflector R was positioned to obtain a reproducible maximum ac signal size.

The entire system was checked by measuring the speed of light over a distance of 240 cm, corresponding to a phase shift of about 15 deg (8×10^{-9} sec). The measurement agreed to 3% with the calculated delay time.

TABLE II. Measured lifetimes and average deviations between four runs.

Compound	Solvent	τ_{obs} (nanoseconds)	Average deviation
Perylene	benzene	4.79	12%
Acridone	EtOH	11.80	6%
9-aminoacridine	EtOH	13.87	4%
9-aminoacridine	EtOH—HCl	14.07	8%
9-aminoacridine	H_2O	16.04	4%
9-aminoacridine	H_2O—HCl	15.45	1%
N-methylacridinium chloride	H_2O	34.78	3%
Fluorescein	H_2O—NaOH	4.02	12%
Rhodamine B	EtOH	6.16	9%
Rhodamine B	EtOH—HCl	4.65	14%
Rubrene	Benzene	16.42	7%

The sample and scattering solutions were contained in rectangular cells of 1-cm path lengths. The sample solutions were dilute enough that the maximum absorbances of the first bands were less than 0.2 or 0.3. Under these conditions, errors due to absorption and re-emission of the fluorescence light should be negligible. One possible exception is the rhodamine B solutions, where the measured lifetime may be long by about 5% due to this factor.

Oxygen was removed from the solutions by bubbling a fine stream of nitrogen through them for about 10 min. Tests indicated that longer bubbling gave no significant change in lifetime.

The lifetime of each compound was measured four times, usually on different days, and the results averaged. Table II gives the measured lifetimes, and the average deviations among the four results. The latter give an indication of the reliability of the measurements. Most of the average deviations are less than 10%, except for the compounds with the shortest lifetimes. The true accuracy might be somewhat better than this, as there are some minor errors which can be deliberately compensated for on different runs.

DISCUSSION OF RESULTS

The comparison of the calculated and observed lifetimes is summarized in Table III. For most of the compounds, the agreement between the two values is rather good. Three of the cases show a somewhat larger error, and these require some comment.

N-methylacridinium chloride is the only molecule for which there is a serious problem of overlap between the first and second transitions. It seems likely that most of the error in this case lies in the measurement of $\int \epsilon d \ln \bar{\nu}$, as the measurement of the area under the absorption curve may easily be wrong by 20%. However, it is also true that this molecule has the weakest first transition of any of the substances considered in

this study, and it is possible that the formula is actually less accurate in this case.

As was mentioned earlier, the fluorescence quantum yield of rhodamine B in acid solution has not been measured. The addition of a proton to the neutral rhodamine B molecule causes a considerable change in absorption spectrum, and it would not be surprising to find a change in fluorescence yield. The differences between the measured and calculated lifetimes would be consistent with a quantum yield of 84%, which would seem to be a reasonable value.

The discrepancy in the case of rubrene is a more serious problem. Considering the agreement for most of the molecules, we do not believe that either the lifetime measurements or the applicability of the formula is at fault. One possible explanation is that the material used is very impure; however, two recrystallizations made a difference of only 2% in the measured extinction coefficient. Another possibility is that the reported quantum yield of unity is in error. This measurement was made by Bowen and Williams[12] using a visual comparison with the yield of another substance. This method may have been less accurate than the photoelectric measurements which they used for some other molecules. They also studied solutions containing oxygen, and reported that the sum of the quantum yields of fluorescence and oxidation became greater than one under some conditions. Our lifetime measurements would indicate a fluorescent quantum yield of about 70%–80% in dilute solution. Such a value would remove part of the discrepancy in the quantum yield observations.

The agreement between the calculated and observed lifetimes in the other cases is much better. However, even among these, there seems to be a slight systematic difference in the direction of long calculated lifetimes. It is our belief that this arises from a combination of several small systematic errors which would tend to

TABLE III. Comparison of observed and calculated lifetimes (nanoseconds).

Compound	Solvent	τ_{obs}	τ_{calc}	Error
Perylene	benzene	4.79	4.29	−10%
Acridone	EtOH	11.80	12.06	+2%
9-aminoacridine	EtOH	13.87	15.43	+11%
9-aminoacridine	EtOH—HCl	14.07	14.19	+1%
9-aminoacridine	H_2O	16.04	16.40	+2%
9-aminoacridine	H_2O—HCl	15.45	16.67	+8%
N-methylacridinium chloride	H_2O	34.78	44.37	+28%
Fluorescein	H_2O—NaOH	4.02	4.37	+9%
Rhodamine B	EtOH	6.16	6.01	−2%
Rhodamine B	EtOH—HCl	4.65	5.55	+19%
Rubrene	benzene	16.42	22.42	+37%

add up. About 1% might be due to errors in the wavelength scale of the fluorometer, as this appeared to read slightly high in wavelength. Any impurities remaining in the compounds would usually give low values of ϵ and thus would also lead to long calculated lifetimes. On the other hand, any O_2 remaining in the solutions would quench the fluorescence and make the measured lifetimes shorter. Also, any scattered exciting light passing through the filters in measurements of fluorescence lifetimes would cause low readings.

There are also several sources of random errors. The largest of these is probably in the lifetime measurements. There are small errors involved in plotting absorption and fluorescence spectra and in measuring areas. The value of $\langle \bar{\nu}_f^{-3} \rangle_{Av}^{-1}$ is probably accurate to about 3% for most of the compounds, and to about 10% for rubrene and rhodamine B.

The agreement between the observed and calculated lifetimes seems to be within experimental error except for the three cases of N-methylacridinium chloride, rubrene, and rhodamine B in acid solution. We believe that formula (22) is actually valid, at least to within a few percent, and that the deviations which do occur arise from various experimental errors.

LIMITATIONS OF THE FORMULA

The principal assumption made in the derivation of Eq. (22) is that only the zeroth-order term in the expansion (17) is significant. This really requires two conditions to be met for singlet–singlet transitions: first that the band be strong, and second that there not be too large a change in configuration in the excited state. The first requirement is easily checked by observing the absorption spectrum. The formula seems to hold for bands with $\epsilon \approx 8000$, though it may be less accurate for much weaker transitions. It is somewhat more difficult to know if the second condition is met, but some idea can be obtained from the position of the Franck–Condon maximum. In the molecules which we have tested, the "vertical" transitions would lie between 0–0 and 0–3 bands in the main progressions. It appears that this much distortion, at least, does not affect the validity of the formula.

The term "configuration" in this connection should be taken to include specific interactions with the solvent. For example, there might be molecules in which the formation or breaking of a hydrogen bond in the excited state would significantly affect the transition probability. It may also be emphasized that the spectra and the lifetime must be measured in the same solvent and under the same conditions, as a change of these may affect the transition probability.

A much more difficult problem is the question of what relationship to expect for weak molecular transitions. In such cases, the higher terms in Eq. (17) become important, and it is almost impossible to make any definite statements about the relation between lifetime and absorption intensity. It seems likely, however, that the factors which determine the transition

probability would not change a great deal in the excited state. Thus, the same equation should give at least the correct order of magnitude for the lifetime, though one cannot expect the accuracy found for the strong transitions.

If the transition is forbidden by symmetry, the zeroth-order term in Eq. (17) vanishes. In many cases, only first-order terms will need to be considered, higher order terms being much smaller yet. If these first-order terms are carried through the succeeding steps, the equation analogous to Eq. (19) becomes

$$B_{l0 \to u} = K \sum_r (\partial \mathbf{M}_{lu}/\partial Q_r)_0^2 \langle Q_r^2 \rangle_{l0}, \qquad (23)$$

where $\langle Q_r^2 \rangle_{l0} = \int \Phi_{l0}^* Q_r^2 \Phi_{l0} dQ$ is the mean-square value of the normal coordinate Q_r in the ground vibronic state. The treatment here is similar to that used by Murrell and Pople[14] in their consideration of the intensities of forbidden transitions. The equation analogous to (20) is

$$A_{u0 \to l} = (8\pi h n^3/c^3) \langle \nu_f^{-3} \rangle_{Av}^{-1} K \sum_r (\partial \mathbf{M}_{lu}/\partial Q_r)_0^2 \langle Q_r^2 \rangle_{u0}.$$

$$(24)$$

There is a problem in comparing Eqs. (23) and (24) due to the fact that the normal coordinates may be different in the ground and excited electronic states. In a rough way, however, the deviations from Eq. (22) might be due to changes in $(\partial \mathbf{M}_{lu}/\partial Q_r)_0^2$ or in $\langle Q_r^2 \rangle$ in the two states. It seems likely that the derivatives would show little change, so that the main effect would lie in differences of the mean square displacements along appropriate antisymmetric normal coordinates. If the molecule is distorted in the excited state, this could make the transition allowed and the lifetime much shorter than calculated from the absorption intensity. If the molecule retains its symmetry in the excited state, then the relationship should depend mainly on the change in force constants for the antisymmetric vibrations, as these determine the mean square displacements.

A particularly interesting example of a forbidden transition is the first singlet–singlet band of benzene (2650 Å), which has been studied in great detail.[15] In this case both the ground and excited states have D_{6h} symmetry. Only one antisymmetric vibration contributes significantly to the intensity; this is a degenerate mode having a frequency of 606 cm^{-1} in the ground state and 521 cm^{-1} in the excited state. Assuming no changes in the derivatives in Eqs. (23) and (24), or in the normal coordinates, the result is simply that the lifetime should be reduced by a factor $\langle Q^2 \rangle_{l0}/\langle Q^2 \rangle_{u0} = 521/606$ compared to the value calculated by Eq. (22) from absorption and fluorescence spectra.

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If these ideas about forbidden transitions are correct, it means that Eq. (22) may be not far from right even when the first-order terms in (17) are involved. This suggests that if a given transition has, let us say, 80% contribution from zero-order terms and 20% from first-order terms, Eq. (22) may be in error by only 3%–4%. This would make the requirements for the strength of transitions much less stringent.

Unfortunately, our apparatus is at present incapable of measuring the lifetime of benzene because of the glass optics. It would, however, be of considerable interest to check the predictions of this type of theory on some molecules with weak or forbidden transitions. It would be very helpful to be able to calculate the fluorescence lifetimes of such molecules with confidence, as seems possible for molecules with strong transitions.

In conclusion, we believe we have shown that Eq. (22) makes possible rather accurate calculation of intrinsic fluorescence lifetimes from data on the absorption and fluorescence spectra, provided that the transitions involved are allowed and fairly strong. Lifetimes for weak transitions can probably be calculated as to order of magnitude, though further studies are needed of the problems involved.

Note added in proof. Since writing this, another paper by E. J. Bowen and E. Coates (J. Chem. Soc. **1947**, 105), has come to our attention. This work suggests that the fluorescence yield of rubrene in benzene is actually about 75%, in good agreement with our results.

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Melting Curves of Five Metals under High Pressure*

Marvin L. McDaniel,† Stanley E. Babb, Jr., and Gene J. Scott

Department of Physics, University of Oklahoma, Norman, Oklahoma

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Techniques have been developed for the determination of the melting curves of metals under pressure and are applied to five metals. These data are used to evaluate the constants appearing in the Simon equation, with and without approximate values of the corrections to be applied to the thermocouples. These corrections can make as much as 20% difference. The values of these constants are compared with the theoretical expressions of Gilvarry, and agreement is close.

INTRODUCTION

A CONSIDERABLE body of literature exists on the almost classical problem of the melting curve. The success of the Simon equation[1] in representing the data has aroused considerable theoretical interest[2–4] from which it has become clear that the metals, as a group, have less agreement with theoretical expressions for the Simon equation constants than for other elements, or compounds. Unfortunately, except for the work of Bridgman[5] on the alkali metals, bismuth, gallium, and mercury, very little work of high precision has been done, due to the difficulties of accurately measuring the melting curves under simultaneous application of high temperatures and pressures. This paper reports the developments of a method of measuring the melting curves of metals with a precision on the order of 0.1°C, and its application to five metals.

APPARATUS AND PROCEDURE

The pressure equipment is standard enough to need little comment. The pressures were provided by a 35:1 intensifier actuated by a hand oil pump. The system was primed by a free piston pump, which was in turn driven by an air-operated oil pump. Thus the system was raised to about 2000 bar before the high-pressure piston was advanced. The pressure transmitting medium was argon in all of the experiments reported in this paper. The cell in which the furnace was located has an inside diameter of $1\frac{1}{16}$ in., and a length of 7 in. Due to the large volume of the pressure cell and the relatively small displacement of the intensifier, a single stroke of the intensifier would yield but 5000 bar pressure in the cell. In order to raise the pressure to our normal working range of 10 000 bar, it was necessary to incorporate a valve between the pressure cell and intensifier so the cell could be isolated during the recycling of the intensifier. Failure of this valve limited

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