Evaluation of Photoluminescence Lifetimes

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A new method is described for calculating emission lifetimes for flash decay data. The technique, based on a linear phase-plane plot, handles the case where the emission lifetime is comparable to the observed flash duration, and its accuracy compares favorably with that of other procedures. It requires only a desk calculator, is rapid, and provides an internal check as to whether or not a single decay time is being observed.

Introduction

Perhaps the most popular and direct method for measuring photoluminescence lifetimes employs a flash procedure. The sample luminescence is excited by a flash lamp or laser pulse, and the emission, monitored by a photomultiplier, is displayed on an oscilloscope.[2] For the most commonly encountered special case where the sample decays by only first-order or pseudo-first-order paths (the decay can thus be characterized by a mean lifetime τ), flash techniques can be especially appealing. If the flash duration and time scale of instrumental distortion are short compared with τ, the transient observed on the oscilloscope is exponential with a lifetime τ; τ may readily be evaluated from a semilogarithmic plot of emission intensity *vs.* time. Unfortunately, when the time scale of instrumental distortion, the flash duration, and τ are comparable, this simple procedure fails; however, in spite of the fact that the observed sample decay now reflects, in a complex fashion, the detailed nature of the flash, the distortions, and τ, various mathematical techniques allow one to extract τ from the flash and sample decay data.[3-5]

For the case where the semilogarithmic plot fails to yield accurate lifetime estimates, we shall present a new method for evaluating τ from the flash and the sample decay data as well as experimental verification of the procedure. The approach is related to, but avoids certain disadvantages of existing procedures and these last will be described briefly so as to provide a proper context.

Three time-dependent functions must first be defined. $F(t)$ is the oscilloscope response to the flash stimulation in the absence of the sample. $D(t)$ is the oscilloscope response when the system views the sample luminescence; $D(t)$ is assumed to contain no direct contribution from the flash. Both $F(t)$ and $D(t)$, however, will contain instrumental distortions such as phototube rise time, RC time constant effects, and amplifier bandwidth limitations. We shall subsequently assume that all distortions are linear and are the same in type and degree in the measurement of both $F(t)$ and $D(t)$. The "true" dependence of the sample decay, $d(t)$, is defined

as that sample decay signal that would be observed if the excitation flash were infinitely short, an impulse, and the optical detector and electronics introduced no signal distortion.

Lifetimes may, for example, be evaluated from the statistical moments of $D(t)$ and $F(t)$;[3-5] computation of a lifetime can be relatively rapid (0.5–2 hr) on a desk calculator. The principal disadvantage of the moments methods is that since only a calculated τ is obtained, no warning is given of multiple decay kinetics.[6,7] Also, since the moments are defined as integrals to infinite time, there is a practical problem associated with taking experimental data to large enough times to ensure that reasonably good convergence is obtained.

Alternatively, the theory of Fourier transformations allows one, in principle, to construct from $F(t)$ and $D(t)$ the true decay curve, $d(t)$.[8] The τ value may then be computed from $d(t)$. For the case where $d(t)$ is not an exponential or a sum of exponentials, this method is the only available one for computing $d(t)$. Implementation of this technique appears to be relatively difficult, however. Munro and Ramsay[8] have mentioned the use of the scarce "optical Fourier transform" computers to carry out the calculations, but to our knowledge the only attempt to employ a digital computer for such evaluations was unsuccessful, presumably due to the difficult programming and ill-conditioned convergence.[9] Digital computer evaluation of the transforms should

(1) National Science Foundation Postdoctoral Fellow.

(2) (a) C. A. Parker, "Photoluminescence of Solutions," Elsevier, New York, N. Y., 1968; (b) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966.

(3) D. H. Cooper, *Rev. Sci. Instrum.*, **37**, 1407 (1966).

(4) J. N. Demas and G. A. Crosby, *Anal. Chem.*, **42**, 1010 (1970).

(5) S. S. Brody, *Rev. Sci. Instrum.*, **28**, 1021 (1957).

(6) An ingenious extension of the moments methods has been described by Isenberg and Dyson.[7] Their method allows one to fit $d(t)$ to a sum of exponentials rather than a single decay. The method requires, however, large numbers of data points of rather high accuracy to obtain meaningful results, thus preventing the use of oscilloscope data collection methods. A digital computer is required to carry out the data reduction.

(7) 1. Isenberg and R. D. Dyson, *Biophys. J.*, **9**, 1337 (1969).

(8) I. H. Munro and I. A. Ramsay, *J. Sci. Instrum.*, **1**, 147 (1968).

eventually be possible since the approach has been successful for similar problems.[10]

Perhaps the most widely used method for evaluating τ under adverse conditions is that of curve simulation, CS.[3,4,11] If $d(t)$ is a simple exponential, then

$$D(t) = Ke^{-t/\tau} \int_0^t F(x)e^{x/\tau}dx \qquad (1)$$

The procedure is to calculate a sample decay curve, $D_{calcd}(t)$, for an assumed value of τ, and to compare this $D_{calcd}(t)$ with the observed function, $D(t)$. The proportionality constant, K, which takes into account the various instrumental, geometric, and sample properties is adjusted to give the best fit between $D_{calcd}(t)$ and $D(t)$. The calculation is repeated for successive τ values until an acceptable fit to the observed $D(t)$ is obtained. Efficient procedures for obtaining a best τ value have been discussed.[4]

The CS method has the advantage that $D_{calcd}(t)$ can be compared with the observed $D(t)$, a procedure which gives insight into how well an exponential describes the emission kinetics. Inability to obtain a satisfactory fit constitutes strong evidence for a more complex decay function and, conversely, a good fit implies simple exponential decay of the emission. The disadvantage is that a large number of calculations is required; thus, the method is usually practical only if a digital computer is available.[12,13] Also, both $D(t)$ and $F(t)$ must be taken to the same zero reference time, which precludes the use of the normal internal triggering mode on the oscilloscope in obtaining the data. The readout must be externally triggered by another pulse of fixed time relation to the initiation of the flash, usually by a signal from a second photomultiplier which views the flash directly.

In summary, there is no available technique which allows *both* the rapid evaluation of a decay constant by means of a desk calculator *and* also a check that $d(t)$ is indeed a simple exponential. The method described below has both attributes.

The Phase-Plane Method. The phase-plane, PP, method is based on the fact that while eq 1 is not linear, it may be converted to a linear form (see Appendix A). This form is

$$Z(t) = -\tau W(t) + K\tau \qquad (2)$$

where

$$Z(t) = \frac{\int_0^t D(y)dy}{\int_0^t F(y)dy}$$

and

$$W(t) = \frac{D(t)}{\int_0^t F(y)dy}$$

The integrals are readily evaluated from the experimental $D(t)$ and $F(t)$, and a plot of $Z(t)$ vs $W(t)$ will then yield a straight line of slope $-\tau$ and intercept $K\tau$.

We have found it convenient to calculate the integrals numerically using the trapezoidal rule and a programmable desk calculator (see Appendix B). With this procedure computation of the PP plot is about as rapid as a moments calculation (20 min for 40 data points using the programmable calculator and about 2 hr otherwise). Further, if the PP plot is not linear, then $d(t)$ is presumably complex in nature; one thus has an internal check on the correctness of the assumption that $d(t)$ is a single exponential decay. In practice, however, $W(t)$ and $Z(t)$ are not accurately defined at short times because of experimental error, and the plot will usually be nonlinear at small $Z(t)$. In a least-squares or visual fitting of a straight line to the PP plot, these early points should be given reduced weight. The entire procedure can, of course, be carried out be means of a digital computer.

Since the PP method is based on eq 1, it shares some of the attributes of the CS method. Thus both $D(t)$ and $F(t)$ must be taken to a common zero time. As with the latter method, linear instrumental distortion (*e.g.*, transit time spread and delay and RC distortion) do not invalidate the results so long as $D(t)$ and $F(t)$ are obtained under identical conditions of distortion. We feel, however, that the PP method allows easier detection of any nonsimple $d(t)$ although, of course, no direct readout of two or more τ values is possible. Also, we suggest that even if the CS method is used, the calculations should be routinely checked by our procedure. Occasionally the integral of eq 1 is evaluated erroneously in the CS method because of convergence problems—the presence of the exponential factor may give the plot of $F(t) \exp(t/\tau)$ vs. t, an irregular shape, and an apparently acceptable simulation can be obtained with an incorrect τ value.[14]

Experimental Test of the Phase-Plane Method. Demas and Crosby[4] tabulated luminescence decay data for tris(2,2'-bipyridine)ruthenium(II) chloride, [Ru-(bipy)$_3$]Cl$_2$, at 77°K, and the corresponding plots of $F(t)$ and $D(t)$ are shown in Figure 1. The flash duration was about 20 μsec, while τ was about 5 μsec.

(9) J. A. McIntosch, "A Pulsed Excitation Method for Determining Nanosecond Fluorescent Lifetimes," National Bureau of Standards Clearing House for Federal Scientific and Technical Information, AD-651-799.

(10) J. B. Bassingthwaghte, *Science*, 167, 1347 (1970).

(11) O. J. Steingraber and I. B. Berlman, *Rev. Sci. Instrum.*, 34, 524 (1963).

(12) An exception is the TRW lifetime computer. This device is an on-line analog computer; visual matching of the synthetic decay curve and the actual curve is carried out on an oscilloscope.[13]

(13) TRW Systems, El Segundo, California, TRW Instruments, Application Note 6, 1967.

(14) Convergence difficulties can be minimized by assuming a functional form for the flash curve between data points and then carrying out the integrations of eq 1 exactly rather than by approximate numerical methods.[4]
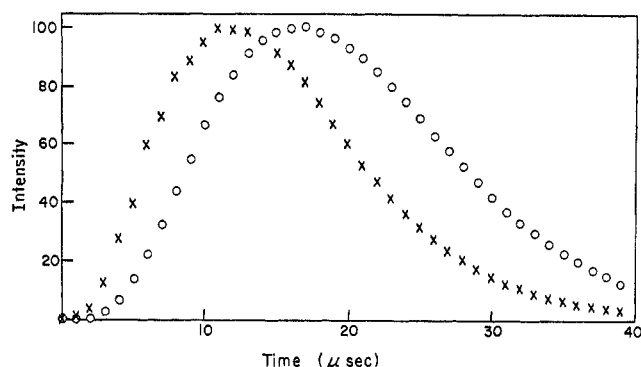
Figure 1. Observed flash and sample decay for $[Ru(bipy)_3]Cl_2$ at 77°K (from ref 4). Curve F (X) is the observed flash. Curve D (O) is the observed sample decay. The true sample lifetime is ~4.92 μsec.
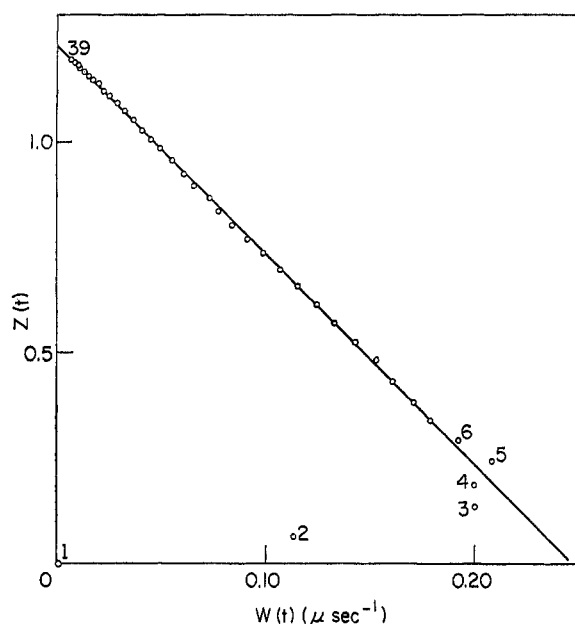

Figure 2. Phase-plane plot for the data of Figure 1. The times (in microseconds) at which the points were evaluated are given by the numbers (those between 7 and 38 being omitted).

These parameters are such, of course, as to preclude a direct evaluation of τ from a semilogarithmic plot of $D(t)$ vs. time. The corresponding PP plot is essentially linear, however, as shown in Figure 2. An unweighted linear least-squares fit through points 3 to 39 gives a line from whose slope τ is 5.00 μsec, with a standard deviation of ±0.06 μsec. The intercept, $K\tau$, is 1.229 ± 0.006. The first two points for very low $Z(t)$ values are clearly unreliable.

The "true" lifetime (from a short flash experiment[4]) is 4.92 ± 0.05 μsec for this system, while other evaluation methods[4] applied to the data of Figure 1 give 4.91 μsec (moments method 1), 4.79 μsec (moments method 2), and 5.15 μsec (CS method). The CS result presumably could have been made more accurate by using a larger number of trial τ values. The PP method

clearly gives accuracy comparable to that of the established techniques.

Conclusion

We feel that the PP plot method is so simple and rapid that it can routinely be applied whenever there is a discernible difference between an observed sample luminescence and the excitation pulse. Then, as long as $F(t)$ and $D(t)$ are not too similar, one obtains an estimate of τ and a good indication of whether or not the decay kinetics are simple. For nearly identical $F(t)$ and $D(t)$, of course, a rough estimate of τ is the only information present.

Appendices

A. Derivation of Equation 2. We first integrate both sides of eq 1 between the limits 0 and t

$$\int_0^t D(y)dy = K \int_0^t e^{-y/\tau}\left[\int_0^y e^{x/\tau}F(x)dx\right]dy \quad (3)$$

Integration of the right-hand side of eq 3 by parts yields

$$\int_0^t D(y)dy =$$

$$-K\tau e^{-t/\tau}\int_0^t e^{x/\tau}F(x)dx + K\tau \int_0^t F(y)dy \quad (4)$$

Equation 4 simplifies since the first term on the right-hand side is just $-\tau D(t)$ (by eq 1), so

$$\int_0^t D(y)dx = -\tau D(t) + K\tau \int_0^t F(y)dy \quad (5)$$

which rearranges to eq 2.[15-18]

B. Calculational Procedure. Our procedure for generating the data points of Figure 2 requires that the flash and emission intensities be measured (that is, read off the curves of Figure 1) at the same equal time intervals. The times are then $t_0, t_1 \ldots t_j \ldots t_n$, each with a corresponding value of $F(t)$ and $D(t)$. The data are taken so that $F(t_0) = D(t_0) = 0$.

(15) Equation 5 is a generalization of the phase-plane method used by Huen.[16,17] Huen's technique applies only when $F(t)$ is a delta function or an impulse so that $\int_0^t F(y)dy$ is a constant. Under this condition eq 2 simplifies and a plot of $\int_0^t D(y)dy$ vs. $D(t)$ gives a straight line with a slope of $-\tau$, Huen's original form.
(16) T. Huen, *Rev. Sci. Instrum.*, **40**, 1067 (1969).
(17) A. Bernalte and J. Le Page, *ibid.*, **40**, 41 (1969).
(18) Dividing both sides of eq 5 by $D(t)$ also yields a linear form; τ is obtained from an intercept rather than a slope. Since the intercept is extrapolated from the data, this alternative form does not appear to be as accurate for evaluating τ as eq 2.

The integrals are then estimated by the trapezoidal rule, which gives

$$\int_0^{t_j} D(y)\,dy \simeq \frac{(t_1 - t_0)}{2} R_j \qquad (6)$$

where

$$R_j = [D(t_j) + D(t_{j-1})] + R_{j-1}; \qquad j \geq 1 \text{ and } R_0 = 0$$

and

$$\int_0^{t_j} F(y)\,dy \simeq \frac{(t_1 - t_0)}{2} Q_j \qquad (7)$$

with

$$Q_j = [F(t_j) + F(t_{j-1})] + Q_{j-1}; \qquad j \geq 1 \text{ and } Q_0 = 0$$

Insertion of the above relationships into the definitions of $Z(t)$ and $W(t)$ then gives

$$W(t_j) = \frac{2D(t_j)}{(t_1 - t_0)Q_j} \qquad (8)$$

and

$$Z(t_j) = R_j/Q_j \qquad (9)$$

Our calculator was a Wang 360 machine equipped with a CP-1 card programmer. The card program for the calculation is available upon request.

The Optical Activity of Alkyl-Substituted Cyclopentanones.

INDO Molecular Orbital Model[1]

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An INDO molecular orbital model is used to compute the oscillator strengths, rotatory strengths, and anisotropy factors for several of the lowest-lying singlet → singlet transitions in seven chiral cyclopentanone systems. The computational model provides for limited configuration interaction and calculates all electric transition moments in the dipole velocity formalism. The structures studied were: (1) unsubstituted cyclopentanone with the five-membered carbocyclic ring twisted into a half-chair conformation (belonging to the C_2 point group); (2) three conformational isomers of (+)-3-methylcyclopentanone—two in which the ring is twisted into a C_2 geometry (the methyl group equatorial to the ring in one and the methyl group axial to the ring in the other), and one in which the ring is planar; (3) two conformational isomers of 2-methylcyclopentanone—one in which the ring is twisted and one in which it is planar; (4) one conformational isomer of 2,3-dimethylcyclopentanone in which the ring is twisted, the 2-methyl group is axial to the ring, and the 3-methyl group is equatorial. The rotatory strengths calculated for the n → π^* transition are in good agreement with the experimentally determined values for several twisted cyclopentanone systems. The computed results indicate that in the β-substituted systems the inherent chirality of the twisted carbocyclic ring is the primary source of optical activity, whereas in the α-substituted systems the substituents exert the dominant influence. The rotatory strengths calculated for higher energy singlet → singlet transitions appear not to be in good agreement with the experimental data, although in these cases the analysis is ambiguous and inconclusive.

I. Introduction

The molecule 3-methylcyclopentanone is of particular interest in theoretical studies concerned with the optical rotatory properties of carbonyl electronic transitions. This saturated, cyclic ketone was selected as the model system for the first detailed one-electron calculation of the rotatory strength associated with the carbonyl n → π^* transition[2] and was also adopted as a test system in several subsequent theoretical studies on the optical activity of carbonyl compounds.[3-5] In each

of these studies, the cyclopentanone ring was assumed to be in a rigid, planar conformation and only the

(1) This work was supported in part by a National Science Foundation grant (CASS Institutional, 3760-2195) administered through the Center for Advanced Studies, University of Virginia.

(2) W. J. Kauzmann, J. Walter, and H. Eyring, *Chem. Rev.*, 26, 339 (1940).

(3) T. Watanabe and H. Eyring, *J. Chem. Phys.*, 40, 3411 (1964).

(4) M. V. Volkenshtein and M. P. Kruchek, *Opt. Spectrosk.*, 9, 243 (1960).

(5) D. Caldwell and H. Eyring, *Ann. Rev. Phys. Chem.*, 15, 281 (1964).