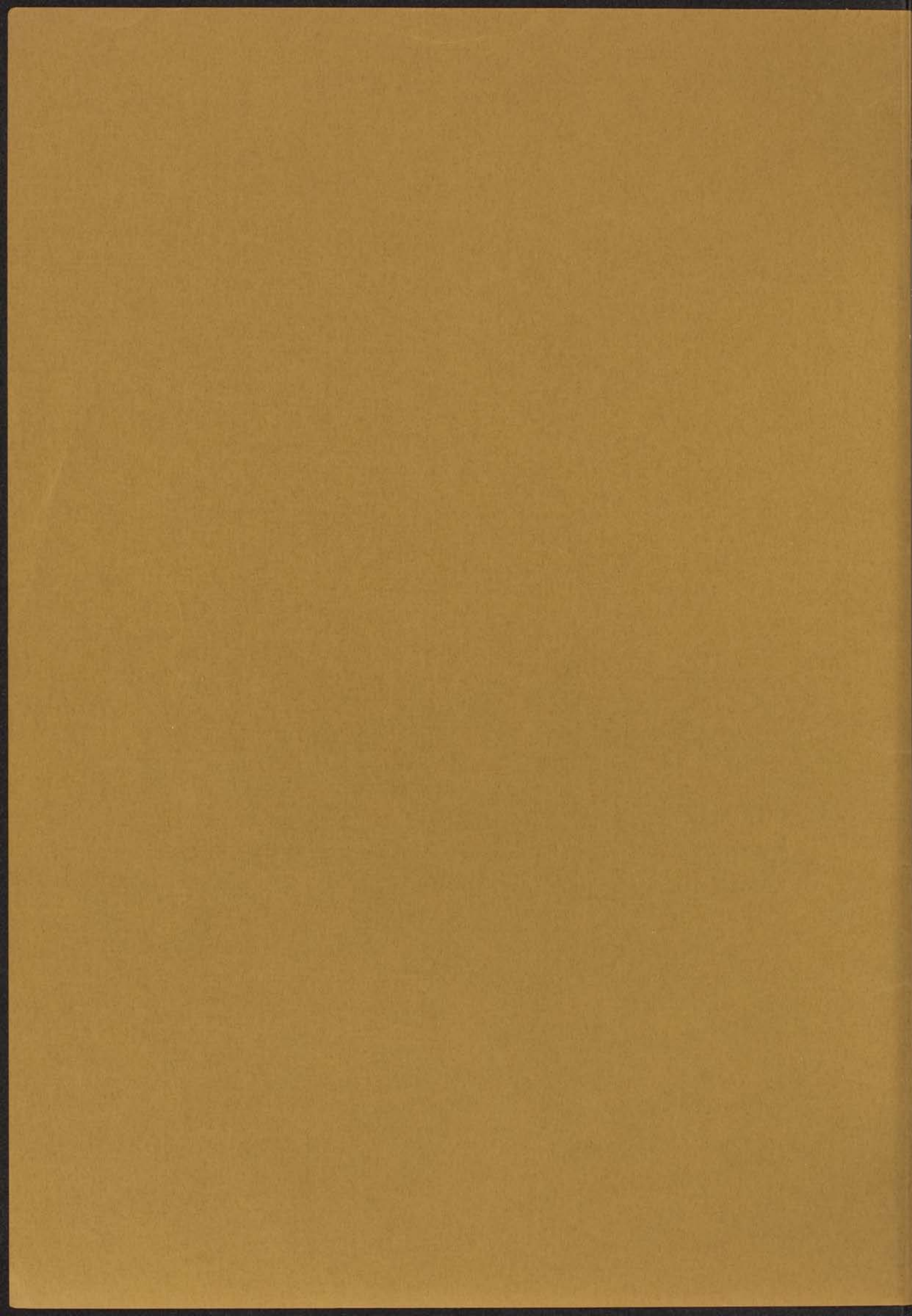


# **The influence of an electric field on molecular electronic spectra**

Directions of transition moments,  
dipole moments and  
polarizabilities in excited states

**C.A.G. O. Varma**



## STELLINGEN

C.A.G.O. Varma

Leiden, 28 april 1971

## I

- a. De beschikbare experimentele gegevens zijn onvoldoende om de onderling sterk afwijkende waarden, die voor het dipoolmoment van 1,4-cyclohexaandion worden gevonden, te kunnen verklaren.
- b. Bij het zoeken naar een verklaring voor deze verschillende waarden bieden de volgende metingen goede vooruitzichten:
  1. De diëlektrische relaxatietijden en de statische diëlektrische constante van oplossingen in verschillende oplosmiddelen.
  2. De chemische relaxatietijden in verschillende media.
  3. Het rotatiespectrum en het Stark-effect in het rotatiespectrum.

A. Mossel, Proefschrift Leiden 1963;

A. Aihara, K. Chitoku, K. Higasi, *Bull. Chem. Soc. Japan* **35**, 2056 (1962);

M.T. Rogers, J.M. Canon, *J. Phys. Chem.* **65**, 1417 (1961);

P. Dowd, T. Dyke, W. Klemperer, *J. A. C. S.* **92**, 6327 (1970).

## II

Vergeleken bij tris-dipivalo-methanato lanthanide complexen kunnen perfluoro-tris-acetylacetonato lanthanide complexen betere verschuivingsreagentia zijn in de kernspin-resonantie-spectroscopie. Het is te verwachten dat laatstgenoemde verbindingen kunnen worden gesynthetiseerd via een combinatie van de methoden beschreven door Fenton e.a. en door Kollonitsch e.a.

D.E. Fenton, M.R. Truter, B.L. Vickery, *Chem. Comm.* (1971) 93;

J. Kollonitsch, L. Barash, G.A. Doldouras, *J. A. C. S.* **92**, 7494 (1970).

## III

Het is zinvol complexen tussen  $\pi$ -electronen donoren en acceptoren te onderzoeken op hun absorpties in het verre infrarood.

## IV

De uit de molecular orbital theorie door Lindholm verkregen resultaten, die betrekking hebben op de fragmentatie van aangeslagen toestanden van methaan, zijn niet in overeenstemming met de meest betrouwbare experimenten.

E. Lindholm, *Arkiv Fysik* **37**, 37 (1968)/*J. C. P.* **52**, 4921 (1970);

W. Braun, J.R. Mc Nesby, A.M. Bass, *J. C. P.* **46**, 2071 (1967);

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## V

Het reactieschema dat Bolton e.a. voorstellen voor de isomerisatie van tert-butylfenolen, is onwaarschijnlijk.

A.P. Bolton, M.A. Lanewala, P.E. Pickert, *J. O. g. Chem.* **33**, 3415 (1968).

## VI

De intermediären die worden gevormd bij de bestraling van een reactiemengsel van ijzerpentacarbonyl en styreen, bieden nieuwe synthetische mogelijkheden in de chemie.

R. Victor, R.B. Shoshan, S. Sarel, *Tetr. Lett.* **49**, 4257 (1970).

## VII

In zijn berekeningen van de door het kation geïnduceerde verschuiving in het u.v. spectrum van het terphenyl ion heeft Biloen een aantal belangrijke factoren buiten beschouwing gelaten.

P. Biloen, *Theor. Chim. Acta* **19**, 365 (1970).

## VIII

Sauter en Albrecht houden, bij de interpretatie van het veldeffect op het spectrum van azuleen in een vaste oplossing, geen rekening met een aantal mogelijk belangrijke bijdragen aan het effect.

H. Sauter, A.C. Albrecht, *Chem. Phys. Lett.* **2**, 8 (1968).

## IX

Het getuigt van argeloosheid dat Thulstrup en Vala de taak op zich nemen om inzicht te verschaffen in het spectroscopisch gedrag van benzeen via polarisatiemetingen aan p-dimethoxybenzeen.

E.W. Thulstrup, M. Vala, *Chem. Phys. Lett.* **7**, 31 (1970).

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19. The nineteenth section of the Act...

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Directions of transition moments,  
dipole moments and  
polarizabilities in excited states

PROEFSCHRIFT

TER VERKRUGING VAN DE GRAAD VAN DOCTOR  
IN DE WISKUNDE EN NATUURWETENSCHAPPEN AAN  
DE RIJESUNIVERSITEIT TE LEIDEN, OP GEZAG VAN  
DE RECTOR MAGNIFICUS DR. C. SOETEMAN, HOOG-  
LEERAAR IN DE FACULTEIT DER LETTEREN, TEN  
OVERSTAAN VAN EEN COMMISSIE UIT DE SENAAT  
TE VERDEDIGEN OP WOENSDAG 28 APRIL 1971 TE  
KLOKKE 15.15 UUR

DOOR

CYRIL ANTON GAJENDRECHANDRE OEDAY RAJSINGH VARMA

GEBOREN TE PARAMARIBO, SURINAME IN 1936

# The influence of an electric field on molecular electronic spectra

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# The influence of an electric field on molecular electronic spectra

Directions of transition moments,  
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polarizabilities in excited states

PROBESCHRIJFT

PROMOTOR: PROF. DR. L.J. OOSTERHOFF

TER VERVOLGENDE EN NATUURWETENSCHAPPEN AAN  
DE RIJKSUNIVERSITEIT TE LEIDEN, OP GEZAC VAN  
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CYRIL ANTON GALENDRACHANDRE OEDAY RAISINGH VARMA

GEBOREN TE PARAMARIBO, SURINAME IN 1938

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INTRODUCTION

CHAPTER 1 The theory of absorption in the presence of a static electric field

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1.2 The influence of an electric field on the intensity of molecules

1.3 The energy change

1.4 The dipole function

1.5 The field dependent transition moment

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1.7 The field dependence of the extinction coefficient

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CHAPTER 2 Experimental technique and data processing

2.1 General considerations

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SUMMARY

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This work has been performed as part of the program of the Foundation for Chemical Research in The Netherlands and has been sponsored by the Organization for the Advancement of Pure Research in The Netherlands.

## INTRODUCTION

It has been recognized that knowledge of the electronic properties of molecules, such as their dipole moments and polarizabilities, may be useful to elucidate the nature of elementary physical and chemical interactions and processes involving molecules in their ground state<sup>1,2</sup>. To this end one may gain insight from suitable experimental studies like measurements of dielectric constant, refractive index, stark effect in rotational spectra etc. On the other hand there is a trend to take advantage of methods to find approximate wavefunctions in order to calculate molecular properties<sup>3,4</sup>. Concerning the latter point of view it should be said that, at least at present, it is not the purpose of quantum mechanics to deliver us accurate values of molecular quantities for large molecules. The essential point of quantum mechanics is still, that it serves as a tool to systematize experimental observations.

After electronic excitation a molecule may behave quite different from the ground state in a physical and chemical sense. Again a knowledge of the dipole moment and polarizability in the excited state may contribute to an understanding of the modifications due to excitation. However, the usual experimental techniques such as measurement of the dielectric constant of solutions are not of any use in this case, since the stationary concentration of excited species which can be obtained, is much too low. Nevertheless there is a way out. The interaction of a strong uniform electric field of the order 100 KV/cm with a molecule of interest leads to a change in its absorption spectrum. By applying a suitable, although complicated, theory it is then possible to derive from the induced changes in an absorption band some molecular quantities like the direction of the transition moment, the dipole moments in the ground- and excited state as well as the polarizability after excitation. Compared to dielectric studies, more trustworthy values of ground state dipole moments of highly polar molecules, which tend to associate as a consequence of dipole-dipole interaction, may be obtained from such spectroscopic experiments, since concentrations can be kept very low e.g.  $C < 10^{-4}$  moles/liter.

In this thesis we are concerned with both theoretical and practical aspects of the quoted electro-optical phenomenon, which has been referred to by some authors<sup>5</sup> as electrochromism. Here we like to remark that the name 'electro-spectroscopy', as an alternative, is more in accordance with the variety of effects encountered in this field. A selection of experimental studies is presented with an eye on their implications for other fields of current research.

The complete derivation of the theory is given in the first chapter, taking into account several effects which may contribute to the observed modification of an absorption band: 1. A lowering of energies of initial and final states arising from the interaction of the dipole moments and polarizabilities of these states with the external field; 2. The field dependence of the transition moment; 3. The induced angular anisotropy in the distribution of molecules in the sample.

The experimental technique, based on modulation by a time dependent external field in conjunction with a ratio detection system, allows the direct determination of the relative change in light intensity, caused by the electric field. The most important features of the spectrometer we have constructed for electro-optical measurements are given in chapter 2.

We discuss in chapter 3 the determination of the absolute direction of the transition moment and the dipole moment in the ground- and first excited singlet state of some conjugated organic molecules. The results are compared with quantum chemical calculations on these molecules. In one case we have related the photochemical behaviour of the molecule with our result.

In order to obtain the magnitude of the change in polarizability of a medium size molecule, we have studied the influence of an electric field on the first absorption band of the nonpolar compound tetracene. Knowing the order of magnitude of this quantity for such molecules one may estimate the consequences of neglecting polarizability changes in the determination of excited state dipole moments. The first paper included in this thesis deals with this subject.

When transparent solutions of anthracene (electron donor) and trinitrobenzene (electron acceptor) are mixed, a colored sample is obtained. The electronic absorption spectrum shows a new band superimposed on the slightly modified spectra of the individual components. Mulliken's theory<sup>6</sup> ascribes the new band to a transition in which an electron is transferred from the donor D to the acceptor A, resulting in a final state which practically resembles that of an ion pair  $D^+A^-$ . This charge transfer state should therefore have a dipole moment of the order of an electron charge times the intermolecular distance, say 3.5 Å, i.e.  $\approx 15$  Debye. However, the resonance theory does not fully explain the ground

state properties of the donor - acceptor pair (complex)<sup>6</sup>. In order to gain insight in the charge distribution in the ground- as well as the charge transfer state of these complexes, we have studied a number of them electro-optically. This investigation is reported in the second paper.

Since we are able to determine dipole moments of excited molecules, it is quite natural to compare them with the values determined by other means. In the last paper we discuss a method to evaluate excited state dipole moments from the influence of solvents on absorption bands. Where possible the results thus derived are compared with electro-optical values. At this point it is appropriate to remark that proper understanding of solute - solvent interactions, together with estimates of excited states dipole moments, might be useful in the explanation of the solvent dependence of photo-chemical reactions in cases, where two states are very close in energy.

Summarizing, the possibilities offered by electrospectroscopic studies are: 1. The evaluation of dipole moments and polarizabilities of electronically excited molecules; 2. More accurate determination of ground state dipole moments in certain cases; 3. The only way to obtain dipole moments in some instances e.g. exciplexes; 4. The resolution of polarizations of electric dipole transitions; 5. The understanding of electric field- and solvent dependency of the intensity of absorption bands.

To bring this section to an end, we present a glossary of symbols frequently encountered in this work. Unless stated otherwise the notation means the following:

$h$	=	Planck's constant
$K$	=	Boltzmann's constant
$c$	=	velocity of light
$\nu$	=	frequency
$\sigma$	=	wavenumber
$T$	=	absolute temperature
$\beta$	=	$1/KT$
$D$	=	Debye unit for dipole moment
$M$	=	the electric dipole operator
$P$	=	the transition moment in a field free case
$P(F)$	=	the transition moment in the presence of a field $F$
$\mu$	=	the molecular dipole moment in the ground state
$\mu(i)$	=	the dipole moment in the $i^{\text{th}}$ excited state of the molecule
$\mu_i$	=	a component of $\mu$
$\Delta\mu$	=	$\mu(i) - \mu$
$a$	=	the polarizability tensor in the molecular ground state
$a(i)$	=	the polarizability in the $i^{\text{th}}$ excited state of the molecule
$a_{ij}$	=	a component of the tensor $a$
$\Delta a$	=	$a(i) - a$
$A, B$	=	are the second and third rank transition polarizabilities, respectively
$\langle \rangle$	=	stands for averaging in general
$\ll \gg$	=	means averaging over an isotropic distribution of orientations
$\epsilon(\nu)$	=	the molar extinction coefficient measured in an isotropic system when there is no external field present
$\epsilon_\chi(\nu, F)$	=	molar extinction measured with light polarized with an angle $\chi$ relative to a uniform field $F$

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## CHAPTER 1

### THE THEORY OF ABSORPTION IN THE PRESENCE OF A STATIC ELECTRIC FIELD

#### 1.1 The molar extinction coefficient

The link between the quantum mechanical treatment of absorption of radiation and its phenomenological description in terms of the molar extinction coefficient can be made by selecting a simple example.

Let us consider a transition between two discrete levels of an atom or molecule. The radiation causing the transition is linearly polarized and has a sharp intensity distribution around the central frequency  $\nu$ .

In a semiclassical treatment one derives, using time dependent perturbation theory, the transition probability per unit time  $W(\nu)$ . We take this expression for an electric dipole transition from H.A. Bethe, 'Intermediate Quantum Mechanics'<sup>1</sup>.

$$W(\nu) = \frac{8\pi^3\nu}{hc} N(\nu) (\underline{e} \cdot \underline{P})^2 \quad 1.1$$

Here  $N(\nu)$  is the number of photons per unit of frequency/sec  $\text{cm}^2$  in the incident radiation;  $\underline{e}$  is a unit vector in the direction of the electric field of the lightwave;  $\underline{P}$  is the transition dipole moment.

With the aid of (1) we can calculate the decrease in intensity  $dI(\nu)$  of the lightwave after it has travelled a distance  $dl$  through a sample containing  $n$  molecules/ $\text{cm}^3$ .

$$dI(\nu) = -h\nu n \langle W(\nu) \rangle dl = -\frac{8\pi^3\nu}{hc} \langle (\underline{e} \cdot \underline{P})^2 \rangle n I(\nu) dl \quad 1.2$$

where we have used the fact that the intensity  $I(\nu)$  of the light is given by  $I(\nu) = h\nu N(\nu)$ . The brackets indicate that one has to average over the molecular orientations in the sample.

The molar extinction coefficient is defined by the law of Lambert-Beer which we write in the form:

$$dI(\nu) = -\epsilon(\nu) C I(\nu) dl \quad 1.3$$

with  $C$  the concentration in moles/liter.

Identifying eqs (2) and (3) we find:

$$\epsilon(\nu) = \frac{N}{1000} \frac{8\pi^3\nu}{hc} \langle (\underline{e} \cdot \underline{P})^2 \rangle \quad 1.4$$

where  $N$  is Avogadro's number.

The relation (4) can be generalized to the case of the broad electronic absorption bands encountered in molecular spectroscopy. For large molecules there may be associated with every electronic state a continuum or quasi continuum of vibrational and rotational sublevels. This leads to the observed band structure in molecular electronic spectra. By introducing the shape function  $S(\nu)$  as a weighting factor we obtain the generalization:

$$\epsilon(\nu) = \frac{N}{1000} \frac{8\pi^3\nu}{hc} \langle (\underline{e} \cdot \underline{P})^2 S(\nu) \rangle \quad 1.5$$

The value of the function  $S(\nu)$  is determined, in the Born-Oppenheimer approximation, by the nuclear parts of the initial and final states involved in transitions occurring in a narrow frequency interval around  $\nu$ . Later in our discussion we will return to this point. It should be noted that  $S(\nu)$  is an average value over states of the molecule in a particular orientation.

## 1.2 The influence of an electric field on an assembly of molecules

We will now consider the modifications in the absorption of light of a whole sample, brought about by an external static electric field. In the subsequent discussion we will deal with absorption bands showing no rotational fine structure and with non-rigid samples i.e. gases and liquid solutions. Further the sample is considered as a system of non-interacting molecules.

Then the individual molecules will suffer a perturbation from the external field  $F$ . Four effects may develop.

1. The energies of initial and final state change.
2. The shape function  $S(\nu)$  is altered.
3. The transition moment  $P$  is modified.
4. The distribution of molecular orientations becomes anisotropic.

## 1.3 The energy change

For a given state  $|k\rangle$  the energy change amounts to  $\Delta E(k)$ .

$$\Delta E(k) = -\underline{\mu}(k) \cdot \underline{F} - \frac{1}{2} \underline{F} \cdot \underline{\alpha}(k) \cdot \underline{F} \quad 1.6$$

where  $\mu(k)$  and  $\alpha(k)$  are the dipole moment and polarizability of the molecule in its  $k^{\text{th}}$  state.

In the case of a sharp absorption line this would be observed as a frequency shift of the line given by:

$$h \Delta \nu = -\Delta \underline{\mu} \cdot \underline{F} - \frac{1}{2} \underline{F} \cdot \Delta \underline{\alpha} \cdot \underline{F} \quad 1.7$$

$$\Delta \underline{\mu} \equiv \underline{\mu}(f) - \underline{\mu}(i) \quad 1.8$$

with

$$\Delta \underline{\alpha} \equiv \underline{\alpha}(f) - \underline{\alpha}(i) \quad 1.9$$

the labels  $f$  and  $i$  indicating final and initial state respectively.

## 1.4 The shape function

Within the manifold of rotational and vibrational sublevels belonging to a certain electronic state the dipole moment and polarizability will be considered as constant. The frequency shift given by (7) will then be uniform i.e. constant within the frequency range of the absorption band. Therefore it seems reasonable to assume that the modification of the shape function  $S(\nu)$  consists merely of a uniform shift  $\Delta \nu$  of the band without changing its shape<sup>2</sup> i.e.

$$S^F(\nu) = S(\nu - \Delta \nu) \quad 1.10$$

However, the justification remains an intriguing problem. At times eq (10) looks very obvious to us and at other instances it seems very questionable. In the following discussion we shall try to trace out the origin of bandshape conservation only to find a somewhat stronger support than intuition provides.

The Born-Oppenheimer approximation<sup>1</sup> leads to a separation of electronic and nuclear motions.

$$\Psi_{j\alpha}(q, Q) = \varphi_j(q, Q) \theta_{j\alpha}(Q) \quad 1.11$$

$$\{T(q) + V(q, Q)\} \varphi_j(q, Q) = E_j(Q) \varphi_j(q, Q) \quad 1.12$$

$$\{T(Q) + E_j(Q) + \dots\} \theta_{j\alpha}(Q) = \epsilon_{j\alpha} \theta_{j\alpha}(Q) \quad 1.13$$



where  $\varphi_j(q, Q)$  and  $\Theta_{j\alpha}(Q)$  represent the electronic and nuclear part of the wavefunction respectively;  $T(q)$  and  $T(Q)$  are the kinetic energy operators for electrons and nuclei respectively.

If the additional assumption is made that the electronic transition moment  $P_e$  does not vary with the nuclear coordinates we get for the transition moment:

$$P(j\alpha, k\beta) = P_e(jk) \langle \Theta_{j\alpha} | \Theta_{k\beta} \rangle \quad 1.14$$

$$\text{with } P_e(jk) \equiv \langle \varphi_j | M_e | \varphi_k \rangle \quad \text{where } M_e \text{ is the electronic part of the dipole operator.} \quad 1.15$$

We consider our system at a temperature of about 300°K. In the electronic ground state only the first vibrational state will be populated appreciably, since vibrational wavenumbers are of the order  $1000 \text{ cm}^{-1}$  and  $KT \approx 200 \text{ cm}^{-1}$ . But still many rotational sublevels pertaining to this vibronic state will be occupied.

For a moment we take the bandwidth of the light equal to zero. Any occupied sublevel may serve as an initial state for absorption at frequency  $\nu$ . If we consider the sublevels of initial and final electronic states as discrete, the frequency  $\nu$  connects the sublevel  $|i\alpha\rangle$  with only one final level, which we therefore indicate by  $|f\alpha'\rangle$ . In reality the bandwidth  $w$  of the light ensures that starting from  $|i\alpha\rangle$  all final levels in the interval  $f\alpha - w \leq f\alpha' \leq f\alpha + w$  are reached (fig 1.1).

By  $g_\alpha$  we denote the number of molecules in the sublevel  $|i\alpha\rangle$ . The contribution of the level  $|i\alpha\rangle$  to the function  $S(\nu)$  is given by

$$S_\alpha(\nu) = g_\alpha \sum_{\alpha'=-w}^{+w} \langle \Theta_{i\alpha} | \Theta_{f\alpha'} \rangle^2 \quad 1.16$$

Summing over all occupied initial states  $|i\alpha\rangle$  we get the total shape function.

$$S(\nu) = \sum_{\alpha}^{occ} g_\alpha \sum_{\alpha'=-w}^{+w} \langle \Theta_{i\alpha} | \Theta_{f\alpha'} \rangle^2 \quad 1.16a$$

Whenever the right hand side of (1.6a) can be considered an invariant quantity with respect to perturbation by the field  $F$ , eq (10) will be valid. Let us examine under what conditions this will happen.

In the presence of the field the Born-Oppenheimer separation still holds i.e.  $\varphi_i \Theta_{i\alpha} \xrightarrow{F} \varphi_i^F \Theta_{i\alpha}^F$ . The perturbation operator  $-M \cdot F$  is now part of the potential in the equation for  $\varphi_i^F$  and leads to a mixing of  $\varphi_i$  with other electronic states  $\varphi_j$ . The correction in the electronic energy, which in first order is given by:

$$E_i^{(1)}(Q) = - \langle \varphi_i | M | \varphi_i \rangle \cdot F \quad 1.17$$

enters as the perturbation in the equation for  $\Theta_{i\alpha}$ .

The field  $F$  causes orthogonal transformations in the manifolds  $\{\Theta_{i\alpha}\}$  and  $\{\Theta_{f\beta}\}$ . In first order of  $F$  we have

$$\Theta_{i\alpha}^F = \Theta_{i\alpha} + \sum_{\mu \neq \alpha} a_{\alpha\mu} \Theta_{i\mu} \quad 1.18$$

$$\Theta_{f\alpha'}^F = \Theta_{f\alpha'} + \sum_{\sigma \neq \alpha'} b_{\alpha'\sigma} \Theta_{f\sigma} \quad 1.19$$

The transformation coefficients are given by relations of the form

$$a_{\alpha\mu} = \frac{N_{\alpha\mu}}{E_{i\alpha} - E_{i\mu}} \quad \alpha \neq \mu \quad 1.20$$

$$\text{where } N_{\alpha\mu} \equiv \langle \Theta_{i\alpha} | E_i^{(1)}(Q) | \Theta_{i\mu} \rangle \quad 1.21$$

$N_{\alpha\mu}$  will in general be of the order of the strength of  $F$ , say  $10^5 \text{ V/cm}$ , times a transition moment encountered in vibration and rotation spectra<sup>3</sup>, say  $\leq 0.1 \text{ Debye}$ , i.e.  $N_{\alpha\mu} \leq 0.2 \text{ cm}^{-1}$ . Therefore convergence of the series (18) and (19) will be satisfactory if the summation is limited to a small energy region  $\delta_\alpha$ , say  $\delta_\alpha \approx 20 \text{ cm}^{-1}$ , around  $E_{i\alpha}$  and  $E_{f\alpha'}$  (fig 1.1).

In experiments we will usually encounter bandwidths  $w \approx 60 \text{ cm}^{-1}$ . This ensures that the domain of summation in eq (16) completely encloses  $\delta_\alpha$  i.e. mixing does not bring us outside the subspace defined by the specified interval.

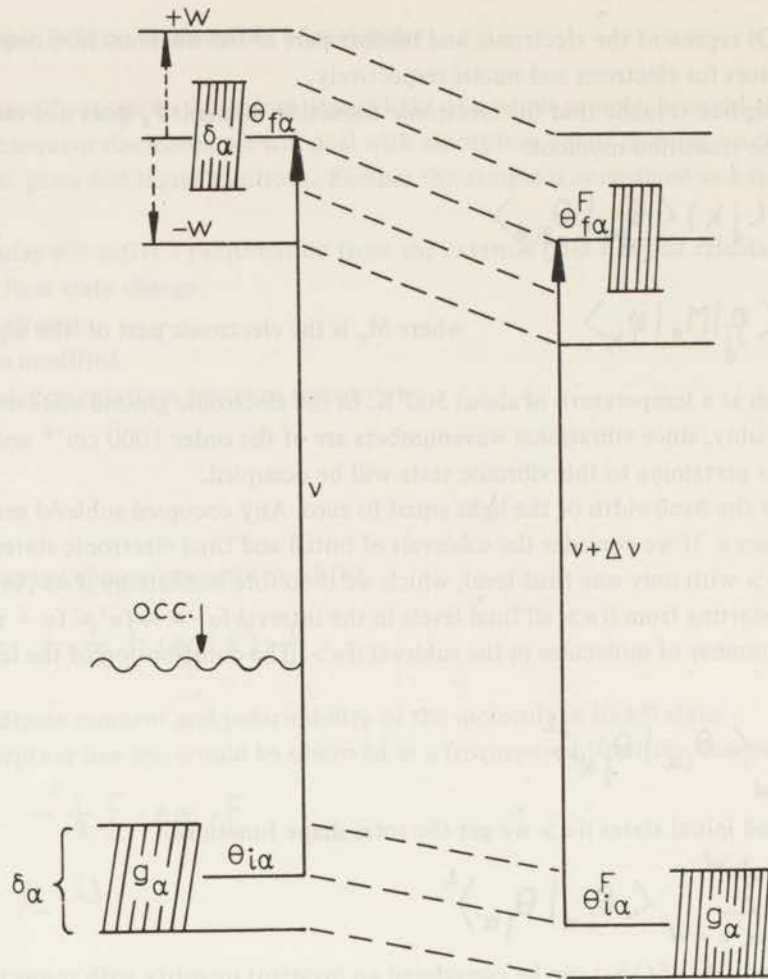


Fig 1.1

Schematic diagram illustrating the influence of an electric field on the molecular energy levels

Let us now turn our attention to the ground state levels. If we may consider  $g_\alpha$  as constant in the region  $\delta_\alpha$  i.e.  $\delta_\alpha \ll KT$ , we can introduce the notion of an invariant partial sum  $S_\alpha(\nu)$ .

$$S_\alpha \equiv g_\alpha \sum_{\alpha \in \delta_\alpha} \sum_{\alpha' = -W}^{+W} \langle \theta_{i\alpha} | \theta_{f\alpha'} \rangle^2 \quad 1.22$$

$S_\alpha$  will remain invariant under the limited orthogonal transformations (18) and (19). Due to the energy changes discussed in section 1.1 this partial sum will be observed in the presence of the field at frequency  $\nu + \Delta\nu$  and hence  $S'(\nu + \Delta\nu) = S(\nu)$ .

At very low temperatures it may happen that  $g_\alpha$  can no longer be considered as constant in the region  $\delta_\alpha$ . Especially the mixing of unoccupied sublevels with the occupied ground state levels may lead to a breakdown of eq (10). Even the bandwidth does not help to guarantee the validity of the approximation.

### 1.5 The field dependent transition moment

As we have just seen in the preceding section the mixing of rovibrational sublevels does not lead to an observable effect at room temperature. The main reason being that in the absence of the field most of these states are already involved in the phenomena. A similar spectroscopy stability<sup>4</sup> is not expected if initial and final electronic states are mixed with other electronic states.

The electronic transition moment given by (15), which from now on will be indicated by  $\mathbf{P}$ , gains a field induced part. Just like an ordinary dipole moment we describe  $\mathbf{P}(\mathbf{F})$  by a power series in  $\mathbf{F}$ :

$$\underline{\mathbf{P}}(\underline{\mathbf{F}}) = \underline{\mathbf{P}} + \underline{\mathbf{A}} \cdot \underline{\mathbf{F}} + \underline{\mathbf{B}} : \underline{\mathbf{F}} \underline{\mathbf{F}}$$

which defines the transition polarizability  $A$  and the transition hyperpolarizability  $B$ . The tensors  $A$  and  $B$  are of second and third rank respectively.

Unlike the polarizability  $\alpha$ , the transition polarizability needs not to be a symmetrical tensor. The components of the tensors  $A$  and  $B$  may in principle be calculated using perturbation or variation methods. The perturbation method may be helpful to study the implications of molecular symmetry on  $A$ . We shall illustrate this for a molecule having  $C_{2v}$  symmetry. This pointgroup is Abelian and therefore the irreducible representations are one dimensional. We choose a cartesian coordinate system with  $z$  along  $C_2$ ,  $y$  in  $\sigma'_v$  and  $x$  in  $\sigma_v$ . Let us consider a  $x$  polarized transition starting from the totally symmetric ground state ( $A_1$ ). We denote by  $F_i\Gamma$  an irreducible representation which enters  $\varphi(F)$  due to the field component  $F_i$ . Realizing that the perturbation operator is  $-\mathbf{M}\cdot\mathbf{F}$ , we obtain by inspecting the character table<sup>5</sup> the following mixing scheme:

$$\varphi_i(\underline{F}) = A_1 + (B_1)F_x + (B_2)F_y + (A_1)F_z \quad 1.24$$

$$\varphi_f(\underline{F}) = B'_1 + (A'_1)F_x + (A'_2)F_y + (B'_1)F_z \quad 1.25$$

In first order of  $F$  we find for the components of  $P(F)$

$$P_x(\underline{F}) = P_x + \langle A_1 | M_x | B'_1 \rangle F_z + \langle B'_1 | M_x | A_1 \rangle F_z$$

$$P_y(\underline{F}) = 0 \quad 1.26$$

$$P_z(\underline{F}) = \langle A_1 | M_z | A'_1 \rangle F_x + \langle B'_1 | M_z | B_1 \rangle F_x$$

This result states that the only nonvanishing components of the transition polarizability  $A$  are:  $A_{xz}$  and  $A_{zx}$  with  $A_{xz} \neq A_{zx}$ .

Along the same lines it follows that for transitions from the ground state which are  $y$  polarized the nonvanishing components of  $A$  are  $A_{yz}$  and  $A_{zy}$ . Transitions from the ground state which are  $z$  polarized have only the diagonal components of  $A$  nonzero.

## 1.6 The induced anisotropy

We suppose that the temperature of our system is high enough for  $KT$  to be much larger than the energy separation between the molecular rotational levels. The problem of the orientational distribution of molecules which are able to rotate in an external field can then be handled by classical statistical mechanics<sup>6</sup>. At equilibrium the number of molecules with a given orientation will be given by a Boltzmann distribution. The molecules acquire a potential energy  $-V(\Omega, F)$  depending on their orientation relative to the field  $F$ .

$$V(\Omega, \underline{F}) = \mu \cdot \underline{F} + \frac{1}{2} \underline{F} \cdot \underline{\alpha} \cdot \underline{F} \quad 1.27$$

The normalized distribution function for molecular orientations is given by

$$f(\Omega, \underline{F}) = \frac{[\exp \beta V(\Omega, \underline{F})]}{\int \exp \beta V(\Omega, \underline{F}) d\Omega} \quad 1.28$$

with  $\beta \equiv 1/KT$  and where the integration is over all orientations.

In view of the development in the next section we emphasize that at zero field eq (28) represents an isotropic distribution of orientations.

### 1.7 The field dependence of the extinction coefficient

We are now ready to calculate the extinction coefficient in the presence of  $F$ . From eq (5) we infer:

$$\epsilon(\nu, F) = K \nu \left\langle \left\{ \underline{e} \cdot \underline{P}(F) \right\}^2 S^F(\nu) \right\rangle \quad 1.29$$

where

$$K = \frac{8\pi^3 N}{1000 k c}$$

With the aid of eq (10), realizing  $\Delta\nu$  given by eq (7) to be small, we expand  $S^F(\nu)$  into a Taylor series in  $\Delta\nu$ .

$$S^F(\nu) = S(\nu) - \Delta\nu \left( \frac{dS}{d\nu} \right)_{\nu} + \frac{1}{2} (\Delta\nu)^2 \left( \frac{d^2S}{d\nu^2} \right)_{\nu} + \dots \quad 1.30$$

The right hand side of eq (30) may be transformed into an expression depending on  $\epsilon(\nu)$  and its derivatives. Averaging in eq (5) over an isotropic distribution of orientations we obtain the extinction coefficient  $\epsilon(\nu)$  related to  $S(\nu)$ .

$$\epsilon(\nu) = \frac{1}{3} K \nu P^2 S(\nu) \quad 1.31$$

Introducing (31) in (29) and using the relations

$$\frac{d \ln \epsilon / \nu}{d \nu} = \left( \epsilon / \nu \right)^{-1} \frac{d \epsilon / \nu}{d \nu} \quad 1.32$$

$$\frac{d^2 \ln \epsilon / \nu}{d \nu^2} = - \left( \frac{d \ln \epsilon / \nu}{d \nu} \right)^2 + \left( \epsilon / \nu \right)^{-1} \frac{d^2 \epsilon / \nu}{d \nu^2} \quad 1.33$$

we get:

$$\epsilon(\nu, F) = \frac{3\epsilon(\nu)}{P^2} \left\langle \left\{ \underline{e} \cdot \underline{P}(F) \right\}^2 \left[ 1 - \Delta\nu \frac{d \ln \epsilon / \nu}{d \nu} + \frac{1}{2} (\Delta\nu)^2 \left[ \left( \frac{d \ln \epsilon / \nu}{d \nu} \right)^2 + \frac{d^2 \ln \epsilon / \nu}{d \nu^2} \right] \right] \right\rangle \quad 1.34$$

The averaging indicated on the R.H.S. of eq (34) will be carried out term by term, using the distribution function (28). For a general term  $Q(F)$  we shall show the route to perform the calculation. We define:

$$T(F) \equiv \int_0 \phi(\Omega, F) \exp \beta V(\Omega, F) d\Omega \quad 1.35$$

$$N(F) \equiv \int_0 \exp \beta V(\Omega, F) d\Omega \quad 1.36$$

$$Q(F) \equiv \langle \phi(\Omega, F) \rangle \quad 1.36a$$

Hence:  $Q(F) = T(F) / N(F)$

Expanding  $Q(F)$  into a Taylor series in the field components  $F_i$ , retaining terms up to the second order in  $F$ , we obtain:

$$Q(F) = Q(0) + \sum_i F_i \left( \frac{\partial Q}{\partial F_i} \right)_{F=0} + \frac{1}{2} \sum_{ij} F_i F_j \left( \frac{\partial^2 Q}{\partial F_i \partial F_j} \right)_{F=0} \quad 1.37$$

The derivatives are given by:

$$\frac{\partial Q}{\partial F_i} = N^{-1} \frac{\partial T}{\partial F_i} - N^{-2} T \frac{\partial N}{\partial F_i} \quad 1.38$$

$$\frac{\partial^2 Q}{\partial F_i \partial F_j} = N^{-1} \frac{\partial^2 T}{\partial F_i \partial F_j} - N^{-2} \frac{\partial T}{\partial F_i} \frac{\partial N}{\partial F_j} - N^{-2} T \frac{\partial^2 N}{\partial F_i \partial F_j} \quad 1.39$$

$$- N^{-2} \frac{\partial N}{\partial F_i} \frac{\partial T}{\partial F_j} + 2 N^{-3} T \frac{\partial N}{\partial F_i} \frac{\partial N}{\partial F_j}$$

$$\frac{\partial T}{\partial F_i} = \int \frac{\partial \phi}{\partial F_i} \exp \beta V d\Omega + \beta \int \phi \frac{\partial V}{\partial F_i} \exp \beta V d\Omega \quad 1.40$$

$$\frac{\partial^2 T}{\partial F_i \partial F_j} = \int \frac{\partial^2 \phi}{\partial F_i \partial F_j} \exp \beta V d\Omega + \beta \int \frac{\partial \phi}{\partial F_i} \frac{\partial V}{\partial F_j} \exp \beta V d\Omega \quad 1.41$$

$$+ \beta \int \frac{\partial \phi}{\partial F_j} \frac{\partial V}{\partial F_i} \exp \beta V d\Omega + \beta \int \phi \frac{\partial^2 V}{\partial F_i \partial F_j} \exp \beta V d\Omega$$

$$+ \beta^2 \int \phi \frac{\partial V}{\partial F_i} \frac{\partial V}{\partial F_j} \exp \beta V d\Omega$$

$$\frac{\partial N}{\partial F_i} = \beta \int \frac{\partial V}{\partial F_i} \exp \beta V d\Omega \quad 1.42$$

$$\frac{\partial^2 N}{\partial F_i \partial F_j} = \beta^2 \int \frac{\partial V}{\partial F_i} \frac{\partial V}{\partial F_j} \exp \beta V d\Omega + \beta \int \frac{\partial^2 V}{\partial F_i \partial F_j} \exp \beta V d\Omega \quad 1.43$$

Inserting eqs (40) to (43) into (38) and (39) and introducing the symbol  $\langle\langle \rangle\rangle$  for averaging over an isotropic distribution, we arrive at:

$$\left( \frac{\partial Q}{\partial F_i} \right)_{F=0} = \langle\langle \left( \frac{\partial \phi}{\partial F_i} \right) \rangle\rangle_{F=0} + \beta \langle\langle \phi(0) \left( \frac{\partial V}{\partial F_i} \right) \rangle\rangle_{F=0} - \beta \langle\langle \phi(0) \rangle\rangle \langle\langle \left( \frac{\partial V}{\partial F_i} \right) \rangle\rangle_{F=0} \quad 1.44$$

$$\left( \frac{\partial^2 Q}{\partial F_i \partial F_j} \right)_{F=0} = \langle\langle \left( \frac{\partial^2 \phi}{\partial F_i \partial F_j} \right) \rangle\rangle_{F=0} + \beta \langle\langle \left( \frac{\partial \phi}{\partial F_i} \right) \left( \frac{\partial V}{\partial F_j} \right) \rangle\rangle_{F=0} \quad 1.45$$

$$+ \beta \langle\langle \left( \frac{\partial \phi}{\partial F_j} \right) \left( \frac{\partial V}{\partial F_i} \right) \rangle\rangle_{F=0} + \beta \langle\langle \phi(0) \left( \frac{\partial^2 V}{\partial F_i \partial F_j} \right) \rangle\rangle_{F=0} +$$

$$\begin{aligned}
& + \beta^2 \ll \phi(0) \left( \frac{\partial V}{\partial F_i} \right)_{\underline{F}=0} \left( \frac{\partial V}{\partial F_j} \right)_{\underline{F}=0} \gg \\
& - \beta \ll \left( \frac{\partial V}{\partial F_i} \right)_{\underline{F}=0} \gg \left\{ \ll \left( \frac{\partial \phi}{\partial F_j} \right)_{\underline{F}=0} \gg + \beta \ll \phi(0) \left( \frac{\partial V}{\partial F_j} \right)_{\underline{F}=0} \gg \right\} \\
& - \beta \ll \left( \frac{\partial V}{\partial F_j} \right)_{\underline{F}=0} \gg \left\{ \ll \left( \frac{\partial \phi}{\partial F_i} \right)_{\underline{F}=0} \gg + \beta \ll \phi(0) \left( \frac{\partial V}{\partial F_i} \right)_{\underline{F}=0} \gg \right\} \\
& - \beta \ll \phi(0) \gg \left\{ \ll \left( \frac{\partial^2 V}{\partial F_i \partial F_j} \right)_{\underline{F}=0} \gg + \beta \ll \left( \frac{\partial V}{\partial F_i} \right)_{\underline{F}=0} \left( \frac{\partial V}{\partial F_j} \right)_{\underline{F}=0} \gg \right\} \\
& + 2\beta^2 \ll \phi(0) \gg \ll \left( \frac{\partial V}{\partial F_i} \right)_{\underline{F}=0} \gg \ll \left( \frac{\partial V}{\partial F_j} \right)_{\underline{F}=0} \gg
\end{aligned}$$

The derivatives of  $V$  with respect to the field components are found by differentiating the form (27). If the fact that  $\ll \mu_i \gg = 0$  is used, the following expressions result.

$$\left( \frac{\partial Q}{\partial F_i} \right)_{\underline{F}=0} = \ll \left( \frac{\partial \phi}{\partial F_i} \right)_{\underline{F}=0} \gg + \beta \ll \mu_i \phi(0) \gg \quad 1.46$$

$$\begin{aligned}
\left( \frac{\partial^2 Q}{\partial F_i \partial F_j} \right)_{\underline{F}=0} &= \ll \left( \frac{\partial^2 \phi}{\partial F_i \partial F_j} \right)_{\underline{F}=0} \gg + \beta \ll \mu_i \left( \frac{\partial \phi}{\partial F_j} \right)_{\underline{F}=0} \gg + \beta \ll \mu_j \left( \frac{\partial \phi}{\partial F_i} \right)_{\underline{F}=0} \gg \quad 1.47 \\
&+ \beta^2 \ll \mu_i \mu_j \phi(0) \gg - \beta^2 \ll \phi(0) \gg \ll \mu_i \mu_j \gg \\
&+ \frac{1}{2} \beta \ll \alpha_{ij} \phi(0) \gg - \frac{1}{2} \beta \ll \phi(0) \gg \ll \alpha_{ij} \gg
\end{aligned}$$

After the expressions (23) for  $P(F)$  and (7) for  $\Delta v$  are inserted and distributed over all terms in (34) we retain terms up to the second order in  $F$  and write:

$$\mathcal{E}(v, F) = \frac{3 \mathcal{E}(v)}{P^2} \left\langle \left\{ \sum_{k=1}^4 \phi_k + \frac{1}{h} \frac{d \ln \epsilon/v}{d v} \sum_{k=1}^3 \phi'_k + \frac{1}{2 h^2} \left[ \left( \frac{d \ln \epsilon/v}{d v} \right)^2 + \frac{d^2 \ln \epsilon/v}{d v^2} \right] \phi'' \right\} \right\rangle \quad 1.48$$

where

$$\begin{aligned}
\phi_1 &= (\underline{e} \cdot \underline{P})^2 & \phi'_1 &= (\underline{e} \cdot \underline{P})^2 (\Delta \underline{\mu} \cdot \underline{F}) \\
\phi_2 &= (\underline{e} \cdot \underline{A} \cdot \underline{F})^2 & \phi'_2 &= 2 (\underline{e} \cdot \underline{P}) (\underline{e} \cdot \underline{A} \cdot \underline{F}) (\Delta \underline{\mu} \cdot \underline{F}) \\
\phi_3 &= 2 (\underline{e} \cdot \underline{P}) (\underline{e} \cdot \underline{A} \cdot \underline{F}) & \phi'_3 &= \frac{1}{2} (\underline{e} \cdot \underline{P})^2 (\underline{F} \cdot \underline{\Delta} \underline{\alpha} \cdot \underline{F}) \\
\phi_4 &= 2 (\underline{e} \cdot \underline{P}) (\underline{e} \cdot \underline{B} : \underline{F} \underline{F}) & \phi'' &= (\underline{e} \cdot \underline{P})^2 (\Delta \underline{\mu} \cdot \underline{F})^2
\end{aligned} \quad 1.49$$

Now relation (37) together with (46) and (47) enable us to calculate any such term as  $Q_k \equiv \langle \Phi_k \rangle$ . The problem of averaging has been reduced to that of finding average values in an isotropic system.

### 1.8 Average values in an isotropic system

Let us agree to choose in a molecule a cartesian coordinate system defined by three orthonormal vectors  $\{i\}$ . The components of a tensor  $T$  of rank  $n$  with respect to this basis are denoted by  $T_{ij\dots}$ .

We select a space-fixed coordinate system defined by the three orthonormal vectors  $\{\xi\}$ . The two coordinate systems are related to each other by the orthogonal transformation  $R$ :

$$\{\underline{\xi}\} = R \{\underline{i}\} \quad \text{or} \quad \underline{\xi} = \sum_i R_{\xi i} \underline{i} \quad \text{with} \quad R_{\xi i} = \underline{\xi} \cdot \underline{i} \quad 1.50$$

The components of the tensor  $T$  in the two coordinate systems are coupled by the following transformation:

$$\begin{aligned} T_{\xi\eta\dots} &= \sum_{ij\dots} R_{\xi i} R_{\eta j} \dots T_{ij\dots} \\ &= \sum_{ij\dots} (\underline{\xi} \cdot \underline{i}) (\underline{\eta} \cdot \underline{j}) \dots T_{ij\dots} \end{aligned} \quad 1.51$$

If the system  $\{i\}$  can take all possible orientations in space, the average value of the component  $\langle T_{\xi\eta\dots} \rangle$  is determined by the average values of quantities of the form  $\langle (\underline{\xi} \cdot \underline{i}) (\underline{\eta} \cdot \underline{j}) \dots \rangle$ . We shall refer to these as a  $n$ -factor product depending on the number  $n$  of scalar products involved. In our problem we shall not exceed  $n = 4$ . The average value of an  $n$  factor product is completely determined by the rotational invariants it contains. At the end of this chapter we shall present in an appendix a method to find these invariants. Here we give the rules which follow from the discussion in the appendix.

$$1. \langle \langle \underline{\xi} \cdot \underline{i} \rangle \rangle = 0 \quad 1.52$$

2. The contribution from a 2-factor product is given by

$$\langle \langle (\underline{\xi} \cdot \underline{i}) (\underline{\eta} \cdot \underline{j}) \rangle \rangle = \frac{1}{3} \delta_{\xi\eta} \delta_{ij} \quad 1.53$$

3. A 3-factor product averages to zero unless the vectors  $\xi, \eta, \zeta$  and  $i, j, k$  appear only once.

$$\langle \langle (\underline{\xi} \cdot \underline{i}) (\underline{\eta} \cdot \underline{j}) (\underline{\zeta} \cdot \underline{k}) \rangle \rangle = \frac{1}{6} \quad 1.54$$

4. A 4-factor product yields a non-vanishing contribution in two cases.

a. One of the vectors  $\xi$  appears in all the factors

$$\langle \langle (\underline{\xi} \cdot \underline{i}) (\underline{\xi} \cdot \underline{j}) (\underline{\xi} \cdot \underline{k}) (\underline{\xi} \cdot \underline{l}) \rangle \rangle = \frac{1}{15} \{ \delta_{ij} \delta_{kl} + \delta_{ik} \delta_{jl} + \delta_{il} \delta_{kj} \} \quad 1.55$$

b. The two vectors  $\xi$  and  $\eta$  each appear twice.

$$\langle \langle (\underline{\xi} \cdot \underline{i}) (\underline{\xi} \cdot \underline{j}) (\underline{\eta} \cdot \underline{k}) (\underline{\eta} \cdot \underline{l}) \rangle \rangle = \frac{2}{15} \delta_{ij} \delta_{kl} - \frac{1}{30} \delta_{ik} \delta_{jl} - \frac{1}{30} \delta_{il} \delta_{kj} \quad 1.56$$

A most convenient choice of the space-fixed coordinate system is to have  $\xi$  in the direction of the external field  $F$ .

The result of the averaging of the quantities listed in (49) will depend on the direction of  $e$  i.e. on the polarization of the lightwave. The job has to be done for two situations, namely  $e \parallel F$  i.e.  $e = \xi$  and  $e \perp F$ , say  $e = \eta$ . From these we shall synthesize the general result for an angle  $\chi$  between  $e$  and  $F$ . All quantities in (49) are quadratic in  $e$  and hence for any  $\Phi$  we have a relation:

$$\phi(\chi) = \phi(0^\circ) \cos^2 \chi + \phi(90^\circ) \sin^2 \chi \quad 1.57$$

For a particular  $\Phi$ , say  $\Phi''$ , we shall present the steps leading to  $\langle\langle \Phi(\chi) \rangle\rangle$  as an example. From (49) it follows:

$$\phi''(0^\circ) = P_\xi P_\xi \Delta\mu_\xi F_\xi \Delta\mu_\xi F_\xi \quad \phi(90^\circ) = P_\eta P_\eta \Delta\mu_\eta F_\eta \Delta\mu_\eta F_\eta \quad 1.58$$

$$\left( \frac{\partial \phi''(0^\circ)}{\partial F_\xi} \right)_{F=0} = 0 \quad \left( \frac{\partial \phi''(90^\circ)}{\partial F_\eta} \right)_{F=0} = 0 \quad 1.59$$

$$\left( \frac{\partial^2 \phi''(0^\circ)}{\partial F_\xi^2} \right)_{F=0} = 2 P_\xi P_\xi \Delta\mu_\xi \Delta\mu_\xi \quad \left( \frac{\partial^2 \phi''(90^\circ)}{\partial F_\eta^2} \right)_{F=0} = 2 P_\eta P_\eta \Delta\mu_\eta \Delta\mu_\eta \quad 1.60$$

$$\begin{aligned} \langle\langle \phi''(0^\circ) \rangle\rangle &= F_\xi^2 \langle\langle P_\xi P_\xi \Delta\mu_\xi \Delta\mu_\xi \rangle\rangle = F_\xi^2 \sum_{ijkl} \langle\langle (\xi \cdot i)(\xi \cdot j)(\xi \cdot k)(\xi \cdot l) P_i P_j \Delta\mu_k \Delta\mu_l \rangle\rangle \\ &= F_\xi^2 \left\{ \frac{1}{15} \sum_{ik} P_i P_i \Delta\mu_k \Delta\mu_k + \frac{1}{15} \sum_{ik} P_i P_k \Delta\mu_i \Delta\mu_k + \frac{1}{15} \sum_{ik} P_i P_k \Delta\mu_k \Delta\mu_i \right\} \end{aligned} \quad 1.61$$

$$\begin{aligned} \langle\langle \phi''(90^\circ) \rangle\rangle &= F_\eta^2 \langle\langle P_\eta P_\eta \Delta\mu_\eta \Delta\mu_\eta \rangle\rangle = F_\eta^2 \sum_{ijkl} \langle\langle (\eta \cdot i)(\eta \cdot j)(\eta \cdot k)(\eta \cdot l) P_i P_j \Delta\mu_k \Delta\mu_l \rangle\rangle \\ &= F_\eta^2 \left\{ \frac{2}{15} \sum_{ik} P_i P_i \Delta\mu_k \Delta\mu_k - \frac{1}{30} \sum_{ik} P_i P_k \Delta\mu_i \Delta\mu_k - \frac{1}{30} \sum_{ik} P_i P_k \Delta\mu_k \Delta\mu_i \right\} \end{aligned} \quad 1.62$$

$$\begin{aligned} \langle\langle \phi''(\chi) \rangle\rangle &= \langle\langle \phi''(0^\circ) \rangle\rangle \cos^2 \chi + \langle\langle \phi''(90^\circ) \rangle\rangle (1 - \cos^2 \chi) \\ &= F^2 \frac{2}{90} \left\{ 5 \text{H} + \text{II} (3 \cos^2 \chi - 1) \right\} \end{aligned} \quad 1.63$$

where

$$\text{H} = P^2 (\Delta\mu)^2 \quad 1.64$$

$$\text{II} = 3 (P \cdot \Delta\mu)^2 - P^2 (\Delta\mu)^2 \quad 1.65$$

Working along this line an expression is finally obtained for  $\epsilon_x(\nu, F)/\epsilon(\nu)$ .

$$\frac{\epsilon_x(\nu, F)}{\epsilon(\nu)} = 1 + F^2 \left\{ A_x + \frac{1}{15h} B_x \frac{d \ln \epsilon/\nu}{d\nu} + \frac{1}{30h^2} C_x \left[ \left( \frac{d \ln \epsilon/\nu}{d\nu} \right)^2 + \frac{d^2 \ln \epsilon/\nu}{d\nu^2} \right] \right\} \quad 1.66$$

The quantities  $A_x$ ,  $B_x$  and  $C_x$  all depend linearly on  $\cos^2 \chi$ . These linear relations are written in the form:

$$A_x = \frac{1}{3} D + \frac{1}{30} E (3 \cos^2 \chi - 1) \quad 1.67$$

$$B_x = 5 F + G (3 \cos^2 \chi - 1) \quad 1.68$$



$$C_{\chi} = 5H + I(3\cos^2\chi - 1) \quad 1.69$$

The coefficients  $D$ ,  $E$ ,  $F$ ,  $G$ ,  $H$  and  $I$  are given in terms of molecular quantities by the following relations:

$$D = 2\beta \frac{P \cdot A \cdot \mu}{P^2} + \frac{1}{P^2} \sum_{ij} A_{ij}^2 + \frac{2}{P^2} \sum_{ij} P_i B_{ijj} \quad 1.70$$

$$E = \beta^2 [3(\underline{\mu} \cdot \underline{p})^2 - \mu^2] + \frac{3}{2} \beta \underline{p} \cdot \underline{\alpha} \cdot \underline{p} - \frac{1}{2} \beta \text{Tr} \underline{\alpha} \quad 1.71$$

$$+ 6\beta \frac{(\underline{\mu} \cdot \underline{P}) \text{Tr} \underline{A}}{P^2} + 6\beta \frac{\underline{\mu} \cdot \underline{A} \cdot \underline{P}}{P^2} - 4\beta \frac{P \cdot A \cdot \mu}{P^2}$$

$$+ \frac{3}{P^2} (\text{Tr} \underline{A})^2 + \frac{3}{P^2} \sum_{ij} A_{ij} A_{ji} - \frac{2}{P^2} \sum_{ij} A_{ij}^2$$

$$+ \frac{6}{P^2} \sum_{ij} P_i B_{jij} + \frac{6}{P^2} \sum_{ij} P_i B_{jji} - \frac{4}{P^2} \sum_{ij} P_i B_{ijj}$$

$$F = \beta \underline{\mu} \cdot \underline{\Delta\mu} + 2 \frac{P \cdot A \cdot \Delta\mu}{P^2} + \frac{1}{2} \text{Tr} \underline{\Delta\alpha} \quad 1.72$$

$$G = \beta [3(\underline{\mu} \cdot \underline{p})(\underline{\Delta\mu} \cdot \underline{p}) - \underline{\mu} \cdot \underline{\Delta\mu}] \quad 1.73$$

$$+ \frac{3}{2} \underline{p} \cdot \underline{\Delta\alpha} \cdot \underline{p} - \frac{1}{2} \text{Tr} \underline{\Delta\alpha}$$

$$+ 3 \frac{(\underline{\Delta\mu} \cdot \underline{P}) \text{Tr} \underline{A}}{P^2} + 3 \frac{\underline{\Delta\mu} \cdot \underline{A} \cdot \underline{P}}{P^2} - 2 \frac{P \cdot A \cdot \Delta\mu}{P^2}$$

$$H = (\Delta\mu)^2 \quad 1.74$$

$$I = 3(\underline{\Delta\mu} \cdot \underline{p})^2 - (\Delta\mu)^2 \quad 1.75$$

Equations (66) to (75) constitute the basis to disentangle the experimental observations we are going to discuss in the following chapters.

To bring this section to an end, we remark that deleting all terms in  $\beta$  in eqs (66) to (75) yields the theory for a system which remains isotropic in the presence of the field  $F$ . Such a situation will occur for instance if the molecules are embodied in an isotropic rigid glass. Note that an isotropic polarizability does not contribute to  $E$  as we expect from the fact that the corresponding terms depend on  $\beta$  and therefore originate from the contribution of  $\alpha$  to the induced anisotropy.

## Appendix

By an  $n$ -factor product we mean a product of  $n$  factors, each of which is a scalar product of two vectors.

We shall derive for an  $n$ -factor product its average value over an isotropic distribution of orientations.

Consider a space-fixed righthanded coordinate system defined by the orthonormal vectors  $\xi, \eta, \zeta$ . We have another rigid system of independent vectors  $\underline{u}, \underline{v}, \underline{w}$ . The two systems have a common origin and the tripod  $\underline{u}, \underline{v}, \underline{w}$  can take all possible orientations with respect to the space-fixed one. Only rotational invariants which are independent of the mutual orientation of the two systems will survive the averaging.

$$1. \langle\langle (\underline{\xi} \cdot \underline{u}) \rangle\rangle = 0 \quad \text{since there is no invariant linear in } \xi \text{ and } \underline{u} \text{ and independent of their mutual orientation.}$$

$$2a. \langle\langle (\underline{\xi} \cdot \underline{u})^2 \rangle\rangle = \lambda (\underline{\xi} \cdot \underline{\xi})(\underline{u} \cdot \underline{u}) \quad \text{i.e. proportional to an invariant which does not depend on the mutual orientation of } \xi \text{ and } \underline{u} \text{ and which is quadratic in both } \xi \text{ and } \underline{u}. \quad 1.76$$

$$\text{We also have } \langle\langle (\underline{\xi} \cdot \underline{u})^2 \rangle\rangle = \langle\langle (\underline{\eta} \cdot \underline{u})^2 \rangle\rangle = \langle\langle (\underline{\zeta} \cdot \underline{u})^2 \rangle\rangle = \lambda (\underline{u} \cdot \underline{u})$$

$$(\underline{u} \cdot \underline{u}) = (\underline{\xi} \cdot \underline{u})^2 + (\underline{\eta} \cdot \underline{u})^2 + (\underline{\zeta} \cdot \underline{u})^2 = 3 \langle\langle (\underline{\xi} \cdot \underline{u})^2 \rangle\rangle$$

thus  $\lambda = \frac{1}{3}$ .

$$b. \langle\langle (\underline{\xi} \cdot \underline{u})(\underline{\xi} \cdot \underline{v}) \rangle\rangle = \lambda' (\underline{\xi} \cdot \underline{\xi})(\underline{u} \cdot \underline{v}) \quad \text{since this should also hold for } \underline{u} = \underline{v} \quad 1.77$$

$$\lambda = \lambda' = \frac{1}{3}.$$

$$c. \langle\langle (\underline{\xi} \cdot \underline{u})(\underline{\eta} \cdot \underline{v}) \rangle\rangle = \lambda'' (\underline{\xi} \cdot \underline{\eta})(\underline{u} \cdot \underline{v}) = 0 \quad \text{since } \xi \cdot \eta = 0 \quad 1.78$$

3. The invariant associated with three vectors  $\xi, \eta, \zeta$  is the volume of the parallelepiped which they span. If in a 3-factor product one of the vectors occurs twice or more the average value will be zero.

$$\langle\langle (\underline{\xi} \cdot \underline{u})(\underline{\eta} \cdot \underline{v})(\underline{\zeta} \cdot \underline{w}) \rangle\rangle = \lambda [(\underline{\xi} \times \underline{\eta}) \cdot \underline{\zeta}][(\underline{u} \times \underline{v}) \cdot \underline{w}] = \lambda (\underline{u} \times \underline{v}) \cdot \underline{w} \quad 1.79$$

The value of  $\lambda$  is determined by the reasoning which follows. An interchange of  $\underline{v}$  and  $\underline{w}$  will introduce a change of sign on the R.H.S. of (79). Hence

$$\begin{aligned} \langle\langle (\underline{\xi} \cdot \underline{u})(\underline{\eta} \cdot \underline{v})(\underline{\zeta} \cdot \underline{w}) \rangle\rangle &= \frac{1}{2} \left\{ \langle\langle (\underline{\xi} \cdot \underline{u})(\underline{\eta} \cdot \underline{v})(\underline{\zeta} \cdot \underline{w}) \rangle\rangle - \langle\langle (\underline{\xi} \cdot \underline{u})(\underline{\eta} \cdot \underline{w})(\underline{\zeta} \cdot \underline{v}) \rangle\rangle \right\} \\ &= \frac{1}{2} \langle\langle (\underline{\xi} \cdot \underline{u}) \left\{ (\underline{\eta} \cdot \underline{v})(\underline{\zeta} \cdot \underline{w}) - (\underline{\eta} \cdot \underline{w})(\underline{\zeta} \cdot \underline{v}) \right\} \rangle\rangle \\ &= \frac{1}{2} \langle\langle (\underline{\xi} \cdot \underline{u}) \left\{ (\underline{\eta} \times \underline{\zeta}) \cdot (\underline{v} \times \underline{w}) \right\} \rangle\rangle \\ &= \frac{1}{2} \langle\langle (\underline{\xi} \cdot \underline{u}) \left\{ \underline{\xi} \cdot (\underline{v} \times \underline{w}) \right\} \rangle\rangle \\ &= \frac{1}{6} \underline{u} \cdot (\underline{v} \times \underline{w}) \end{aligned}$$

In the last step the result (77) has been applied and the conclusion is  $\lambda = \frac{1}{6}$ .

4. A 4-factor product of the type  $\langle\langle (\underline{\xi} \cdot \underline{u})(\underline{\xi} \cdot \underline{z})(\underline{\eta} \cdot \underline{v})(\underline{\zeta} \cdot \underline{w}) \rangle\rangle$  has an average value zero, because non-vanishing would require an invariant linear in  $\eta$  and independent of its orientation with respect to the  $u, v, w$  system, which obviously does not exist. There are two cases delivering a non-vanishing average.

a. Only one of the vectors  $\xi, \eta$  or  $\zeta$  occurs in the product.

$$\langle\langle (\underline{\xi} \cdot \underline{u})(\underline{\xi} \cdot \underline{v})(\underline{\xi} \cdot \underline{w})(\underline{\xi} \cdot \underline{z}) \rangle\rangle = \lambda \{ (\underline{u} \cdot \underline{v})(\underline{w} \cdot \underline{z}) + (\underline{u} \cdot \underline{w})(\underline{v} \cdot \underline{z}) + (\underline{u} \cdot \underline{z})(\underline{v} \cdot \underline{w}) \} \quad 1.80$$

from  $\underline{u} = \underline{v} = \underline{w} = \underline{z}$  it follows:

$$\langle\langle (\underline{\xi} \cdot \underline{u})^4 \rangle\rangle = 3 \lambda (\underline{u} \cdot \underline{u})^2 \quad 1.81$$

On the other hand we have:

$$(\underline{u} \cdot \underline{u})^2 = \{ (\underline{\xi} \cdot \underline{u})^2 + (\underline{\eta} \cdot \underline{u})^2 + (\underline{\zeta} \cdot \underline{u})^2 \}^2 = 3 \langle\langle (\underline{\xi} \cdot \underline{u})^4 \rangle\rangle + 6 \lambda (\underline{u} \cdot \underline{u})^2 \quad 1.82$$

where the last step arises from the application of (80) to  $\langle\langle (\underline{\xi} \cdot \underline{u})^2 (\underline{\eta} \cdot \underline{u})^2 \rangle\rangle$ .  
Substitution of (81) into (82) yields  $\lambda = \frac{1}{15}$ .

b. Two vectors from the set  $\xi, \eta, \zeta$  appear in the product.

$$\langle\langle (\underline{\xi} \cdot \underline{u})(\underline{\xi} \cdot \underline{v})(\underline{\eta} \cdot \underline{w})(\underline{\eta} \cdot \underline{z}) \rangle\rangle = \lambda (\underline{u} \cdot \underline{v})(\underline{w} \cdot \underline{z}) + \rho \{ (\underline{u} \cdot \underline{w})(\underline{v} \cdot \underline{z}) + (\underline{u} \cdot \underline{z})(\underline{v} \cdot \underline{w}) \} \quad 1.83$$

Consider  $u = v$  and  $w = z$ .

$$\langle\langle (\underline{\xi} \cdot \underline{u})^2 (\underline{\eta} \cdot \underline{w})^2 \rangle\rangle = \lambda (\underline{u} \cdot \underline{u})(\underline{w} \cdot \underline{w}) + 2 \rho (\underline{u} \cdot \underline{w})^2 \quad 1.84$$

On the other hand we have

$$\begin{aligned} (\underline{u} \cdot \underline{u})(\underline{w} \cdot \underline{w}) &= \{ (\underline{\xi} \cdot \underline{u})^2 + (\underline{\eta} \cdot \underline{u})^2 + (\underline{\zeta} \cdot \underline{u})^2 \} \{ (\underline{\xi} \cdot \underline{w})^2 + (\underline{\eta} \cdot \underline{w})^2 + (\underline{\zeta} \cdot \underline{w})^2 \} \\ &= 3 \langle\langle (\underline{\xi} \cdot \underline{u})^2 (\underline{\xi} \cdot \underline{w})^2 \rangle\rangle + 6 \langle\langle (\underline{\xi} \cdot \underline{u})^2 (\underline{\eta} \cdot \underline{w})^2 \rangle\rangle \end{aligned} \quad 1.85$$

Application of the previous result (80) to the first term on the R.H.S. of (85) yields

$$6 \langle\langle (\underline{\xi} \cdot \underline{u})^2 (\underline{\eta} \cdot \underline{w})^2 \rangle\rangle = \frac{12}{15} (\underline{u} \cdot \underline{u})(\underline{w} \cdot \underline{w}) - \frac{6}{15} (\underline{u} \cdot \underline{w})^2 \quad 1.86$$

Comparing (86) with (84) we see that  $\lambda = \frac{2}{15}$  and  $\rho = -\frac{1}{30}$ .

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## EXPERIMENTAL TECHNIQUE AND DATA PROCESSING

## 2.1 General considerations

Let us estimate the relative change in intensity  $I_\chi$  of a light beam leaving the sample when there is a field  $F$  present. From eq (1.66) we obtain

$$I_{\chi,F} = I_\chi^0 \exp(-\epsilon C l) \exp(-\epsilon F^2 \zeta_\chi C l) \quad 2.1$$

where  $I_\chi^0$  is the intensity of the linearly polarized light entering the sample in a direction perpendicular to  $F$ .

$$\zeta_\chi \equiv A_\chi + \frac{1}{15h} B_\chi \frac{d \ln \epsilon / \nu}{d\nu} + \frac{1}{30h^2} C_\chi \left\{ \left( \frac{d \ln \epsilon / \nu}{d\nu} \right)^2 + \frac{d^2 \ln \epsilon / \nu}{d\nu^2} \right\} \quad 2.2$$

Expanding the second exponential in eq (2.1) into a Taylor series, retaining the first two terms, we get:

$$I_{\chi,F} = I_{\chi,F=0} \left\{ 1 - \epsilon F^2 \zeta_\chi C l \right\} \quad 2.3$$

In order to eliminate the concentration we introduce the optical density  $D$  of the sample.

$$D \equiv {}^{10} \log \frac{I_\chi^0}{I_{\chi,F=0}} = \epsilon C l / 2.303 \quad 2.4$$

Combining (2.3) and (2.4) we find for the relative intensity change:

$$\left( \frac{\Delta I}{I} \right)_\chi \equiv \frac{I_{\chi,F=0} - I_\chi}{I_{\chi,F=0}} = 2.303 D F^2 \zeta_\chi \quad 2.5$$

We consider an absorption band, whose shape is described by a gaussian function centered at  $\sigma_m$ , having a maximum  $\epsilon_m$  and a width  $2w$ .

$$\epsilon(\sigma) = \epsilon_m \exp - \frac{(\sigma - \sigma_m)^2}{w^2} \quad 2.6$$

A reasonable choice for an electronic absorption band without vibrational structure is  $\sigma_m \approx 2.10^4 \text{ cm}^{-1}$  and  $w = 10^3 \text{ cm}^{-1}$

$$\frac{d \ln \epsilon / \nu}{d\nu} \sim \frac{1}{c} \left( \frac{d \ln \epsilon / \sigma}{d\sigma} \right)_{\sigma_m - w} \sim \frac{1}{c} \left\{ \frac{2}{w} - \frac{1}{\sigma_m - w} \right\} \sim \frac{2 * 10^{-3}}{c} \text{ cm} \quad 2.7$$

Now we shall perform our measurements at  $300^\circ \text{ K}$  with  $F = 120 \text{ KV/cm}$ . Suppose we selected a sample of optical density  $D = 1$ , consisting of absorbing molecules having  $p, \mu$  and  $\Delta\mu$  parallel with  $\mu = \Delta\mu = 1.D$ . Neglecting all polarizability effects, using (1.67) to (1.73) we estimate that the relative intensity change will have a magnitude of the order  $7 \times 10^{-5}$ . If the absorbing molecules in the sample were nonpolar with an isotropic polarizability and  $\frac{1}{3} \text{Tr } \Delta\alpha = 50 \text{ \AA}^3$  the relative intensity change would have been of the order  $9 \times 10^{-5}$ .

What we learn from these estimates is that the relative intensity change is so small that we must efficiently conquer all sources of fluctuations in detector output. The influence of shot noise in the incident radiation must be kept to a minimum. We therefore select a combination of a high intensity light source (high pressure Xenon, XBO 900) and a monochromator with high transmittance (Bausch and Lomb 500 mm, grating 1200 lines/m.m). The optical density of the sample should be between 0.5 and 2, considering that  $\Delta I/I$  is proportional to  $D$  and that  $I$  is already reduced to 1% of the original intensity at  $D = 2$ . The instability in arc position, well known for large Xenon lamps, may introduce strong fluctuations in the output of the monochromator. We cope with these by applying a technique to record directly the ratio  $\Delta I/I$ , which does not depend on intensity. At the same time the recorded signal does not depend on the supply voltage of the photomultiplier. Another advantage is that one can work at maximum attainable intensity, in contrast to

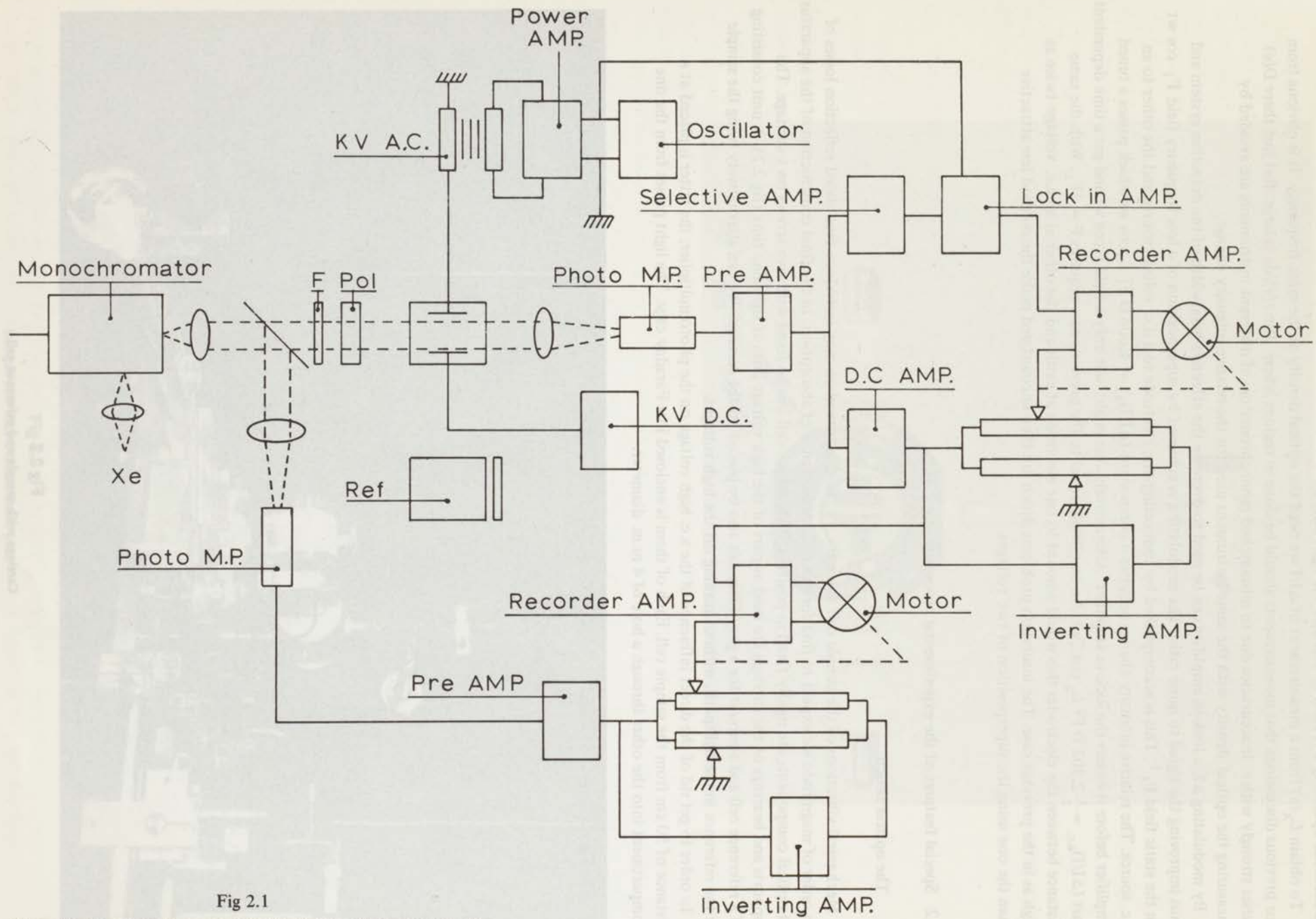


Fig 2.1

Schematic diagram of the spectrometer for electro-optical measurements

all methods operating a system to stabilize the light output.

To obtain  $L_{\chi}(v)$  from a measurement of  $\Delta I/I$  we need the optical density at the same frequency. It is obvious from our previous discussions that measurements should be done in regions where  $d(\ln \epsilon/v)/dv$  is large. But just there  $D(v)$  varies strongly with  $v$ . Inaccuracies due to mismatched monochromators of different instruments are avoided by measuring the optical density with the same instrument used for the relative intensity change.

By modulating  $\Delta I$ , a lock-in amplifier can be used to decrease the effective bandwidth of the detection system and thus improving the signal to noise ratio. The modulation is achieved by superposition of a low frequency field  $F_1 \cos \omega t$  on the static field  $F_1^1$ . This is accomplished by connecting one electrode to a d.c. voltage source and the other to an a.c. source. The relative intensity change acquires a component  $(\Delta I/I)_{a.c.} = 4.606 D F_1^2 L_{\chi} \cos \omega t$  which passes a tuned amplifier before it enters the lock-in amplifier. Alternatively one might use only a field  $F \cos \omega t$  and get a time dependent part  $(\Delta I/I)_{a.c.} = \frac{1}{2} 2.303 D F^2 L_{\chi} \cos 2\omega t$ . An amplitude equal to the previous case requires  $F = 2F_1$ . With the same distance between the electrodes this would amount to one electrode at earth and the other at an a.c. voltage twice as high as in the previous case. The insulation problems which are then encountered make the method less attractive than the one using the superposition of two voltages.

## 2.2 Special features of the experimental procedure (fig 2.1)

### a. The optical bench

Mechanical vibrations of the sample cell when the a.c. field is turned on may introduce modulated reflection losses of an order of magnitude we expect to find for the field dependence of absorption. In the final construction of the apparatus all optical components are rigidly fixed in position. The sample cell can be fixed with two screws on a carriage. The supports and bearings of the carriage are used as part of the high voltage lines at the same time (fig 2.2). A unit consisting of a reference cell and a mount for a gray filter can also be placed on the carriage. We can alternatively bring the sample or the reference in the lightpath, without turning off the high voltages.

In order to get rid of the direct influence of the a.c. high voltage on the photomultiplier, the latter is placed at a distance of 50 cm from the sample cell. Each of them is enclosed in a Faraday cage. The light passes from the one compartment into the other through a hole of 4 m.m. diameter.

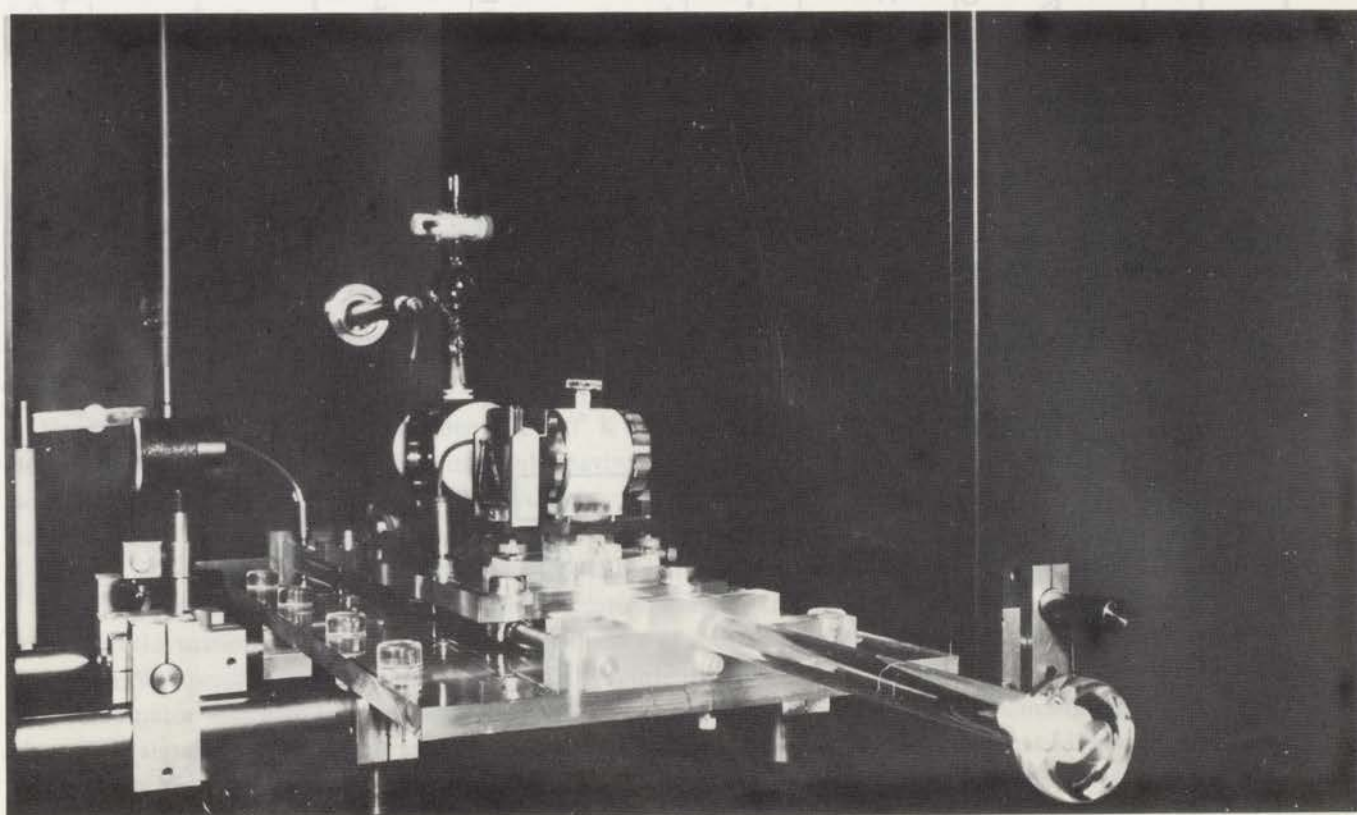


Fig 2.2

Carriage with sample and reference cell

b. The sample cell (from 2.3 and 2.4)

The two electrodes are cylindrical rods of diameter 0.5 mm. Both electrodes are 20 mm long. A constant current source (Fig 2.4) the sample cell. Electrodes are fixed in the cell. The size of the cell is 20 mm diameter and 20 mm high. The cell is made of stainless steel. The cell is driven by a pressure driven liquid nitrogen filled cell. The cell is filled with liquid nitrogen.

c. The high voltage

For the stable operation of the detector, the high voltage must be stable. The a.c. high voltage input to the amplifier is required because the frequency and amplitude of the high voltage between electrodes. A high voltage transformer is used. Shunting the primary section with an inductor's component, the phase shift at a certain frequency while resonance is obtained. By trial and error we managed to obtain a stable system of 125 v/a. We measure the high voltage with an electrostatic voltmeter (Trib T4001, Zephrus) having an accuracy of 0.5%. Using a completely shielded voltage divider we monitor the a.c. high voltage on an oscilloscope. By shunting the lower end of the divider with a suitable capacitor we have compensated the phase shift between its input and output signals. The output which has the same phase as the modulated signal serves to calibrate the gain of the detector system. The voltage divider has been made according to our specifications by Sams, Grenobles, France.

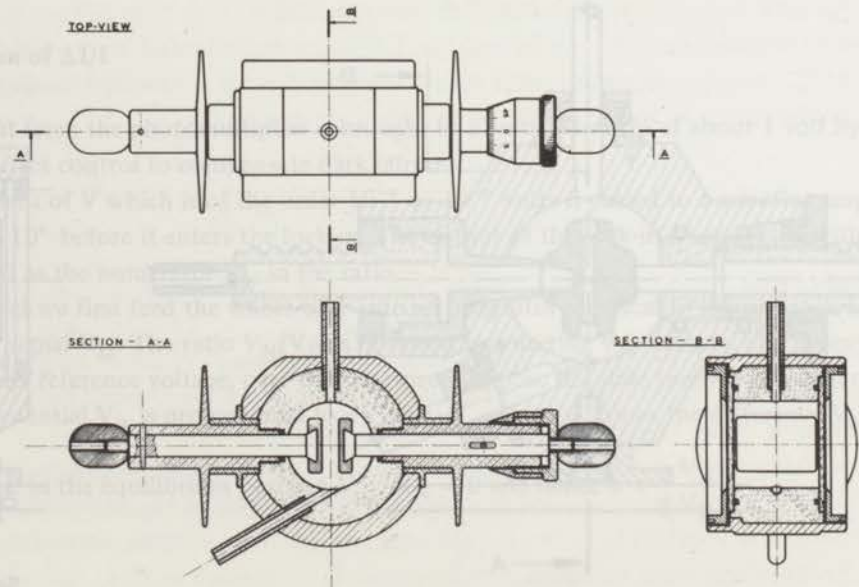
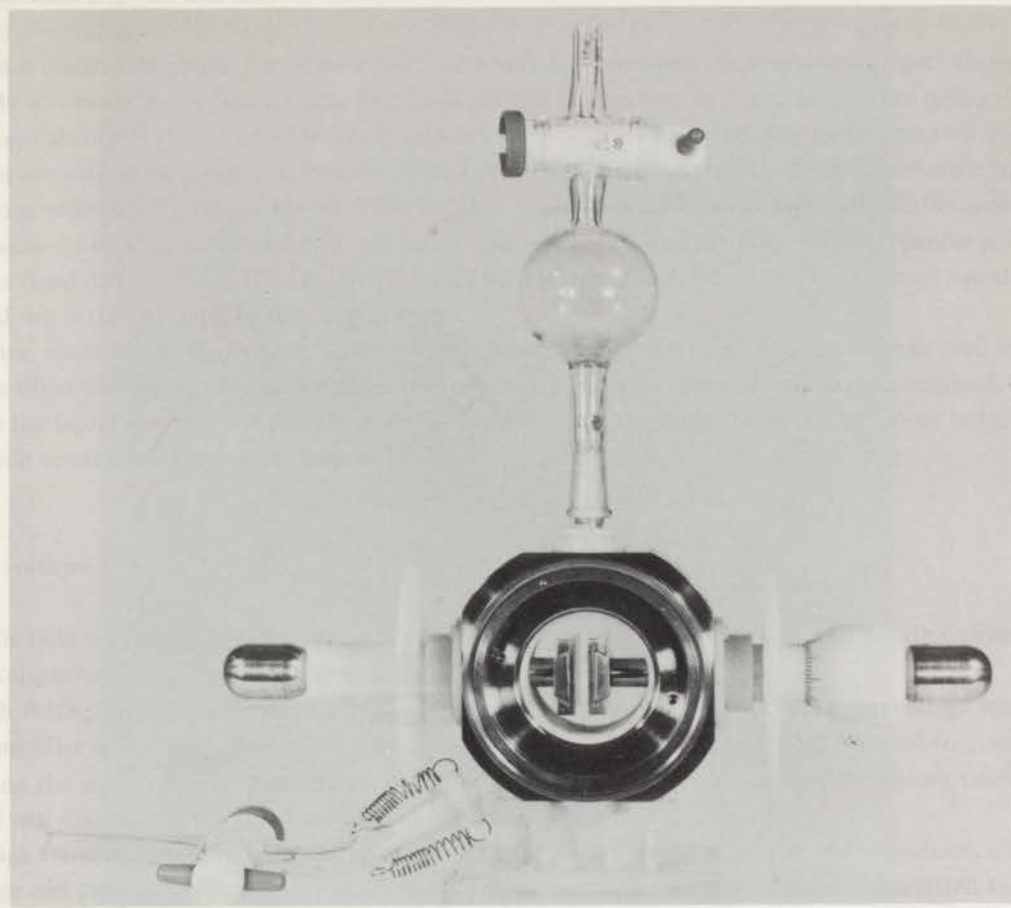


Fig 2.3

Sample cell with a teflon inner part

all methods operating a system for stabilizing the light source.

To obtain  $L_{\text{eff}}$  (to be used in our previous discussion) we will refer strongly with the beam measuring the optical flow.

By modulating  $\Delta I_{\text{eff}}$  thus improving the signal on the static field  $\Delta I_{\text{eff}}$ . The a.c. source. The reference amplifier before  $\Delta I_{\text{eff}}$  part  $(\Delta I)_{\text{eff}} = \Delta I_{\text{eff}}$  distance between the two high as in the present case than the one using the high

2.2 Special features of the

a. The optical system

Maximum resolution is an order of magnitude. All optical components are supports and bearings of a reference cell and a cell of the reference is the

In order to avoid the direct influence of the a.c. high voltage on the photomultiplier, the latter is placed at a distance of 30 cm from the sample cell. Each of them is enclosed in a Faraday cage. The light passes from the one compartment into the other through a hole of 4 mm diameter.

is a 20 cm from the sample cell. The light is collected by

photo systems and is measured by a photomultiplier. The latter is an order of magnitude more sensitive than the one used in the present case. The signal is then amplified by a low-noise amplifier.

The collection losses of the light of the apparatus are negligible. The light path consists only of the sample

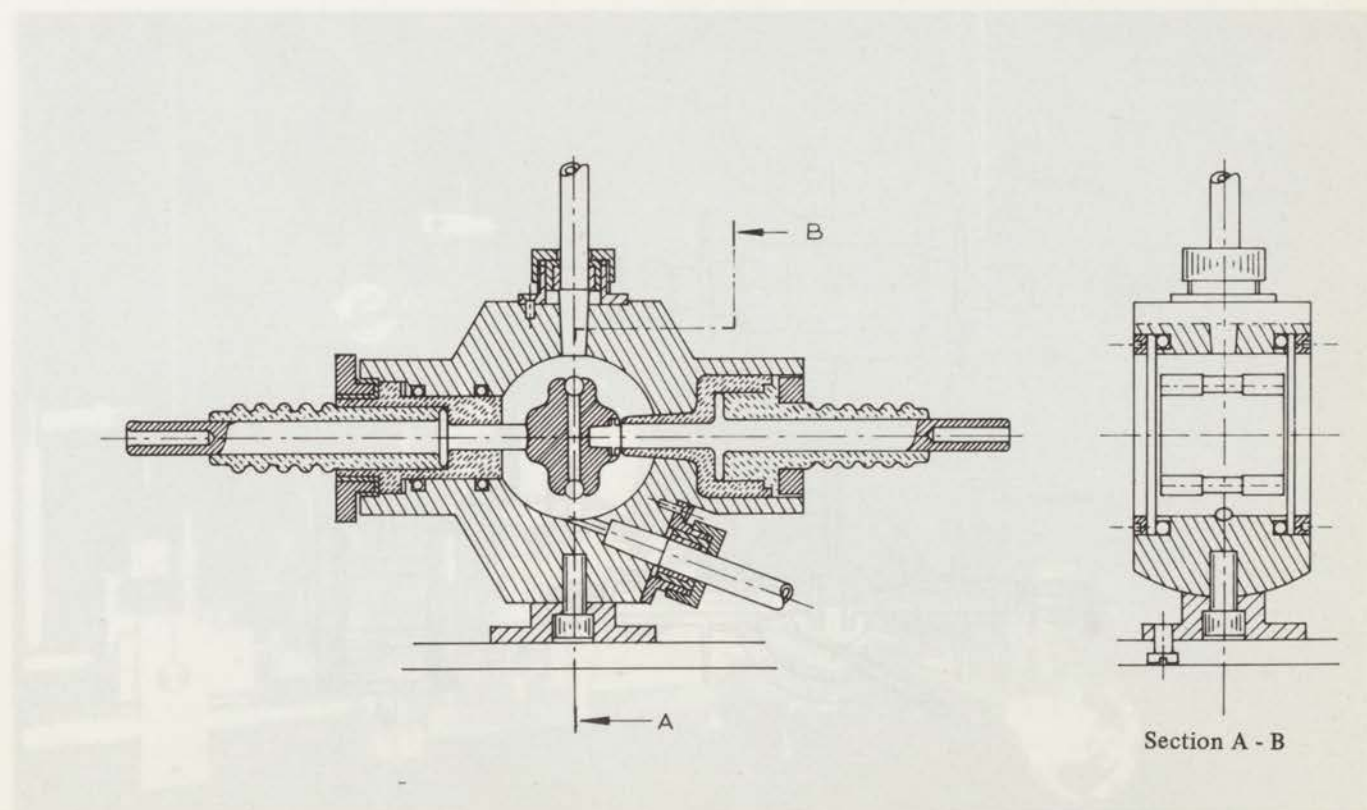
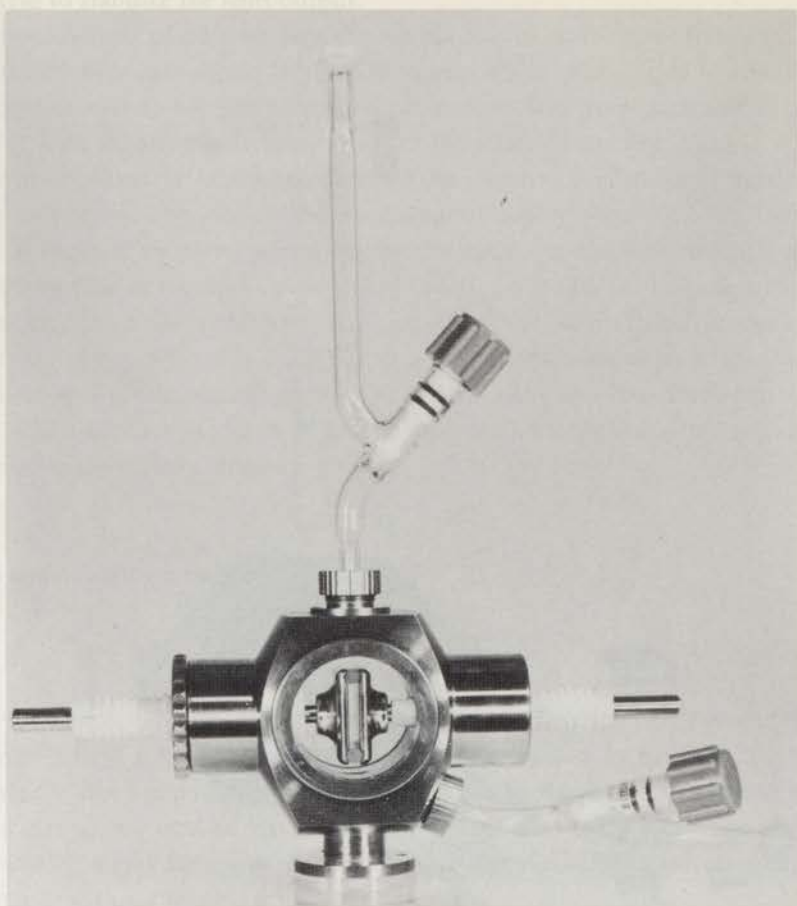


Fig 2.4  
Sample cell with a stainless steel body



## b The sample cells (figs 2.3 and 2.4)

The first cell is constructed from a massive teflon rod which had been pressed into a brass pipe. Afterwards a cylindrical hole was made in the teflon (fig 2.3). The brass mantle prevents deformations of the teflon. One of the electrodes is fixed and the other adjustable; the displacement from the fixed electrode can be read on a micrometer. Both electrodes are carried on sledges so that they can be removed easily and repaired after an electric breakdown.

A disadvantage of teflon is that it gives off fluff, which may move around in the lightpath. In the second sample cell (fig 2.4) the amount of teflon is reduced to a minimum. The whole cell body is made out of stainless steel and the electrodes are a fixed distance of 3.33 m.m. apart. Again the electrodes can be replaced with ease. Another advantage of the all metal cell is that overall stability is guaranteed.

The size of the electrodes is the same in both cells, the length being 30.0 m.m. and the height 20.0 m.m.

The cells are filled through the lower opening by connecting them to a vertically mounted container. The hydrostatic pressure drives the liquid into the cell and all air drifts away through the upper hole, so that no air bubbles are left in the filled cell. Teflon cocks are used to close the cell.

## c The high voltages

For the static field we use a d.c. high voltage supply manufactured by Brandenburg Ltd, South Croydon, Surrey, England. The output voltage is continuously adjustable between 0 and 50 KV.

The a.c. high voltage we obtain by using a 100 watt power amplifier to drive a 25 KV high voltage transformer. The input to the amplifier is obtained from an oscillator with a frequency stability of 0.05%. A good frequency stability is required because the signal passes a selective preamplifier. Large phase shifts accompany deviations from the central frequency and will destroy the phase relation in the lock-in system.

A high voltage transformer represents a large capacitive load to the power amplifier and introduces a large phase shift between voltage and current in the primary section. As a consequence nearly no power is transmitted to the transformer. Shunting the primary section with an inductance compensates the phase shift at a certain frequency where resonance is established. By trial and error we managed to obtain a stable system at 135 c/s.

We measure the high voltages with an electrostatic voltmeter (Trüb Täuber, Zurich), having an accuracy of 0.5%. Using a completely shielded voltage divider we monitor the a.c. high voltage on an oscilloscope. By shunting the lower end of the divider with a suitable capacitor we have compensated the phase shift between its input and output signals. The output which has the same phase as the modulated signal serves to calibrate the gain of the detection system. The voltage divider has been made according to our specifications by Sames, Grenoble, France.

## d Ratio detection of $\Delta I/I$

The photocurrent from the photomultiplier is brought to a voltage level  $V$  of about 1 volt by a low drift d.c. amplifier provided with an offset control to compensate dark current.

The a.c. component of  $V$  which is of the order  $10^{-4}$  to  $10^{-6}$  volts is passed to a selective amplifier with a variable gain in the range  $10^4$  to  $10^6$  before it enters the lock-in. The output of the lock-in is integrated with a time constant of 10 seconds and used as the numerator  $V_N$  in the ratio.

In another channel we first feed the whole of  $V$  into an integrator identical to the previous one and then we convert it to a symmetrical signal  $V_D$ . The ratio  $V_N/V_D$  is obtained by entering  $V_N$  as signal in a potentiometer recorder which has  $V_D$ , instead of its reference voltage, over the slidewire. Suppose the slide (pen) is at a distance  $\alpha$  from the zero position, then its potential  $V_\alpha$  is proportional to  $\alpha V_D$  i.e.  $V_\alpha = g\alpha V_D$ . Since the difference  $V_\alpha - V_N$  drives the servo-

system we shall have in the equilibrium position  $V_\alpha - V_N = 0$  and hence  $\alpha = \frac{1}{g} \frac{V_N}{V_D}$ .

## e Calibration of the angle $\chi$

The parallel light beam from the monochromator is polarized by a 20 x 20 m.m. Glan prism P before it enters the sample cell. P is mounted in the centre of a rotatable disc, provided with a scale indicating the angle of rotation.

In order to calibrate the angle  $\chi$  between the electric vector of the light and the field  $F$  we take advantage of the Kerr effect. We introduce an auxiliary Glan prism  $A$  as an analyser behind the sample and cross it with respect to  $P$ . A concentrated solution of nitrobenzene in benzene, as the sample, becomes birefringent upon application of a static field. As a consequence the analyser will transmit some light. A minimum in transmitted intensity will occur when  $P$  is either parallel or perpendicular to  $F$ , while  $A$  is still crossed with respect to  $P$  (fig 2.5). The discrimination between  $\chi = 0^\circ$  or  $90^\circ$  is a rather trivial matter. The minimum transmittance can be determined nicely if the incident radiation passes an auxiliary chopper. The transmitted intensity can then be measured with the aid of the lock-in amplifier.

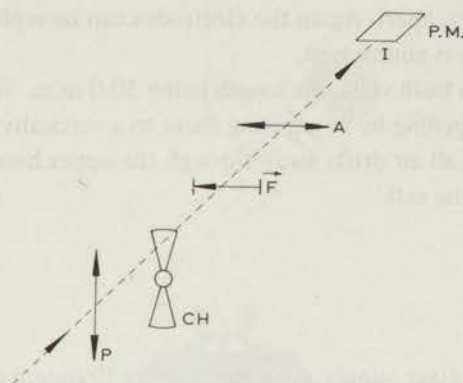


Fig 2.5  
Calibration of the angle of polarization

#### f Determination of the optical density

We use a ratio recording system similar to the one described above to get rid of intensity fluctuations in the light source.

The light emerging from the monochromator first passes a filter, removing second and higher order frequencies, and is then divided by a beamsplitter into two mutual perpendicular beams. If the intensity before the splitting is  $I^\circ$ , the intensities of the main beam  $I_m^\circ$  and of the side beam  $I_s$  are proportional to  $I^\circ$  i.e.  $I_m^\circ = mI^\circ$  and  $I_s = sI^\circ$ . The intensity of the side beam is converted to a voltage  $V_s = sg_s I^\circ$ . The intensity  $I_m^\circ$  is attenuated by the optical density  $D$  of the sample and yields a voltage  $V_m = mg_m I^\circ 10^{-D}$ . The ratio  $R \equiv V_m/V_s$  does not depend on light intensity:

$R = 10^{-D} mg_m / sg_s$ . Keeping  $mg_m / sg_s$  constant the sample can be replaced by a reference with optical density  $D_r$  which then gives the ratio  $R_r$ . If  $D_r$  is known we obtain  $D$  from the relation  $D = D_r - {}^{10} \log R/R_r$ .

The calibration of  $D_r$  can be accomplished in a similar manner. The factor  $m$  is reduced by the addition of a suitable gray filter in such a way that  $I_m^\circ$  can be measured directly, without causing damage to the photomultiplier. When no absorption is compared with absorption by the reference we are able to determine  $D_r$ .

### 2.3 Collecting and handling of data

Throughout this work we investigate the behaviour of electronic absorption bands of solute molecules in transparent nonpolar liquids. The local field acting on the solute molecules is approximated by the Lorentz field  $F = F_e(\epsilon_D + 2)/3$ , where  $\epsilon_D$  is the dielectric constant of the solvent and  $F_e$  the externally applied field.

Since the monochromator has a scale linear in wavelength  $\lambda$ , we obtain all measurements directly as a function of  $\lambda$ . However, in view of eq (1.66) it is more appropriate to collect the data as functions of the wavenumber  $\sigma$ .

At a fixed angle  $\chi$  we determine at a certain  $\lambda_i$  within the absorption band of interest the relative change in intensity  $(\Delta I/I)_i$  and the optical density  $D_i$ . From these two quantities we obtain  $L_\chi(i)$  through eq (2.5). Scanning  $\lambda_i$  from point to point through the band we generate an array of numbers  $L_\chi(i)$ . We use a bandwidth of  $1 \text{ m}\mu$  and select a number of points, usually more than 15, over a region where there is a sufficient variation of  $d(\ln \epsilon/\sigma)/d\sigma$ . To give the reader an impression of the signal to noise ratio encountered in the measurement of  $\Delta I/I$  we present in fig 2.6 the result obtained, by continuously scanning  $\lambda$ , for the first band of  $pp'$  nitroaminobiphenyl.

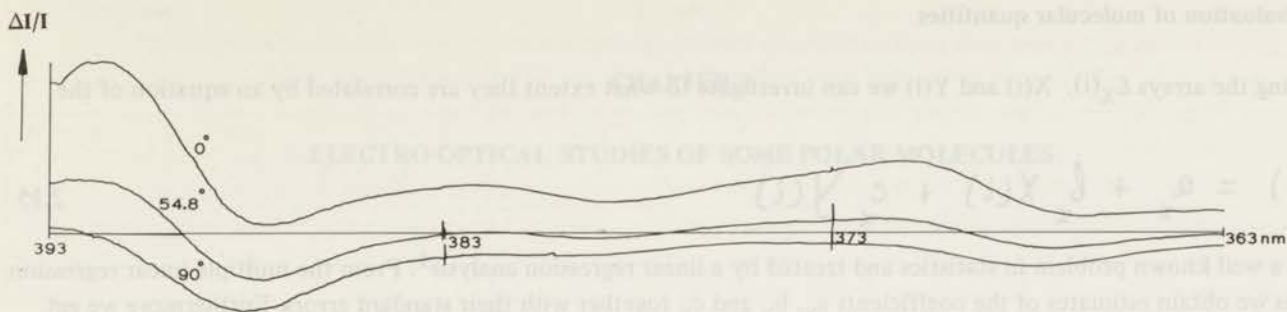


Fig 2.6

Continuously scanned spectra  $\Delta I/I$  of the first absorption band of pp' nitroaminobiphenyl

Subsequently we create two other arrays X(i) and Y(i)

$$X(i) \equiv \left( \frac{d \ln \epsilon / \sigma}{d \sigma} \right)_{\sigma_i} \quad 2.8$$

$$Y(i) \equiv \left( \frac{d \ln \epsilon / \sigma}{d \sigma} \right)_{\sigma_i}^2 + \left( \frac{d^2 \ln \epsilon / \sigma}{d \sigma^2} \right)_{\sigma_i} \quad 2.9$$

The quantities on the R.H.S. of eqs (2.8) and (2.9) are determined numerically from a table of optical densities D tabulated as a function of  $\lambda$ . Let us pursue this point somewhat. The derivatives of  $\ln \epsilon / \sigma$  are related to  $dD/d\lambda$  and  $d^2D/d\lambda^2$ .

$$\left( \frac{d \ln \epsilon / \sigma}{d \sigma} \right)_{\sigma_i} = -\lambda_i - \frac{\lambda_i^2}{D_i} \left( \frac{dD}{d\lambda} \right)_{\lambda_i} \quad 2.10$$

$$\left( \frac{d^2 \ln \epsilon / \sigma}{d \sigma^2} \right)_{\sigma_i} = \lambda_i^2 + \frac{2\lambda_i^3}{D_i} \left( \frac{dD}{d\lambda} \right)_{\lambda_i} - \frac{\lambda_i^4}{D_i^2} \left( \frac{dD}{d\lambda} \right)_{\lambda_i}^2 + \frac{\lambda_i^4}{D_i} \left( \frac{d^2 D}{d\lambda^2} \right)_{\lambda_i} \quad 2.11$$

The derivatives of D with respect to  $\lambda$  are approximated by the following expressions.

$$\left( \frac{dD}{d\lambda} \right)_{\lambda_i} = \frac{8[D_{+1} - D_{-1}] - [D_{+2} - D_{-2}]}{12\eta} \quad 2.12$$

$$\left( \frac{d^2 D}{d\lambda^2} \right)_{\lambda_i} = \frac{16[D_{+1} + D_{-1}] - [D_{+2} + D_{-2}] - 30D_0}{12\eta^2} \quad 2.13$$

The first corrections on eqs (2.12) and (2.13) are respectively  $0.033\eta^4 D^{(5)}$  and  $0.011\eta^4 D^{(6)}$ .

Equations (2.12) and (2.13) are obtained by combining the Taylor series expansions of D around  $\lambda_i$  for the points  $\lambda_i + k\eta$  for  $k = -2, -1, 0, +1, +2$

$$D_k \equiv D(\lambda_i + k\eta) = D_i + \sum_{q=1}^{\infty} \frac{1}{q!} (k\eta)^q D^{(q)} \quad 2.14$$

In practice we take  $\eta = 1 \text{ m}\mu$  and measure the optical densities in the points around  $\lambda_i$ . In order to obtain the derivatives as accurate as possible we select for every point  $\lambda_i$  a sample which has  $0.8 \leq D_i \leq 1.5$ .

## 2.4 Evaluation of molecular quantities

Having the arrays  $L_X(i)$ ,  $X(i)$  and  $Y(i)$  we can investigate to what extent they are correlated by an equation of the form:

$$L_X(i) = a_X + b_X X(i) + c_X Y(i) \quad 2.15$$

This is a well known problem in statistics and treated by a linear regression analysis<sup>2</sup>. From the multiple linear regression analysis we obtain estimates of the coefficients  $a_X$ ,  $b_X$  and  $c_X$  together with their standard errors. Furthermore we get the multiple correlation coefficient, which is a direct measure of the quality of the correlation. Its value ranges from 0 (no correlation) to 1 (perfect correlation).

All numerical work indicated so far is performed on a IBM 360/50 computer. The regression analysis is based on a IBM program.

Comparing eqs (2.2) and (2.15) we see that for a perfect correlation we have:

$$A_X = a_X \quad 2.16$$

$$B_X = 15 h c b_X \quad 2.17$$

$$C_X = 30 h^2 c^2 c_X \quad 2.18$$

By studying now  $A_X$ ,  $B_X$  and  $C_X$  as a function of the angle  $\chi$ , we find from the linear relations (1.67) to (1.69), at least if they are satisfied, the quantities  $D$ ,  $E$ ,  $F$ ,  $G$  etc. Usually we give  $\chi$  the three values  $0^\circ$ ,  $54.8^\circ$  and  $90^\circ$ .

The point of view adopted here is quite different from Liptay's<sup>3</sup>, who in principle starts with the assumption that the experimental observations are perfectly correlated with the theory. He then applies an iterative procedure based on eqs (1.66) to (1.75) to find  $A_X$ ,  $B_X$ ,  $C_X$ ,  $\mu$  and  $\Delta\mu$ . In cases where the transition moment is independent of the external field  $F$ , we applied his method and obtained results in agreement with those derived by the method we have just explained. However, when the transition moment is strongly field dependent his method can not be used without additional knowledge.

## References

1. H. Labhart, *Chimia* **15**, 20 (1961)
2. M. Spiegel 'Statistics', Schaum's outline series, Mc Graw Hill.
3. W. Liptay *Z.f. Naturf.* **20a**, 272 (1965).

## ELECTRO-OPTICAL STUDIES OF SOME POLAR MOLECULES

## 3.1 Introduction

An important class of organic compounds, known as conjugated molecules, have received considerable attention of both experimental and theoretical chemists. There are many methods to study their ground state properties, but there are very few leading to an understanding of the excited states. The field influence on absorption bands provides a tool to determine dipole moments of electronically excited molecules.

Knowledge of the change in charge distribution due to electronic excitation may contribute to the understanding of the photochemical behaviour of these compounds. In the present state of affairs one can only rely on experimental determinations.

Various methods of approximation have been launched to find the wavefunctions for the first states of conjugated molecules. The semi empirical treatments are the most in vogue<sup>1</sup>. In addition to the dipole moments, the directions of the transition moments, found from electro-optical measurements, may be used to verify computations.

We have restricted the choice to planar molecules, having the symmetry of the  $C_{2v}$  point group. The symmetry provides us with necessary additional information, required in the analysis of our experimental data. The dipole moment is always along the twofold axis; transitions are polarized either parallel or perpendicular to this axis.

## 3.2 Experimental results

Working along the lines indicated in section 2.2, we have determined  $A_\chi$  and  $B_\chi$  in the first absorption band of the compounds listed in table 3.1. In fig 3.1 we give the structural formulae of these molecules. From the dependence of the quantities  $A_\chi$  and  $B_\chi$  on  $(3\cos^2\chi - 1)$  we have determined the values of  $D$ ,  $E$ ,  $F$  and  $G$  given in table 3.2. The relative error with which  $C_\chi$  is found from the regression analysis is too large to make a further analysis of it worthwhile.

Table 3.1 presents the following information: a. solvents used, b. the wavelength region where the  $L_\chi$  values have been determined, c.  $A_\chi$ ,  $B_\chi$  and their standard errors  $S_a$  and  $S_b$  respectively, d. the multiple correlation coefficient M.C.C. connected with the description of the observed  $L_\chi(v)$  curve by eq(2.2).

In an appendix we briefly review our determinations of ground state dipole moments from dielectric measurements.

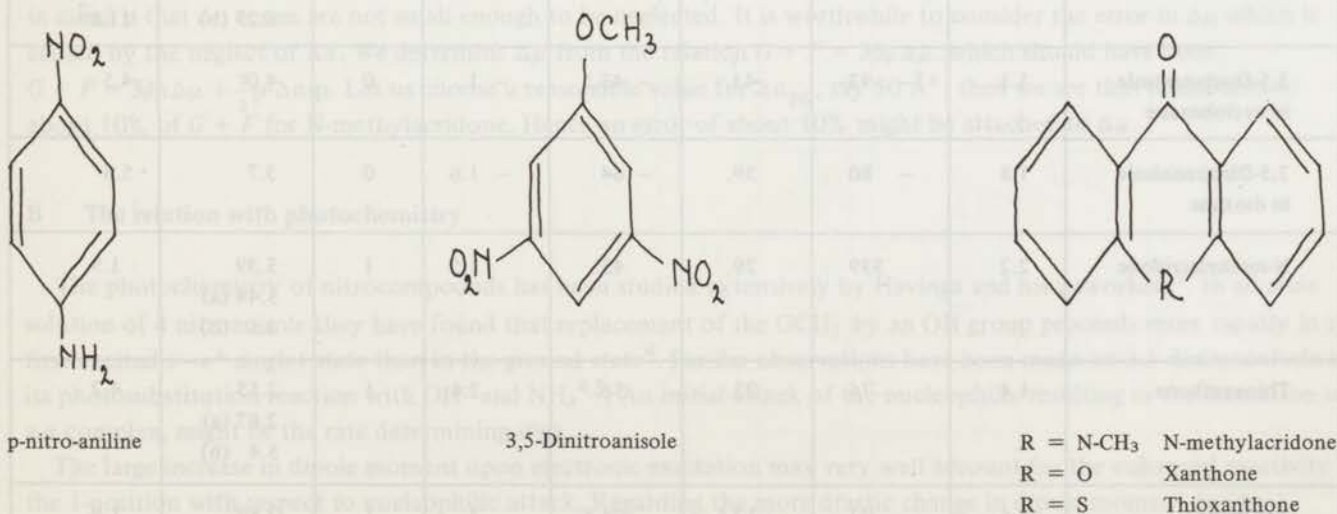


Fig 3.1

Structural formulae of the compounds treated in this chapter

Table 3.1

Electro-optical data for some polar  $\pi$  electron systems, observed in their first  $\pi$ - $\pi^*$  absorption band at 300° K.  
M.C.C. = Multiple Correlation Coefficient;  $S_a$  and  $S_b$  are the standard errors in  $A$  and  $B$ .

	$\chi$	M.C.C.	$10^{10}$ $A_\chi$	$10^{10}$ $S_a$	$10^{23}$ $B_\chi$	$10^{23}$ $S_b$
p-Nitroaniline in benzene 335 - 380 $\mu$	0°	0.976	36.3	1.4	1526	87
	54.8°	0.977	1.9	0.7	807	45
	90°	0.976	- 13.6	0.4	484	27
3,5-Dinitroanisole in cyclohexane 300 - 346 $\mu$	0°	0.991	- 5.9	0.2	128	5
	54.8°	0.999	0.4	0.1	216	3
	90°	0.999	3.4	0.1	258	3
3,5-Dinitroanisole in dioxane 312 - 360 $\mu$	0°	0.865	- 4.8	0.3	83	13
	54.8°	0.995	0.7	0.1	213	6
	90°	0.998	3.2	0.1	276	4
N-methylacridone in cyclohexane 363 - 395 $\mu$	0°	0.995	23.3	0.4	236	5
	54.8°	0.988	0.7	0.3	144	4
	90°	0.961	- 10.5	0.4	104	6
Thioxanthone in cyclohexane 346 - 384 $\mu$	0°	0.997	5.5	0.2	178	3
	54.8°	0.998	0.4	0.1	109	2
	90°	0.995	- 2.0	0.1	74	2
Xanthone in cyclohexane 310 - 340 $\mu$	0°	0.978	7.6	0.3	109	5
	54.8°	0.931	1.1	0.3	69	6
	90°	0.871	- 2.1	0.2	33	4

Table 3.2

Molecular properties

(a): From our dielectric measurements; (b): From A.L. McClellan 'Tables of experimental dipole moments'

	$10^{10}$ $D$	$10^{10}$ $E$	$10^{23}$ $F$	$10^{23}$ $G$	$G/F$	$(p\cdot\mu)^2$	$\mu$ [D]	$\Delta\mu$ [D]
p-Nitroaniline	7.9	501	165	349	2.1	1	6.55 6.29 (b)	10.8 11.8 <sup>2</sup>
3,5-Dinitroanisole in cyclohexane	1.1	- 93	- 43	- 43.5	- 1.	0	4.0	4.5
3,5-Dinitroanisole in dioxane	1.8	- 80	39.	- 64	- 1.6	0	3.7	5.8
N-methylacridone	2.2	339	29.	45.	1.5	1	5.39 5.44 (a) 3.5 (b)	1.9
Thioxanthone	1.4	76.	22.	56.	2.6	1	2.55 2.67 (a) 5.4 (b)	4.2
Xanthone	3.4	97.	12.5	24.6	2.	1	2.89 2.99 (a) 3.0 (b)	1.8

### 3.3 Discussion

#### A Molecular properties

We stress that the theory developed in chapter 1 is only valid for an absorption band whose envelope covers a single electronic transition. The direction of the transition moment should not change within the band i.e. vibronic coupling of electronic states should be negligible. In transitions which gain their intensity mainly from vibronic mixing, such as  $n-\pi^*$  transitions, one should be aware of possible variations of polarization throughout the band. For a medium strong ( $P \approx 2.5D$ ) or very strong ( $P \approx 10D$ )  $\pi-\pi^*$  transition we will assume the electronic transition moment to be a constant for the corresponding band. This assumption applies to all the bands listed in table 3.1, since  $\epsilon_m$  exceeds or is of the order  $7 \times 10^3$ .

A good correlation of eq (2.2) and the observed  $L_\chi(v)$  curves indicates that only one final electronic state is involved in the absorption. All the more reason for this when  $\mu$ , derived from  $E$ , agrees with values determined by other methods.

The values of  $D$  listed in table 3.2 are all small compared to the corresponding magnitudes of  $E$  and are of the order of the estimated error in  $E$ . It therefore makes sense to neglect all contributions from the tensors  $A$  and  $B$ . In solutions of nonpolar solutes, treated in chapter 4, no anisotropy in molecular orientations has been found. As a consequence we drop the terms arising from the polarizability  $\alpha$ . For reasonable polar molecules it may be expected, at least if  $\Delta\mu \neq 0$ , that the frequency shift arising from  $\Delta\alpha$  may be ignored relative to the shift due to  $\Delta\mu$ . If the  $\Delta\alpha$  terms are also deleted the equations (1.70) to (1.73) are simplified to:

$$D = 0 \quad 3.1$$

$$E = \beta^2 [3(\underline{\mu} \cdot \underline{p})^2 - \mu^2] \quad 3.2$$

$$F = \beta \underline{\mu} \cdot \underline{\Delta\mu} \quad 3.3$$

$$G = \beta [3(\underline{\mu} \cdot \underline{p})(\underline{\Delta\mu} \cdot \underline{p}) - \underline{\mu} \cdot \underline{\Delta\mu}] \quad 3.4$$

Knowing that the symmetry of our molecules is such that  $\underline{p}$  is either parallel or perpendicular to  $\underline{\mu}$ , the sign of  $E$  is sufficient to discriminate between the two possibilities.

In the case  $\underline{p} \parallel \underline{\mu}$  we have  $E = 2\beta^2\mu^2$  and  $G = 2F = 2\beta\mu\Delta\mu$ . When  $\underline{p} \perp \underline{\mu}$  we have  $E = -\beta^2\mu^2$  and  $F = -G = \beta\mu\Delta\mu$ . The values of  $\mu$  and  $\Delta\mu$  derived from these relations are presented in table 3.2.

By inspection of table 3.2 we see that the agreement of  $\mu$  values with those found from dielectric measurements is very good. The ratio  $G/F$  deviates in some instances significantly from the expected value. The explanation we have in mind is that  $\Delta\alpha$  terms are not small enough to be neglected. It is worthwhile to consider the error in  $\Delta\mu$  which is caused by the neglect of  $\Delta\alpha$ . We determine  $\Delta\mu$  from the relation  $G + F = 3\beta\mu\Delta\mu$ , which should have been  $G + F = 3\beta\mu\Delta\mu + \frac{3}{2}\underline{p} \cdot \underline{\Delta\alpha} \cdot \underline{p}$ . Let us choose a reasonable value for  $\Delta\alpha_{pp}$ , say  $50 \text{ \AA}^3$ , then we see that it amounts to about 10% of  $G + F$  for N-methylacridone. Hence an error of about 10% might be attached to  $\Delta\mu$ .

#### B The relation with photochemistry

The photochemistry of nitrocompounds has been studied extensively by Havinga and his coworkers<sup>3</sup>. In alkaline solution of 4 nitroanisole they have found that replacement of the  $\text{OCH}_3$  by an  $\text{OH}$  group proceeds more rapidly in the first excited  $\pi-\pi^*$  singlet state than in the ground state<sup>4</sup>. Similar observations have been made on 3,5 dinitroanisole in its photosubstitution reaction with  $\text{OH}^-$  and  $\text{NH}_3$ <sup>4,5</sup>. An initial attack of the nucleophile, resulting in the formation of a  $\sigma$ -complex, might be the rate determining step.

The large increase in dipole moment upon electronic excitation may very well account for the enhanced reactivity of the 1-position with respect to nucleophilic attack. Regarding the more drastic change in dipole moment due to  $\pi-\pi^*$  excitation of 4-nitroaniline into  $S_1$ , we should expect the 1-position in 4-nitrodimethylaniline to be even more reactive towards nucleophilic substitution. The possibility that 4-nitroaniline may behave as an acid and lose a proton from the  $\text{NH}_2$  group in the excited state makes it less attractive for the desired test.

### C Comparison with quantumchemical calculations

The point of view adopted in semi empirical treatments of the many electron problem encountered in (planar) aromatic molecules is to separate the electrons in two independent groups. A number of electrons, usually more tightly bound to the nuclear frame, are collected in the  $\Sigma$  core. The core electrons occupy  $\sigma$  orbitals which are symmetric with respect to reflection in the molecular plane  $\sigma_h$ . Another class of more mobile electrons constitute the  $\Pi$  electron system and occupy  $\pi$  orbitals, antisymmetric with respect to  $\sigma_h$ . Most of the visible and near ultraviolet absorption bands are interpreted in terms of transitions to excited states, having the  $\Pi$  part excited to  $\Pi^*$ , whereas the  $\Sigma$  part remains unaffected.

The main difficulty in these methods is to find a suitable set of parameters which, after calibration on selected molecules, may be transferred to other ones. We have collected two sets of parameters in table 3.3, known to give reasonable results in Pariser, Parr, Pople type calculations<sup>1</sup>. The one-centre core integrals and the one-centre electronic repulsion integrals are denoted by  $U_\mu$  and  $\gamma_{\mu\mu}$  respectively. The integral  $\gamma_{\mu\mu}$  is taken as the difference between the valence state ionization potential  $I_\mu$  and electron affinity  $A_\mu$ . The two centre repulsion integrals  $\gamma_{\mu\nu}$  are found from  $\gamma_\mu$  and  $\gamma_\nu$  according to a well known formula of Nishimoto and Mataga<sup>7</sup>. The two centre core integral  $\beta_{\mu\nu}$  is calculated from  $\beta_{\mu\nu} = \frac{1}{2}S_{\mu\nu}(U_\mu + U_\nu)$  if  $\mu$  and  $\nu$  are nearest neighbours and is zero otherwise. Here  $S_{\mu\nu}$  is the overlap integral between the two  $2p_z$  atomic orbitals on the atoms  $\mu$  and  $\nu$ .

One set of parameters, based on the work of Van der Lugt, has been given the code name LNMIA and the other, derived from the work of Billingsley and Bloor, carries the code name BBNMIA<sup>6</sup>. With each set of parameters we have performed a selfconsistent field calculation for the  $\Pi$  system, followed by a configuration interaction of 49 singly excited  $\Pi^*$  states. The results are summarized in table 3.4. In figures 3.2 to 3.4 we have indicated in the experimental absorption spectra the positions of transitions calculated with LNMIA. The heights of the vertical bars are proportional to the calculated oscillator strengths. The dashed parts in the curves refer to the regions where the electro-optical measurements play a part.

The results obtained with the two different sets do not differ much. We might say that the first transition compares favourably with the experimental observations with regard to energy, polarization and change in dipole moment. A glance at figs 3.2 to 3.4, however, gives a sad feeling regarding the other transitions. Other parameter choices did not improve the results.

Taking the consequences of the discrepancy we assume that the breakdown of the approximation with a constant  $\Sigma$  state causes the trouble. A certain amount of negative feedback coupling will be present between the  $\Pi$  and  $\Sigma$  system i.e. a redistribution of  $\Pi$  charge will automatically be counteracted by a  $\Sigma$  charge modification.

Atom	LNMIA		BBNMIA	
	U[eV]	$\gamma$ [eV]	U[eV]	$\gamma$ [eV]
C <sup>+</sup>	- 9.6	11.13	- 9.6	11.13
N <sup>++</sup>	-21.0 Amino	12.34	-23.24 Pyrrole	16.76
H <sub>3</sub> C-N <sup>++</sup>	-19.0	12.34	-21.64	16.76
O <sup>+</sup>	-15.58 Keto	15.23	-15.58 Keto	15.23
O <sup>++</sup>	-27.52 Hydroxy	15.23	-31.44 Furan	21.53
S <sup>++</sup>	-18.4 Thiol	9.94	-20.64 Thiophene	13.05
CH <sub>3</sub> inductive effect	2.0		1.6	
$r_{C-N}=1.39 \text{ \AA}$ , $r_{C-O}=1.37 \text{ \AA}$ , $r_{C=O}=1.2 \text{ \AA}$ , $r_{C-S}=1.7 \text{ \AA}$ , $r_{C-C}=1.40 \text{ \AA}$ .				

Table 3.3

Two sets of parameters for  $\pi$  electron calculations



Table 3.4

Results of quantumchemical computations; y and x axes are in the molecular plane, y being along the dipole moment

R	State	LNMIA				BBNMIA				Experiment	
		[eV]	P <sub>x</sub> [D]	P <sub>y</sub> [D]	Δμ[D]	[eV]	P <sub>x</sub> [D]	P <sub>y</sub> [D]	Δμ[D]	[eV]/p	Δμ[D]
H <sub>3</sub> C-N	S <sub>1</sub>	3.55		4.4	2.7	3.45		4.4	2.1	3.2±0.1/y	1.9
	S <sub>2</sub>	3.88	5.2		1.0	3.65	6.5		0.1		
	S <sub>3</sub>	4.10	3.8		-1.3	3.94	3.3		-1.3		
	S <sub>4</sub>	5.18		2.9	-1.1	5.24		1.2	-0.8		
O	S <sub>1</sub>	4.12		3.6	2.2	3.98		3.9	1.9	3.7±0.1/y	1.8
	S <sub>2</sub>	4.53	0.6		0.4	4.41	0.97		1.0		
	S <sub>3</sub>	4.87	0.6		-0.1	4.57	3.6		-3.0		
	S <sub>4</sub>	5.14		2.9	-1.1	5.22		2.5	-1.5		
S	S <sub>1</sub>	3.87		4.4	3.2	3.80		4.5	2.9	3.3±0.1/y	4.2
	S <sub>2</sub>	4.39	0.2		1.5	4.27	2.3		1.7		
	S <sub>3</sub>	4.55	3.5		-1.2	4.40	4.1		-1.8		
	S <sub>4</sub>	5.13		3.2	-1.7	5.19		2.9	-2.0		

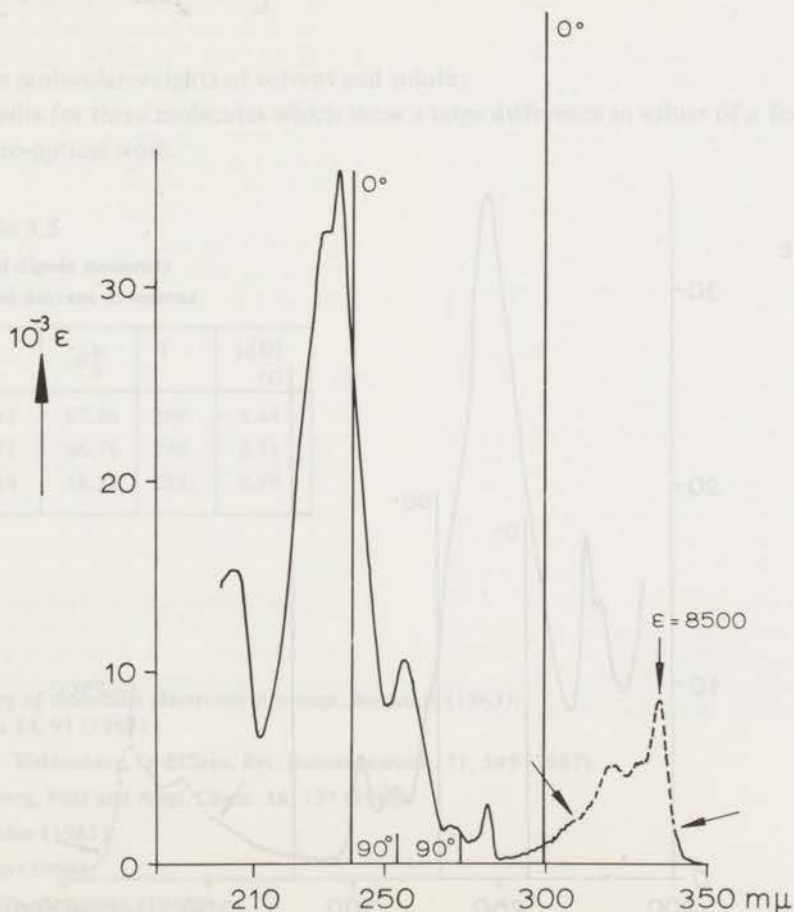


Fig 3.2

Absorption spectrum of Xanthone in cyclohexane solution; the dashed part indicates the region of electro-optical measurements; the vertical lines indicate the calculated transitions, their heights being proportional to the oscillator strengths.

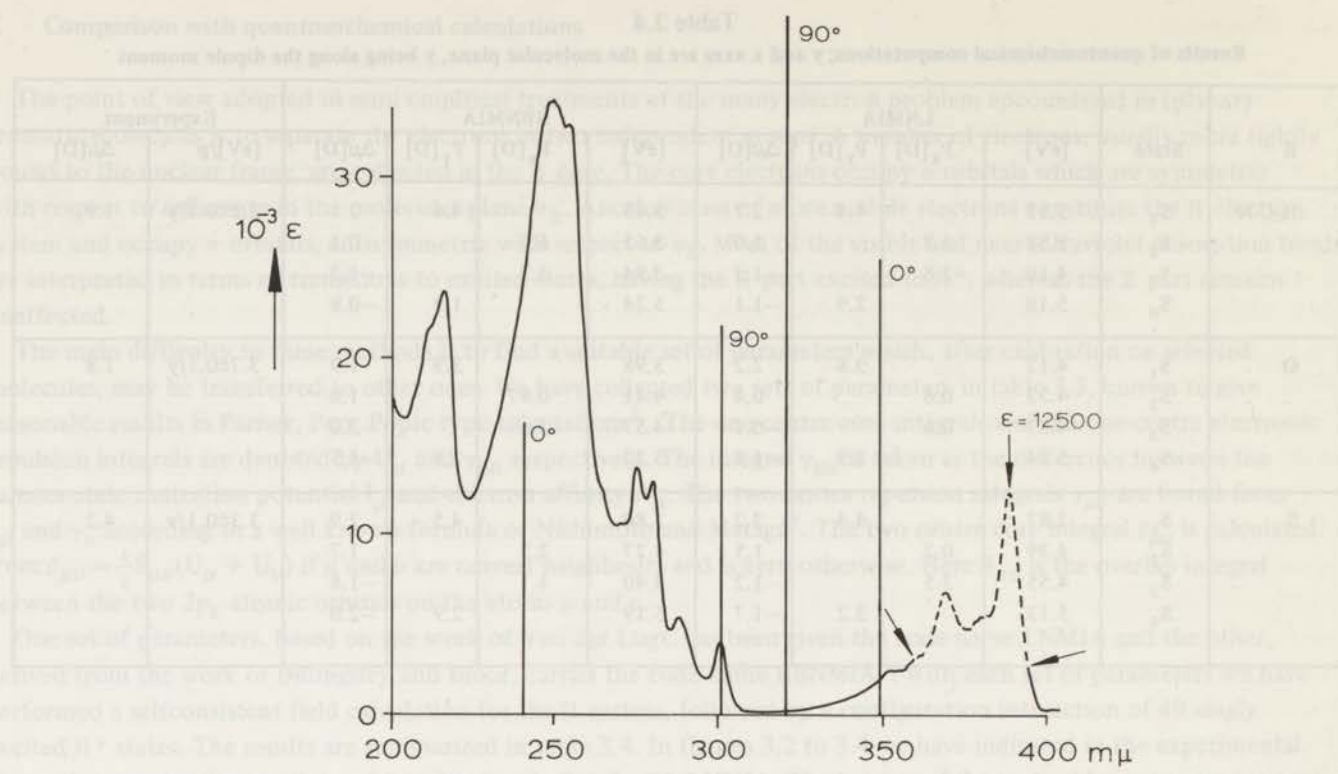


Fig 3.3

Absorption spectrum of N-methylacridone in cyclohexane solution; the dashed part indicates the region of electro-optical measurements; the vertical lines indicate the calculated transitions, their heights being proportional to the oscillator strengths.

comparability with the experimental observations with regard to energy, polarization and change in dipole moment. A glance at Figs 3.2 to 3.4, however, gives a good feeling regarding the other derivatives. Other parameter choices did not improve the results.

Taking the consequences of the discrepancy we assume that the breakdown of the approximation with a constant  $\Sigma$  state causes the trouble. A certain amount of negative feedback coupling will be present between the  $\Pi$  and  $\Sigma$  systems, i.e. a redistribution of  $\Pi$  charge will automatically be counteracted by a  $\Sigma$  charge redistribution.

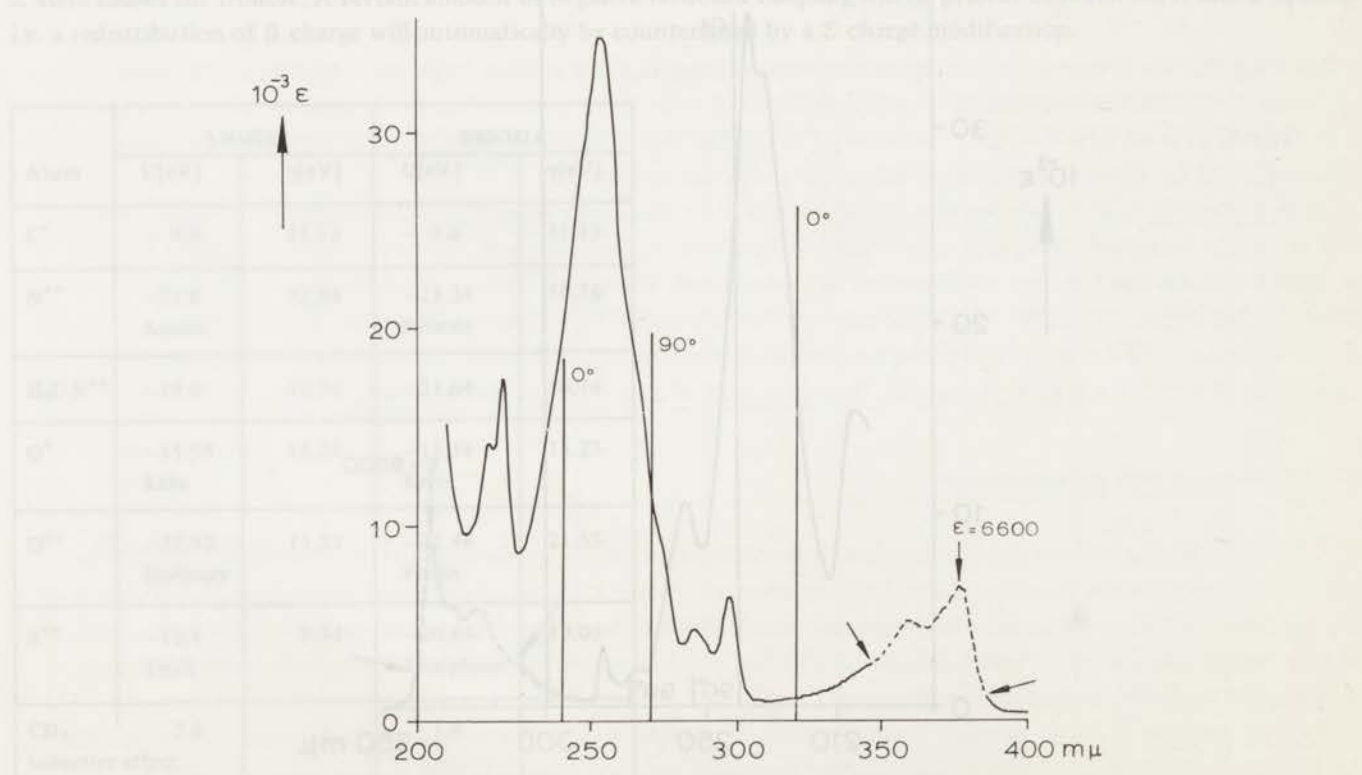


Fig 3.4

Absorption spectrum of Thioxanthone in cyclohexane solution; the dashed part indicates the region of electro-optical measurements; the vertical lines indicate the calculated transitions, their heights being proportional to the oscillator strengths.

## Appendix

The most frequently applied method to obtain dipole moments is based on measurements of the static dielectric constant  $\epsilon(1,2)$ , the refractive index  $n(1,2)$  and the specific volume  $v(1,2)$  of dilute solutions as a function of the mole-fraction  $x_2$  of the solute. The labels 1 and 2 refer to the pure solvent and the solute respectively.

In nonpolar solvents the method of Halverstadt and Kumler, which derives from the theory of Debye<sup>8</sup>, may be used to find the dipole moment of the solute. The procedure is summarized in the formulae presented below.

$$P = \frac{\epsilon(1) - 1}{\epsilon(1) + 2} \left\{ M_2 v(1) + M_1 \left( \frac{\partial v(1,2)}{\partial x_2} \right)_{x_2=0} \right\} + \frac{3 M_1 v(1)}{\{\epsilon(1) + 2\}^2} \left( \frac{\partial \epsilon(1,2)}{\partial x_2} \right)_{x_2=0} \quad 3.5$$

$$R^D(1,2) = \left\{ \frac{n^2(1,2) - 1}{n^2(1,2) + 2} \right\} \{ M_1 x_1 + M_2 x_2 \} v(1,2) \quad 3.6$$

$$R^D(2) = R^D(1) + \left( \frac{\partial R^D(1,2)}{\partial x_2} \right)_{x_2=0} \quad 3.7$$

$$P_{ind} = 1.05 R^D(2) \quad 3.8$$

$$\mu = 0.01281 \left\{ (P - P_{ind}) T \right\}^{1/2} \quad 3.9$$

where  $M_1$  and  $M_2$  are the molecular weights of solvent and solute.

Table 3.5 gives our results for three molecules which show a large difference in values of  $\mu$  found in the literature<sup>9</sup> and those from our electro-optical work.

Table 3.5  
Determination of dipole moments  
with freshly purified dioxane as solvent

	$P$	$R_2^D$	$T$	$\mu[D]$
N-methylacridone	677.43	67.86	298	5.44
Thioxanthone	220.41	66.76	298	2.71
Xanthone	244.48	58.33	298	2.99

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## CHAPTER 4

THE POLARIZABILITY OF TETRACENE  
IN ITS FIRST EXCITED SINGLET STATEC. A. G. O. VARMA and L. J. OOSTERHOFF  
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Received 11 November 1970

The polarizability of tetracene in the first excited singlet state relative to the ground state has been determined from electro-optical studies of the first absorption band of tetracene in benzene solution. The theory of electro-optical effects for nonpolar molecules is reformulated and for comparison with experiment a calculation of the polarizability, due to the  $\pi$  electron system has been performed.

A very useful method to study the change in polarizability of a molecule due to electronic excitation is based on the measurement of the effects of an external electric field on its absorption spectrum. We shall consider the theory for nonpolar molecules with absorption bands, which are broad compared to the bandwidth of the light, used in the measurement. For an absorption at frequency  $\nu$  the molar extinction coefficient is given by

$$\epsilon(\nu) = K\nu \langle (\mathbf{e} \cdot \mathbf{P})^2 S(\nu) \rangle. \quad (1)$$

Here  $K$  is a constant,  $\mathbf{e}$  is the electric field of the incident light wave,  $\mathbf{P}$  is the electronic transition moment,  $S(\nu)$  is a function describing the shape of the absorption band,  $\langle \rangle$  means averaging over the given distribution of molecules in the sample.

The shape function can be evaluated from measurements of  $\epsilon(\nu)$  in an isotropic system, yielding

$$S(\nu) = 3\epsilon(\nu) / K\nu P^2. \quad (2)$$

The introduction of an electric field  $\mathbf{F}$  will in general show the following effects.

- 1) A change in the distribution of molecular orientations as a result of the interaction of the field with the anisotropic polarizability of the molecules in their electronic ground states.
- 2) An energy shift for each level, given by

$$\Delta E_k = -\frac{1}{2} \mathbf{F} \cdot \boldsymbol{\alpha}(k) \cdot \mathbf{F}, \quad (3)$$

with  $\boldsymbol{\alpha}(k)$  the polarizability in the state  $k$ .

- 3) A change in the transition moment.
- 4) A change in the function  $S(\nu)$ .

Up to field strengths of 120 kV/cm no effects due to orientation could be found. This fact has

also been established by Seibold et al. [1]. For the sake of simplicity we shall therefore maintain an isotropic distribution in the description of the field effects. All sublevels belonging to the initial electronic state are considered to have the same polarizability  $\alpha(i)$ . Similarly  $\alpha(f)$  is taken constant for all sublevels pertaining to the final state. The perturbed transition moment may conveniently be described by

$$\mathbf{P}(\mathbf{F}) = \mathbf{P} + \mathbf{A} \cdot \mathbf{F} + \mathbf{B} : \mathbf{F}\mathbf{F}, \quad (4)$$

where  $\mathbf{A}$  is the transition polarizability and  $\mathbf{B}$  the third rank transition hyperpolarizability.

Following the arguments given by Labhart [2] we assume that the shape function is uniformly shifted over a frequency  $\Delta\nu$ , i.e., the shape function satisfies the following relation

$$S^F(\nu) = S(\nu - \Delta\nu), \quad (5)$$

with  $\hbar\Delta\nu = \Delta E_f - \Delta E_i$ .

Now the extinction coefficient for the sample subjected to the field can be evaluated from

$$\epsilon(\mathbf{F}, \nu) = K\nu \langle \langle (\mathbf{e} \cdot \mathbf{P}(\mathbf{F}))^2 S^F(\nu) \rangle \rangle. \quad (6)$$

The double brackets mean averaging over an isotropic distribution. Expanding  $S^F(\nu)$  into a Taylor series in  $\Delta\nu$ , using eqs. (2)-(4), retaining terms up to the second order in  $\mathbf{F}$ , we arrive at

$$\begin{aligned} \epsilon(\mathbf{F}, \nu) = & \frac{3\epsilon(\nu)}{P^2} \langle \langle (\mathbf{e} \cdot \mathbf{P})^2 + 2(\mathbf{e} \cdot \mathbf{P})(\mathbf{e} \cdot \mathbf{A} \cdot \mathbf{F}) \\ & + (\mathbf{e} \cdot \mathbf{A} \cdot \mathbf{F})^2 + 2(\mathbf{e} \cdot \mathbf{P})(\mathbf{e} \cdot \mathbf{B} : \mathbf{F}\mathbf{F}) \\ & - \frac{1}{2\hbar} (\mathbf{e} \cdot \mathbf{P})^2 (\mathbf{F} \cdot \Delta\boldsymbol{\alpha} \cdot \mathbf{F}) \frac{d \ln \epsilon / \nu}{d\nu} \rangle \rangle. \quad (7) \end{aligned}$$

Here  $\Delta\alpha = \alpha(f) - \alpha(i)$ .

After averaging we end up with the relation, valid for the extinction measured with linearly polarized light, travelling in a direction perpendicular to the external field and polarized under an angle  $\chi$  with respect to the field  $F$ :

$$\frac{\epsilon_{\chi}(F, \nu)}{\epsilon(\nu)} = 1 + F^2 \left\{ \mathcal{A}_{\chi} + \frac{1}{15h} \mathcal{B}_{\chi} \frac{d \ln \epsilon/\nu}{d\nu} \right\}. \quad (8)$$

The quantities  $\mathcal{A}_{\chi}$  and  $\mathcal{B}_{\chi}$  satisfy linear relations of the form

$$\mathcal{A}_{\chi} = \frac{1}{3} \mathcal{D}, \quad (9)$$

$$\mathcal{B}_{\chi} = 5\mathcal{F} + \mathcal{G} (3 \cos^2 \chi - 1), \quad (10)$$

where the coefficients on the right-hand sides of these equations are given by

$$\mathcal{D} = \frac{1}{P^2} \sum_{ij} A_{ij}^2 + \frac{2}{P^2} \sum_{ij} P_i B_{ijj}, \quad (11)$$

$$\mathcal{F} = \frac{1}{2} \text{Tr } \Delta\alpha, \quad (12)$$

$$\mathcal{G} = \frac{3}{2} \frac{P \cdot \Delta\alpha \cdot P}{P^2} - \frac{1}{2} \text{Tr } \Delta\alpha. \quad (13)$$

In eqs. (11)-(13) all components may be considered to be related to molecular coordinate axes.

At this point we introduce the connection between the theory, described above, and experiment. With the aid of the relative intensity change, caused by the field, a quantity  $L_{\chi}(\nu)$  is defined:

$$L_{\chi}(\nu) = \frac{I_{\chi, F=0} - I_{\chi, F}}{I_{\chi, F=0}} \frac{1}{2.303 D F^2}. \quad (14)$$

Here  $I_{\chi, F}$  is the intensity of the linearly polarized light beam leaving the sample, when the field has a value  $F$ ;  $D$  represents the optical density of the solution at the frequency involved.

Considering the fact that the second term on the right-hand side of eq. (8) is very small compared to unity, we find

$$L_{\chi}(\nu) = \mathcal{A}_{\chi} + \frac{1}{15h} \mathcal{B}_{\chi} \frac{d \ln \epsilon/\nu}{d\nu}. \quad (15)$$

It might be mentioned in passing that the dependence of  $L_{\chi}$  on  $\cos^2 \chi$  is already evident from general considerations on the symmetry of the macroscopic system. If we keep all experimental conditions fixed and rotate the sample, which was originally isotropic,  $I_{\chi, F}$  should remain constant. As a consequence  $I_{\chi, F}$  can only depend on invariants constructed from the external fields. Bearing in mind that in our experiments  $I_{\chi, F}$  should depend linearly on the light intensity, the invariants are  $(e \cdot e)$ ,  $(e \cdot F)^2$ ,  $(e \cdot e)(F \cdot F)$

etc. Therefore, only terms independent of  $\chi$  or depending on  $\cos^2 \chi$  will occur. In the application of eq. (14), a knowledge of the local field acting on the solute molecules is necessary. For non-polar solvents we take the Lorentz field as a sufficient approximation to the local field. We have determined experimentally the quantity  $L_{\chi}(\nu)$  as a function of frequency  $\nu$  and angle  $\chi$ . The derivative of  $\ln \epsilon/\nu$  has been evaluated numerically from the absorption curve and has been used in a linear regression analysis of  $L_{\chi}(\nu)$ , to obtain  $\mathcal{A}_{\chi}$  and  $\mathcal{B}_{\chi}$ .

Results for the first singlet excitation of tetracene in a solution of benzene are presented in table 1. Within experimental error no  $\chi$  dependence of  $\mathcal{A}$  has been found, in accordance with formula (9).

Table 1

Electro-optical effects of the first  $\pi$ - $\pi^*$  singlet transition of tetracene observed in the first two vibrational sub-bands between 482 and 435 nm in benzene solution. All quantities are given in electrostatic units

$\chi$	$10^{10} \mathcal{A}_{\chi}$	$10^{10} s_a^a$	$10^{24} \mathcal{B}_{\chi}$	$10^{24} s_b^a$
$0^\circ$	-1.05	0.19	276	15
$54.8^\circ$	-1.25	0.17	319	14
$90^\circ$	-1.13	0.17	341	14
	$10^{10} \mathcal{D} = -3.43 \pm 9\%$		$10^{24} \mathcal{F} = 63.8 \pm 3\%$	
	$10^{24} \mathcal{G} = -21.5 \pm 32\%$		$10^{24} \overline{\Delta\alpha} = 42.5 \pm 3\%$	

<sup>a</sup>  $s_a$  and  $s_b$  are the standard errors in  $\mathcal{A}_{\chi}$  and  $\mathcal{B}_{\chi}$ , respectively.

The value of  $\mathcal{D}$  turns out to be negative, which indicates, since  $(1/P^2) \sum A_{ij}^2$  is positive, that there is a contribution from the transition hyperpolarizability determining the sign of  $\mathcal{D}$ . It is noteworthy that a negative value of  $\mathcal{D}$  also applies to crocetindimethylester as follows from fig. 1 in the paper by Seibold et al. [1], without being mentioned explicitly. From  $\mathcal{F}$  we calculate the average change in polarizability  $\overline{\Delta\alpha}$ . This value is roughly of the order of magnitude one finds quantumchemically for the  $\pi$ -electron contribution. Bauer and Nicol estimate from solvent effects a much lower value ( $3 \text{ \AA}^3$ ), which must certainly be in error [3].

In table 2 we present the result of a  $\pi$ -electron calculation of the Pariser-Parr-Pople (P.P.P.) type, including the first 16 excited singlet states. The calculation yields an excitation energy of 2.9 eV for the first  $\pi$ - $\pi^*$  band, which shows its first two vibrational sub-bands in benzene solution at 2.6 and 2.8 eV. The transition

Table 2  
Results of a  $\pi$  electron calculation for the first  $\pi-\pi^*$  transition

Excitation energy = 2.9 eV	
$\alpha^{(i)}_{xx}$ <sup>a)</sup>	= 18.58 Å <sup>3</sup>
$\alpha^{(f)}_{xx}$	= 15.26 Å <sup>3</sup>
$\alpha^{(i)}_{yy}$	= 46.08 Å <sup>3</sup>
$\alpha^{(f)}_{yy}$	= 218.88 Å <sup>3</sup>
$\Delta\alpha_{xx}$	= -3.32 Å <sup>3</sup>
$\Delta\alpha_{yy}$	= 172.8 Å <sup>3</sup>
$\overline{\Delta\alpha}$	= 56.6 Å <sup>3</sup>
$\mathcal{F}$	= 84.7 Å <sup>3</sup>
$\mathcal{G}$	= -89.7 Å <sup>3</sup>

a) Axes in the molecular plane:  
 $x$  = short,  $y$  = long.

moment determined theoretically lies along the short axis in the molecular plane, in agreement with the experimental determination of Sidman [4]. This direction is also consistent with the electro-optical observations. A little reflection reveals that if  $\Delta\alpha$  has its main component along the long axis, the largest frequency shift will occur, when the molecule lies with its long axis parallel to the field  $F$  and at the same time maximum absorption will be observed when the light is polarized perpendicularly to the field, i.e.,  $\mathcal{B}_{900}$  must be largest, as is the case.

The absolute values for  $\mathcal{F}$  and  $\mathcal{G}$  derived from  $\pi$  electron theory are too large compared to experiment. In general P.P.P. type calculations do not reproduce the magnitudes of dipole moments and transition moments very well and the same feature is to be expected for induced moments. A treatment including the  $\sigma$  electrons may improve the calculation in two respects:

(i) The polarizability perpendicular to the molecular plane. An important contribution will originate from  $\sigma-\pi^*$  and  $\pi-\sigma^*$  excited states. This component is not negligible as may be seen from the individual components of the tensor, determined experimentally by Le Fèvre and Le Fèvre for naphthalene [5]

$$\alpha_{xx} = 17.6 \text{ \AA}^3, \quad \alpha_{yy} = 21.5 \text{ \AA}^3, \quad \alpha_{zz} = 10.3 \text{ \AA}^3;$$

for benzene [6]

$$\alpha_{xx} = \alpha_{yy} = 11.12 \text{ \AA}^3, \quad \alpha_{zz} = 7.37 \text{ \AA}^3,$$

where  $z$  refers to the direction perpendicular to the molecular plane.

(ii) The in-plane components may be reduced by a drift of charge in the  $\sigma$  core, opposed in direction to the movement of  $\pi$  electrons [7,8].

In the computation of the in-plane  $\pi$  electron polarizability we have treated the influence of an external electric field as a modification of the  $\pi$  electron core hamiltonian:

$$\langle \mu | H_C | \mu \rangle = \langle \mu | H_C^0 | \mu \rangle - R_\mu \cdot F;$$

$$\langle \mu | H_C | \nu \rangle = \langle \mu | H_C^0 | \nu \rangle \quad \text{if } \mu \neq \nu.$$

With this modification we have calculated the dipole moments, induced by fields in  $x$  and  $y$  directions. The induced moments turn out to be approximately linear in the field up to a strength of  $10^7$  V/cm. We used this field strength in the evaluation of the polarizability to escape from rounding errors at lower fields. Two center electronic repulsion integrals have been calculated according to the well known formula of Mataga and Nishimoto. The values of the parameters used in the calculation are [9]

$$\begin{aligned} \text{one center core integral} &= -9.6 \text{ eV;} \\ \text{two center core integral} &= -2.4 \text{ eV;} \\ \text{one center electron repulsion integral} &= \\ &10.9 \text{ eV.} \end{aligned}$$

A modulation technique introduced by Labhart [10] has been chosen to get a good signal recovery from noise by using a lock-in amplifier. By applying a ratio recording system,  $L_\chi$  could be determined without disturbances from fluctuations in light intensity.

One of us (V.) is indebted to the Netherlands Organisation for the Advancement of Pure Research (Z.W.O.) for the sponsorship of his work under the auspices of the Netherlands Foundation for Chemical Research (S.O.N.).

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## CHAPTER 5

### THE BEHAVIOUR OF THE CHARGE TRANSFER BAND OF E.D.A. COMPLEXES IN A STRONG ELECTRIC FIELD

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A revised theory of electro-optical effects in the absorption spectra of solute molecules is presented. Measurements on a series of electron donor-acceptor complexes show a strong field dependence of the transition moment of the charge transfer absorption band. With the aid of a special model for these complexes it has been possible to evaluate the dipole moments in the electronic ground- and excited states. The ground state dipole moments are in good agreement with the values derived from dielectric measurements. It has been found that in some cases the directions of the excited state dipole moment and the ground state moment are antiparallel.

#### Introduction

Since a larger number of molecular compounds have been recognized as E.D.A. complexes<sup>1,2</sup> many attempts have been made to evaluate the charge transfer model quantitatively<sup>3,4</sup>. The main source of information has been the study of the electronic spectra. In addition dielectric polarization<sup>5</sup> has furnished valuable data about the charge distribution in the ground state of E.D.A. complexes. In this respect the importance of dielectric relaxation should not be ignored<sup>6</sup>.

Here we want to show the merits of electro-optical studies as a tool to determine ground state as well as excited state dipole moments and transition polarizabilities of such systems. All these quantities may contribute to the understanding of the structure of E.D.A. complexes. Our studies refer to the change in light absorption of solutions induced by strong electric fields of the order of 120 kV/cm.

#### Theory

We present the theory in a form, more suitable for our purposes than the existing formulation<sup>7</sup>.

In the presence of an electric field  $F$  the following effects may influence the light absorption of the solute molecules in a liquid solution.

1. A change in the distribution of molecular orientations as a result of the interaction of the field  $F$  with the dipole moment and anisotropic polarizability in the ground state.
2. A shift in energy for each state, given by:

$$\Delta E(k) = -\underline{\mu}(k) \cdot \underline{F} - \frac{1}{2} \underline{F} \cdot \underline{\alpha}(k) \cdot \underline{F} \quad 5.1$$

with  $\mu(k)$  and  $\alpha(k)$  the dipole moment and polarizability in the state  $k$ .

3. A change in the transition moment  $P$ .
4. A change in the function  $S(\nu)$ , describing the shape of the absorption band.

We recall that for an absorption at frequency  $\nu$ , the molar extinction coefficient is:

$$\epsilon(\nu) = K \nu \langle (\underline{e} \cdot \underline{P})^2 S(\nu) \rangle \quad 5.2$$

Here the constant  $K = \frac{8\pi^3 N}{h c 10^3}$

$\underline{e}$  is a unit vector along the electric field of the incident light wave.  $\langle \rangle$  means averaging over the existing distribution of solute molecules in the sample. From measurements of  $\epsilon(\nu)$  in an isotropic system, the shape function may be

evaluated:

$$S(\nu) = \frac{1}{K} \frac{3 \epsilon(\nu)}{\nu} \frac{1}{\rho^2} \quad 5.3$$

Now the following assumptions are introduced:

1. All sublevels belonging to the initial electronic state are attributed the same dipole moment  $\mu(i)$  and polarizability  $a(i)$ . Similarly  $\mu(f)$  and  $a(f)$  are related to the sublevels of the final state.
2. The field dependence of the transition moment is described by:

$$\underline{P}(\underline{F}) = \underline{P} + \underline{A} \cdot \underline{F} + \underline{B} : \underline{F} \underline{F} \quad 5.4$$

where  $A$  is the transition polarizability and  $B$  the third rank transition hyperpolarizability.

3. As has been suggested by Liptay and Czekalla<sup>8</sup> and made plausible by Labhart<sup>9</sup>, the shape function is uniformly shifted over a frequency  $\Delta\nu$  i.e. the field dependent function satisfies the relation:

$$S^F(\nu) = S(\nu - \Delta\nu) \quad \text{with} \quad 5.5$$

$$h\Delta\nu = \Delta E(f) - \Delta E(i)$$

The extinction coefficient for the sample subjected to the field  $F$  may now be evaluated from:

$$\epsilon(F, \nu) = K\nu \langle \{ \underline{e} \cdot \underline{P}(\underline{F}) \}^2 S^F(\nu) \rangle \quad 5.6$$

After averaging over a Boltzmann distribution, retaining terms upto the second order in  $F$ , we arrive at the relation valid for the extinction observed with linearly polarized light, travelling in a direction perpendicular to the field  $F$  and polarized with an angle  $\chi$  with respect to this field:

$$\frac{\epsilon_x(F, \nu)}{\epsilon(\nu)} = 1 + F^2 \left\{ A_x + \frac{1}{15h} B_x \frac{d \ln \epsilon / \nu}{d\nu} + \frac{1}{30h^2} C_x \left[ \left( \frac{d \ln \epsilon / \nu}{d\nu} \right)^2 + \frac{d^2 \ln \epsilon / \nu}{d\nu^2} \right] \right\} \quad 5.7$$

The quantities  $A_x$ ,  $B_x$  and  $C_x$  have the following dependance on the angle  $\chi$ :

$$A_x = \frac{1}{3} D + \frac{1}{30} E (3 \cos^2 \chi - 1) \quad 5.8$$

$$B_x = 5 F + G (3 \cos^2 \chi - 1) \quad 5.9$$

$$C_x = 5 H + I (3 \cos^2 \chi - 1) \quad 5.10$$

In a previous communication<sup>10</sup> we have derived from general symmetry considerations, that  $\chi$  will always enter these formulae as  $\cos^2 \chi$ .

Before explaining the symbols  $D$ ,  $E$ , etc. in terms of molecular quantities we will first pay attention to their experimental determination.

With the aid of the relative intensity change induced by the field  $F$  a function  $L_x(\nu)$  may be defined, which depends on measurable quantities only.

$$L_x(\nu) \equiv \frac{I_{x, F=0} - I_{x, F}}{I_{x, F=0}} \frac{1}{2.303 D F^2} \quad 5.11$$

Here  $I_{x, F}$  represents the intensity of the linearly polarized light beam, leaving the sample, when the field has a value  $F$ ;  $D$  is the optical density of the solution at frequency  $\nu$ . Owing to the fact, that the second term on the right hand side of equation (5.7) is small compared to unity, we find:

$$L_x(\nu) = A_x + \frac{1}{15h} B_x \frac{d \ln \epsilon / \nu}{d\nu} + \frac{1}{30h^2} C_x \left\{ \left( \frac{d \ln \epsilon / \nu}{d\nu} \right)^2 + \frac{d^2 \ln \epsilon / \nu}{d\nu^2} \right\} \quad 5.12$$

In (5.11) the strength of the local field acting on the solute molecules is required. For this we take the Lorentz field as



a sufficient approximation in nonpolar solvents.

From the experimental results, which will be discussed later, it follows, that in (5.12) the term containing  $C_\chi$  makes a relative small contribution.

In view of the following discussion we introduce the notation listed below:

$$\beta \equiv 1/kT \quad \underline{\mu} \equiv \underline{\mu}(i)$$

$$\underline{\Delta\mu} \equiv \underline{\mu}(f) - \underline{\mu}(i) \quad \underline{\alpha} \equiv \underline{\alpha}(i)$$

$$\underline{\Delta\alpha} \equiv \underline{\alpha}(f) - \underline{\alpha}(i) \quad \underline{p} \equiv \frac{P}{P}$$

Tr Q  $\equiv$  trace of the second rank tensor Q.

For an arbitrarily chosen molecule the expressions for  $D$ ,  $E$ ,  $F$  and  $G$  are unwieldy. They will be given in the appendix. A special model may simplify them considerably. The charge transfer complexes studied in this paper consist of aromatic moieties and therefore are assumed to be of a sandwich type, having their transition moment, dipole moments in the ground and charge transfer state, along the same axis, to which we shall refer as  $z$  direction. Such a model seems sensible, considering the experimental observations of parallel molecular planes<sup>3</sup> and  $z$  polarized charge transfer transitions<sup>11</sup>. In addition only the  $A_{zz}$  and  $B_{zzz}$  components of the transition polarizabilities are considered to be nonzero. Realizing that  $A_{zz}/P$  must be very small compared to unity, we disregard terms in  $(A_{zz}/P)^2$  and as a consequence also terms in  $B_{zzz}/P$ . We reported in a previous paper<sup>10</sup> that no molecular orientation due to an anisotropic polarizability could be detected in fields of 120 KV/cm. Since one expects a very large  $\Delta\mu$  the contribution of  $\Delta\mu$  to the frequency shift may also be ignored. With these assumptions the following very simple relations are obtained:

$$D = 2\beta \frac{A_{zz}}{P} \mu \quad 5.13$$

$$E = 2\beta^2 \mu^2 + 4D \quad 5.14$$

$$F = \frac{1}{2} G = \left\{ \beta\mu + 2 \frac{A_{zz}}{P} \right\} \Delta\mu \quad 5.15$$

Within this picture these equations provide a means to determine the molecular quantities appearing on the right hand sides. The relation  $F = \frac{1}{2} G$  may be used for direct experimental verification of the model.

## Results

We have examined the charge transfer band of a number of complexes by measuring the relative intensity change due to an external field of 120 KV/cm. The samples were kept at room temperature. The curves for  $L_\chi(\sigma)$  are all smooth, showing no scatter of experimental points around the curve. A typical example is presented in fig 5.1. The derivatives

$\frac{d \ln \epsilon/\sigma}{d\sigma}$  and  $\frac{d^2 \ln \epsilon/\sigma}{d\sigma^2}$  have been evaluated numerically from point by point measurements of

the optical density at a bandwidth  $\leq 0.3 \mu\mu$ , using our spectrometer designed for electro-optical work. The quantities

$\frac{d \ln \epsilon/\sigma}{d\sigma}$  and  $\left\{ \left( \frac{d \ln \epsilon/\sigma}{d\sigma} \right)^2 + \frac{d^2 \ln \epsilon/\sigma}{d\sigma^2} \right\}$  have been used as independent variables in a

linear multiple regression analysis of  $L_\chi$  to obtain  $A_\chi$ ,  $B_\chi$  and  $C_\chi$  (table 5.1). From a statistical point of view this method is to be preferred over the iterative procedure proposed by Liptay<sup>7</sup>, which does not provide a test on the validity of the theory. The values found for  $C_\chi$  do always show such a large relative error that it is not worthwhile considering them. From  $A_\chi$  and  $B_\chi$ , plotted as a function of  $3 \cos^2 \chi - 1$  (fig 5.2), the quantities  $D$ ,  $E$ ,  $F$  and  $G$  are determined. The results are tabulated in table 5.2. The estimated error in  $G/F$  is about 10%.

Table 5.1

Results of the regression analysis of  $L_\chi$  for a number of complexes.

Abbreviations for compounds are explained under table 5.2.

M.C.C. = Multiple Correlation Coefficient;  $S_a$  and  $S_b$  are the standard errors in  $A$  and  $B$ .

	$\chi$	M.C.C.	$10^{10}A_\chi$	$10^{10}S_a$	$10^{23}B_\chi$	$10^{23}S_b$
HMB + CA in $CCl_4$	$0^\circ$	0.97	- 6.55	0.47	549	34
	$54.8^\circ$	0.97	- 3.54	0.27	311	19
	$90^\circ$	0.97	- 2.12	0.16	197	11
HMB + CA in benzene	$0^\circ$	0.95	- 5.17	0.46	455	37
	$54.8^\circ$	0.95	- 2.83	0.26	257	21
	$90^\circ$	0.95	- 1.15	0.14	125	11
Naphtalene + CA in benzene	$0^\circ$	0.97	- 8.97	0.41	665	42
	$54.8^\circ$	0.97	- 5.07	0.23	380	24
	$90^\circ$	0.96	- 2.64	0.17	228	17
Anthracene + TNB in benzene	$0^\circ$	0.98	-14.78	2.0	734	37
	$54.8^\circ$	0.98	- 8.92	1.3	437	24
	$90^\circ$	0.98	- 5.72	0.8	286	15
PPDA + TNB in benzene	$0^\circ$	0.98	2.20	0.17	352	18
	$54.8^\circ$	0.96	0.61	0.14	195	14
	$90^\circ$	0.94	- 0.20	0.11	127	12
Naphtalene + TCNE in $CCl_4$	$0^\circ$	0.98	-10.42	0.59	657	31
	$54.8^\circ$	0.98	- 5.91	0.33	370	18
	$90^\circ$	0.98	- 3.71	0.22	228	11
H.M.B. + TCNE in $CCl_4$	$0^\circ$	0.94	6.95	0.40	258	22
	$54.8^\circ$	0.95	2.81	0.22	153	12
	$90^\circ$	0.96	0.78	0.13	95	7
Mesitylene + TCNE	$0^\circ$	0.97	-18.13	0.83	789	60
	$54.8^\circ$	0.98	-10.41	0.43	436	31
	$90^\circ$	0.97	- 6.93	0.30	290	21
Benzene + TCNE	$0^\circ$	0.99	-11.48	0.53	727	37
	$54.8^\circ$	0.99	- 6.65	0.27	407	18
	$90^\circ$	0.99	- 4.28	0.18	264	12

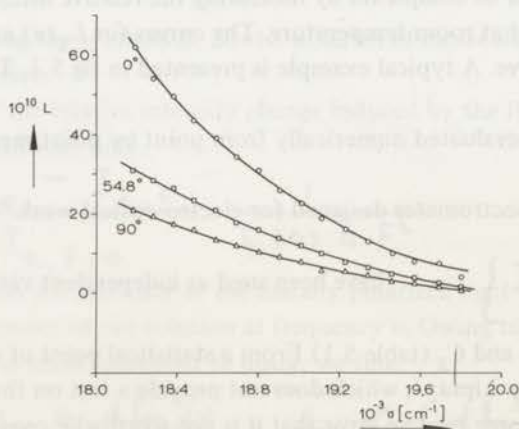


Fig 5.1

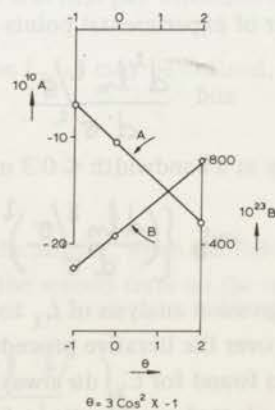
Mesitylene-TCNE in mesitylene as solvent;  $L' = fL$  where  $f$  is the Lorentz field factor.

Fig 5.2

Mesitylene-TCNE

Table 5.2  
Molecular quantities derived from the charge transfer band of some complexes

	$10^{10}D$	$10^{10}E$	$10^{23}F$	$10^{23}G$	$G/F$	$10^{10}E-4D$	$10^{18}\mu$	$10^{18}\Delta\mu$
HMB + CA in $CCl_4$	-10.7	- 44.3	62.6	118	1.9	- 1.4	< 0.6 1. <sup>3</sup>	
HMB + CA in $C_6H_6$	- 7.8	- 39.5	48.5	109	2.2	- 8.1		
Naphtalene + CA	-14.5	- 63	74.3	146	2.	- 4.9		
Anthracene + TNB	-26.4	- 90.3	87.2	149	1.7	15.3	1.1	-10.9
PPDA + TNB	1.8	24.	39.9	75.7	1.9	16.8	1.2	11.2
Naphtalene + TCNE	-17.8	- 67.2	74.2	143	1.9	4.	0.6	- 6.4
HMB + TCNE	9.	64.6	29.9	53.9	1.8	28.8	1.6	4.5
							1.35 <sup>3</sup>	5.0 <sup>16</sup>
							1.5 <sup>14</sup>	
							1.64 <sup>15</sup>	
Mesitylene + TCNE	-31.7	-112.6	89.9	168	1.9	14.2	1.1	- 9.4
							1.1 <sup>14</sup>	
							1.12 <sup>15</sup>	
Benzene + TCNE	-20.	- 72.	82.8	155	1.9	8.	0.8	- 9.8
							1.0 <sup>14</sup>	
							0.75 <sup>15</sup>	

HMB = Hexamethylbenzene  
 CA = Chloranil  
 TNB = Trinitrobenzene  
 PPDA = Paraphenylenediamine  
 TCNE = Tetracyanoethylene

All quantities are in electrostatic units.

### Discussion

The multiple correlation coefficients indicate that the model leading to eq (5.15) covers the experimental data nearly perfectly. A remarkable high value for  $D$  has been found in most cases, which means that the field  $F$  affects the intensity of the transition significantly. There are three effects, one may think of as causing an intensity change:

1. A deviation from the equilibrium distance between the molecular planes of donor and acceptor.
2. A field dependence of the equilibrium constant.
3. The mixing of electronic states.

Points 1 and 2 can be ruled out as we shall show, by estimating their magnitudes.

#### Ad 1

Let us consider the interaction energy  $W_{int}$  of the dipole moments  $\mu_d$  and  $\mu_a$ , induced in donor and acceptor by an external field in the  $z$  direction, as a function of the intermolecular distance  $R$ .

$$W_{int}(R) = - \frac{2 \mu_a \mu_d}{R^3} \quad 5.16$$

The total energy of the complex may be written as

$$V(F, R) = V_0(R) - \frac{2 \mu_a \mu_d}{R^3} \quad 5.17$$

If we choose for  $V_0(R)$  a harmonic potential, the new equilibrium distance may be determined from the condition

$$d V(F, R) / dR = 0$$

For the system benzene - tetracyanoethylene we estimate the relative change in intermolecular distance to be  $\Delta R_e/R_e \approx -1 \times 10^{-7}$ . We have assumed a field of 120 KV/cm,  $a_{zz} = 10 \text{ \AA}^3$ <sup>12</sup> for benzene,  $a_{zz} = 20 \text{ \AA}^3$  for TCNE and a fundamental frequency as low as  $100 \text{ cm}^{-1}$  for the oscillator.

In the same manner we can estimate the increase in intermolecular distance due to the repulsive interaction  $W'_{\text{int}}$  of the dipoles  $\mu'_d$  and  $\mu'_a$  induced in the planes of donor and acceptor respectively.

$$W'_{\text{int}} = \frac{\mu'_a \mu'_d}{R^3} \quad 5.18$$

The in-plane components of  $a$  for benzene are  $a_{xx} = a_{yy} \approx 10 \text{ \AA}^3$ <sup>12</sup>. If we take an average in-plane polarizability  $\frac{1}{2}(a_{xx} + a_{yy}) \approx 40 \text{ \AA}^3$  for TCNE we estimate the relative change in  $R$  to be  $\Delta R_e/R_e \approx 1 \times 10^{-7}$ .

The simple description<sup>4</sup> of the complex in terms of a covalent state  $\Psi_0$  and a charge transfer state  $\Psi_1$  leads to a ground state  $\Psi_N = a\Psi_0 + b\Psi_1$  and an excited state  $\Psi_E = a'\Psi_1 - b'\Psi_0$ . In sufficient approximation the transition moment is given by  $P \approx a'b\mu(1)$ , which is in the  $z$  direction. The dipole moment  $\mu(1)$  of the charge transfer state may be approximated by  $\mu(1) \approx -eR$ . Usually  $a' \approx 1$  and  $b \approx \frac{\beta}{\Delta}$ , where  $\beta \equiv \langle \Psi_1 | H | \Psi_0 \rangle$  and  $\Delta \approx E_1 - E_0$ , so that to estimate the variation of  $P$  with  $R$ , we shall start from  $P \approx \frac{\beta}{\Delta} \mu(1)$ .

$$\frac{dP}{dR} \approx \frac{d\beta}{dR} \frac{\mu(1)}{\Delta} + \frac{\beta}{\Delta} \frac{d\mu(1)}{dR} = \left\{ \frac{1}{\beta} \frac{d\beta}{dR} + \frac{1}{R} \right\} P \quad 5.19$$

If we take  $\beta \sim S_{01} \sim R^4 \exp(-1.6R)$ , where the last expression represents the overlap between two  $2p$  orbitals at large distance with  $R$  in atomic units<sup>18</sup>, we estimate that a relative change in equilibrium distance of  $10^{-7}$  causes  $\Delta P \approx 10^{-6}P$ . When  $P \approx 1$  Debye this corresponds to a component of the transition polarizability  $A_{zz} \approx 10^{-27}$ , whereas an observable contribution to  $D$  would require  $A_{zz} > 10^{-23}$ .

#### Ad 2

The theory of the field dependence of an equilibrium constant, developed by Bergman et al<sup>13</sup>, may be used to obtain an order of magnitude. Assuming nonpolar components and a dipole moment of 1 Debye for the complex, we estimate

$${}^{10} \log \frac{k_F}{k_0} \approx 4 \times 10^{-16} \text{ in a field of } 120 \text{ KV/cm.}$$

#### Ad 3

The mixing of electronic states remains as the most probable origin of intensity changes. In an idealized system with  $C_{2v}$  symmetry the transition polarizability  $A$  will be diagonal for a transition moment along the twofold axis of symmetry ( $z$  direction). If for a transition of this type the relation  $G = 2F$  holds, then it is obvious from the general expressions that only the  $A_{zz}$  component should be nonzero. Since such an idealization may be very close to reality for certain donor-acceptor pairs, it provides some justification for our model proposed at the beginning.

The equations (5.13) to (5.15) enable in principle the determination of  $A_{zz}/P$ ,  $\mu$  and  $\Delta\mu$ . Results are given in table 5.2. For comparison the magnitudes obtained by other methods are also presented in this table. The ground state dipole moments of the complexes of TCNE with the substituted benzenes are in excellent agreement with our dielectric measurements<sup>14</sup> and also with the values of R.K. Chan and S.C. Liao<sup>15</sup>. The  $\Delta\mu$ -value for HMB-TCNE is about equal to what we find from solvent induced shifts of the absorption maximum<sup>16</sup>. The very surprising result that in some cases the vectors  $\mu$  and  $\Delta\mu$  are antiparallel may be explained by small deformations in the constituents. If the CN groups in TCNE are bent a little out of plane in the direction of the donor, this will introduce a dipole opposed to the 'mesomeric moment'. Since the partial moment of the CN group is about 4 Debye, an inclination of  $6^\circ$  for the four CN groups will already yield a dipole moment of 1.6 Debye. In the series of substituted benzenes with TCNE we see that the charge transfer has overcome this effect in HMB-TCNE.

Considering  $\mu$  to be in the positive  $z$  direction, we see by inspecting the  $D$  values in table 2 that  $\Delta\mu$  and  $A_{zz}/P$  always have the same sign. Since the simple theory (see ad 1) predicts  $P$  to be in the direction of  $\Delta\mu$ , we infer that in all cases the transition moment increases when a field  $F$  is applied in the direction of  $P$ .

#### Experimental

In our spectrometer we have used a 500 m.m. Bausch and Lomb 1200 lines/m.m. grating monochromator and a XBO 900 lamp. The field modulation introduced by Labhart<sup>17</sup> has been used in conjunction with a Lock-in amplifier and a ratio recording system. We have measured point by point, using a time constant of 12 sec.

## Chemicals

Hexamethylbenzene, anthracene and naphthalene were zone refined. Tetracyanoethylene and paraphenylenediamine were sublimed in a stream of dry nitrogen. PPDA obtained in this way was absolutely white. Chloranil was sublimed in vacuum and trinitrobenzene has been recrystallized from ethanol. Mesitylene was treated with concentrated sulphuric acid.

## Acknowledgement

One of us (V) is indebted to the Netherlands Foundation for Chemical Research (S.O.N.) for sponsoring his work.

## Appendix

The general expressions for the coefficients  $D$ ,  $E$ ,  $F$ ,  $G$ ,  $H$  and  $I$  are:

$$A_x = \frac{1}{3} D + \frac{1}{30} E (3 \cos^2 \chi - 1) \quad 5.20$$

$$B_x = 5 F + G (3 \cos^2 \chi - 1) \quad 5.21$$

$$C_x = 5 H + I (3 \cos^2 \chi - 1) \quad 5.22$$

$$D = 2\beta \frac{P \cdot A \cdot \mu}{P^2} + \frac{1}{P^2} \sum_{ij} A_{ij}^2 + \frac{2}{P^2} \sum_{ij} P_i B_{ijj} \quad 5.23$$

$$E = \beta^2 [3(\underline{\mu} \cdot \underline{p})^2 - \mu^2] + \frac{3}{2} \beta \underline{p} \cdot \underline{\alpha} \cdot \underline{p} - \frac{1}{2} \beta \text{Tr} \underline{\alpha} \quad 5.24$$

$$+ 6\beta \frac{(\underline{\mu} \cdot \underline{P}) \text{Tr} \underline{A}}{P^2} + 6\beta \frac{\underline{\mu} \cdot \underline{A} \cdot \underline{P}}{P^2} - 4\beta \frac{P \cdot A \cdot \mu}{P^2}$$

$$+ \frac{3}{P^2} (\text{Tr} \underline{A})^2 + \frac{3}{P^2} \sum_{ij} A_{ij} A_{ji} - \frac{2}{P^2} \sum_{ij} A_{ij}^2$$

$$+ \frac{6}{P^2} \sum_{ij} P_i B_{jij} + \frac{6}{P^2} \sum_{ij} P_i B_{jji} - \frac{4}{P^2} \sum_{ij} P_i B_{ijj}$$

$$F = \beta \underline{\mu} \cdot \underline{\Delta} \underline{\mu} + 2 \frac{P \cdot A \cdot \Delta \mu}{P^2} + \frac{1}{2} \text{Tr} \underline{\Delta} \underline{\alpha} \quad 5.25$$

$$\zeta = \beta [3(\underline{\mu} \cdot \underline{p})(\underline{\Delta\mu} \cdot \underline{p}) - \underline{\mu} \cdot \underline{\Delta\mu}] \quad 5.26$$

$$+ \frac{3}{2} \underline{p} \cdot \underline{\Delta\alpha} \cdot \underline{p} - \frac{1}{2} T_h \underline{\Delta\alpha}$$

$$+ 3 \frac{(\underline{\Delta\mu} \cdot \underline{p}) T_h A}{p^2} + 3 \frac{\underline{\Delta\mu} \cdot A \cdot \underline{p}}{p^2} - 2 \frac{\underline{p} \cdot A \cdot \underline{\Delta\mu}}{p^2}$$

$$H = (\Delta\mu)^2 \quad 5.27$$

$$II = 3(\underline{\Delta\mu} \cdot \underline{p})^2 - (\Delta\mu)^2 \quad 5.28$$

It should be noted that in these expressions all components may be considered as related to molecular coordinate axis.

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## CHAPTER 6

### A METHOD TO EVALUATE DIPOLE MOMENTS OF ELECTRONICALLY EXCITED MOLECULES FROM SOLVENT FIELD EFFECTS ON ABSORPTION SPECTRA

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Starting from the existing theory of long range solute solvent interactions we have derived a method to estimate dipole moments of excited molecules. The advantage over other methods is that it is not restricted to fluorescent molecules. The results compare favourably with those found from the influence of a strong electric field on absorption bands. It is shown that the usual method which combines fluorescence and absorption measurements is not always adequate.

#### Introduction

The basic theory treating the implications of electrostatic solute-solvent interactions on the spectra of solute molecules has been presented in a paper by Ooshika<sup>1</sup>. Various modifications of his theory have been applied to evaluate dipole moments of first electronically excited singlet states from observed shifts in both absorption and fluorescence spectra. For a review the reader is referred to an article by Liptay<sup>2</sup>.

It is the purpose of this work to present a procedure which may be used to determine the dipole moment in any excited state, provided the corresponding bands do not overlap other electronic transitions. The experimental part involves the measurements of absorption spectra in different solvents. Consequently the method is not restricted to molecules showing fluorescence in liquid solutions and leads the way to a wide range of applications.

#### Theoretical background

For the sake of convenience we give a list of symbols used frequently in this paper.

$n_i$  and  $\epsilon_i$  are refractive index and dielectric constant of the  $i^{\text{th}}$  solvent respectively.

$$Q_i \equiv \frac{n_i^2 - 1}{2n_i^2 + 1}$$

$$S_i \equiv \frac{\epsilon_i - 1}{2\epsilon_i + 1}$$

$a_0$  and  $a$  are the radii of the cavities needed to store a solute molecule in its ground- and excited state respectively;

$\Delta a \equiv a - a_0$ .

$\sigma(O)$  is the wavenumber of the O—O transition observed in the gasphase;  $\delta_a$  and  $\delta_f$  measure the energy separation from the O—O transition of the maximum in absorption and fluorescence respectively;  $e$  and  $m$  are charge and mass of an electron.

$h$  is Planck's constant

$f$  is the oscillator strength

$\mu_g$  and  $\mu_e$  are dipole moments in ground- and excited state respectively.

$\Delta\mu \equiv \mu_e - \mu_g$

The solute molecule is treated as a nonpolarizable point dipole situated in a spherical cavity in the solvent, which is considered as a continuous dielectric body. In the course of absorption the radius  $a_0$  of the cavity is determined by the size of the solute in its ground state. Possible changes in equilibrium distances in the solute after excitation necessitate the introduction of another radius  $a$  for the process of fluorescence.

Apart from the dispersion energy, the solute-solvent interactions may be treated classically as an interaction of the Onsager reaction field with the dipole moment of the solute<sup>2,3</sup>. The dispersion interaction between the solute and the surrounding solvent molecules leads to a shift  $\Delta E_d$  in the transition energy, given by  $\Delta E_d = -2Q_i D/a^3$ .

According to Liptay<sup>2</sup> D is approximately given by:

$$D = \frac{1}{2} \frac{E_e - E_g}{(\bar{E}_m - E_g)(\bar{E}_m - E_e)} \left\{ \frac{3}{2\pi} \frac{\hbar e^2}{m} + (\lambda \bar{E}_m - E_e - E_g) P^2 \right\} \quad 6.1$$

Here  $E_e$  and  $E_g$  are unperturbed energies of final- and initial state involved in the transition, while  $\bar{E}_m$  is some average energy for all other states of the solute.  $P$  is the transition moment.

In fact a detailed expression for  $D$  is not needed for our purpose. What really matters, is whether the dispersion contribution can be factorized in a factor  $2 Q_i/a^3$  depending on the solvent and a factor  $D$  determined completely by the solute. Regarding fluctuations in molecular charge densities as responsible for dispersion interaction, one would expect such a separation to hold. In the factor which stems from the solute one would anticipate a term in  $P$ , arising during the transition and a term independent of it, caused by charge fluctuations in each of the two states. Because the fluctuations are faster than the orientational relaxation of the solvent molecules, the factor arising from the solvent should be the same as in the induction part of a reaction field. One may consider the observed linear relation<sup>2</sup> between  $\sigma_i$  and  $Q_i$  for nonpolar solutes as an empirical justification for the separation (eq 6.2).

Realizing that different vibronic states are involved in the maxima of absorption and fluorescence we shall discriminate between the corresponding dispersion shifts by labelling them respectively as  $D^a$  and  $D^f$ .

Knowledge of some experimentally estimated  $D^a$  values as a function of the oscillator strength may be useful in view of the results to be discussed. From table 1 in the article by Liptay<sup>2</sup> we derive the following  $D$  values for three absorption bands of naphthalene by assuming a cavity radius  $a_0 = 3.5 \text{ \AA}$ .

	f	$10^{36}D$
${}^1L_b$	0.002	6.5
${}^1L_a$	0.18	20.6
${}^1B_b$	1.7	48.6

Accounting for the interaction of the dipole moments in the ground- and excited states with the corresponding reaction fields the complete expression for the wavenumber  $\sigma_i^a$  of an absorption maximum observed in the  $i^{\text{th}}$  solvent is given by:

$$\sigma_i^a = \sigma(0) + \frac{\delta_a}{hc} - \frac{2D^a}{hc} \frac{Q_i}{a_0^3} - \frac{(\Delta\mu)^2}{hc} \frac{Q_i}{a_0^3} - \frac{2(\Delta\mu \cdot \mu_g)}{hc} \frac{S_i}{a_0^3} \quad 6.2$$

A similar equation holds for the fluorescence maximum  $\sigma_i^f$

$$\sigma_i^f = \sigma(0) - \frac{\delta_f}{hc} - \frac{2D^f}{hc} \frac{Q_i}{a_0^3} + \frac{(\Delta\mu)^2}{hc} \frac{Q_i}{a_0^3} - \frac{2(\Delta\mu \cdot \mu_e)}{hc} \frac{S_i}{a_0^3} \quad 6.3$$

If we consider  $\Delta a/a_0$  as small compared to unity we obtain from a Taylor series expansion of eq (6.3) around  $a_0$ , retaining the first two terms

$$\sigma_i^f = \sigma(0) - \frac{\delta_f}{hc} - \frac{2D^f}{hc} \frac{Q_i}{a_0^3} + \frac{(\Delta\mu)^2}{hc} \frac{Q_i}{a_0^3} - \frac{2(\Delta\mu \cdot \mu_e)}{hc} \frac{S_i}{a_0^3} - \frac{3\Delta a}{a_0} \left\{ -\frac{2D^f}{hc} \frac{Q_i}{a_0^3} + \frac{(\Delta\mu)^2}{hc} \frac{Q_i}{a_0^3} - \frac{2(\Delta\mu \cdot \mu_e)}{hc} \frac{S_i}{a_0^3} \right\} \quad 6.4$$

Equations (6.2) and (6.3) differ from previously reported formulae<sup>2</sup> so far as the introduction of different cavities and dispersion terms for absorption and fluorescence is concerned.

#### Procedure

The wavenumber for the absorption maximum is determined in a number of solvents, labeled by the index  $i$ . We now define the difference quotients  $Y(ij)$  and  $X(ij)$ .

$$Y(ij) \equiv \frac{\sigma_i^a - \sigma_j^a}{Q_i - Q_j} \quad X(ij) \equiv \frac{S_i - S_j}{Q_i - Q_j} \quad 6.5$$



From eq (6.2) we derive the following linear relation between Y(ij) and X(ij):

$$Y(ij) = \frac{\lambda D^a + (\Delta\mu)^2}{hca_0^3} + \frac{\lambda (\Delta\mu \cdot \mu_g)}{hca_0^3} X(ij) \quad 6.6$$

With the experimentally determined values  $\sigma_i^a$ ,  $n_i$  and  $\epsilon_i$  at hand, a number of Y(ij) and X(ij) values can be generated. The slope of the straight line obtained by plotting Y(ij) against X(ij) gives according to eq (6.6) the inner product  $2(\Delta\mu \cdot \mu_g)/hca_0^3$ . If  $a_0$  and  $\mu_g$  are known  $\Delta\mu$  may be determined and used to evaluate  $D^a$  from the intercept.

## Applications

The linear behaviour described by eq (6.6) has been verified by locating the maxima of the first absorption band in different solvents for a number of compounds. Values of  $\sigma_j^a - \sigma_i^a$  smaller than  $50 \text{ cm}^{-1}$  and  $Q_i - Q_j < 0.01$  have not been considered in the plots, presented in figs 6.2 to 6.9. In all cases the observed linearity is satisfactory. We summarize the experimental data in table 6.1 and the final results in table 6.2. Throughout this work dipole moments are given in Debye units, D in electrostatic units.

Table 6.1  
Survey of experimental data. Wavenumbers are given in  $[\text{cm}^{-1}]$ .

Solvent	$\epsilon$	n	NMA		PDM	PB	SMC	DAMC	HMB - TCNE	Mes - TCNE
			$10^{-3}\sigma_a$	$10^{-3}\sigma_f$	$10^{-3}\sigma_a$	$10^{-3}\sigma_a$	$10^{-3}\sigma_a$	$10^{-3}\sigma_a$	$10^{-3}\sigma_a$	$10^{-3}\sigma_a$
n-Hexane	1.89	1.372							19.14	
iso-Octane	1.95	1.391							19.05	22.31
Cyclohexane	2.02	1.424							18.94	22.12
Methylcyclohexane	2.07	1.421	25.77	25.00						
Carbon tetrachloride	2.24	1.459	25.38	24.75	23.34	17.86			18.74	21.83
Mesitylene	2.27	1.497								22.47
Anisole	4.3	1.515	25.06	24.30						
Diethylether	4.34	1.352	25.58	24.94						
Chloroform	4.81	1.444			24.51				18.55	21.53
Chlorobenzene	5.62	1.523	25.09		24.13	17.23		19.32		
Ethylacetate	6.02	1.370	25.30	24.54	24.81	17.59		19.57		
Morpholine	7.33	1.455	25.00	24.15			16.61			
Tetrahydrofuran	7.39	1.404	25.32	24.60						
Dichloromethane	9.08	1.424	25.03	24.24	24.72	17.05		19.18		
o-Dichlorobenzene	9.80	1.551	25.06	24.39						
Pyridine	12.3	1.507		24.16		16.91	16.56	18.76		
Acetone	20.7	1.357	25.16	24.36	25.25					
Acetonitrile	37.5	1.342	25.08	24.27		17.24	17.62	18.80		
Dimethylformamide	38.0	1.427				16.94	17.18	18.38		

Table 6.2  
Summary of the results

$M_a$ ,  $N_a$  and  $M_f$ ,  $N_f$  are intercept and slope in eqs (6.6) and (6.9) respectively;  
(b): values obtained from solvent effects; (c): values from electro-optical studies.

	$[\text{cm}^{-1}]$ $10^{-3}M_a$	$[\text{cm}^{-1}]$ $10^{-3}M_f$	$[\text{cm}^{-1}]$ $10^{-3}N_a$	$[\text{cm}^{-1}]$ $10^{-3}N_f$	$[\text{\AA}]$ a	[D] $\mu_g$	[D] $\Delta\mu(b)$	[D] $\Delta\mu(c)$	[e.s.u.] $10^{36}D$
N-methylacridone	4.6	4.9	2.1	2.7	3.6	5.4	1.8	1.9	20
Pyridiniumdicyanomethylide	11.2		-6.2		3.3	8.0	-2.8	-2.6	36
Phenolblue	7.9		4.1		5.0	5.8	$\geq 8.9$		$\leq 59$
Stilbene-merocyanine	15.5		-5.6		5.5	26.	-3.6		250
Diaza-merocyanine	7.6		9.5		4.6	13.2	7.0	7.3	50
Hexamethylbenzene - TCNE	10.2		2.0		3.5	1.6	5.3	4.5	30
Mesitylene - TCNE	15.7		3.1		3.3	1.1	10.1		6

## Discussion

### A. General

Some workers in the field of solvent induced spectral shifts<sup>4</sup> have unjustly assumed that electrostatic interactions fully account for the observed solvent effects. In general specific chemical interactions due to charge overlap between solvent and solute will be superimposed on long range interactions. The idea of Chakrabarti and Basu<sup>4</sup> that the choice of three solvents leads to three equations of the type (6.2), sufficient to determine  $\sigma_o$ ,  $\mu_g$  and  $\Delta\mu$ , may lead to serious errors.

The advantage of the method described above is that to a certain extent it reveals strong specific interactions (e.g. Mesitylene - TCNE) and averages over weak chemical effects.

As in all theories working with the Onsager reaction field we are confronted with the proper choice of the cavity radius. However, independent of the choice one may already see from the sign of  $\Delta\mu \cdot \mu_g$  whether an increase or decrease of dipole moment accompanies excitation. In molecules where there is no pronounced difference in short and long axis, the volume of the spherical cavity may be estimated by adding the Van der Waals volume increments<sup>5</sup>. In the case of molecules with the dipole moment along the long axis we rely for the determination of the radius on the method of Lippert<sup>6</sup>. He takes the diameter of the sphere equal to 80% of the long axis of the most suitable ellipsoidal cavity.

It is instructive to compare the magnitudes of  $\Delta\mu$  with those derived by an alternative and more precise method. A strong external electric field  $F$  causes a frequency shift of the absorption band  $h\Delta\nu = -\Delta\mu \cdot F$  which may be determined. For an extensive treatment of this sort of electro-optical phenomena the reader is referred to work of Labhart<sup>7</sup>, Liptay<sup>8</sup> and Varma<sup>9</sup>. At the end of this paper a short discussion of this topic will be presented, as far as it is related to the present work. Although electro-optical studies are more precise, the present method remains attractive in view of its wider scope of applicability and its experimental simplicity. Eventually it may be used to test peculiar results obtained electro-optically.

### B. Special features

#### 1. N-methylacridone (= NMA, fig 6.2)

N-methylacridone is a compound showing a structured fluorescence band in several liquid solutions, which is the mirror image of the first absorption band (fig 6.1). It is therefore probable that the absorption band covers transitions to only one electronic level. Other evidence is found from electro-optical studies.

In fig 6.2 a plot of  $Y(ij)$  versus  $X(ij)$  is presented from which  $\Delta\mu = 1.8$  and  $D^a = 20 \times 10^{-36}$  are derived. The increase in dipole moment is correct compared to the electro-optical value  $\Delta\mu = 1.9$  and  $D^a$  is compatible with the oscillator strength ( $f \approx 0.1$ ) of the transition.

The existence of fluorescence provokes the application of the method already mentioned in the introduction, which combines the shifts of the maxima in absorption and fluorescence. We define  $Z(i) \equiv \sigma_i^a - \sigma_i^f$  and obtain from eqs (6.2) and (6.4):

$$Z(i) = \frac{\delta_a + \delta_f}{hc} + \frac{2(\Delta\mu)^2}{a_o^3 hc} \Delta f(i) + C_i \quad 6.7$$

where

$$\Delta f(i) \equiv S_i - Q_i$$

$$C_i \equiv \frac{2D^f - 2D^a}{hc} \frac{Q_i}{a_o^3} + \frac{3\Delta a}{a_o} \left\{ -\frac{2D^f}{hc} \frac{Q_i}{a_o^3} + \frac{(\Delta\mu)^2}{hc} \frac{Q_i}{a_o^3} - \frac{2(\Delta\mu \cdot \mu_e)}{hc} \frac{S_i}{a_o^3} \right\} \quad 6.8$$

It is clear from fig 6.2 that observed  $Z$  values are very badly correlated with  $\Delta f$ . This is surprising in view of the results previously reported by Lippert<sup>6</sup> and others, but it might have been expected from our eqs (6.7) and (6.8).

In order to check our suggestion as to the origin of the scatter in fig 6.2, we shall apply the same method, proposed for absorption, but now in the case of fluorescence. If in eq (6.5) the wave numbers are related to the maxima of the fluorescence band, we derive from (6.3) an equation analogous to (6.6).

$$Y_f(ij) = \frac{2D^f - (\Delta\mu)^2}{hc a^3} + \frac{2(\Delta\mu \cdot \mu_e)}{hc a^3} X \dots \quad 6.9$$

Figure 6.2a confirms the linearity predicted by eq (6.9). Since eqs (6.6) and (6.9) are both very well satisfied and the Z values are not all correlated with  $\Delta f$ , it follows that (6.2) and (6.3) must contain terms proportional to  $Q_i$  in addition to the terms in D and  $(\Delta\mu)^2$ . We have tried to write these terms as in eq (6.4), which finally yielded the correction  $C_i$  in eq (6.8). Taking an optimistic view we looked whether a plot of  $Z_i - C_i$  showed a linear behaviour. Bearing in mind that  $\mu_g$  and  $\mu_e$  should be nearly independent of the vibrational part of the wavefunctions, we determine  $a$  from the slope in (6.9) and the already available values  $\mu_g$  and  $\Delta\mu$  and obtain  $a = 3.64 \text{ \AA}$ . Since the cavity radii  $a_0$  and  $a$  turn out to be practically equal, the first part in  $C_i$  may be estimated from the difference ( $300 \text{ cm}^{-1}$ ) between the intercepts in (6.9) and (6.6), which yields  $D^f - D^a = 4.6 \times 10^{-36}$ . It turned out that  $Z_i - C_i$  did not show a significant improvement in correlation with  $\Delta f$ .

Maybe the large errors in the estimated  $C_i$  values have caused the failure, but the misfortune might have originated from a term not yet included in (6.8). If we consider the guest molecule surrounded by the first solvent shell acting as the solute, we expect  $D^f$  to be a function of  $a$ . Equation (6.8) then gains an additional term

$$\frac{3\Delta a}{a_0^3} \left( \frac{dD^f}{da} \right)_{a_0} Q_i$$

In the present state of the investigation this remains only a suggestion.

Regarding the previous discussions it is worthwhile to comment on the method proposed by Baba et al<sup>10</sup>. By proper choice of two solvents in which the dispersion term is supposed to be equal, they derive values for  $a$  and  $\Delta\mu$  from the maxima of absorption and fluorescence in the solutions. Such practice does not provide an internal check on the applicability of a pure electrostatic model and leads to unreliable results. Especially in the case of small  $\Delta\mu$  values one should be careful in this respect. Application of their method yields a magnitude  $\Delta\mu = 3.2$ , which is much too large.

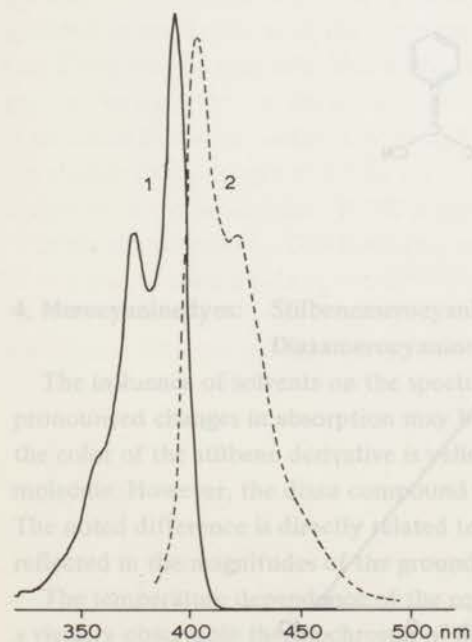


Fig 6.1

Absorption (curve 1) and fluorescence (curve 2) of N-methylacridone in  $\text{CCl}_4$

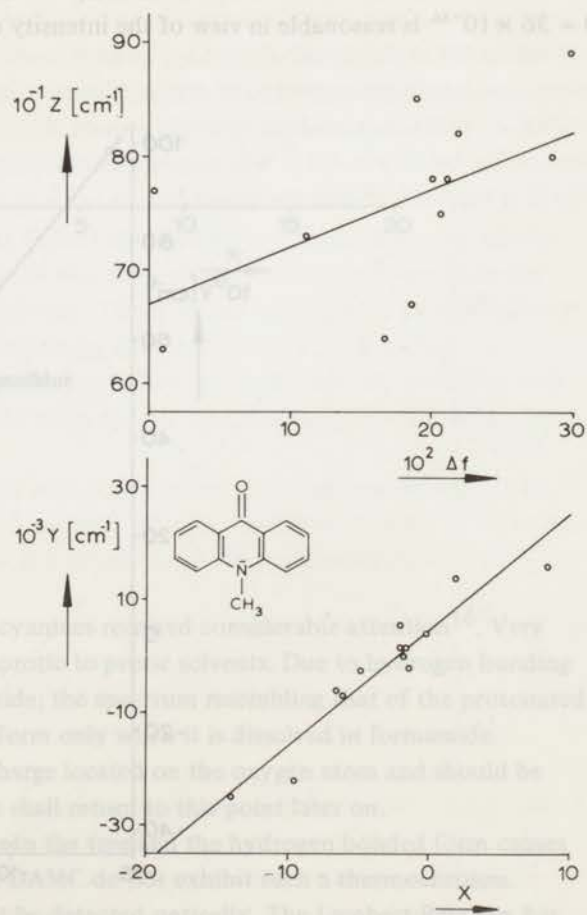


Fig 6.2

N-methylacridone. Plots to verify eqs 6.6 and 6.7

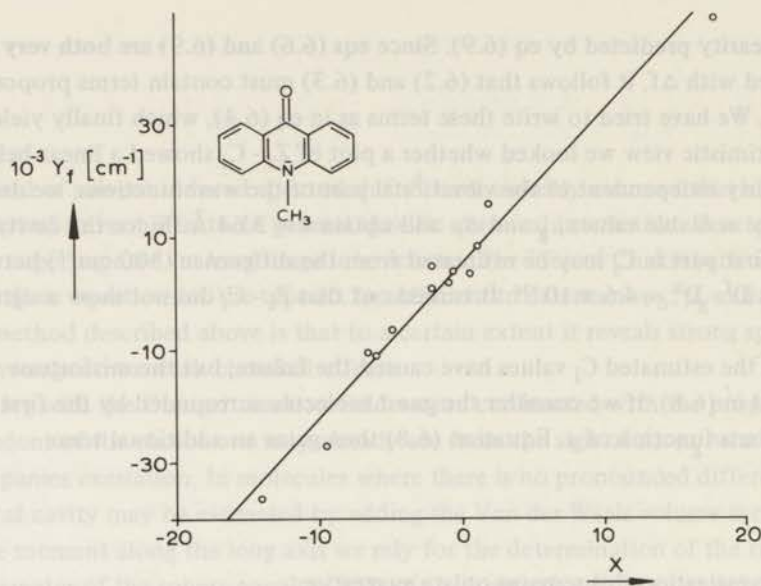


Fig 6.2a

N-methylacridone. Plot to verify eq 6.9

## 2. Pyridiniumdicyanomethylide (= PDM, fig 6.3)

Treiner et al<sup>11</sup> obtained the dipole moment in the ground state from a dielectric study of the monomer-dimer equilibrium in dioxane. Their value  $\mu_g = 9.2$  might be inaccurate, because solubility limited the range of dielectric increments to relative small values, leading to some scatter in the plots. From electro-optical studies of the absorption band we find  $\mu_g = 8$ , and  $\Delta\mu = -2.6$ . Very dilute solutions in  $\text{CCl}_4$  ( $C \leq 7 \times 10^{-5}$  moles/liter) have been used, where dimer formation does not complicate the situation.

We derive from the solvent induced shifts  $\Delta\mu = -2.8$ , in agreement with our electro-optical result. The magnitude  $D = 36 \times 10^{-36}$  is reasonable in view of the intensity of the band ( $f \approx 0.1$ ).

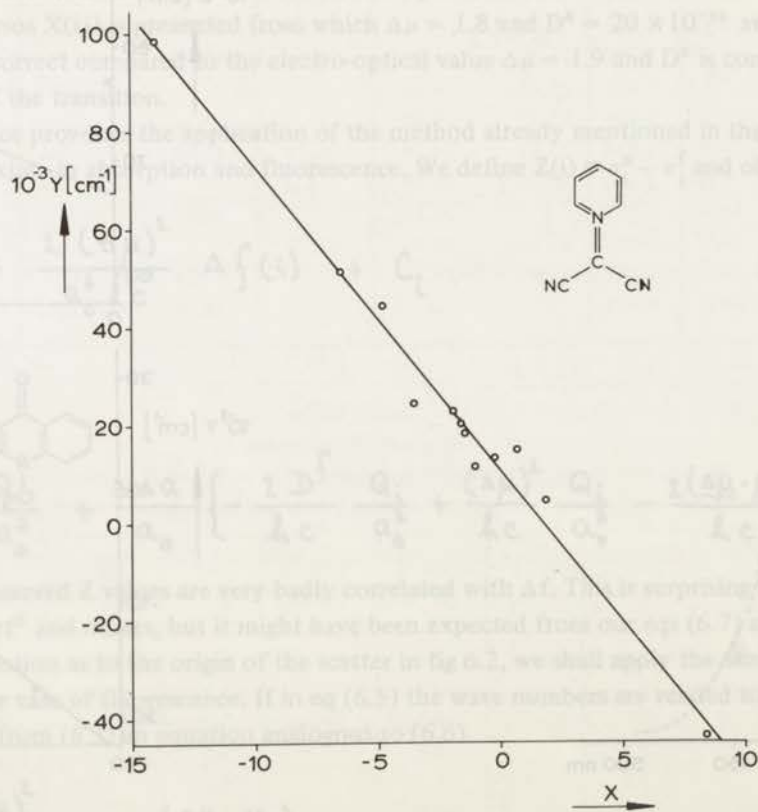


Fig 6.3

Verification of eq 6.6 for Pyridiniumdicyanomethylide

### 3. Phenolblue (= PB, fig 6.4)

Phenolblue has been known for some time<sup>12</sup> to exhibit strong solvent induced spectral shifts. Although several workers<sup>13</sup> tried to give a quantitative interpretation, it is still worthwhile to reconsider the behaviour in this respect. McRae<sup>14</sup> derived a relation for the shift in absorption, which he applied in a rather obscure method to evaluate molecular quantities. Powers et al<sup>14</sup> studied the influence of a strong electric field on the absorption of phenolblue embedded in a rigid matrix. Neither their experiment nor their theory is consistent with current ideas about quantitative interpretation of electro-optical experiments. Kosower<sup>15</sup> presents a treatment on the basis of his Z value theory, which itself has no sound physical basis.

We derive from the slope  $\mu \cdot \Delta\mu = 51.6$ . Since the directions of  $\mu$  and  $\Delta\mu$  are not determined by molecular symmetry a separation of the two will only be possible if the angle  $\theta$  between the two vectors is known. Considering  $\theta = 0^\circ$  we may determine a lower bound  $\Delta\mu = 8.9$  and an upper bound  $D = 59 \times 10^{-36}$ . A value of D larger than in the previous cases is in accordance with the higher intensity of the transition ( $f \approx 0.25$ ).

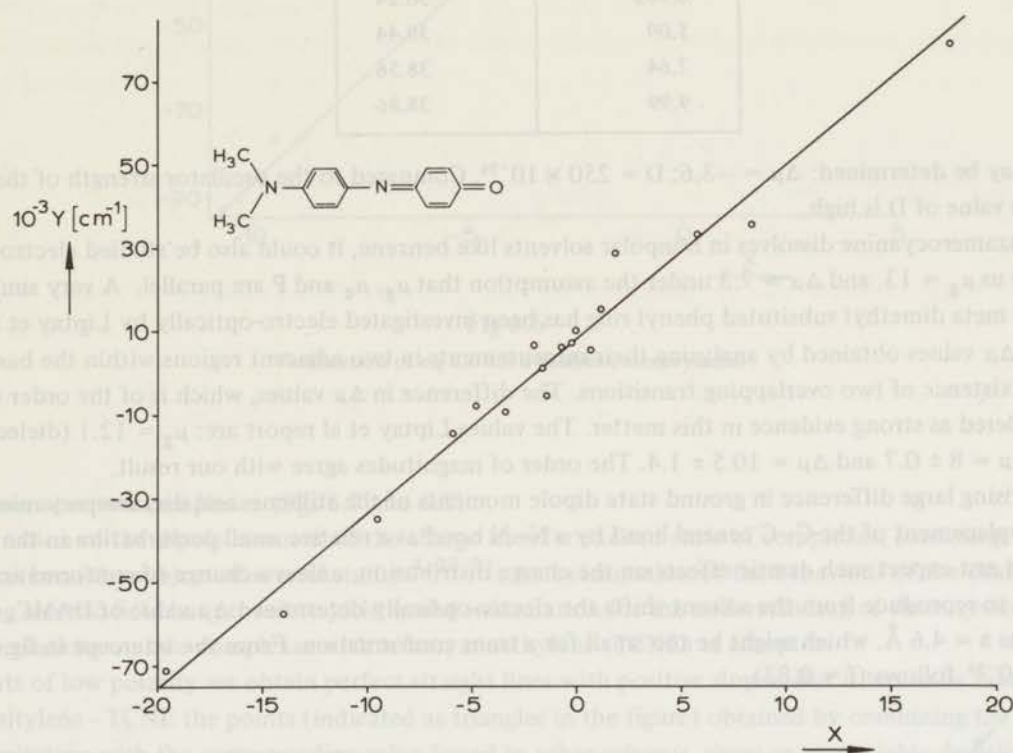


Fig 6.4

Verification of eq 6.6 for Phenolblue

### 4. Merocyaninedyes: Stilbenemerocyanine (= SMC, fig 6.5)

Diazamerocyanine (= DAMC, fig 6.6)

The influence of solvents on the spectra of the highly polar merocyanines received considerable attention<sup>16</sup>. Very pronounced changes in absorption may be observed in going from aprotic to protic solvents. Due to hydrogen bonding the color of the stilbene derivative is yellow in alcohols and formamide; the spectrum resembling that of the protonated molecule. However, the diaza compound resembles the protonated form only when it is dissolved in formamide. The noted difference is directly related to the amount of negative charge located on the oxygen atom and should be reflected in the magnitudes of the ground state dipole moments. We shall return to this point later on.

The temperature dependence of the equilibrium in alcohols between the free and the hydrogen bonded form causes a visually observable thermochroism of SMC. Alcoholic solutions of DAMC do not exhibit such a thermochroism.

Formation of dimers<sup>17</sup> due to dipole-dipole interaction could not be detected optically. The Lambert-Beer law has been verified and holds for concentrations up to  $5 \times 10^{-4}$  moles/liter of the stilbene compound. In order to eliminate disturbances from dimerization we restricted the optical measurements to concentrations below  $2 \times 10^{-5}$  moles/liter.

The extremely high dipole moment of SMC limits its solubility to very polar solvents. Therefore only a small number of points appear in fig 6.5, nevertheless distributed over a sufficiently large range to allow a determination of molecular quantities. If we assume  $\mu_g$  and  $\mu_e$  to be in the same direction, then it follows from the negative slope that the dipole moment decreases upon excitation. We need  $\mu_g$  in order to obtain  $\Delta\mu$ . Since SMC is completely insoluble in nonpolar solvents, we have determined the dielectric constant as a function of concentration in dimethylformamide. From the very simple relation derived by Kirkwood<sup>18</sup>  $\mu_g$  is found in Debye units:

$$\mu_g = 3.30 \left( \frac{d\epsilon}{dC} \right)^{1/2} = 26$$

Table 6.3 summarizes the dielectric measurements.

$10^3 \times C$ [mole/l]	$\epsilon$
0.000	38.17
0.962	38.24
5.09	38.44
7.64	38.56
9.99	38.86

Table 6.3

Now  $\Delta\mu$  and  $D$  may be determined:  $\Delta\mu = -3.6$ ;  $D = 250 \times 10^{-36}$ . Compared to the oscillator strength of the absorption band,  $f \approx 0.6$ , the value of  $D$  is high.

Because the diazamerocyanine dissolves in nonpolar solvents like benzene, it could also be studied electro-optically. These studies give us  $\mu_g = 13$ , and  $\Delta\mu = 7.3$  under the assumption that  $\mu_g$ ,  $\mu_e$  and  $P$  are parallel. A very similar compound with a meta dimethyl substituted phenyl ring has been investigated electro-optically by Liptay et al<sup>19</sup>. On the basis of different  $\Delta\mu$  values obtained by analysing their measurements in two adjacent regions within the band separately, they suggest the existence of two overlapping transitions. The difference in  $\Delta\mu$  values, which is of the order of the error, is not to be considered as strong evidence in this matter. The values Liptay et al report are:  $\mu_g = 12.1$  (dielectric measurements),  $\Delta\mu = 8 \pm 0.7$  and  $\Delta\mu = 10.5 \pm 1.4$ . The order of magnitudes agree with our result.

There is a surprising large difference in ground state dipole moments of the stilbene- and diazamerocyanine. Considering the replacement of the C-C central bond by a N-N bond as a relative small perturbation in the  $\pi$  electron system, one would not expect such drastic effects on the charge distribution, unless a change of conformation is involved. In order to reproduce from the solvent shifts the electro-optically determined  $\Delta\mu$  value of DAMC, we have to take a cavity radius  $a = 4.6 \text{ \AA}$ , which might be too small for a trans conformation. From the intercept in fig 6.6 the value  $D = 50. \times 10^{-36}$  follows ( $f \approx 0.83$ ).

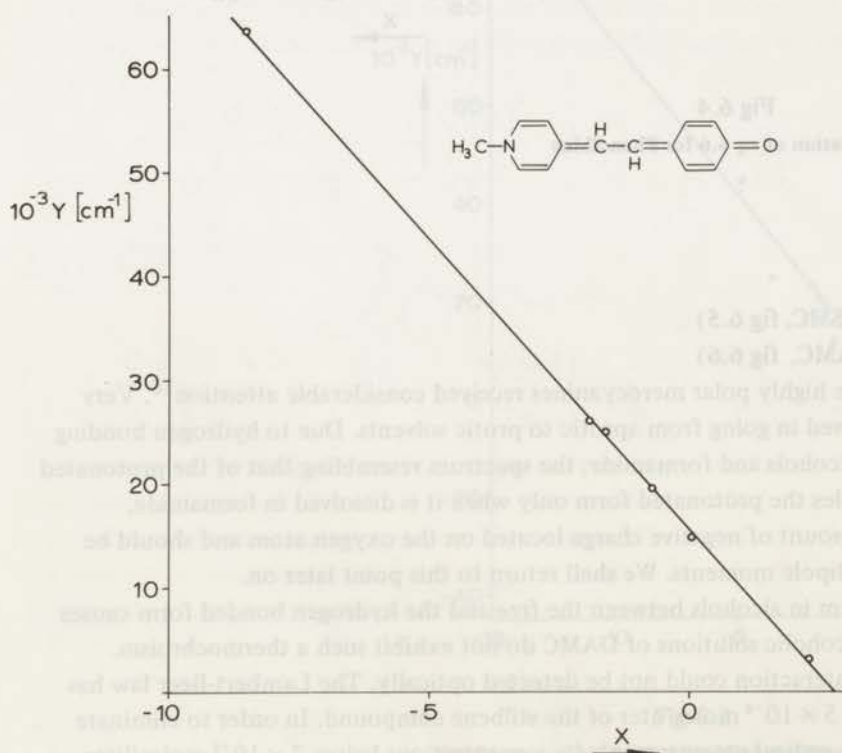


Fig 6.5

Verification of eq 6.6 for a Stilbene-merocyanine

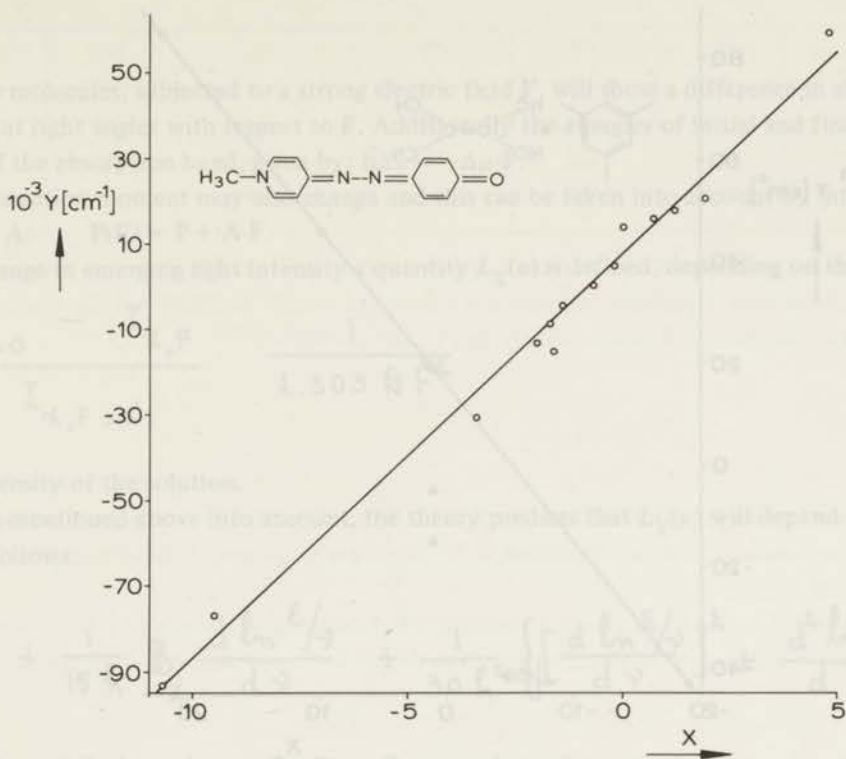


Fig 6.6

Verification of eq 6.6 for a Stilbene-merocyanine

### 5. Electron donor acceptor complexes (figs 6.7 and 6.8)

The determination of the dipole moment of the charge transfer excited state of complexes, consisting of aromatic components, has been the subject of several studies<sup>4, 20, 21</sup>. An examination of the behaviour of the charge transfer band in a strong electric field has proved to yield useful information for the understanding of these systems. We will discuss the observations on two complexes with tetracyanoethylene (TCNE) as acceptor.

Using solvents of low polarity we obtain perfect straight lines with positive slopes. But it has to be mentioned that in the case of mesitylene - TCNE the points (indicated as triangles in the figure) obtained by combining the wavenumber observed in mesitylene with the corresponding value found in other solvents, show an appreciable deviation from the line. From this we may infer that in the two component system mesitylene - TCNE we are dealing with a quite different species. An analysis<sup>22</sup> of the electro-optical behaviour of this two component system gives  $\Delta\mu \cdot \mu_g < 0$  and  $\mu_g = 1.1$ . If we adopt this as the order of magnitude of the ground state moment in the three component system, we derive from the solvent shifts, using  $a = 3.3 \text{ \AA}$ :  $\Delta\mu = 10.1$  and  $D = 6 \times 10^{-36}$ . The value of  $D$  is in accordance with the weak ( $f \approx 0.07$ ) transition in the mesitylene - TCNE complex.

Hexamethylbenzene - TCNE behaves as one should expect from the results of electro-optical measurements in  $\text{CCl}_4$ <sup>22</sup>. With a ground state dipole  $\mu_g = 1.6$ <sup>22, 23</sup> and a cavity radius  $a = 3.5 \text{ \AA}$  we find:  $\Delta\mu = 5.3$  and  $D = 30 \times 10^{-36}$ . The value  $\Delta\mu = 4.5$ , found previously<sup>22</sup>, matches the present result very nicely.  $D$  is larger than in the case mesitylene - TCNE, in accordance with the stronger transition ( $f \approx 0.18$ ).

### Experimental

Absorption spectra have been recorded on a Cary 15 spectrophotometer at a scan speed  $\leq 5 \text{ \AA}/\text{sec}$  and a wavelength scale of  $25 \text{ \AA}/\text{chart division}$ . Fluorescence spectra have been measured on a home made instrument. The emitted light is passed through a Bausch and Lomb 500 mm, 1200 lines/mm grating monochromator and detected on a EMI 6256 photomultiplier. The slitwidth of the emission monochromator was adjusted to obtain a bandwidth  $\leq 4 \text{ nm}$ . In the measurements of the dielectric constant of solutions in dimethylformamide we used a sample cell and bridge, designed for work with conducting liquids. The complete set up has been described by D. Rosen et al<sup>25</sup>.

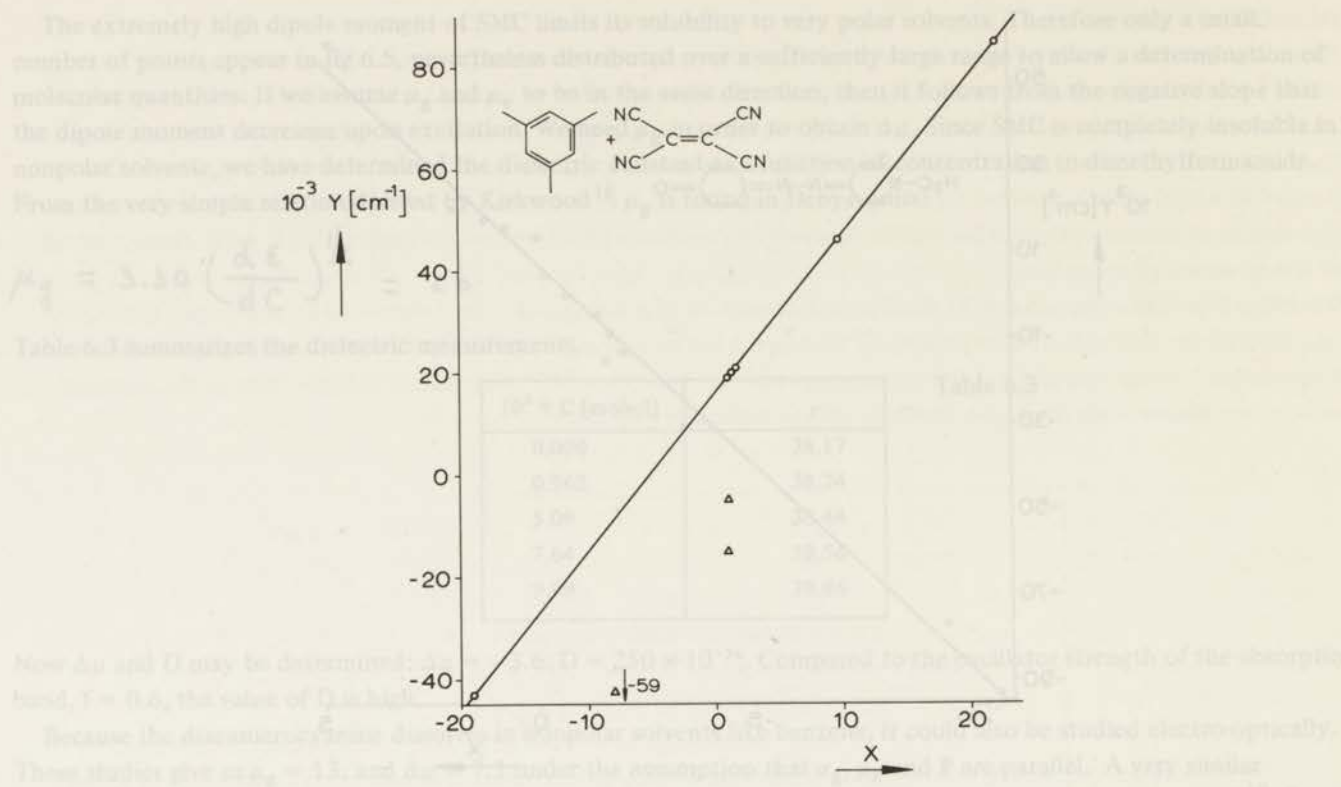


Fig 6.7  
Verification of eq 6.6 for the Mesitylene-TCNE complex

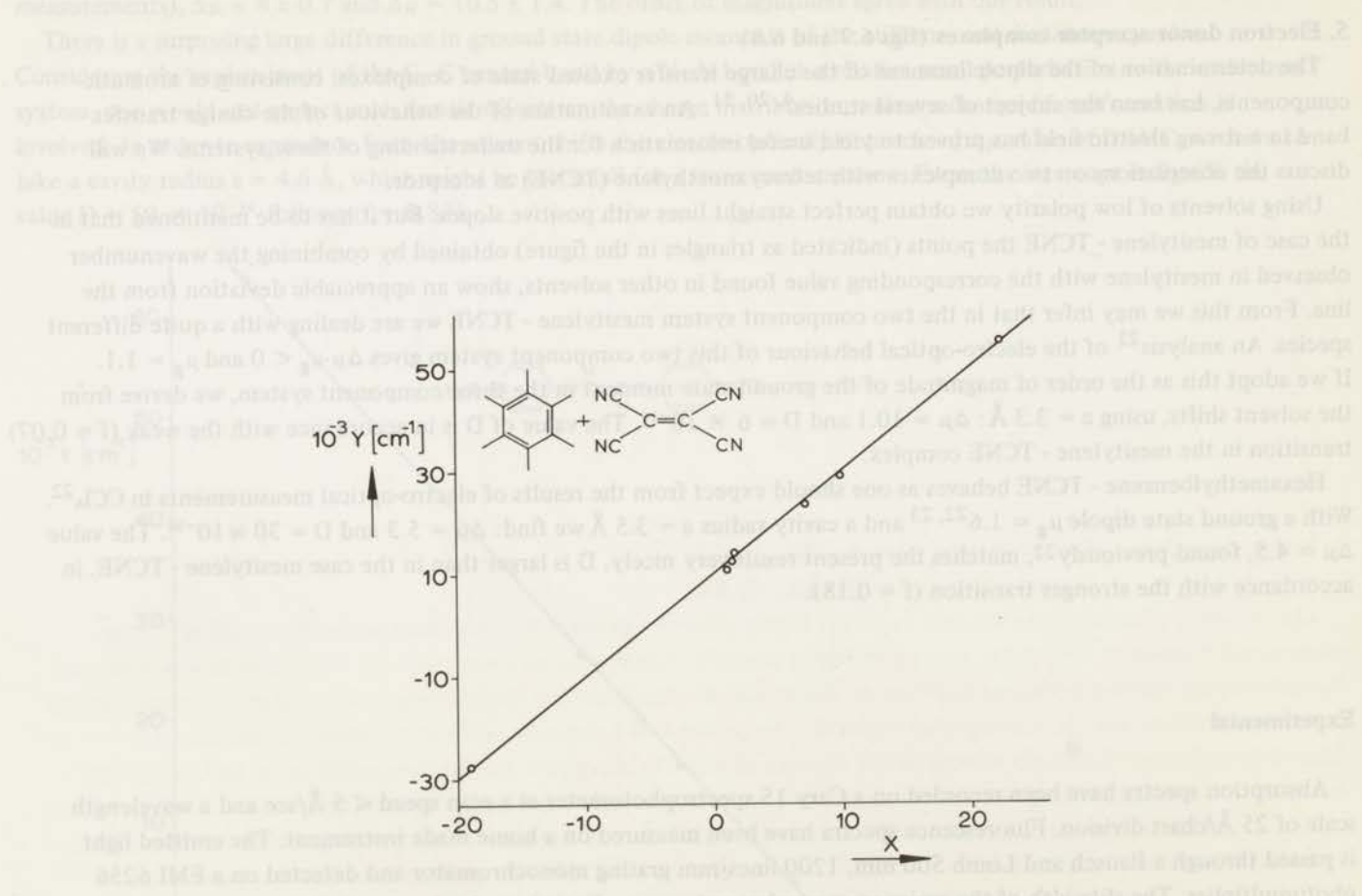


Fig 6.8  
Verification of eq 6.6 for the Hexamethylbenzene-TCNE complex



## Appendix

Solutions of polar molecules, subjected to a strong electric field  $F$ , will show a difference in absorption for light, polarized parallel or at right angles with respect to  $F$ . Additionally the energies of initial and final state will be altered and lead to a shift of the absorption band, given by:  $h\Delta\nu = -\Delta\mu \cdot F$ .

In principle the transition moment may also change and this can be taken into account by introducing the transition-polarizability tensor  $A$ :  $P(F) = P + A \cdot F$ .

Using the relative change in emerging light intensity a quantity  $L_\chi(\nu)$  is defined, depending on the angle of polarization  $\chi$

$$L_\chi(\nu) \equiv \frac{I_{\chi, F=0} - I_{\chi, F}}{I_{\chi, F=0}} \cdot \frac{1}{2.303 AF^2} \quad (6.10)$$

with  $D$  the optical density of the solution.

Taking the effects mentioned above into account, the theory predicts that  $L_\chi(\nu)$  will depend on the derivatives of the absorption band as follows:

$$L_\chi(\nu) = A_\chi + \frac{1}{15h} B_\chi \frac{d \ln \epsilon/\nu}{d\nu} + \frac{1}{30h^2} \left\{ \left[ \frac{d \ln \epsilon/\nu}{d\nu} \right]^2 + \frac{d^2 \ln \epsilon/\nu}{d\nu^2} \right\} \quad (6.11)$$

The quantities  $A_\chi$ ,  $B_\chi$  and  $C_\chi$  depend on  $\cos^2\chi$ . Since  $C_\chi$  can only be determined very inaccurately, we will omit it in the subsequent discussion.

$$A_\chi = \frac{1}{3} D + \frac{1}{30} E (3 \cos^2\chi - 1) \quad (6.12)$$

$$B_\chi = 5 F + G (3 \cos^2\chi - 1) \quad (6.13)$$

The coefficients on the right hand sides of eqs (6.12) and (6.13) depend on molecular quantities. We present the expressions obtained, when only first order terms in  $A$  are considered.

$$D = 2\beta \frac{P \cdot A \cdot \mu}{P^2} \quad (6.14)$$

$$E = \beta^2 [3(\mu \cdot p)^2 - \mu^2] + 6\beta \frac{(\mu \cdot P) T_A A}{P^2} + 6\beta \frac{\mu \cdot A \cdot P}{P^2} - 4\beta \frac{P \cdot A \cdot \mu}{P^2} \quad (6.15)$$

$$F = \beta (\mu \cdot \Delta\mu) + 2 \frac{P \cdot A \cdot \Delta\mu}{P^2} \quad (6.16)$$

$$G = \beta [3(\mu \cdot p)(\Delta\mu \cdot p) - \mu \cdot \Delta\mu] + 3 \frac{(\Delta\mu \cdot P) T_A A}{P^2} + 3 \frac{\Delta\mu \cdot A \cdot P}{P^2} - 2 \frac{P \cdot A \cdot \Delta\mu}{P^2} \quad (6.17)$$

Here  $\beta \equiv 1/kT$  and  $p$  is a unit vector along  $P$ . We shall pay special attention to the molecules having  $C_{2v}$  symmetry.

In such cases one usually derives from the sign of  $E$  the relative directions of  $\mu$  and  $p$ . For a transition moment parallel to  $\mu$  the tensor  $A$  will be diagonal and hence  $E = 2\beta^2 \mu^2 + 4D$ . If only the component of  $A$  corresponding to the direction of  $\mu$  is nonzero than  $G = 2F$ .

The first $\pi-\pi^*$ transition of	$10^{10}D$	$10^{10}E$	$10^{23}F$	$10^{23}G$	$G/F$	$\mu$	$\Delta\mu$
NMA in cyclohexane	2.2	338.7	29.2	44.5	1.5	5.4	1.9
PDM in $\text{CCl}_4$	- 4.	742.	- 58.	- 94.	1.6	8.0	-2.6
DAMC in $\text{C}_6\text{H}_6$	13.	2019.	221.	468.	2.1	13.	7.3

It should be noted that the ratio  $G/F$  shows a significant deviation from the value expected in the case of NMA and PDM. The small values of  $D$  indicate a negligible contribution from the tensor  $A$ . Therefore the explanation should be sought in terms, arising from the change in polarizability due to the excitation<sup>24, 9</sup>.

### Acknowledgement

We gratefully acknowledge the opportunity offered by J.D.M. Wisse (dept. of Phys. Chem. Leiden) to use his equipment for dielectric measurements. We are indebted to W. Furnée who prepared the diazamerocyanine and assisted in the electro-optical studies.

One of us (V) is most grateful to the Netherlands Foundation for Chemical Research (S.O.N.) for sponsoring his work.

Finally we like to express our gratitude to Prof. Dr. L.J. Oosterhoff for many valuable discussions concerning this work.

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## SUMMARY

The first $\pi-\pi^*$ transition of	10 <sup>19</sup> V/cm	10 <sup>18</sup> V/cm	10 <sup>17</sup> V/cm	10 <sup>16</sup> V/cm	0 V/cm	$\mu$	$\mu^*$
PMA in CHCl <sub>3</sub>	2.2	174.7	285.2	46.4	1.3	3.4	1.8
PMA in CCl <sub>4</sub>	4	74.2	78	108	1.8	1.8	1.2
DMSO in CCl <sub>4</sub>	15	201.9	179	108	2.1	1.8	1.2

The investigations, reported in this thesis, are concerned with properties of molecules in both their electronic ground- and excited states. The interaction between molecules, either in solution or in the gasphase, with an external uniform field of the order 100 KV/cm causes a change in their absorption spectrum in the visible and ultraviolet wavelength region. Several effects contribute to the modification of the spectrum: 1. The energies of the different electronic states are changed by the perturbation, depending on the permanent dipole moments and polarizabilities in these states; 2. The transition moment may gain a field induced part; 3. An angular anisotropy arises in the distribution of molecules relative to the applied field. The theory treating the modifications in absorption spectrum is presented. The field dependence of the transition moment has been accounted for by the use of a transition polarizability and a transition hyperpolarizability. Special attention has been paid to the conservation of bandshape in the field. Finally an expression has been derived for the change in molar extinction coefficient.

A beam of light emerging from the sample acquires a relative change in intensity due to the field of an order from 10<sup>-5</sup> to 10<sup>-4</sup>, which can be detected accurately, using a spectrometer we have constructed for the purpose. By applying a ratio detection system the measurements are not disturbed by the strong fluctuations in intensity of the light source. In addition, this method has the advantage, over stabilizing the light source, that the maximum output of the lamp is used. Special features of the equipment are discussed.

Applying the theory to the observed relative changes in intensity, one may determine certain molecular quantities like the absolute directions of transition moments, dipole moments in ground- and excited states as well as the change in polarizability due to excitation. For the nonpolar molecule tetracene the polarizability-change, accompanying excitation to the first excited singlet, has been determined. The dipole moment in the first  $\pi-\pi^*$  singlet of a number of conjugated organic molecules has been evaluated. Results of these electro-optical investigations are compared with quantum-chemical calculations. Quantitatively the results of such calculations are not very satisfactory.

The behaviour of the charge-transfer band of a number of electron donor - acceptor complexes in an electric field has been studied, in order to obtain the dipole moments in the ground- and charge transfer state. The dipole moments found for the ground state are in good agreement with their magnitudes as determined from dielectric measurements. In certain complexes the direction of the ground state dipole moment is opposed to that of the excited state, which is not to be expected from Mulliken's theory for these compounds. The transition moment in all molecular compounds shows a pronounced field dependence.

Starting from the existing theory for the influence of solute - solvent interactions on the spectrum of the solute, we have been able to determine the dipole moment in the excited state by locating the absorption maximum in different solvents. Experimentally the method is very simple and at the same time the results are in good agreement with values determined electro-optically. On the contrary, the well known method which combines fluorescence and absorption in various solvents, is shown to be inadequate in certain cases.

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## SAMENVATTING

De onderzoeken in dit proefschrift hebben betrekking op de eigenschappen van moleculen, die zich in de grondtoestand of in een aangeslagen electronen-toestand bevinden. De wisselwerking tussen moleculen, in oplossingen of in de gasfase, met een uitwendig homogeen elektrisch veld van de orde 100 KV/cm, veroorzaakt een verandering van hun absorptie spectrum in het zichtbare en ultraviolette golflengtegebied. Verschillende effecten dragen aan de wijziging van het spectrum bij: 1. De energieën van de verschillende electronen-toestanden veranderen ten gevolge van de storing, in afhankelijkheid van de in die toestanden optredende permanente dipoolmomenten en polariseerbaarheden; 2. Een verandering van het overgangsmoment kan door het veld worden geïnduceerd; 3. Er treedt een anisotropie op in de oriëntatie van moleculen ten opzichte van het aangelegde veld. De theorie die de verandering van het absorptie spectrum beschrijft, wordt gegeven. Hierbij is de veldafhankelijkheid van het overgangsmoment behandeld met behulp van een overgangspolariseerbaarheid en overgangshyperpolariseerbaarheid. Er wordt uitvoerig aandacht besteed aan het behoud van de bandenvorm in het veld. Tenslotte wordt er een uitdrukking afgeleid voor de verandering van de molaire extinctie coefficient.

Een uit de oplossing tredende lichtbundel ondergaat een relatieve intensiteitsverandering, ten gevolge van het veld, van de orde  $10^{-5}$  à  $10^{-4}$ , die met een door ons gebouwde spectrometer nauwkeurig kan worden bepaald. Door toepassing van een ratio detectie systeem worden de metingen niet verstoord door de sterke fluctuaties in de intensiteit van de lichtbron. Bovendien heeft deze methode het voordeel, boven stabilisatie van de lichtbron, dat de maximale intensiteit van de lamp bij de metingen wordt gebruikt. Bijzonderheden van de apparatuur zijn vermeld.

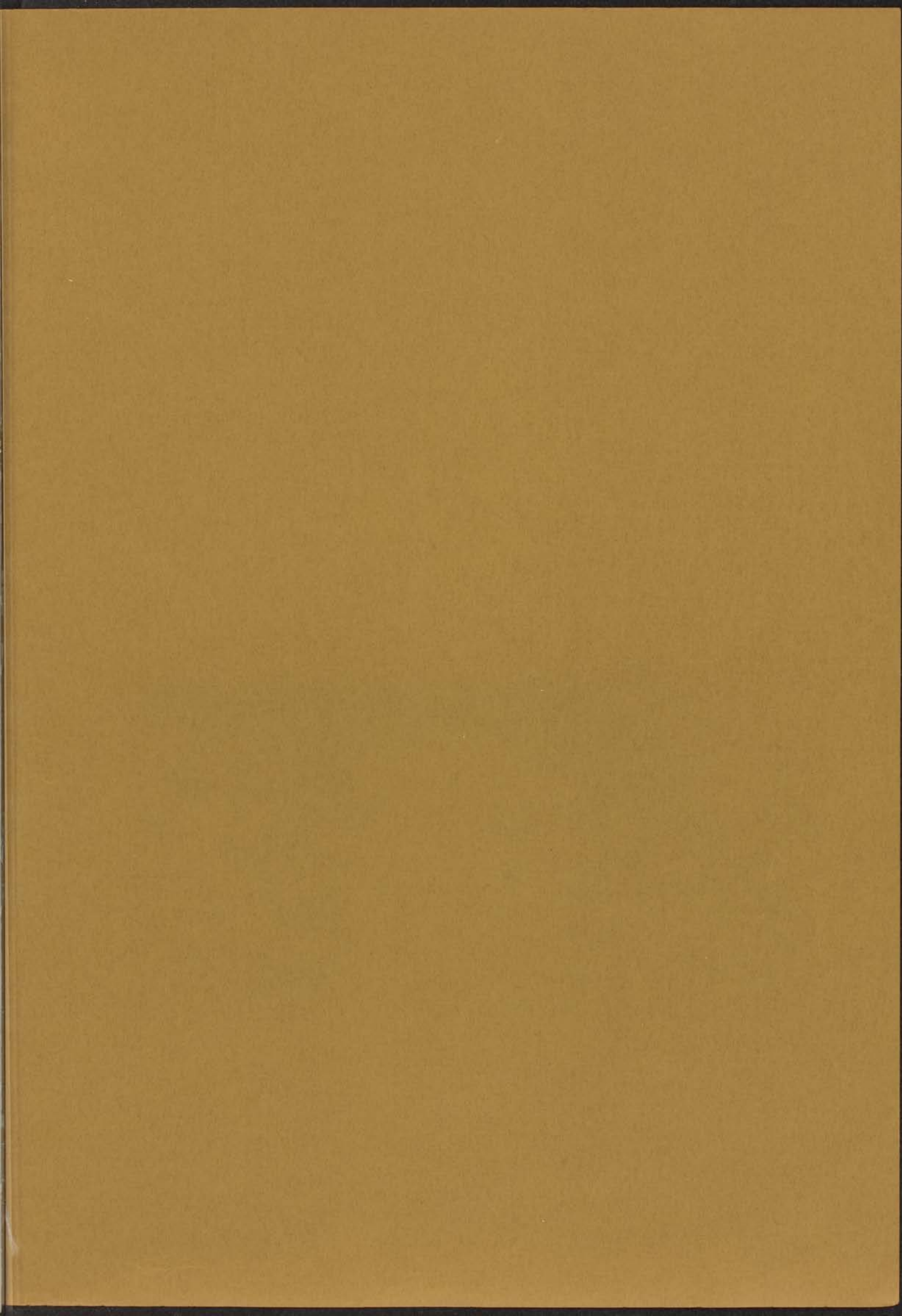
Uit de waargenomen relatieve intensiteitsveranderingen kunnen door toepassing van de theorie enkele moleculaire grootheden worden bepaald, zoals de absolute richtingen van overgangsmomenten, de dipoolmomenten in de grond- en aangeslagen toestanden en de verandering van de polariseerbaarheid bij excitatie. Voor het niet polaire molecuul tetraceen hebben wij de verandering van de polariseerbaarheid bepaald bij excitatie naar de eerste aangeslagen singulet. Het dipoolmoment in de eerste  $\pi-\pi^*$  singulet van een aantal geconjugeerde organische moleculen werd eveneens bepaald. De uitkomsten van deze electro-optische onderzoeken hebben wij vergeleken met quantum-chemische berekeningen. Kwantitatief bekeken, zijn de resultaten van dergelijke berekeningen niet erg bevredigend.

Door het gedrag van de 'charge transfer' band van een aantal electron donor - acceptor complexen in een elektrisch veld te bestuderen hebben wij de dipoolmomenten van de grond- en aangeslagen toestand in enkele gevallen kunnen bepalen. De dipoolmomenten voor de grondtoestand zijn in goede overeenstemming met de waarden die uit dielectrische metingen zijn bepaald. In sommige complexen is de richting van het dipoolmoment in de grondtoestand tegengesteld aan die van de aangeslagen toestand. Op grond van de theorie van Mulliken voor deze molecuulverbindingen zou men dit niet verwachten. Het overgangsmoment blijkt in alle complexen duidelijk van het veld af te hangen.

Uitgaande van de bestaande theorie, die de invloed van het oplosmiddel op het spectrum van een opgelost molecuul beschrijft, hebben wij het dipoolmoment van de aangeslagen toestand kunnen vaststellen, door bepaling van het absorptie maximum in verschillende oplosmiddelen. De methode is experimenteel zeer eenvoudig en de resultaten stemmen goed overeen met electro-optisch bepaalde waarden. Daarentegen blijkt de bekende methode, die metingen van zowel absorptie als fluorescentie in verschillende oplosmiddelen combineert, niet altijd tot een goed resultaat te leiden.

Na het behalen van het einddiploma van de Algemene Middelbare School te Paramaribo begon ik in januari 1955 met de studie aan de Rijksuniversiteit te Leiden. Het kandidaatsexamen in de chemie (letter f) legde ik in juli 1959 af. Mijn studie werd daarna voortgezet op de afdeling voor theoretische organische chemie onder leiding van Prof. Dr. L.J. Oosterhoff. De studie voor de bijvakken wiskunde en theoretische natuurkunde werd begeleid door de hoogleraren in de wiskunde Dr. W.T. van Est en Dr. C. Visser, en door de hoogleraar in de theoretische natuurkunde Dr. S.R. de Groot. Het doctoraalexamen legde ik af in januari 1962. In 1964 heb ik gedurende een half jaar met Prof. Dr. H. Labhart, in Basel, samengewerkt aan een onderzoek over triplet-triplet absorptiespectra van aromatische koolwaterstoffen.

Dit onderzoek werd gedeeltelijk gesubsidieerd door de Stichting Scheikundig Onderzoek in Nederland. De apparatuur werd in eigen beheer ontwikkeld met medewerking van de instrumentmakerij van de chemische laboratoria van de Rijksuniversiteit te Leiden. Aan zowel de technische als de administratieve staf van dit instituut ben ik dank verschuldigd voor de terzake kundige wijze waarop zij aan het tot stand komen van dit proefschrift hebben meegewerkt. Vooral voor het geduld en de zorgvuldigheid die men daarbij heeft getoond, heb ik grote bewondering.



*Bindwerk: Benco, Leiden*