

(see paper I, Sec. 5] in coordinate space by

$$\begin{aligned} &\langle \mathbf{k}_1', \dots, \mathbf{k}_l' | U_l | \mathbf{k}_1, \dots, \mathbf{k}_l \rangle \\ &= \Omega^{-l} \int \langle \mathbf{r}_1' \dots \mathbf{r}_l' | U_{l,\Omega} | \mathbf{r}_1 \dots \mathbf{r}_l \rangle \\ &\times \exp[i \sum_{\alpha} (\mathbf{k}_{\alpha}' \cdot \mathbf{r}_{\alpha}' - \mathbf{k}_{\alpha} \cdot \mathbf{r}_{\alpha})] \prod_{\alpha} d^3 r_{\alpha} d^3 r_{\alpha}'. \quad (\text{IV.123}) \end{aligned}$$

The $U_{l,\Omega}$ functions in momentum space are defined by

$$\begin{aligned} &\langle \mathbf{k}_1', \dots, \mathbf{k}_l' | U_{l,\Omega} | \mathbf{k}_1, \dots, \mathbf{k}_l \rangle \\ &= (8\pi^3)^{-l} \int \langle \mathbf{r}_1', \dots, \mathbf{r}_l' | U_{l,\Omega} | \mathbf{r}_1, \dots, \mathbf{r}_l \rangle \\ &\times \exp[i \sum_{\alpha} (\mathbf{k}_{\alpha}' \cdot \mathbf{r}_{\alpha}' - \mathbf{k}_{\alpha} \cdot \mathbf{r}_{\alpha})] \prod_{\alpha} d^3 r_{\alpha} d^3 r_{\alpha}', \quad (\text{IV.124}) \end{aligned}$$

where $U_{l,\Omega}$ in the coordinate space was defined in paper I. Thus if we define u_l by Eq. (I.54), then as $\Omega \rightarrow \infty$,

$$\begin{aligned} &[\Omega/(8\pi^3)]^{l-1} \langle \mathbf{k}_1', \dots, \mathbf{k}_l' | U_l | \mathbf{k}_1, \dots, \mathbf{k}_l \rangle \\ &\rightarrow \langle \mathbf{k}_1', \dots, \mathbf{k}_l' | u_l | \mathbf{k}_1, \dots, \mathbf{k}_l \rangle \delta_{\mathbf{K}, \mathbf{K}'}, \quad (\text{IV.125}) \end{aligned}$$

where $\mathbf{K} = \sum \mathbf{k}_{\alpha}$ and $\mathbf{K}' = \sum \mathbf{k}_{\alpha}'$. Similarly we find, as $\Omega \rightarrow \infty$,

$$\begin{aligned} &[\Omega/(8\pi^3)]^{l-1} \langle \mathbf{k}_1', \dots, \mathbf{k}_l' | \Upsilon_l^S | \mathbf{k}_1, \dots, \mathbf{k}_l \rangle \\ &\rightarrow \delta_{\mathbf{K}, \mathbf{K}'} \langle \mathbf{k}_1', \dots, \mathbf{k}_l' | v_l^S | \mathbf{k}_1, \dots, \mathbf{k}_l \rangle, \quad (\text{IV.126}) \end{aligned}$$

where v_l^S is defined by (IV.54). Both u_l and v_l^S are independent of volume.

Some explicit forms of Υ_l^S and v_l^S for hard spheres have been given in papers II and III.

Theory of Fluorescence Time Constant Measurements in Liquid and Rigid Solutions*

HARTMUT KALLMANN

Department of Physics, New York University, New York, New York

(Received June 16, 1959)

Formulas are derived for the dependence of fluorescence upon time for the case when energy transfer from the solvent to the solute is involved. Three cases are considered: excitation by single fast particles, excitation by one burst of particles during a given period, and periodic excitation. One important point is that in the rise and decay of fluorescence from a burst of particles, it is the difference of two exponential functions and not their sum which occurs. The results are compared with the experiments of Burton and Dreeskamp, of Swank and Buck, and of Knau. These experiments are in general accordance with the derived formulas.

A THEORY of light emission from a liquid or rigid solution which is energized by a fast particle has been given by Brucker and Kallmann.¹ It shows that in a solution containing a single solute and solvent where the fluorescence is emitted mainly by the solute, the light emission, I , varies with time according to the formula

$$I = N\alpha\kappa\frac{\tau_s}{\tau_s - \tau_u} \left[\exp\left(\frac{-t}{\tau_s}\right) - \exp\left(\frac{-t}{\tau_u}\right) \right]. \quad (1)$$

This formula holds if the solute is excited via energy transfer only. N is the total number of excited molecules of the bulk material, $\alpha\kappa$ is the probability per unit time that energy is transferred to the solute, and τ_u is the decay time of the solute as measured under direct light excitation (not via energy transfer). $1/\tau_s = 1/\tau_0 + \alpha\kappa$, where τ_0 is the time constant of the solvent in the absence of solute. κ is the product of the quantum efficiency of the solute when directly excited by light and the efficiency of energy transfer. According to recent measurements, this latter efficiency is close to

one.² Often, however, the solution is not energized by a single particle but by a burst of particles during a period of time, T , as is the case in the experiments of Burton and Dreeskamp³ and Swank and Buck⁴; or, the solution is continuously excited with an excitation intensity varying with the period ω . This is the case in the experiments of Knau.⁵

Formula (1) cannot be applied directly to these cases, but the theory can be extended by a straightforward procedure to include the effect of a burst of particles or of periodic excitation.

If the excitation is extended over a period of T seconds, then the following formulas for the light emission are obtained:

$$t < T: \quad I = \frac{N_0\alpha\kappa\tau_s}{T(\tau_s - \tau_u)} \left\{ \tau_s \left[1 - \exp\left(\frac{-t}{\tau_s}\right) \right] - \tau_u \left[1 - \exp\left(\frac{-t}{\tau_u}\right) \right] \right\}, \quad (2)$$

² Brown, Furst, and Kallmann, *Discussions Faraday Soc.* (to be published).

³ M. Burton and H. Dreeskamp, *Discussions Faraday Soc.* (unpublished).

⁴ W. L. Buck and R. K. Swank, Argonne National Laboratory, Physics Division, Summary Report, 1958 (unpublished).

⁵ H. Knau, *Z. Naturforsch.* **12a**, 881 (1957).

* This work was supported by the Signal Corps Engineering Laboratories, Fort Monmouth, New Jersey.

¹ G. Brucker and H. Kallmann, *Phys. Rev.* **108**, 1122 (1957).

$$t > T: I = \frac{N_0 \alpha \epsilon \kappa \tau_s}{T(\tau_s - \tau_u)} \left\{ \tau_s \exp\left(\frac{-t'}{\tau_s}\right) \left[1 - \exp\left(\frac{-T}{\tau_s}\right) \right] - \tau_u \exp\left(\frac{-t'}{\tau_u}\right) \left[1 - \exp\left(\frac{-T}{\tau_u}\right) \right] \right\}, \quad (3)$$

where $t' = t - T$ and N_0/T is the number of solvent molecules excited per second.

For periodic excitation with the intensity $n_0[1 - \cos \omega t]$, where n_0 = excited solvent molecules produced per second, one obtains for the light emission

$$I = \frac{n_0 \alpha \epsilon \kappa \tau_s}{\tau_s - \tau_u} [(\tau_s - \tau_u) - A \cos(\omega t + \varphi_{su})], \quad (4)$$

where

$$A = \frac{\{\tau_s(1 + \delta_u^2) - \tau_u(1 + \delta_s^2)\}^2 + [\tau_s \delta_s(1 + \delta_u^2) - \tau_u \delta_u(1 + \delta_s^2)]^2\}^{\frac{1}{2}}}{(1 + \delta_s^2)(1 + \delta_u^2)}, \quad (5)$$

τ_s and τ_u are the above-defined lifetimes, $\delta_s = \omega \tau_s$, $\delta_u = \omega \tau_u$, and

$$\tan \varphi_{su} = \frac{\delta_s \tau_s(1 + \delta_u^2) - \delta_u \tau_u(1 + \delta_s^2)}{\tau_s(1 + \delta_u^2) - \tau_u(1 + \delta_s^2)}. \quad (6)$$

Equation (4) goes over into the well-known formula for direct excitation of the solute if $\tau_s \ll \tau_u$.

It is noteworthy that although two time constants occur in Eq. (1), nevertheless the light emitted by the solute varies in (4) as the incoming intensity except that it is altered by a phase shift φ_{su} , (φ_{su} is, of course different from the value of φ_u when only one time constant is involved as under direct excitation of the solute by light).

The application of these equations leads to the following conclusions:

Instantaneous excitation (high-energy particle), produces a flash, the decay time of which is essentially always the longer of the two time constants involved. Thus for dilute solutions, and $\tau_0 > \tau_u$, the time constant of the solvent (or more precisely τ_s which is always smaller than τ_0) is observed as the decay time of the emitted light. When $\tau_s > \tau_u$, direct light excitation of the solute and high-energy excitation of the solute yield different decay times as observed by Knau.

For constant excitation during a period T , comparable to τ_s and τ_u or longer, formula (2) gives the rise of the emission and formula (3) its decay. Both contain two time constants. In both rise and decay curves the longer time constant accounts for most of the emission. One must, however, consider that it is not the sum but the difference of two exponential functions which occurs in the rise and decay curves, the longer time constant having the greater effect when excitation is carried out almost to equilibrium ($T > \tau_s$ and τ_u). On a plot of $\log I$ against t an extrapolation to $t' = 0$ of the linear portion of the curve which represents the longer time constant will intersect the I axis only slightly above the equilibrium intensity.

If the two time constants are in the ratio 2 to 1, the extrapolated line intersects the I axis at an intensity twice as large as the actual equilibrium intensity (1.3 on the logarithmic scale). This means that the actual

light emission curve lies only slightly below the extrapolated curve for the longest time constant. In a logarithmic representation, the smaller time constant only shows up as a small downward bending at the beginning of the decay curve because the two time constants occur as differences in formula (3). This agrees with the form shown by Burton's measurements.¹ Even for the special case in which the time constants are equal, the curve will not deviate greatly from a straight line in the logarithmic representation. In this case the decaying intensity is proportional to the formula $[1 + (t/\tau)] \exp(-t/\tau)$.

This analysis shows that two different time constants do not show up as sharply as one might expect in the decay curve. A greater difference is obtained when excitation is not to equilibrium. ($T < \tau_s$ and τ_u). The difference between the strength of excitation of the two time constants becomes smaller; however, the exponential with the longer time constant always remains the larger one. Burton's measurements for crystals and plastics are found to display the effects of two time constants. These cannot be readily identified with the time constant of transfer and light emission of the solute since the curves do not show the down curving at the beginning and since the longer time constant component is not always the larger one. The longer time constant in this case must have another origin than energy transfer. We conjecture that it is due to a long-time component of light emission observed in scintillators especially under excitation with high density of excitation. This long-time excitation probably comes about because of a delayed recombination of charges or perhaps by trapping of charges or excitation energy. One can describe this delayed excitation in this theory as equivalent to two types of excitation which are superimposed upon each other; their respective light emissions also are superimposed. If the light emission of the short-time excitation has already decayed, the weaker emission of the long-time component becomes observable. A long-time exciting component of this type may be responsible for the form of Burton's curves for crystals and plastics.⁶

⁶ Buck and Swank⁴ have also pointed out that simple energy transfer considerations cannot explain their results in plastics.

The dependence of the time constant given by the straight-line portion of Burton's curves of time constants as function of the benzene concentration in cyclohexane can be interpreted in accordance with the above equations. At zero benzene concentration the measured τ is that of terphenyl in cyclohexane since τ_s of cyclohexane (assumed to be determined essentially by τ_0 of cyclohexane) is expected, because of the small energy transfer of cyclohexane, to be smaller than τ_u (terphenyl). The amount of energy going to benzene and from benzene to terphenyl increases with benzene concentration. The time constant involved in the energy transfer to terphenyl in the combination solvent is always essentially the τ_s for benzene, since the transfer time from cyclohexane is always shorter than τ_0 of cyclohexane which is assumed very short. Thus when most of the emitted light stems from energy transfer from benzene, formula (3) is used with τ_s that of benzene (plus terphenyl) and τ_u the time constant of terphenyl in the benzene-cyclohexane combination.

τ_0 is larger for small concentrations of benzene than for higher concentrations because of concentration quenching; this is known from the fluorescence of benzene. In addition, αc for a given terphenyl concentration is smaller for benzene-cyclohexane combinations than for benzene alone; this is concluded from our general observation that Q values in such solutions are larger than for a solution with a single solvent. On account of both effects it is to be expected that τ_s (benzene) is relatively large for small benzene concentrations and may even be larger than τ_u . This is a possible explanation of the increase in τ observed by Burton at small benzene concentration. At larger benzene concentrations τ_s becomes small, and the observed time constants decrease in agreement with observations of Burton. A more accurate comparison

between the proposed theory and experiment can be made only when many more time-constant data are available, especially those obtained under light excitation.

The measurements with periodic excitation as given by Knau can also be analyzed with the theory. He finds that the time constants change with concentration from large magnitudes to small. The time constant at very small solute concentrations is interpreted as that of the solvent; at large concentration the time is that of the solute as is verified by direct light excitation of the solute. Actually his equipment does not measure time constants but phase shifts, and apparently he determines the equivalent time constants from the formula $\varphi = \omega t$ which gives an apparent time constant. The true time constants must be calculated by means of Eq. (6). From this equation τ_s can be determined if τ_u is known. For small concentration Eq. (6) yields indeed $\varphi_{\text{measured}} = \omega \tau_0$, and for large concentration $\varphi_{\text{meas}} = \omega \tau_u$. However, in the intermediate range (6) must be employed in order to determine τ_s . The phase shift curve given by Knau should be given by Eq. (6) if τ_s is given by $(\tau_0^{-1} + \alpha c)^{-1}$ or, using the relationship between αc and the " Q " of the intensity *versus* concentration curve, by $\tau_s = \tau_0(1 + c/\alpha)^{-1}$ since $Q = (\alpha \tau_0)^{-1}$.⁵ It would be interesting to see whether such a relationship follows from the experimental data. At the moment one can only say that the general trend of Knau's agrees with Eq. (6) and the value given above for τ_s . It would also be particularly interesting to consider types of energy transfer other than by diffusion or migration, for instance that by jumps. The latter would give a slightly different dependence of τ_s upon the concentrations. Thus this method may help to discriminate between the various types of transfer processes.