CORRECTION FOR REFRACTIVE INDEX IN THE COMPARISON OF RADIATIVE LIFETIMES IN VAPOUR AND SOLUTION PHASES

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Summary

Different expressions in the literature for electronic transition probabilities are compared, with emphasis placed on their dependence on the refractive index n of the medium. It is shown that, in cases where the experimental integrated area under the absorption curves is essentially independent of the medium, the radiative rate constant k_r should depend on n^2; this is verified experimentally in a comparison of the gas phase and solution phase fluorescence from 9-methylanthracene.

1. Introduction

Although the effect of the medium on the oscillator strength for electronic transitions has been extensively investigated [1 - 4], no clear concensus on corrections for this effect appears to have emerged. Morris *et al.* [5] have pointed out recently the importance of correction for the refractive index n in calculations of the oscillator strength in 9,10-diphenylanthracene in various solvents. Different methods have been used to correct for the refractive index in the calculation of radiative lifetimes. The method of Strickler and Berg [6] uses integration of areas under absorption spectra, and it should be noted that equations are sometimes used improperly in this regard [5, 7, 8]. One means of testing such corrections would be the comparison of measured radiative lifetimes in the vapour phase and in solution. However, there have been few such comparisons made [9], even though it is well documented that the radiative lifetimes of some benzene derivatives are shorter in the vapour phase than in solution [10]. In this work we do not develop yet another correction factor for refractive index effects, but merely summarize the methods in the literature in the hope that this will prove to

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be useful to other research workers, and we compare the results with those determined experimentally for 9-methylanthracene.

2. Experimental

Fluorescence decay times of 9-methylanthracene were measured using time-correlated single-photon counting techniques [11]. Absorption and emission spectra were recorded on a Unicam SP 1800 spectrophotometer and on a home-built fluorimeter respectively. Freshly sublimed 9-methylanthracene was used. Weighed solid samples were introduced into a cell and the temperature was raised to 171 °C when no further increase in absorbance was observed [12]. Samples with optical densities above 0.5 were rejected. The bottom of the cell was cooled after measurement of the gas phase spectrum causing the sample to solidify. The top of the cell was cut off, 4 ml of spectroscopic grade cyclohexane was added and the absorption spectrum was remeasured in that solvent (Fig. 1). The areas under the absorption curves were measured by integration using a computer.
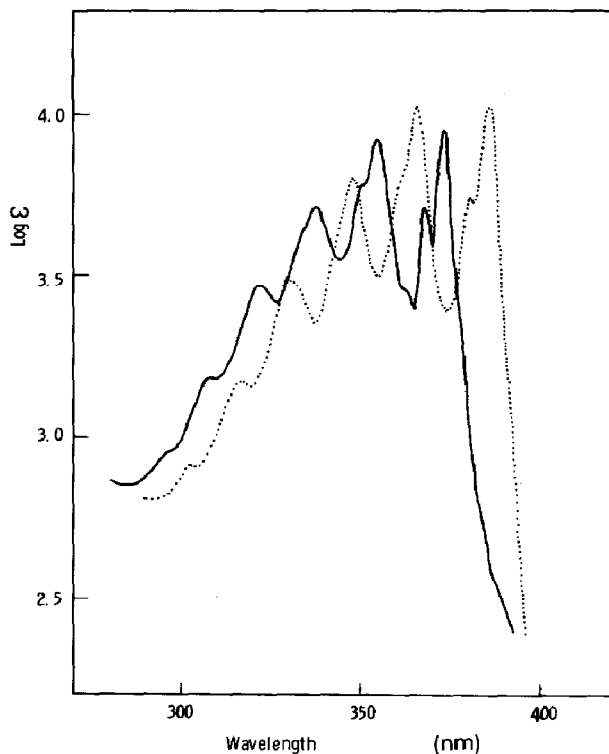

Fig. 1. Absorption spectra of 9-methylanthracene in the gas phase at 171 °C (———) and in cyclohexane solution at room temperature (· · ·).

3. Results and discussion

Since there is confusion in the literature about the effects of the refractive index of a medium on radiative lifetimes and oscillator strengths, it is worth summarizing the results of different approaches. In Table 1 are shown explicit formulae for the Einstein emission A and absorption B probabilities, the oscillator strength $f(\nu)$, the molar extinction coefficient $\epsilon(\nu)$ and the radiative rate constant k_r. In order to discuss the formulations given in Table 1 it is necessary to recognise three main effects of the refractive index on electronic transition moments. These are (1) a reduction in the velocity of light in a medium of refractive index n relative to that *in vacuo*, (2) a change in the effective electric field experienced by the light absorbing molecule and (3) a change in the photon state density with the medium. In addition, some solvents may perturb the molecular eigenstates and this must also be considered [14, 15]. However, this effect is often ignored, and has been used by some authors as a basis for a discussion of the effects of the solvent on electronic spectra [16, 17].

Many of the misconceptions concerning the use of the different correction factors given in Table 1 stem from ambiguities in the definitions of terms used rather loosely in the literature. Thus there are two definitions of oscillator strength. The first, given by Förster [14, 18] and used by Mataga and Kubota [16], is based on the Einstein B coefficient *in vacuo* divided by the quantity $\pi e^2/mh\nu$. Because it is defined as an *in vacuo* quantity, the solvent refractive index is not involved. In contrast, when the oscillator strength is related to a molar decadic extinction coefficient (not an *in vacuo* quantity), an apparent dependence on n results. However, this dependence is cancelled if $\epsilon(\nu)$ is defined as being inversely proportional to n [13, 16] and in these circumstances the arguments of Morris *et al.* [5] are inappropriate. In the second definition of oscillator strength the value of the Einstein B coefficient used is that in a medium of refractive index n, and it is not an *in vacuo* quantity [2]. In this case, the oscillator strength depends explicitly on n.

Because of these different definitions, it is clear from Table 1 that expressions of B, A, $f(\nu)$ and $\epsilon(\nu)$ have different dependences on n, and thus care must be exercised in their use. In contrast, all the approaches give the same expression for the radiative rate constant k_r. However, this agreement is illusory, since the common expression depends on an integral involving $\epsilon(\nu)$. It can be shown readily that $k_r(\nu)$ is related uniquely to $\epsilon(\nu)$. By definition

$$k_r(\nu_f) = 1/\tau_r = A(\nu_f)$$

and thus

$$k_r(\nu_f) = \frac{8\pi n^3 h\nu_f{}^3}{c^3} \; B(\nu_f) \tag{1}$$

since by common agreement

TABLE 1

Formulations for electronic transition probabilities

Parameter	Formulation				Notes
	Ref. 13	Ref. 7	Ref. 2	Ref. 4	
B^{a}	$\dfrac{8\pi^3}{3n^2h^2}\lvert M_{01}\rvert^2$	$\dfrac{8\pi^3}{3h^2}\lvert M_{01}\rvert^2$ [b]	$\dfrac{(n^2+2)^2}{9}\dfrac{8\pi^3}{3n^2h^2}\lvert M_{01}\rvert^2$ [b]	$\dfrac{9n^2}{(2n^2+1)^2}\dfrac{8\pi^3}{3h^2}\lvert M_{01}\rvert^2$ [b]	$\lvert M_{01}\rvert^2$ is the transition dipole strength
A^{a}	$\dfrac{64\pi^4 n\nu^3}{3hc^3}\lvert M_{01}\rvert^2$	$\dfrac{64\pi^4 n^3\nu^3}{3hc^3}\lvert M_{01}\rvert^2$	$\dfrac{(n^2+2)^2}{9}\dfrac{64\pi^4 n\nu^3}{3hc^3}\lvert M_{01}\rvert^2$ [b]	$\dfrac{9n^5}{(2n^2+1)^2}\dfrac{64\pi^4\nu^3}{3hc^3}\lvert M_{01}\rvert^2$ [b]	
$f(\nu)^{c}$	$\dfrac{8\pi^2 m\nu}{e^2h}\lvert M_{01}\rvert^2$	$\dfrac{8\pi^2 m\nu}{3e^2h}\lvert M_{01}\rvert^2$	$\dfrac{(n^2+2)^2}{9n^2}\dfrac{8\pi^2 m\nu}{3e^2h}\lvert M_{01}\rvert^2$	$\dfrac{9n^2}{(2n^2+1)^2}\dfrac{8\pi^2 m\nu}{3e^2h}\lvert M_{01}\rvert^2$ [b]	
$\epsilon(\nu)^{d}$	$\dfrac{1}{n}C_1\nu\lvert M_{01}\rvert^2$	$nC_1\nu\lvert M_{01}\rvert^2$ [b]	$\dfrac{(n^2+2)^2}{9n}C_1\nu\lvert M_{01}\rvert^2$	$\dfrac{9n^3}{(2n^2+1)^2}C_1\nu\lvert M_{01}\rvert^2$	$C_1 = \dfrac{1}{3}\dfrac{8\pi^3 N}{2303hc}$
$\epsilon(\nu)$ in terms of $f(\nu)$	$\dfrac{1}{3n}C_2f(\nu)$	$nC_2f(\nu)$	$nC_2f(\nu)$ [b]	$nC_2f(\nu)$ [b]	$C_2 = \dfrac{\pi e^2 N}{2303mc}$
k_r^{e}	$C_3n^2\displaystyle\int\dfrac{\epsilon(\nu)\,d\nu}{\nu}$	$C_3n^2\displaystyle\int\dfrac{\epsilon(\nu)\,d\nu}{\nu}$	$C_3n^2\displaystyle\int\dfrac{\epsilon(\nu)\,d\nu}{\nu}$	$C_3n^2\displaystyle\int\dfrac{\epsilon(\nu)\,d\nu}{\nu}$	$C_3 = 2303\,\dfrac{8\pi\widetilde{\nu}_f^{\,3}}{Nc^2}$

[a] A and B correspond to $n_e(\nu)$ and $n_a/\sigma(\nu)$, defined by Förster [13], and satisfy the relation $A \propto n^3B$.
[b] Expressions derived in this work using the terms given in the references.
[c] $f(\nu)$ is the oscillator strength and is defined differently by different authors. Only the expression given in ref. 13 relates to the value *in vacuo.*
[d] Based on eqn. (2) (see ref. 4).
[e] Based on eqn. (5).

$$A(\nu_f) = \frac{8\pi n^3 h \nu_f{}^3}{c^3} B(\nu_f)$$

The experimentally observable molar extinction coefficient $\epsilon(\nu)$ is related to the Einstein B coefficient by eqn. (2) [7]:

$$\epsilon(\nu_a) = \frac{n}{c}\frac{1}{1000 \ln 10} N h \nu_a \frac{n_a(\nu_a)}{\sigma(\nu_a)} \tag{2}$$

$$= \frac{n}{c}\frac{N h \nu_a}{2303} B(\nu_a)$$

where $n_a(\nu_a)/\sigma(\nu_a) = B(\nu_a)$, $n_a(\nu_a)$ is the absorption transition probability, $\sigma(\nu_a)$ is the radiation density and N is the Avogadro number. The subscripts a and f denote absorption and fluorescence respectively.

For molecular systems the total rate constant k_r must be derived from eqn. (1) integrated over the whole fluorescence band, *i.e.*

$$k_r = \int k_r(\nu_f) d\nu_f$$

$$= \frac{8\pi n^3 h}{c^3} \int \nu_f{}^3 B(\nu_f) d\nu_f$$

$$= \frac{8\pi n^3 h}{c^3} \tilde{\nu}_f{}^3 \int B(\nu_f) d\nu_f \tag{3}$$

In eqn. (3) $\tilde{\nu}_f{}^3$ is some mean value of $\nu_f{}^3$ which can be given by the term $\langle \nu_f{}^{-3} \rangle_{av}{}^{-1}$ following Strickler and Berg [6]. It has also been shown [6] that the following equation is valid for strong transitions in rigid molecules:

$$\int B(\nu_a) d\nu_a = \int B(\nu_f) d\nu_f \tag{4}$$

Combination of eqns. (2), (3) and (4) gives the expression for k_r shown in Table 1, namely

$$k_r = \frac{8\pi n^2 2303}{Nc^2} \tilde{\nu}_f{}^3 \int \frac{\epsilon(\nu_a)}{\nu_a} d\nu_a \tag{5}$$

Equation (5) shows that k_r has an explicit n^2 dependence plus whatever n dependence $\epsilon(\nu_a)$ carries. Therefore on an analytical basis, k_r will have a linear dependence on n in the Förster formulation, whereas it depends on n^3 in the Birks formulation. Thus, it is difficult to choose an appropriate expression; in the Birks treatment one of the medium effects was ignored (that of effective electric field changes), whereas Förster solved an incomplete equation of motion of an oscillator in a medium to obtain his correction factor [13, 16]. Use of a more appropriate expression [19] leads to Chako's formulae [2] which, although they are frequently used, do not appear to be realistic.

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TABLE 2

Spectral and kinetic data for 9-methylanthracene in the gas phase and in solution

Quantity	Gas phase	Cyclohexane solution
$\int \epsilon d\nu \times 10^{-7}$	2.69[a]	2.78[b]
$\int \epsilon d\ln\nu \times 10^{-2}$	9.21[a]	9.86[b]
ϕ_f[c]	0.26	0.36
τ_f[d] (ns)	6.3	4.6
τ_r[e] (ns)	24.2	12.7
$\tau_{r(gas)}/\tau_{r(solution)}$	1.94	

[a]Integration between the limits 280 - 410 mm.
[b]Integration between the limits 290 - 420 mm.
[c]Fluorescence quantum yield.
[d]Fluorescence decay time.
[e]Radiative lifetime ($= \tau_f/\phi_f$).

Until much more experimental evidence is available, these analytical expressions should be used with caution. In cases where $\int\epsilon(\nu_a)d\ln\nu_a$ can be shown experimentally to be independent of the medium, *e.g.* in a variety of solvents for some molecules [5, 7, 20], k_r should have the n^2 dependence (see eqn. (5)). However, comparisons between polar and non-polar media are not appropriate because of dielectric effects [4]. A better test of the n^2 dependence (assuming invariance of $\int\epsilon(\nu_a)d\ln\nu_a$) should be obtained by a comparison of data obtained in the vapour phase and in non-polar solvents. Such data for 9-methylanthracene are shown in Table 2. It is evident that $\int\epsilon d\ln\nu$ does not vary greatly in the two phases, and the value of $\tau_{r(gas)}/\tau_{r(solution)}$ is satisfactorily close to the value of n^2, as expected from eqn. (5). However, it must be stressed that the apparent agreement of experiment with theory in this case cannot be taken as a demonstration of the general validity of an n^2 dependence, since this will be the case only when $\int\epsilon d\ln\nu$ is independent of the medium. Much more experimental evidence in the form of comparisons between gas phase and solution phase data are needed. The establishment of a generally valid analytical expression is a worthwhile goal, in that it will be useful for discussions of the radiative lifetimes of weak transitions, for understanding variations in the radiative lifetimes of exciplexes and excimers in different media [11], and for understanding energy transfer in solution [21].

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