

Electric Field Dependence of the Fluorescence Intensity of Solute Molecules and Fourth Order Effects

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The effect of an external electric field on the total fluorescence of solute molecules is studied up to fourth order theoretically, and is checked experimentally with 4'-N,N-dimethylamino-4-nitrostilbene in dioxane at room temperature.

I. Introduction

In previous papers [1–5] electro-optical emission measurements have been developed, theoretically and experimentally. With these methods the influence of an external electric field on the fluorescence of solutes is measured and from the resulting quantities electric moments in the fluorescent excited state and in the corresponding Franck-Condon (FC) ground state can be determined. These measurements can be done spectrally resolved, or optically integrating over the whole fluorescence band, in this way defining “electro-optical emission measurements (EOEM)” and “integral electro-optical emission measurements (IEOEM)”. The latter method is preferentially used since the measuring accuracy is much better because of the better photon statistics. On the other hand, less information on molecular quantities can be derived. Because of the high relative accuracy of this latter method especially with highly polar molecules, the attempt has been made to detect an effect of fourth order in the electric field applied to the solution.

Hence the first theory of IEOEM is extended to the fourth order and then the results from measurements are analysed with respect to second and fourth order terms. Molecular quantities derived from second and fourth order then should give values equal within the measuring errors if the molecular model used is sufficiently elaborated. In this way a further test of the model connecting molecular quantities with macroscopic values can

be performed, as well as of the experimental quality of the method.

II. The Photon Current in a Modulated Electric Field

The experimentally observed photon current $p^E(\varphi)$ in an electric field E_a can be expanded to fourth order with respect to E_a

$$p^E(\varphi) = p [1 + {}^2X(\varphi) E_a^2 + {}^4X(\varphi) E_a^4], \quad (1)$$

where the expansion coefficients ${}^2X(\varphi)$ and ${}^4X(\varphi)$ can be determined by varying the applied electric field. φ is the angle between E_a and the polarization direction given by an analyzing polarizer. With the used method [3], the electric field is modulated in order to be able to detect even small changes of p due to an electric field

$$E_a = E_g + E_w \cos \omega t. \quad (2)$$

Putting E_a from (2) into (1), after some trigonometric transformation and rearrangement, $p^E(\varphi)$ results:

$$p^E(\varphi) = p [1 + X_{\omega}(\varphi) \cos \omega t + X_{2\omega}(\varphi) \cos 2\omega t + X_{3\omega}(\varphi) \cos 3\omega t + X_{4\omega}(\varphi) \cos 4\omega t], \quad (3)$$

where p is the photon current without an external field,

$$X_{\omega}(\varphi) = {}^2X(\varphi) 2 E_g E_w + {}^4X(\varphi) (4 E_g^3 E_w + 3 E_g E_w^3), \quad (4)$$

$$X_{2\omega}(\varphi) = {}^2X(\varphi) \frac{1}{2} E_w^2 + {}^4X(\varphi) (3 E_g^2 E_w^2 + \frac{1}{2} E_w^4), \quad (5)$$

$$X_{3\omega}(\varphi) = {}^4X(\varphi) E_g E_w^3, \quad (6)$$

$$X_{4\omega}(\varphi) = {}^4X(\varphi) \frac{1}{8} E_w^4. \quad (7)$$

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With the apparatus described in [3], the quantity

$$X(\varphi) = \frac{X_\omega(\varphi)}{2E_g E_w} \quad (8)$$

can be measured.

Putting X_ω , from (4) into (8) yields

$$X(\varphi) = {}^2X(\varphi) + {}^4X(\varphi) (2E_g^2 + \frac{3}{2}E_w^2). \quad (9)$$

The following (independent) linear combinations of $X(\varphi)$ values are important experimentally:

$$\begin{aligned} \mathbf{X2} &= X(\varphi = 0^\circ) + 2X(\varphi = 90^\circ) \\ &= {}^2\mathbf{X3} + {}^4\mathbf{X3} (2E_g^2 + \frac{3}{2}E_w^2), \end{aligned} \quad (10)$$

$$\begin{aligned} \mathbf{X3} &= 6X(\varphi = 0^\circ) - 18X(\varphi = 90^\circ) \\ &= {}^2\mathbf{X2} + {}^4\mathbf{X2} (2E_g^2 + \frac{3}{2}E_w^2), \end{aligned} \quad (11)$$

in this way defining the following terms

$${}^2\mathbf{X2} = {}^2X(\varphi = 0^\circ) + 2{}^2X(\varphi = 90^\circ), \quad (12)$$

$${}^2\mathbf{X3} = 6{}^2X(\varphi = 0^\circ) - 18{}^2X(\varphi = 90^\circ), \quad (13)$$

$${}^4\mathbf{X2} = {}^4X(\varphi = 0^\circ) + 2{}^4X(\varphi = 90^\circ), \quad (14)$$

$${}^4\mathbf{X3} = 6{}^4X(\varphi = 0^\circ) - 18{}^4X(\varphi = 90^\circ). \quad (15)$$

Hence, once $X(\varphi)$ has been determined at different field strengths, from a regression analysis of the $X(\varphi)$ with respect to the field strength term $(2E_g^2 + \frac{3}{2}E_w^2)$ the experimental quantities ${}^2X(\varphi)$ and ${}^4X(\varphi)$ and thus ${}^2\mathbf{X2}$, ${}^2\mathbf{X3}$, ${}^4\mathbf{X2}$ and ${}^4\mathbf{X3}$ can be determined.

III. The Second Order Effect Terms ${}^2\mathbf{X2}$ and ${}^2\mathbf{X3}$

In order to be able to determine molecular quantities, like the permanent dipole moment μ_e^0 of a free molecule in its fluorescent state, from the measured values of macroscopic quantities, like ${}^2X(\varphi)$ or ${}^2\mathbf{X2}$ and ${}^2\mathbf{X3}$, a suitable model must be used to connect the quantities. A rigorous and general discussion of such considerations has been given recently by Liptay et al. [6]. The basic model used here with IEOEM is that developed originally for electro-optical absorption measurements by Liptay. It is based on the Onsager reaction field model that connects the electric field \mathbf{E} acting on a solute with the externally applied field \mathbf{E}_a . The theory of IEOEM has been published [3, 4]. It was shown there, that in the case of strongly polar mole-

cules the following relations between the experimental ${}^2\mathbf{X2}$ and ${}^2\mathbf{X3}$ values and the molecular dipole moment μ_e^0 hold, if the transition dipole moment involved in the considered fluorescence process, the dipole moment in the fluorescent state and that in the corresponding FC-ground state are at least approximately parallel:

$${}^2\mathbf{X2} \approx 0, \quad (16)$$

$${}^2\mathbf{X3} = \frac{2}{(kT)^2} \mu_e^2, \quad (17)$$

where

$$\mu_e = f_e (1 - f \alpha_e^0)^{-1} \mu_e^0. \quad (18)$$

With a spherical approximation to the molecular shape one has

$$f_e = \frac{3\varepsilon}{2\varepsilon + 1}, \quad (19)$$

$$f = \frac{1}{4\pi\varepsilon_0} \frac{2}{a^3} \frac{\varepsilon - 1}{2\varepsilon + 1}, \quad (20)$$

where $4\pi a^3/3$ is about the solute's molecular volume, ε the dielectric constant, ε_0 the permittivity of the vacuum and α_e^0 the polarizability of the solute in its fluorescent state.

IV. The Fourth Order Effect

The theoretical model given in [3, 4] can be extended to fourth order without any problem. But with today's and the near future's measuring accuracy only effects of the permanent dipole moment can be determined experimentally from the fourth order effects. Hence the theory, although developed taking into account minor effects of polarizabilities and transition polarizabilities [7], is displayed here for the mere dipole term only, which is by far the most significant one. Also, parallelity of the dipole moment and the transition dipole moment involved in the fluorescence process is assumed. With this simplification, the calculation gives

$${}^4\mathbf{X2} \approx 0, \quad (21)$$

$${}^4\mathbf{X3} = -\frac{4}{21} \frac{1}{(kT)^4} \mu_e^4, \quad (22)$$

using the definitions already given. Hence, μ_e can be determined independently of ${}^2\mathbf{X3}$ and ${}^4\mathbf{X3}$.

V. Experimental Check

In order to be able to detect a fourth order effect well above the photon noise level, the experimental check was done with the well-investigated molecule 4'-N,N-dimethylamino-4-nitrostilbene (DMANS) in dioxane at 298 K.

Table 1 shows one set of nine values for **X3** and **X2** at nine different field strengths E_a , for which the determining terms $2E_g E_w$ and $2E_g^2 + \frac{3}{2}E_w^2$ are given, too. The relative error of a single **X3** value within a given set is less than 3%, the error between independent sets of **X3** values is about 2.5%. Hence a single set has been given and analyzed further.

X2 is about 3% of **X3** what justifies that minor terms could have been omitted with (17) (see [3], too). The values of $^2\mathbf{X2}$ and $^2\mathbf{X3}$ as well as those of $^4\mathbf{X2}$ and $^4\mathbf{X3}$ determined from a linear regression according to (10) and (11) are given in Table 2, together with the resulting dipole moments.

The agreement between the results from the second and fourth order effects must be looked at as pretty good, having in mind that the fourth order effect amounts to only about 1.5% of the total measuring effect. The error given in Table 2 is derived from the standard error of the respective regression coefficients within one set of **X3** values. One should add about 2.5% due to statistical errors between sets of **X3** values and about 4% due to calibration errors. μ_e^0 can be determined using an estimate for α_e^0/a^3 . But this is not within the scope of this paper (see [8]). The agreement with previously determined values for μ_e of DMANS in dioxane solutions is also good ([3, 8], and references cited therein).

VI. Conclusions

The extension of the model used with IEOEM to interpret experimental effects of fourth order in the electric field strength has mainly been done to check and prove the quality and applicability of the

Table 1. Values of **X2** and **X3** at different field strengths, represented by the field strength terms $2E_g E_w$ and $2E_g^2 + \frac{3}{2}E_w^2$.

| $2E_g E_w$ | $2E_g^2 + \frac{3}{2}E_w^2$ | X2 | X3 |
|--------------------------------------|--------------------------------------|---------------------------------------|---------------------------------------|
| $10^{12} \text{ m}^{-2} \text{ V}^2$ | $10^{12} \text{ m}^{-2} \text{ V}^2$ | $10^{-20} \text{ m}^2 \text{ V}^{-2}$ | $10^{-17} \text{ m}^2 \text{ V}^{-2}$ |
| 10.3 | 21.4 | − 5920 | 191.1 |
| 22.9 | 48.1 | − 5900 | 191.0 |
| 40.6 | 90.2 | − 5870 | 190.8 |
| 51.3 | 107.2 | − 5900 | 190.6 |
| 63.4 | 133.1 | − 5860 | 190.2 |
| 73.9 | 155.4 | − 5800 | 189.4 |
| 81.8 | 173.3 | − 5820 | 189.3 |
| 99.1 | 208.4 | − 5850 | 188.9 |
| 122.2 | 257.2 | − 5840 | 188.2 |

Table 2. Results from a linear regression according to (10) and (11).

| | | |
|---|---------------|-------------------------|
| $^2\mathbf{X2}/10^{-17} \text{ m}^2 \text{ V}^{-2}$ | − 5.91 ± 0.02 | |
| $^2\mathbf{X3}/10^{-17} \text{ m}^2 \text{ V}^{-2}$ | 191.69 ± 0.18 | |
| $^4\mathbf{X2}/10^{-34} \text{ m}^4 \text{ V}^{-4}$ | 40 ± 20 | |
| $^4\mathbf{X3}/10^{-34} \text{ m}^4 \text{ V}^{-4}$ | − 1330 ± 2 | |
| $\mu_e/10^{-30} \text{ Cm}$ | 127.5 ± 0.1 | (from $^2\mathbf{X3}$) |
| $\mu_e/10^{-30} \text{ Cm}$ | 111 ± 1 | (from $^4\mathbf{X3}$) |

model. From the results – the regression coefficients and their errors – it can be seen that this model is well suited for the description of fourth order effects, too, with IEOEM on small molecules. Having in mind the complexity of the fluorescence process and therefore the various ways of possible effects of an external electric field on the fluorescence intensity, then this result cannot be considered trivial as it could be looked at, at a first glance. In addition, the experimental set-up has proven to be of adequate quality even for the detection of a small fourth order effect.

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