

# SOME NEW THERMODYNAMIC CONSIDERATIONS CONCERNING THE UPPER LIMIT OF PHOTOLUMINESCENCE ENERGY YIELD

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As a result of the re-examination of previous thermodynamic considerations eight assumptions are set and whenever these are fulfilled an upper limit can be given for the luminescence energy yield of solutions in agreement with experimental data. The theoretical results are tested by experimental data obtained for the energy yield of rhodamine 6G solutions.

## *Introduction*

1. There is a great deal of contraversion in the literature concerning the upper limit of photoluminescence energy yield  $\eta$  as a function of excitation frequency [1]. Based on an earlier work [2], a re-examination of the problem seemed to be worthwhile. As described in the present paper more exact and careful calculations have led to relations that will be checked by experimental data. This topic has gained particular interest since cooling accompanied with resonance fluorescence was reported for certain gases.

To obtain a lucid survey of this problem the present work will be confined to rigorously defined systems that represent a widely applied category of luminescing systems.

## *Theoretical Considerations*

2. The following set of assumptions will be introduced.

(a) Any absorbed photon can yield at most a single luminescence photon.

(b) The intensity of photoluminescence is strictly proportional to the intensity of the exciting light.

(c) The sample is a solution that fills a sphere of  $r$  radius;  $r$  is larger than the wavelength  $\lambda$  of radiation by many orders of magnitude [3], so that light diffraction can be neglected. The sample solution is surrounded by a diathermanous medium of infinite size and identical refractive index  $n$ .

(d) For the coefficient of absorption  $\alpha_\nu$  and scattering  $\beta_\nu$  of the luminescing solution and  $r \alpha_\nu \ll 1$  and  $\beta_\nu r \ll 1$  is fulfilled at any  $\nu$  frequency.

(e) Since according to (b) the energy yield does not depend on the intensity of the exciting light, for the precise determination of the sample's temperature  $T$  and

the most advantageous application of the entropy law it is also assumed that the sample is exposed to uniform radiation from all directions, the spectrum of which is given in Fig. 1.

Throughout the present paper we shall follow the notions and units of Planck's monograph [3], i.e. with reference to Fig. 1,  $K_b$  denotes the specific intensity of the equilibrium radiation corresponding to temperature  $T$ ;  $K_0$  and  $K_n$  refer to the specific intensity of the exciting light (at  $\nu_e$ ) and the compensating radiation (at  $\nu_n$ ,  $\nu_e \gg \nu_n$ ), both being constant over the interval  $\Delta\nu_e$  and  $\Delta\nu_n$ , respectively. This latter one compensates the warming or cooling of the sample and takes, thus, negative or positive values. It is also assumed that the following inequalities hold:  $K_0 \ll K_b$ ,  $K_n \ll K_b$ ; furthermore (f)  $\alpha_{\nu_e} = \alpha_{\nu_n}$ , and for  $\nu_n$  values in the infrared the luminescence yield vanishes. Due to the presence of solvent this latter assumption is reasonable.

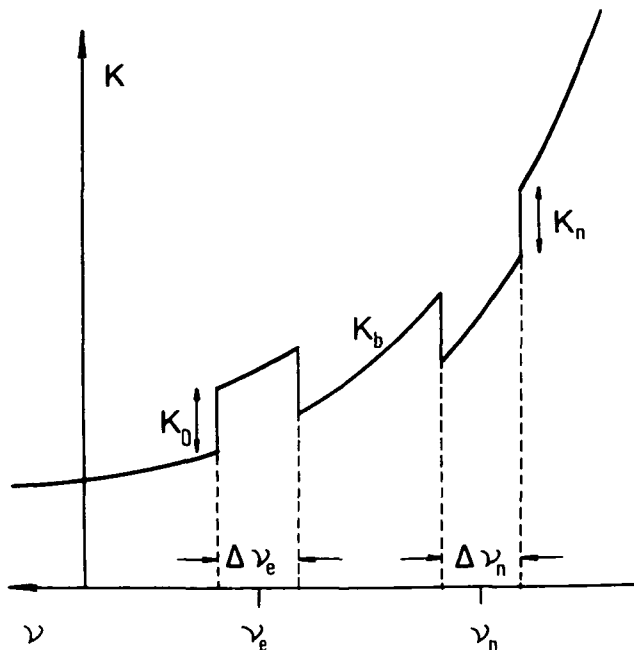


Fig. 1. The specific intensity of the radiation field in the sample

(g) During photoluminescence no chemical changes are brought about in the sample solution.

(h) In order to simplify the calculations below, it is assumed that the product of the exciting bandwidth  $\Delta\nu_e$  and the normalized fluorescence spectrum  $f(\nu)$  is negligible:  $f(\nu_e)\Delta\nu_e \ll 1$ , since  $\int_0^\infty f(\nu)d\nu = 1$ .

From the set of assumptions (a)—(g) it follows that the photoluminescence emitted from any volume element, having the energy spectrum  $f(\nu)$ , should be unpolarized

and have uniform specific intensity in all directions. In the limiting case of  $K_0 \rightarrow 0$  (and  $K_n \rightarrow 0$ ), the sample should return to the thermodynamic equilibrium.

3. When applying the entropy law for luminescing solutions, the following internal entropy changes (i.e. entropy productions inside the system) [4] are taken into account.

(A) The solution absorbs and scatters the incoming radiation, and the non-absorbed outgoing part of this radiation remains coherent with the incident beam.

(B) Due to the sample, photoluminescence and scattered radiation is superimposed onto the outgoing radiation. Apart from the above processes (A) and (B), no other processes should be taken into account. Re-absorption and secondary luminescence [5] can be neglected whenever assumption (d) is fulfilled.

4. As easily shown it is sufficient to analyze the entropy changes of the radiation field with respect to an arbitrarily chosen direction. In an earlier communication [2] we have arrived at the conclusion that the entropy changes of the radiation field inside a luminescing sample are not determined by the difference of incoming and outgoing entropy intensities (since this difference provides information about the surroundings of the sample). Instead, we derived a formula which includes, apart from  $K_b$ , the specific intensity of absorbed, scattered, and emitted radiations, but excludes that part of the exciting radiation, which traverses the sample unchanged.

Because  $\alpha_v$  denotes the total absorption coefficient of the luminescing medium, it is useful to decompose this quantity according to the contribution of the dye  $\alpha'_v$  and the solvent  $\alpha''_v$ :  $\alpha_v = \alpha'_v + \alpha''_v$ . It should be noted that our earlier assumptions, namely  $\alpha''_v = 0$ ,  $\beta_v = 0$ , will not be included into the present calculations. Furthermore as to the size of the sample ( $r$ ) and its concentration, assumptions (c) and (d) set serious limitations, in the forthcoming calculations entropy changes due to processes (A) and (B) will be re-examined.

5. Apparently, in the above-defined conditions the emitted and scattered light of any volume element  $\Delta V$  into the conical element  $d\Omega$  can be considered as due to that part of the exciting radiation which passes that particular volume element in the conical element  $d\Omega$ . With tedious, although elementary algebra, it can be shown that for obtaining the internal production of entropy it is sufficient to calculate this quantity for  $\Delta V$  and  $d\Omega$ . (In other words, the entropy changes can be written into product form, because the space coordinates are separable from the optical parameters and can, thus, be eliminated from the final formulae.)

Without affecting the generality of the results,  $\Delta V$  will be taken to be a cube (of dimension  $a$ ) as shown in Fig. 2,  $d\Omega$  is defined as an infinitesimal solid angle. The luminescing solution in  $\Delta V$ , that attenuates the linearly polarized exciting radiation ( $K_0$ ) propagating along  $d\Omega$ , can be described by an optical device (Fig. 2) that fills the cube with a diathermanous medium (refractive index  $n$ ). Additional features of this optical device are two black-body sides ( $f_1$  and  $f_2$ , Fig. 2), and a thin diathermanous plate  $d$  of  $n + \Delta n$  refractive index. This diathermanous plate is constructed in such a way that it reflects part of  $K_0$  towards  $f_1$  which is equal to the absorption and scattering of the solution in the volume element  $\Delta V$ . One part of process A, namely the attenuation of  $K_0$ , can be divided into the following set of events:

- I. Partial reflection on plate  $d$ .
- II.  $f_2$  absorbs radiation of  $K_b$  specific intensity and emits radiation of the same intensity.

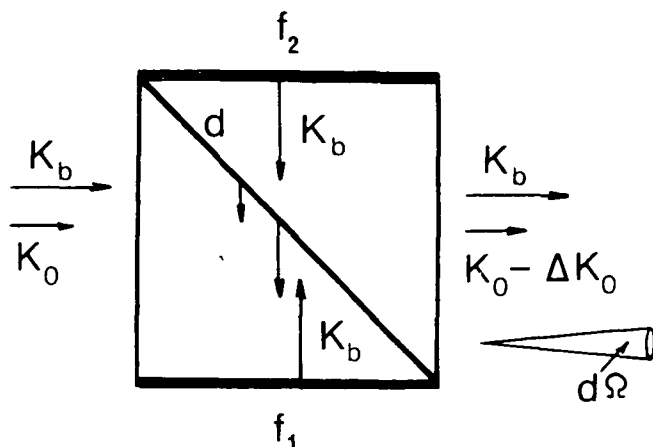


Fig. 2. Scheme of an optical device for modelling elementary processes in luminescing solutions.

III. Radiation enters the cube from its left side and leaves through its right side (Fig. 2).

None of these events are accompanied by internal entropy production.

IV.  $f_1$  absorbs radiation of  $K_b + \Delta K_0$  specific intensity and emits radiation of  $K_b$  specific intensity, giving rise thereby, with respect to the conical and surface element, to an entropy change (a decrease) of

$$\Delta L_1 = L(K_b) - L(K_b + \Delta K_0). \quad (1)$$

For definition of  $L$  the reader is referred to [3]. Eq. (1) expresses an interesting relation between the internal entropy production of the electromagnetic radiation field and the absorption (scattering processes *cf.* 4.§).

To the photoluminescence of  $K_1$  and the light scattering of  $K_s$  specific intensity, the following intrinsic entropy change will be attributed (with respect to the conical and surface element)

$$\Delta L_2 = L(K_b + K_s + K_1) - L(K_b) \quad (2)$$

this latter equation can be derived straightforwardly without the model. Finally, the attenuation of the radiation, maintaining the sample temperature can be taken into account by writing on analogy of Eq. (1)

$$\Delta L_3 = L(K_b) - L(K_b + \Delta K_n). \quad (3)$$

The luminescence yield and scattering coefficient were taken vanishing in the  $\Delta \nu_n$  interval.

6. For the expansion and integration for  $\nu$  of Eqs. (1)–(3), the absorption coefficient of the solution is given as a sum of that of the dye ( $\alpha'_\nu$ ) and the solvent ( $\alpha''_\nu$ );  $\alpha_\nu = \alpha'_\nu + \alpha''_\nu$ . Taking into account

$$\Delta K_0 = K_0 a(\alpha_{\nu_a} + \beta_{\nu_a}) = K'_a + K''_a + K_s \quad (4)$$

and using the following notations

$$K'_a = K_0 a \alpha'_{v_e}, \quad K''_a = K_0 a \alpha''_{v_e}, \quad K_s = K_0 a \beta_{v_e}, \quad (5)$$

$K_1$  can be expressed with the photoluminescence parameters

$$K_1 = K'_a \Delta v_e \eta f(v). \quad (6)$$

In spite of the excitation, the temperature will be maintained providing

$$\Delta K_n \Delta v_n = K_n a \alpha_{v_n} \Delta v_n = K'_a \Delta v_e (\eta - 1) - K''_a \Delta v_e \quad (7)$$

is fulfilled. From the above line of reasonings the rate of intrinsic entropy change for processes (A) and (B) is given as

$$\begin{aligned} d\dot{S} &= 2a^2 d\Omega \left\{ \int_{\Delta v_e} \Delta L_1 dv + \int_0^\infty \Delta L_2 dv + \int_{\Delta v_n} \Delta L_3 dv \right\} \approx \\ &\approx 2a^2 d\Omega \left\{ \Delta L_1 \Delta v_e + \int_0^\infty \Delta L_2 dv + \Delta L_3 \Delta v_n \right\} \end{aligned} \quad (8)$$

with respect to  $\Delta V$  and  $d\Omega$ .  $L_1$ ,  $L_2$ , and  $L_3$  contain  $L(K_b + y)$  type of expressions<sup>1</sup> that can be expanded about  $K_b$  as

$$L(K_b + y) = L(K_b) + \frac{1}{T} y - \frac{kc^2}{h^2} v^{-4} y^2 \exp(hv/kT). \quad (9)$$

This expansion was carried to the second power of  $y$ , since  $y$  is assumed to be much smaller than the cavity radiation (*cf.* assumption (e)). New notations are  $k$  Boltzmann-constant,  $h$  Planck-constant,  $c$  light velocity in the medium. From Eqs. (8)—(9),  $L(K_b)$  terms drop out, the first order terms cancel, and thus  $d\dot{S}$  will be determined by the second order terms of the specific intensities. Among the second order terms any  $K_n^2$ -containing term can be neglected, because  $v_e \gg v_n$ , and therefore we can write

$$\begin{aligned} d\dot{S} &= 2a^2 d\Omega (K_0 a)^2 \frac{kc^2}{h^2} \left\{ v_e^{-4} \exp(hv_e/kT) [\alpha'_{v_e}{}^2 + \alpha''_{v_e}{}^2 + \right. \\ &+ 2\alpha'_{v_e} \beta_{v_e} + 2\alpha'_{v_e} \alpha''_{v_e} + 2\beta_{v_e} \alpha''_{v_e} - \alpha'_{v_e} \beta_{v_e} \eta f(v_e) \Delta v_e] \Delta v_e - \\ &\left. - (\alpha'_{v_e} \eta \Delta v_e)^2 \int_0^\infty v^{-4} \exp(hv/kT) [f(v)]^2 dv \right\}. \end{aligned} \quad (10)$$

The entropy law requires that  $d\dot{S}$  be always non-negative:

$$d\dot{S} \geq 0 \quad (11)$$

and when this inequality is written out in full the scaling factors, including  $K_0^2$ , can be omitted. Furthermore, assumption (h), namely  $f(v_e) \Delta v_e \ll 1$ , guarantees that the  $f(v_e) \Delta v_e$ -containing terms can be neglected with respect to those of containing

$$^1 L(K) = \frac{kv^2}{c^2} \left\{ \left( 1 + \frac{c^2 K}{hv^3} \right) \ln \left( 1 + \frac{c^2 K}{hv^3} \right) - \frac{c^2 K}{hv^3} \ln \frac{c^2 K}{hv^3} \right\}$$

$2\alpha'_{\nu_e}\beta_{\nu_e}$ . Therefore, from Eqs. (10) and (11) we obtain for  $\eta$ , the energy yield, the following inequality:

$$\eta \cong \left\{ \frac{v_e^{-4} \exp(hv_e/kT)(\Delta v_e)^{-1} \left[ \left( \frac{\alpha_{\nu_e}}{\alpha'_{\nu_e}} \right)^2 + 2 \frac{\alpha_{\nu_e}\beta_{\nu_e}}{\alpha'^2_{\nu_e}} \right]}{\int_0^\infty v^{-4} \exp(hv/kT)[f(v)]^2 dv} \right\}^{1/2} = l(\nu_e). \quad (12)$$

In the limiting case of  $\alpha'_{\nu_e} = \alpha_{\nu_e}$  and  $\beta_{\nu_e} = 0$ , this expression will reduce to the simpler form previously found.

### Conclusion

7. Because of assumptions (c) and (d), strictly speaking the obtained relation (Eq. (12)) can only be applied to very weakly absorbing, *i.e.* very dilute, luminescing solutions. (These assumptions guarantee namely that the dimension of the cube  $a$  is much larger than the radiation wavelength  $\lambda$  in the spectral region investigated.) However, by decreasing the dye concentration ( $c_M$ ) the scattering coefficient of the solvent ( $\beta_{\nu_e}$ ) may exceed the absorption coefficient of the dye ( $\alpha'_{\nu_e}$ ), so that for  $c_M \rightarrow 0$  the expression  $\alpha_{\nu_e}\beta_{\nu_e}/\alpha'^2_{\nu_e} \rightarrow \infty$ , and thus  $l(\nu_e)$  diverges. To verify Eq. (12) optimally high dye concentrations should be chosen, for which assumptions (c) and (d) are fulfilled. In the case of the ethanol solution of rhodamine 6G  $c_M$  is best kept around  $10^{-6}$  M. At higher concentrations (*e.g.*  $10^{-3}$  M) any upper limit  $l(\nu_e)$  obtained for more dilute solutions equally well holds, because the energy yield, according to laboratory experiences as yet, decreases with increasing concentration in similar conditions.

Another point to be noted is that with increasing  $\Delta v_e$   $l(\nu_e)$  decreases and therefore the entropy law could be used more advantageously for larger  $\Delta v_e$ . In this instance, however, assumption (h) breaks down and  $l(\nu_e)$  takes a more complicated form. According to numerical calculations the upper limit has its lowest value for  $\Delta v_e \approx \approx 10^{13}$  Hz at any frequency.

An analysis of this inequality (Eq. (12)) suggests that the entropy law does not exclude the possibility that the energy yield exceeds unity. This is best illustrated by writing Eq. (12) into the following form, assuming  $\beta_{\nu_e} = 0$  and  $\alpha''_{\nu_e} = 0$ ,

$$\eta \cong \sqrt{\frac{\Delta v_f}{\Delta v_e} \frac{v_f^2}{v_e^2} \exp[h(\nu_e - \nu_f)/2kT]}. \quad (13)$$

The meaning of the new notations can be given as follows. The integral in Eq. (12) is replaced by  $v_f^{-4} \exp(hv_f/kT)f(v_f)$  and  $f(v_f)$  by  $1/\Delta v_f \cdot (v_f$  is near to the frequency of the maximum of the emission spectrum.  $\Delta v_f$  the approximate half width of the fluorescence spectrum.) As seen from Eq. (12) whenever  $\Delta v_f > \Delta v_e$  and  $v_e \cong v_f$  hold,  $\eta$  may well exceed unity.

The main conclusion of the present paper is that whenever the above given set of assumptions (a) through (h) is fulfilled; an upper limit can be found for the energy yield by calculating Eq. (12). As shown below with the example of rhodamine 6G, this upper limit levels off rapidly in the anti-Stokes region with increasing exciting wavelength, providing the luminescence spectrum is independent of  $\nu_e$ .

### Experimental

8. To estimate upper limits on the basis of Eq. (12), we measured the absorption and emission spectrum of rhodamine 6G, a dye of nearly unity quantum yield, and calculated its absolute quantum and energy yield as a function of wavelength. A particular reason for our choice of rhodamine 6G was that previous investigators arrived at the conclusion that its energy yield might exceed unity [6]. This conclusion was based on the assumption that the quantum yield of rhodamine 6G might not decrease significantly from unity when it is excited at lower frequencies than the average frequency of its fluorescence. It should be noted that the above-mentioned authors did not measure energy yields higher than unity, but extrapolated experimental data obtained for carefully purified dyes and extremely diluted solutions.

As solvents the azeotropic mixture of ethanol and water, and water were used. We found absolute ethanol to be less appropriate solvent, particularly in the case of very dilute solutions. The scattering ( $\beta_v$ ) and absorption ( $\alpha_v''$ ) coefficient of the solvents were determined using the data of ref. [7]. Since water has considerably higher absorption coefficient than ethanol, it is assumed that  $\alpha_v'' = 0.04 \alpha_{H_2O}''$  approximately holds.

Rhodamine 6G was obtained from Merck (West Germany) and chromatographically purified; all solvents used were bidistilled.

The absorption spectra of the solutions were measured with a Zeiss PMQ 3 spectrophotometer, if necessary utilizing special technique which allows the determination of very small absorption coefficients precisely [8]. The emission spectra and the wavelength dependence of the energy yield were measured with a Perkin—Elmer MPF 44 A fluorimeter.

Absolute energy yields were measured as described in ref. [9]. In each experiment the effect of secondary luminescence was negligible. Dye concentrations ranged between  $1 \times 10^{-5}$  and  $5 \times 10^{-7}$  M.

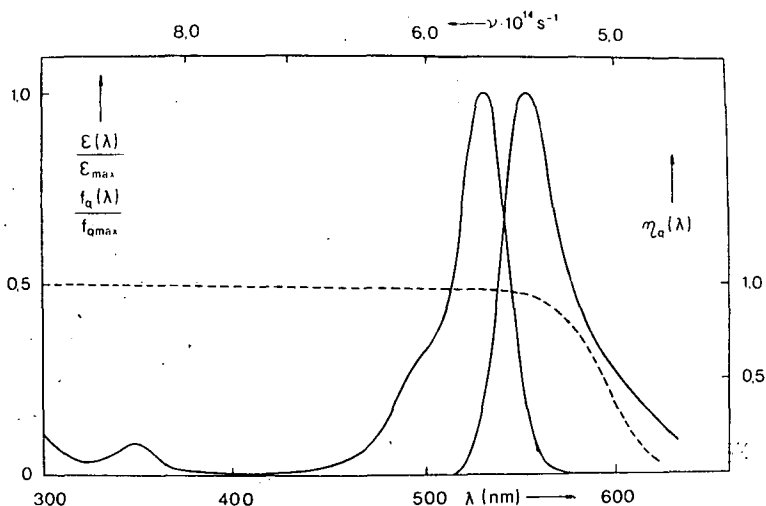


Fig. 3. Absorption and emission spectrum, and quantum yield of the ethanol solution of rhodamine 6G

The absorption spectrum, the fluorescence quantum-spectrum, and the wavelength dependence of the absolute quantum yield of rhodamine 6G in 96% (v/v) ethanol are shown in Fig. 3. In aqueous solution the fluorescence spectrum was almost identical with that in ethanol, whereas the absorption maximum was blue-shifted by about 5 nm, and therefore the onset of quantum yield decrease was also blue-shifted. The maximum value of the quantum yield for rhodamine 6G in ethanol and water is  $\eta_{q\max}=0.98$  and 0.94, respectively.

9. To illustrate how Eq. (12) depends on the absorption and scattering coefficient of the solvent,  $l(\nu_e)$  was calculated using the experimental data obtained for a series of ethanol solutions of rhodamine 6G (Fig. 4a). The concentration of the solu-

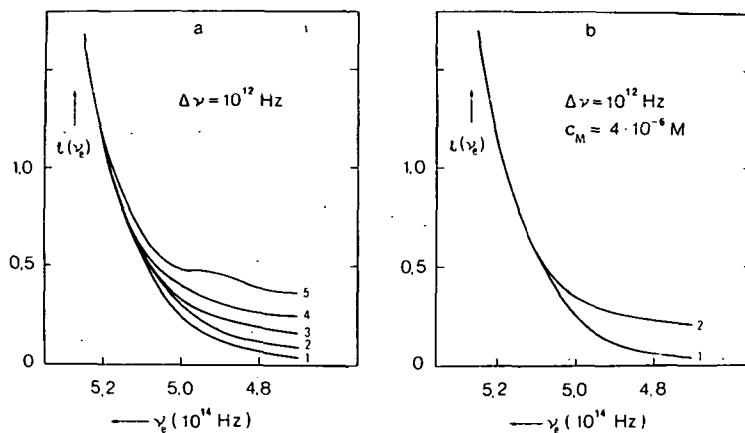


Fig. 4. Calculated limit functions  $l(\nu_e)$  for ethanol solutions of rhodamine 6G.  
 a) Concentrations: (1)  $1 \times 10^{-4}$  M, (2)  $2 \times 10^{-5}$  M, (3)  $5 \times 10^{-6}$  M, (4)  $3 \times 10^{-6}$  M, (5)  $2 \times 10^{-6}$  M.  
 b) The contribution of scattering ( $\alpha''_{\nu_e} = 0$  and  $\beta_{\nu_e} \neq 0$ , curve (1)) and solvent absorption ( $\alpha''_{\nu_e} \neq 0$  and  $\beta_{\nu_e} = 0$ , curve (2)) to  $l(\nu_e)$

tions, *cf.* curves (1) through (5) in Fig. 4a, was  $1 \times 10^{-4}$ ,  $2 \times 10^{-5}$ ,  $5 \times 10^{-6}$ ,  $3 \times 10^{-6}$ , and  $2 \times 10^{-6}$  M, respectively. As apparent from this set of curves, with decreasing dye concentration  $l(\nu_e)$  significantly increases due to solvent absorption and scattering, in the low frequency region. In the case of  $10^{-7}$  M  $l(\nu_e)$  amounts to approximately 1 in the studied frequency region. Solvent absorption gives a larger contribution to  $l(\nu_e)$  than scattering in 96% (v/v) ethanol. This is shown in Fig. 4b where curves (1) and (2) were calculated for  $\alpha''_{\nu_e} = 0$ ,  $\beta_{\nu_e} \neq 0$  and  $\alpha''_{\nu_e} \neq 0$ ,  $\beta_{\nu_e} = 0$ , respectively.

Representative  $l(\nu_e)$  plots for aqueous solutions are shown in Fig. 5. Curve (1) corresponds to the condition  $\beta_{\nu_e} = 0$  and  $\alpha''_{\nu_e} = 0$ ; whereas curves (2) through (5) correspond to dye concentrations of  $1 \times 10^{-4}$ ,  $5 \times 10^{-5}$ ,  $2.5 \times 10^{-5}$  and  $1 \times 10^{-5}$  M, respectively. For calculating curves (2) through (5), the experimentally observed  $\beta_{\nu_e}$  and  $\alpha''_{\nu_e}$  values were inserted into Eq. (12). Because of the relatively large absorption coefficient of water ( $10^{-3} \text{ cm}^{-1}$ ) the effect of solvent absorption ( $\alpha''_{\nu_e}$ ) is apparent in even high concentrations. ( $c_M > 5 \times 10^{-5}$  M). The maximum at  $5 \times 10^{14}$  Hz (Fig. 5, curve (5)) is due to steeply increasing water absorption in this frequency region.



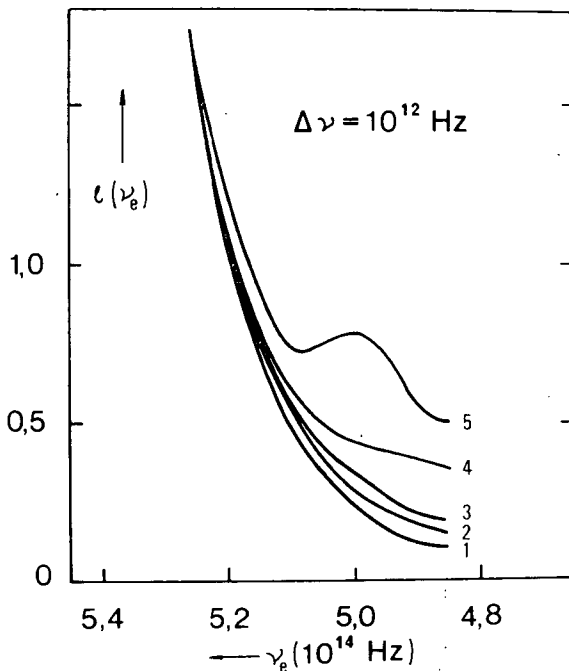


Fig. 5. Calculated limit functions  $I(v_e)$  for aqueous solutions of rhodamine 6G. (1)  $\alpha''_{v_e} = 0$ ;  $\beta_{v_e} = 0$ ; in the cases (2—5) the concentrations: (2)  $1 \times 10^{-4}$  M, (3)  $5 \times 10^{-5}$  M, (4)  $2.5 \times 10^{-5}$  M, (5)  $1 \times 10^{-5}$  M

The experimentally measured energy yield and the calculated  $I(v_e)$  function, that sets an upper limit to the energy yield, is shown in Figs. 6 and 7 for ethanol and aqueous solution, respectively. For the sake of completeness the limit  $I_1(v_e)$  set by assumption (a), is also given as calculated from the formula  $I_1(v_e) = \eta_{q \max} \frac{\bar{\nu}_f}{\nu_f}$ . ( $\bar{\nu}_f$  is the average fluorescence frequency.) In the first case (Fig. 6)  $I(v_e)$  was calculated for  $2 \times 10^{-6}$  M concentration, whereas in the latter one (Fig. 7) both  $\alpha''_{v_e}$  and  $\beta_{v_e}$  was set to zero.

10. Summing up we conclude that the  $I(v_e)$  limit-function, which was derived from the entropy law, requires the decrease of the energy yield in the anti-Stokes region in each investigated case, and especially in the spectral region where  $I_1(v_e) > 1$  is. Our experimental data, in agreement with theory, demonstrate the leveling off of the energy yield in the anti-Stokes region.

However, it is worth mentioning that the energy yield of a solution ( $\eta_0$ ) always levels off faster than that of the dye ( $\eta$ ) due to solvent absorption and scattering;  $\eta_0 = \eta \frac{\alpha'_{v_e}}{\alpha_{v_e}}$ . Thus, in real diluted solutions it is anticipated that the energy yield will be well below this upper limit, and so cooling of luminescing solutions by inducing anti-Stokes radiation can hardly be achieved.

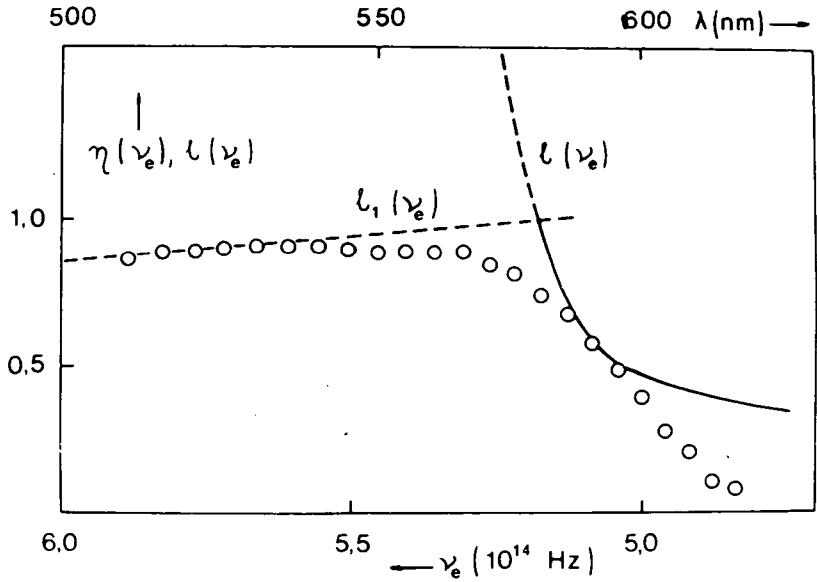


Fig. 6. The energy yield of rhodamine 6G in ethanol and the limit functions  $l(\nu_e)$  and  $l_1(\nu_e)$

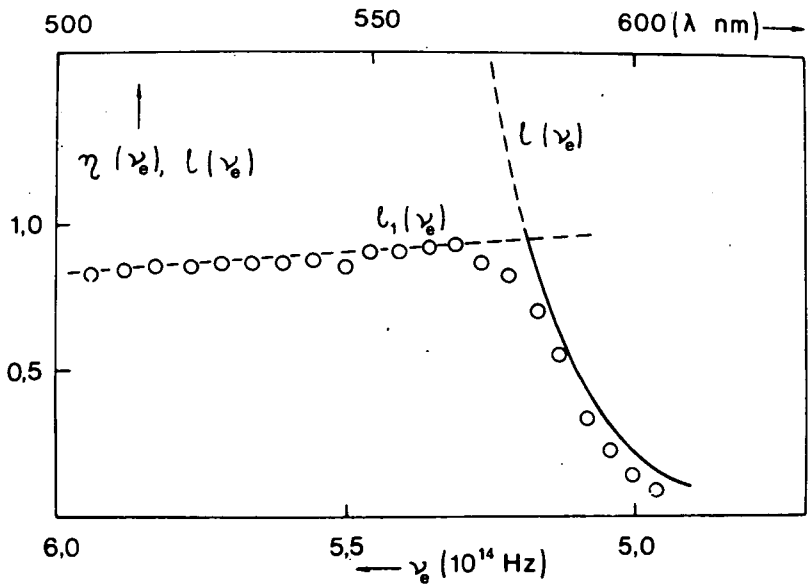


Fig. 7. The energy yield of rhodamine 6G in water and the limit functions  $l(\nu_e)$  and  $l_1(\nu_e)$

Finally, we have to comment on the set of assumptions introduced in 2. Those proved to be most powerful in studying the fluorescence of solutions, but cannot be applied in their present form to the luminescence of vapours and gases [10]. The generalization of these results obtained for solutions is intensively investigated by the present authors.

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### НЕСКОЛЬКО НОВЫХ ТЕРМОДИНАМИЧЕСКИХ СООБРАЖЕНИЙ ОТНОСИТЕЛЬНО ВЫСШЕЙ ГРАНИЦИ ЭНЕРГЕТИЧЕСКОГО ВЫХОДА ФОТОЛЮМИНЕСЦЕНЦИИ

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В результате критического рассмотрения ранее опубликованных термодинамических соображений удалось выделить восемь условий при выполнении которых может быть вычислена высшая граница выхода фотолюминесценции растворов, что согласуется с экспериментальными данными. Теоретические результаты сравниваются с экспериментально полученными значениями выхода для растворов родамина б Ж.