

Photoinduced charge transfer as revealed by ground and excited state dipole moments

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Abstract

As a measure of photoinduced charge transfer the excited state dipole moments of rigid molecules are determined from the quantitatively observed effect of an external electric field on their fluorescence in various solvents. The observed solvent dependence of the excited state dipole moment is interpreted in terms of solvent induced moments which may be described by polarizabilities. The resulting excited state polarizability densities α_e/a^3 (a = Onsager's interaction radius) are determined to be around 0.1 to $0.2 \cdot 10^{-10} \text{ CV}^{-1}\text{m}^{-1}$ and do not add considerably to the excited state dipole moment in nonpolar solvents.

INTRODUCTION

There are not many experimental methods available to study photoinduced charge transfer in molecules directly which means that the electric dipole moment of molecules before and after the absorption of a photon has to be measured. Usually, the solvent polarity induced shift of the absorption or fluorescence band is observed quantitatively from which excited state electric dipole moments can be derived. With a non-rigid compound the geometric and electronic structure may depend on the solvents dielectric constant ϵ and therefore the resultant value for an excited state dipole moment can only be a poorly defined average value.

This drawback is avoided by electrooptical measurements with which the effect of an external electric field on the absorption (ref. 1) or fluorescence intensity (ref. 2) of solute molecules is studied. Careful evaluation of the effects measured in a single solvent yield Franck Condon (FC) excited state dipole moments μ_e^{FC} of the solute in this solvent from electrooptical absorption measurements (EOAM) and equilibrated excited state dipole moments μ_e from electrooptical emission measurements (EOEM). In this communication EOEM and its specialized version IEOEM (integral electrooptical emission measurements) (refs. 3 and 4) are used to show the effect of the solvent polarity on the electric dipole moment μ_e of rigid compounds which are assumed not to undergo severe structural or electronic relaxation before fluorescence takes place to a considerable amount, as it is assumed with TICT fluorescence emitting compounds (ref. 5). From the solvent dependent excited state dipole moment the excited state polarizability can be determined. Such results are extremely useful for the discussion of TICT state dipole moments of non-rigid compounds.

THEORETICAL MODEL OF EOEM

The complete theory of EOEM basing on early work of Liptay (ref. 6) is presented in (ref. 2) and its specialized version IEOEM in (refs. 3 and 4). In the present communication, IEOEM only is used. With this method, the electric field dependence of the total fluorescence intensity optically integrated over the fluorescence band is observed through a linear polarizer which determines the angle φ between the polarization direction of the fluorescence light and the direction of the externally applied electric field. The experimental setup is described for example in (ref. 7).

If minor effects are assumed to be negligible for the consideration of relatively large dipole moments in this communication, the total fluorescence intensity ϕ^{F} in an external electric field F is given by (ref. 3) by

$$\phi^{\text{F}} = \phi^{\text{F}=0} [1 + IX(\varphi) F^2] \quad (1)$$

where $\phi^{\text{F}=0}$ is the fluorescence intensity without electric field and

$$IX(\varphi) = \text{const.} + (3\cos^2\varphi - 1) E/30 \quad (2)$$

where

$$E = (1/kT)^2 f_e^2 [3(m\mu)^2 - \mu^2] \quad (3)$$

with the Boltzmann constant k and the temperature T .

$$f_e = 3\epsilon / (2\epsilon + 1) \quad (4)$$

describes the cavity field which is present in an empty sphere in the solvent, and m is a unit vector in the direction of the transition moment of the considered fluorescence transition. The total dipole moment μ effective in a given solution is defined as

$$\mu = \mu_e (1 - f\alpha_e)^{-1} \quad (5)$$

with

$$f = (4\pi \epsilon_0)^{-1} (2/a^3) (\epsilon - 1)(2\epsilon + 1) \quad (6)$$

where ϵ_0 is the absolute and ϵ the relative permittivity of the solvent used and where "a" is the interaction radius or Onsager radius in the spherical Onsager reaction field model which was introduced to electro optical measurements by Liptay [8]. In this model f determines the reaction field F_R induced by the total dipole moment μ of the solute in the surrounding homogeneous solvent

$$F_R = f \mu \quad (7)$$

which in turn induces a moment in addition to the total dipole moment μ via the solute's polarizability α_e which finally yields eq. 5.

μ_e and α_e are the permanent dipole moment and the polarizability of the free compound. With a rigid compound, α_e mainly consists of the electronic polarizability but with non-rigid ones α_e contains all solvent induced amounts to the total dipole moment μ .

Assuming the transition moment m parallel to the total dipole moment μ which is valid in at least good approximation for all compounds studied in this communication, the value of the total dipole moment μ follows immediately from eq. 3

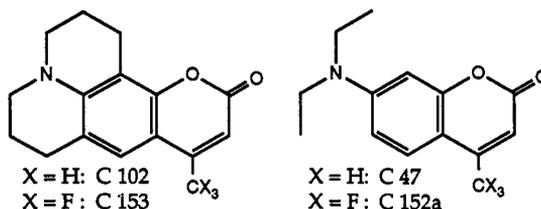
$$\mu = kT f_e^{-1} \sqrt{E/2} \quad (8)$$

Obviously, E has to be determined experimentally following eq. 2 by determining $I^X(\varphi)$ from measurements of $\phi^F(\varphi)$ and $\phi^{F=0}$ with at least two angles φ - see fore (ref. 3).

EXPERIMENTAL RESULTS

Compounds. The following compounds have been studied:

1-methyl-5-cyanoindoline (MIN) which was prepared following (ref. 9), and the following coumarin dyes which have been bought in laser dye quality from Lambda Physics and have been used without further purification.



MIN was chosen as a planar compound of the family related to the double fluorescent compound *N,N*-dimethyl-4-cyanoaniline (DMCA=DMABN) and the coumarins have been chosen as compounds that are not expected to emit from a TICT state, too. Each two coumarins are corresponding pairs where the diethylamino group is more or less free or fixed to an essentially rigid structure.

RESULTS

Table 1 represents the experimental data for the studied compounds in some solvents. The experimental error is of the order of $2 \cdot 10^{-30}$ Cm.

TABLE 1. Total fluorescent excited state dipole moment μ of some coumarins and of MIN determined from IEOEM in various solvents. All dipole moment values are given in units of 10^{-30} Cm.

Solvent	ϵ	MIN	C47	C102	C152a	C153
Cyclohexane	2.02	21.2	39.1	39.9	46.6	47.4
Amylether	2.77	23.0	40.9	43.6	48.8	50.4
iso-Propylether	3.88	23.7	44.4	46.7	52.7	53.4
Fluorobenzene	5.42	23.8	42.2	42.2	48.1	48.8
Dioxane	6.00*	23.2	44.1	42.5	51.5	51.5
Benzotrifluoride	9.04	22.4	42.2	43.6	47.8	48.5

* microscopically effective relative permittivity

DISCUSSION

The fluorescent excited state dipole moments μ represented in Table 1 show the expected tendencies. The value of $\mu(\text{MIN})$ is around $22 \cdot 10^{-30}\text{Cm}$, similar to the ground state dipole moment of the compounds of this class around DMABN (ref. 10) and in good agreement with what is reported in the literature, e.g. in (ref. 10), for the excited state emitting the normal fluorescence of this class of compounds.

The excited state dipole moment of the coumarins show a considerable photoinduced charge transfer characterized by the ground state dipole moment of these compounds reported around $20 \cdot 10^{-30}\text{Cm}$ (ref. 11) and the much larger excited state dipole moments of around $50 \cdot 10^{-30}\text{Cm}$ reported here. The comparison of the rigid and the twistable coumarin reveals that there is no difference between such a pair and the comparison of the fluorinated compound with the standard methyl compound shows a roughly 10% larger dipole moment μ for the respective fluorinated compound.

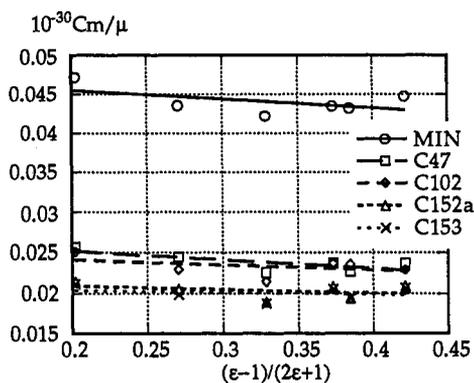


Figure 1. Linear fit to the values of $1/\mu$ plotted against the solvent parameter $(\epsilon-1)/(2\epsilon+1)$.

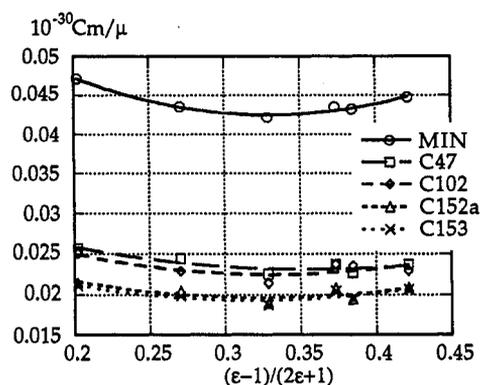


Figure 2. Second order polynomial fit to the values of $1/\mu$ plotted against the solvent parameter $(\epsilon-1)/(2\epsilon+1)$.

At least with rigid compounds the value for μ in different solvents should depend on the solvent relative permittivity according to eq. 5 with eq. 6. Hence, a plot of $1/\mu$ against $(\epsilon-1)/(2\epsilon+1)$ should yield straight lines

$$1/\mu = 1/\mu_e - (2\pi\epsilon_0\mu_e)^{-1} (\alpha_e/a^3) (\epsilon-1)/(2\epsilon+1) \quad (9)$$

Figure 1 shows such a plot. From a respective regression analysis the excited state dipole moment μ_e and the polarizability density α_e/a^3 may be determined. Results from such treatment of the data from Table 1 are presented in Table 2. Overall, these results are important since they show that the excited state total dipole moment μ determined in nonpolar solvents, e.g. in cyclohexane, tab. 1, do not differ much from the values μ_e tab. 2. This means, that μ does not contain considerable amounts of induced moments - experimental values of μ determined in nonpolar solvents therefore may be understood as correct values for the excited state dipole moments of the respective free molecules.

The polarizability densities α_e/a^3 have reasonably small values with a tendency of smaller values for the rigid compounds, but with large experimental uncertainty. Their values determined around 0.1 to $0.2 \cdot 10^{-10} \text{CV}^{-1}\text{m}^{-1}$ are in agreement with the value $\alpha_e/a^3 = (0.15 \pm 0.05) \cdot 10^{-10} \text{CV}^{-1}\text{m}^{-1}$ reported for 2,6,N,N-tetramethyl-4-cyanoaniline (ref. 12) but not with the very large value reported for DMABN (ref. 13) or for 4-(9-anthryl)-N,N-dimethylaniline (ref. 14) as $\alpha_e/a^3 \approx 0.9 \cdot 10^{-10} \text{CV}^{-1}\text{m}^{-1}$ or for 9-(4-dimethylaminophenyl)-10-cyanoanthracene (ref. 15) as $\alpha_e/a^3 \approx 0.74 \cdot 10^{-10} \text{CV}^{-1}\text{m}^{-1}$ or for 9,9'-bianthryl as $\alpha_e/a^3 \approx 1.14 \cdot 10^{-10} \text{CV}^{-1}\text{m}^{-1}$ (ref. 16). This latter value had been calculated for 9,9'-bianthryl assuming a one species or one state emitting rigid system and was already discussed in (ref. 16) as due to a not appropriate description of the system. The value reported in this communication for α_e/a^3 for the rigid compounds also is in agreement with the value of $0.2 \cdot 10^{-10} \text{CV}^{-1}\text{m}^{-1}$ reported for the first Franck-Condon excited singlet state of p-nitroanisole by Kriebel and Labhart (ref. 17).

Hence, the big literature values reported by our group for non-rigid systems that are assumed to fluoresce from locally excited states as well as from TICT states most probably is due an improper model: evaluation of EOEM data with the aim of determining α_e/a^3 most probably is not possible with non-rigid molecules and of course not, if two species emit.

TABLE 2. Dipole moment μ_e and polarizability density α_e/a^3 of MIN and some coumarins. Errors are standard errors.

compound	$\mu_e/10^{-30}$ Cm	$(\alpha_e/a^3)/10^{-10}$ CV ⁻¹ m ⁻¹
MIN	20.9 ± 1.2	0.133 ± 0.11
C 47	36.8 ± 2.1	0.213 ± 0.1
C 102	39.4 ± 3.3	0.140 ± 0.15
C 152a	46.1 ± 3.7	0.100 ± 0.150
C 153	48.3 ± 3.8	0.057 ± 0.150

At a closer view at the data Table 1 it becomes evident that a linear approximation of the data is not the best type of fit. Figure 2 shows that a second order polynomial is a much better fit. Although it is a better fit with the rigid compounds as well as with the more flexible ones or with the coumarins as well as with MIN this finding should not be overinterpreted towards solvent induced structural changes or solvent dependent average distributions since it might simply be due to specific interaction of the solvents, e.g. with the amino nitrogen. Hence the main lecture from this plot is that deriving α_e/a^3 from only two solvents as was done in (ref. 13) will yield doubtful results.

Acknowledgements

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