

# Electric Field Effects on Oriented Molecules and Molecular Crystals

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The interaction of an electric field with a molecule or a crystal causes spectral effects that can often be readily related to important parameters of the charge distribution. Electric field influences on spectra are called Stark effects, and in this Account attention is focused on the optical spectrum (visible and ultraviolet). The field-induced spectral changes often lead to new knowledge of molecular dipole and higher moments of the charge distribution, polarizabilities of excited electronic states, and parameters describing intermolecular interactions in crystals.

The measurement of dipole moments of molecules in dielectrics and the associated phenomena of dielectric relaxation have long been an important branch of physical chemistry. An early (1929) but continuing stimulus to progress in this field was Debye's classic, "Polar Molecules,"<sup>1</sup> and the impact of electric moment and polarization experiments in the earlier days of structural chemistry is evident in, for example, Van Vleck's "The Theory of Electric and Magnetic Susceptibilities."<sup>2</sup> In the present day using microwave and molecular beam electron resonance methods the electric moments of isolated small molecules in their ground electronic-vibrational states can, in favorable cases, be obtained with four or five significant figures. In addition there is a continuing improvement in our knowledge of higher electric moments<sup>3</sup> and polarizabilities, leading to a more complete understanding of the ground-state charge distribution.

Not nearly the same amount of information is available for excited electronic states,<sup>4</sup> but it is badly needed both as a testing ground for theory and to help to rationalize a chemistry of excited states. In the 1967 NBS tabulation of dipole moments<sup>5</sup> information is given for electronically excited states of only four molecules—NH,<sup>6</sup> CO,<sup>7</sup> formaldehyde,<sup>8</sup> and propynal<sup>9</sup>—although that tabulation does not include data inferred from electric dichroism experiments in solutions.<sup>10,11</sup> A major drawback in extending low-pressure gas or beam techniques to the study of significantly more complex excited molecules lies in the fact that the rotational fine structure cannot be completely resolved by conventional spectroscopic meth-

ods when the moment of inertia becomes as large as, say, that of benzene. Lombardi,<sup>12</sup> using high-resolution spectroscopy, has had success in unravelling gas-phase Stark effects of a number of monosubstituted benzenes, and new Stark modulation techniques are likely to contribute significantly not only to the list of electric moments but also to the spectral analysis of complex molecules. However these methods are not likely to expose properties of the higher excited states of the larger molecules because severe spectral congestion and perturbations between different electronic states cause all but the lowest excited-state region to be unresolvably diffuse in many cases.<sup>13,14</sup>

There are significant advantages in using molecular crystals for electric field studies. Not only can anisotropic features be easily explored, but the spectra themselves are less complex. Individual vibronic transitions are usually sharp<sup>15</sup> ( $0.1 \text{ cm}^{-1}$  to  $3.0 \text{ cm}^{-1}$ ) in low-temperature solids, and the spectroscopic signals are strengthened compared with the vapor due to the absence of rotational structure. Thus the purpose of this Account is to explore different manifestations of electric fields on the optical spectra of space-fixed molecules.

## The Effect of an Electric Field on Polarizable Molecules

The change in potential energy  $V(F_1)$  that arises because a molecule is placed in a uniform electric

(1) P. Debye, "Polar Molecules," Chemical Catalogue Co., New York, N. Y., 1929.

(2) J. H. Van Vleck, "The Theory of Electric and Magnetic Susceptibilities," Oxford University Press, Oxford, 1965 (reprint of 1932 edition).

(3) A. D. Buckingham in "Physical Chemistry; Advanced Treatise," Vol. IV, H. Eyring, D. Henderson, and W. Jost, Ed., Academic Press, New York, N. Y., 1970, Chapter 8, p 349.

(4) A. D. Buckingham, *MTP Int. Rev. Sci., Phys. Chem., Ser. One*, 3 (1973).

(5) "Selected Values of Electric Dipole Moments for Molecules in the Gas Phase," *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, No. 10, 1967.

(6) T. A. R. Irwin and F. W. Dalby, *Can. J. Phys.*, 43, 1766 (1965).

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(9) D. E. Freeman, J. R. Lombardi, and W. Klemperer, *J. Chem. Phys.*, 45, 58 (1966).

(10) W. Liptay and J. Czekalla, *Z. Naturforsch. A*, 15, 1072 (1960); *Z. Elektrochem.*, 65, 721 (1961).

(11) H. Labhart, *Helv. Chim. Acta* 44, 447, 571 (1961); *Chimia* 15, 20 (1961); *Tetrahedron Suppl.*, 2, 223 (1963).

(12) J. R. Lombardi, *J. Amer. Chem. Soc.*, 92, 1831 (1970).

(13) R. M. Hochstrasser and C. J. Marzocco, *J. Chem. Phys.*, 49, 971 (1968); R. M. Hochstrasser, *Accounts Chem. Res.*, 1, 266 (1968).

(14) J. P. Byrne and I. G. Ross, *Aust. J. Chem.*, 24, 1107 (1971).

(15) There are many possible contributions to this finite line width, but an important one is that crystalline samples are always slightly inhomogeneous, no matter how perfect a crystal we try to grow. There is considerable evidence to show that this is frequently a dominant factor.<sup>16</sup>

(16) R. M. Hochstrasser and P. N. Prasad, "Optical Spectra and Relaxation in Molecular Solids," in "Excited States," E. Lim, Ed., Academic Press, New York, N. Y., 1973.

Robin Hochstrasser was born and educated in Edinburgh, Scotland, receiving his Ph.D. from Edinburgh University in 1955. After 2 years in the R.A.F. he joined the faculty at the University of British Columbia, where his research interests in molecular spectroscopy began. During 1961-1962 he worked at the National Research Council (Ottawa) and at Florida State University (with M. Kasha) and in 1963 he moved to the University of Pennsylvania where he is currently Blanchard Professor of Chemistry. His research interests center around the molecular spectroscopy of aromatic molecules, particularly in the solid state. Dr. Hochstrasser was an Alfred P. Sloan Foundation Fellow (1963-1967) and a Guggenheim Fellow (1972).

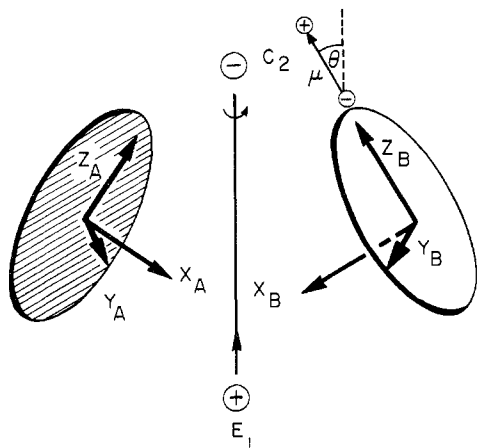


Figure 1. Conventions for axes, dipoles, and fields. Note that the dipole vector is positive along the direction from minus to plus.

field,  $F_1$ , directed in a space-fixed 1-direction, which could, for example, be one of three principal crystal axes, is the work done on the dipole by changing the field from 0 to  $F_1$  (eq 1), where  $m_1$  is the 1-compo-

$$V(F_1) = - \int_0^{F_1} m_1 dF_1 = -\mu F_1 \cos \theta - \frac{1}{2} \alpha_{11} F_1^2 + \dots \quad (1)$$

ponent of the dipole moment in the presence of the field (eq 2),  $\mu$  is the permanent dipole moment that

$$m_1 = \mu \cos \theta + \alpha_{11} F_1 \quad (2)$$

is presumed to make an angle  $\theta$  with the electric field, and  $\alpha_{11}$  is one of the six independent components of the polarizability. The definitions of the field and dipole moment and their relative orientation shown in Figure 1 are such that the potential energy is lowered when  $\theta$  lies between 0 and  $\pi/2$ . The second term in (1) is not dependent on the polarity of the applied field. If there are two noninteracting molecules, related by a symmetry operation such as meant in Figure 1, the polarizability contribution to the energy is the same for each if the field is along or perpendicular to 1, but the dipole term is only the same for each molecule when the field is along a symmetry axis that interchanges molecules.

### Stark Effect in Molecular Crystals<sup>17</sup>

We now consider an idealized crystal having one molecule as the crystal asymmetric unit and  $n$  noninteracting molecules per unit cell. Each molecule in the unit cell is identical with the others in the sense that a test charge exploring one molecule would be unable to distinguish it from the others. The various molecules in the unit cell differ only in their orientations to space-fixed axes determined by their orientation to crystal axes or external fields and the orientation of the crystal in the laboratory. The remaining molecules in the crystal are  $n$  sets of molecules translationally equivalent to each of the  $n$  molecules in the unit cell, and as such they add no new orientational features to the problem. The crystal can be regarded as an  $n$ -fold orientationally degenerate system and, if there are no interactions between the molecules, each nondegenerate state of a molecule

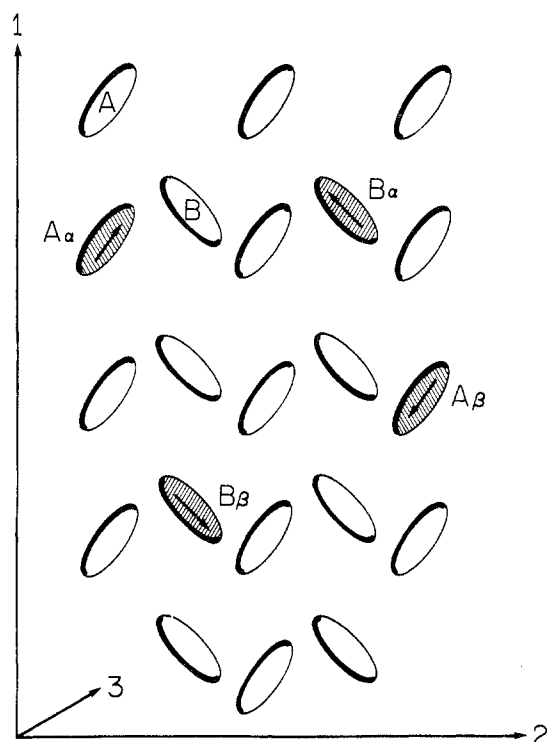


Figure 2. Orientation of molecules in a model molecular crystal.

becomes an  $n$ -fold orientationally degenerate state of the crystal. In principle such degeneracies can be completely lifted by subjecting the crystal to appropriately directed electric or magnetic fields, the latter effect occurring when the molecules have magnetic dipole moments, and the former when they have electric moments.

The approximation of noninteracting molecules is partly realized in practice by using dilute mixed crystals which have the molecule of interest, the guest, dispersed randomly throughout a host of known structure. The various possible guest orientations, assuming that the guests occupy only one set of equivalent lattice points (usually called a site), are as shown schematically in Figure 2 for the case of two molecules per unit cell, two interpenetrating translational sublattices A and B, and each host molecule assumed to be centrosymmetric. Figure 2 shows the four possible equivalent guest dipole orientations  $A_\alpha$ ,  $A_\beta$ ,  $B_\alpha$ ,  $B_\beta$ .

If a uniform electric field  $F$  is now imagined to exist in the neighborhood of the guest molecules, it is of interest to trace its effect on their states. First consider a field  $F_1$  (see Figure 2) and its effect on the ground state of the guest at energy  $E_0$  for every type of guest in the structure. The change in energy per molecule, neglecting the polarizability for the present, is given by  $-\mu_0 F_1 \cos \theta$  for each molecule where its ground-state dipole moment,  $\mu_0$ , makes an angle  $\theta$  with field. Accordingly molecules of type  $A_\alpha$  and  $B_\alpha$  have their energies lowered (attractive interaction with the field) while  $A_\beta$  and  $B_\beta$  have their energies increased by field. The effect on the ground-state  $\Gamma_0$  of the whole system can be represented as the splitting shown in Figure 3. Similarly the excited-state orientational degeneracy will be split but by  $2\mu_e F_1 |\cos \theta|$  where  $\mu_e$  is the dipole moment of the excited-state  $\Gamma_e$ . A spectrum of the mixed crystal

(17) R. M. Hochstrasser and L. J. Noe, *J. Chem. Phys.*, 48, 514 (1968).

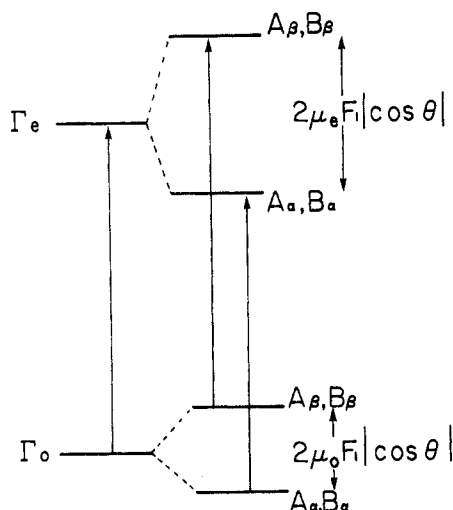


Figure 3. Model energy level diagram for oriented polar molecules of a crystal in an electric field assuming a nonpolarizable lattice.

with  $F = 0$  would consist of a single line at  $(E_e - E_o)$ ; in the presence of the field two transitions will be observed, one from  $\alpha$  and the other from  $\beta$  molecules with

$$\Delta E = E_\beta - E_\alpha = 2F_1(\mu_e - \mu_o)|\cos \theta| \quad (3)$$

This energy difference is observed as a symmetric splitting of the single transition at  $(E_e - E_o)$ .

The Stark splitting predicted here is expected for a transition between any two states that have  $\Delta\mu = (\mu_e - \mu_o) \neq 0$ . This includes not only electronic states but vibrational states so these effects are also expected for infrared and Raman spectra. To obtain  $\Delta\mu$  we need to know  $F_1$ , which can be more complex than simply the applied field, and  $|\cos \theta|$ , which requires some knowledge of the guest orientation, but will be known exactly for neat crystal Stark effects.

### The Effective Field at a Molecule in an Anisotropic Dielectric

We usually assume that the field is uniform over each molecule and that the fluctuations in field due to the nonuniformity of the electronic distribution around a given molecule can be neglected, and that each polar molecule may be treated as a point dipole, and each polarizable molecule treated as a point-induced dipole. Then the average fields in the crystal can be used to describe the effective field  $F$ . In a compact parallel plate condenser the average field in the dielectric due to external charges is precisely the applied field  $E = V/d$  where  $V$  is the applied potential and  $d$  is the thickness of the dielectric. The effective field  $F$  acting on a molecule is different from  $E$  because of the field due to induced dipole moments on host molecules. This contribution to the average field can be obtained by a variety of summing techniques, though the dipole sum generally depends on the nature of Bravais lattice of induced dipoles and on the shape of the volume containing the dipoles included in the sum.<sup>18</sup> In general we may write  $F_1 = L_1 E_1$ , where  $L_1$  is a constant of the material that can be calculated. An additional

important use for the Stark effect methods outlined here is to explore the validity of various local field approximations as applied to molecular crystals.

### Parameters of the Stark Effect

For a dielectric of thickness  $d$  cm, a spectroscopic Stark splitting of  $\Delta = \Delta E/hc$  cm<sup>-1</sup> from eq 3, and an applied potential difference  $V$  (volt), the change in dipole moment  $\Delta\mu$  is given by eq 4. The experi-

$$|\Delta\mu| = 2.978 \times 10^4 \left\{ \frac{d\Delta}{V L_1 |\cos \theta|} \right\} \text{debye} \quad (4)$$

mental uncertainty in the splitting is about 0.03 cm<sup>-1</sup> using conventional spectroscopic techniques on favorable cases, so for an applied potential of 10<sup>4</sup> V,  $d = 0.1$  cm,  $L_1 = 1.4$ , and  $\cos \theta = 1.0$ ,  $|\Delta\mu|$  can be obtained with a precision of 0.006 D: Needless to say there is an inherent uncertainty due to  $L_1$  which is often approximated by  $\frac{1}{3}(n_1^2 + 2)$ , where  $n_1^2$  is the refractive index.

### Stark Effect for a Polarizable Molecule in a Polar Solid

For a polar lattice the total field ( $z$  component) at each molecule is actually  $(F_z + F_z)$ , where  $F_z$  is the field due to the permanent moments of the host molecules, so the total energy of the  $f$ th state, at  $E_f^\circ$  in the free molecule, is readily obtained from (1) for the special case where  $F_1 = F_z$

$$E_f = E_f^\circ - \mu_f^\circ(F_z + F_z) - \frac{1}{2}\alpha_{zz}^f(F_z + F_z)^2 \quad (5)$$

where  $\mu_f^\circ$  is the dipole moment of the unperturbed molecule. Note that at  $F_z = 0$  there is a spectral shift. Now we consider a simplified crystal in which the A molecules have dipoles along  $+1$  ( $z$  in this case) and the B molecules have dipoles along  $-1$  so that there are still two molecules per unit cell. From (5), and the comparable expression for B molecules in which only the sign of  $F_z$  is changed, the Stark splitting between polar molecules in the A and B sublattices is found to be

$$\Delta E_p = 2F_z|\Delta\mu + F_z\Delta\alpha_{zz}| \quad (6)$$

where  $\Delta\alpha_{zz} = \alpha_{zz}^f - \alpha_{zz}^\circ$ : the change in polarizability on excitation contributes to the linear splitting. Given the sign of  $\Delta\alpha$ , the sign of  $\Delta\mu$  is immediately specified by comparing  $\Delta E_p$  of the polar lattice with  $\Delta E$  of the nonpolar lattice. The sign of  $F_z$  can be obtained from a dipole lattice sum and used to calculate  $\Delta\alpha$  from (6) and (3).

There are other methods of measuring the polarizability of the excited state, the most direct being to obtain the energy shift  $\frac{1}{2}\Delta\alpha F^2$  of a spectral line;  $\Delta\alpha$  is expected in the range  $10^{-22}$  to  $10^{-23}$  cm<sup>3</sup> in molecules with normally spaced states, so this shift can be in the range  $4 \times 10^{-2}$  to  $4 \times 10^{-3}$  cm<sup>-1</sup> for fields of  $10^5$  V cm<sup>-1</sup>. At the higher end these are just measurable directly, but in any case  $\Delta\alpha$  should be readily obtainable by measuring the intensity fluctuations at a fixed wavelength caused by the spectral line shifting in an alternating electric field (*i.e.*, Stark modulation). Work of this sort is in progress, and there has been some very recent work on these effects in rigid glasses.<sup>19</sup>

Additional information about the sign of  $\Delta\mu$  can

(18) See, for example, C. Kittel, "Introduction to Solid State Physics," Wiley, New York, N. Y., Chapter 12, 1966.

be obtained from the spectral shifts of the lines in question between vapor, nonpolar, and polar hosts. In crystals of polar molecules the fields of the permanent dipoles can be expected to decrease the total potential energy. If the dipole moment of one molecule in the crystal is then decreased by electronic excitation, the potential energy will be increased and the electronic transition for that molecule will appear at higher energy than that found in gases or nonpolar solids.

### Stark Effect for Excitons and Nonpolar Molecules

In cases where there is a resonance interaction between the molecules the observed spectroscopic transitions no longer signal states of isolated molecules. It is quite common for dipolar molecules to form centrosymmetric crystals, so it is readily seen that the dipole moment of a crystal state may vanish even if the component molecules are strongly polar. In general, for crystals having nonpolar space groups (just as for nonpolar molecules) there is no first-order Stark effect (no dipole moment), but the electric field may mix states: these are second-order Stark effects. Such coupling causes an energy shift ( $\alpha F^2$ ) and a field-induced intensity borrowing. These useful effects have been observed for the triplet exciton states of *p*-dichlorobenzophenone<sup>20</sup> and they are expected for even nonpolar molecules that have very nearby states.<sup>21</sup>

When an electric field acts on an exciton state, or a composite molecule state, the direct resonance between components of the system is modified. Accordingly the energy transfer can be modified and information can be obtained regarding its anisotropy.

### Stark Effect for Oriented Molecules in Degenerate States

A space-fixed molecule in a definite parity degenerate state of symmetry species  $\Gamma$  will have a first-order Stark effect (a dipole moment) whenever the direct product  $\Gamma \times \Gamma$  contains the species of the dipole moment. This is the interesting case of molecules that are normally considered to be nonpolar displaying polar properties, for such is always possible if the molecule is not centrosymmetric. An appropriately directed electric field can reduce the symmetry of any (spin-free) molecular system sufficiently to remove in principle all electronic and vibrational degeneracies. The field must be in a direction perpendicular to the axis of symmetry ( $z$ ). The Stark splitting gives important information on the charge distribution and vibronic coupling in the degenerate state. The most common symmetries to show these effects are  $S_3$ ,  $C_3$ ,  $C_{3v}$ ,  $D_3$ , and  $D_{3h}$  for which  $E \times E$  always contains the  $E$  representation of  $x$  and  $y$ .

The first excited singlet state of *s*-triazine ( $D_3$ ) shows a first-order Stark effect<sup>22</sup> when the electric field is applied parallel to the molecular plane. The observed linear splitting is  $3.5 \text{ cm}^{-1}$  for a field of  $10^5 \text{ V cm}^{-1}$  which, incidentally, suggests that the state is doubly degenerate, and gives a clue to the nature

of the nonbonding orbital.<sup>21</sup> Crystals of aromatics and heteroaromatics having threefold symmetry and common ions such as  $\text{NO}_3^-$  are expected to show similar effects in their  $E$  states.

### The Determination of Molecular Orientations Using Electric Fields

Equation 3 shows that spectra for only one field orientation need be studied if it is assumed that  $|\cos \theta|$  is known. In neat crystals this will be the case, but for mixed crystals there is no guarantee that the guest is aligned with its principal axes parallel to those of the host. Measurements of the Stark splitting for three mutually orthogonal applied field directions can establish the length and orientation in space of the dipole moment change  $|\Delta\mu|$ . In many cases  $\mu_0$  and  $\mu_e$  are parallel, in which case the orientation of  $\mu_0$  is automatically obtained from such measurements, which therefore lead to a determination of features of the molecular orientation. Such information is vital to understanding intermolecular forces in molecular crystals and was previously only available from magnetic resonance studies, and therefore limited to states having angular momentum. Optical dichroism can be used to get approximations to the orientation, but then one has to consider carefully crystal field perturbations on the measured intensity, and internal field problems that may be more serious than in the static field case.

At present there are three complete studies from which orientation data may be extracted; these are azulene in naphthalene,<sup>23</sup> pyridine in benzene,<sup>24</sup> and pyridine *N*-oxide in *p*-dichlorobenzene.<sup>25</sup> The results show that azulene and naphthalene are essentially aligned (see Table I) as intuitively expected. In the other two cases such alignment was not found, and the rationalization of such results in terms of structural detail is a fascinating new aspect of solid state chemistry.

### Field-Induced Molecular Motion

In a real solid the guest molecules are not rigidly fixed: they are in motion about an equilibrium configuration. In the presence of an electric field that changes the potential energy by  $V(F)$  there is a torque, tending to increase the angle  $\theta$ , that is given by

$$-(dV/d\theta) = -\mu F_1 \sin \theta \quad (7)$$

Thus if the guest molecule is at an equilibrium orientation  $\theta_0$  in zero field and is making small harmonic oscillations about  $\theta_0$  characterized by a restoring force  $k(\theta_0 - \theta)$ , then the change in equilibrium position,  $\delta\theta$ , induced by the field is

$$\delta\theta = \theta_0' - \theta_0 = -(\mu F \sin \theta_0/k) \text{ radian} \quad (8)$$

where  $k$  is in ergs radian<sup>-2</sup>. A model force constant,  $k$ , can be estimated by assuming that a typical lattice librational mode has a frequency of  $\bar{\nu} = 50 \text{ cm}^{-1}$  for a molecule having a moment of inertia about that of benzene ( $I \sim 10^{-38} \text{ g cm}^2$ ). In that case  $(k/hc) = 4\pi^2 I \bar{\nu}^2 c/h$ , which is about  $5000 \text{ cm}^{-1} \text{ radian}^{-2}$ , so if

(19) R. Mathies and A. C. Albrecht, *Chem. Phys. Lett.*, **16**, 231 (1972).

(20) R. M. Hochstrasser and J. W. Michaluk, *J. Mol. Spectrosc.*, **42**, 197 (1972).

(21) R. M. Hochstrasser, *Mol. Phys.*, **24**, 597 (1972).

(22) Unpublished results from this laboratory.

(23) R. M. Hochstrasser and L. J. Noe, *J. Chem. Phys.*, **50**, 1684 (1969).

(24) R. M. Hochstrasser and J. W. Michaluk, *J. Chem. Phys.*, **55**, 4668 (1971).

(25) R. M. Hochstrasser and D. A. Wiersma, *J. Chem. Phys.*, **55**, 5339 (1971).

Table I

Molecule	Host <sup>a</sup>	$\Delta\mu$ , debye <sup>b</sup>	Ref
Azulene	Naphthalene	-1.21 ± 0.05 ( <sup>1</sup> B <sub>2</sub> ) -1.10 ± 0.05 ( <sup>1</sup> A <sub>1</sub> )	22
Benzophenone	Neat	-1.52 ± 0.05 ( <sup>1</sup> nπ*) -1.19 ± 0.05 ( <sup>3</sup> nπ*)	29, 37
<i>p</i> -Chloroaniline	Durene	+1.26 ± 0.2 ( <sup>1</sup> B <sub>2</sub> )	38
4,4'-Dichlorobenzophenone	Neat	-1.29 ± 0.06 ( <sup>1</sup> nπ*) -0.68 ± 0.05 ( <sup>3</sup> nπ*)	20
<i>cis</i> -2,2'-Bipyridine	Biphenyl	-1.26 ± 0.06 ( <sup>1</sup> nπ*)	36
Phenanthrene	Biphenyl	0.34 ± 0.1 ( <sup>1</sup> A <sub>1</sub> , ππ*) 0 ± 0.12 ( <sup>3</sup> B <sub>2</sub> , ππ*)	28
Phthalazine	Naphthalene	-3.05 ± 0.1 ( <sup>1</sup> nπ*) -3.05 ± 0.1 ( <sup>1</sup> nπ* + 1670 cm <sup>-1</sup> )	31
Pyridine	Benzene	-3.2 ± 0.1 ( <sup>1</sup> nπ*)	23
Pyridine <i>N</i> -oxide	<i>p</i> -Dichlorobenzene	-0.71 ± 0.03 ( <sup>1</sup> B <sub>2</sub> , ππ*)	24
Pyrimidine	Benzene	-0.88 ( <sup>1</sup> B <sub>1</sub> , nπ*) -1.0 ( <sup>3</sup> B <sub>1</sub> , nπ*) -1.8 ( <sup>3</sup> B <sub>1</sub> , nπ*)	26
Quinoxaline	Neat	-1.8 ( <sup>3</sup> B <sub>1</sub> , nπ*)	
	Durene	-0.65 ± 0.05 ( <sup>1</sup> nπ*) +1.10 ± 0.08 ( <sup>3</sup> ππ*)	33
	Naphthalene	-0.61 ± 0.05 ( <sup>1</sup> nπ*)	33
Sulfur dioxide	Neat	-0.39 ± 0.25 ( <sup>3</sup> B <sub>1</sub> )	39
<i>s</i> -Triazine <sup>c</sup>	Neat	1.02 ( <sup>1</sup> E'')	21, 41
		0.71 ( <sup>3</sup> E'')	40

<sup>a</sup> Single crystal at 4.2 K or lower. <sup>b</sup> The uncertainty due to the local field is not included, and an anisotropic Lorentz correction is used in each case. Numbers can usually be corrected for a better field approximation by straight proportion. The signs are inferred from spectral shifts or from comparisons of neat with mixed crystal experiments. <sup>c</sup> In this case  $\Delta\mu$  is  $2(E''|er|E'')$  if the splitting is due to a doubly degenerate state of *s*-triazine.

$E_1 \mu \sin \theta_0/hc$  is chosen as  $5 \text{ cm}^{-1}$ , we find  $\delta\theta \sim -0.06^\circ$ . This is much less than the root-mean-square angular displacements ( $\sim 3^\circ$ ) of the molecule at 0 K through zero-point motion. Accordingly there should be only slight effects due to the couple exerted on the dipole moment and only in cases when either the ground- or the excited-state dipole moment is rather large or in crystals that are very easily deformable. For those cases where the guest seriously deforms the host the motional effects may be 10–20 times larger than the above estimate. In fact, there are a number of cases of field-induced line broadening at relatively low fields, for example, the luminescence and absorption of pyrimidine in benzene.<sup>22</sup>

### Relationship between the Dipole Moment of a Molecule in Free Space and in a Molecular Crystal

When a dipolar molecule is placed into a polarizable medium its dipole moment is changed. If there is a uniform field at the lattice site where the molecule is situated, then a dipole,  $\mu_\alpha$ , is induced. The direction and number of components of  $\mu_\alpha$  depend on the crystal symmetry; for example,  $\mu_\alpha = 0$  if the host molecules are centrosymmetric and with neglect of the reaction field;  $\mu_\alpha$  must be directed along any axis of symmetry that is shared by the molecule and the crystal. Only to the extent that the polarizabilities of the ground and excited states are different will these internal fields contribute to our measured values of  $|\Delta\mu|$  as shown by eq 6.

In nonpolar host lattices there is a more important effect due to the reaction field of the guest dipole. Host molecules at a distance  $R$  from the guest experience a field on the order of  $\mu R^{-3}$  which therefore induces a dipole in the host of  $\alpha_H \mu R^{-3}$ . The guest thereby experiences a field on the order of  $\alpha_H \mu R^{-6}$  which induces a dipole moment of  $\alpha_G \alpha_H \mu R^{-6}$  in the

guest. This induced moment is proportional to the guest dipole moment and therefore the percentage increase in the  $\Delta\mu$  value is at most  $(6 \times 10^2) \alpha_G \alpha_H R^{-6}$  for six nearest neighbors, or 3% of  $\Delta\mu$  for  $\alpha \sim 10^{-23} \text{ cm}^3$ ,  $R = 5 \text{ \AA}$ , neglecting anisotropy and geometrical factors.

Pyrimidine<sup>26</sup> presents an interesting use of eq 6. From Table I it follows that  $|\Delta\mu| = 1.0 \text{ D}$ , whereas  $|\Delta\mu + F\Delta\alpha| = 1.8 \text{ D}$ . Since the pyrimidine crystal contains card-pack stacks with an intermolecular spacing of only  $3.8 \text{ \AA}$ ,  $F_z$  can be guessed at  $2\mu_0 R^{-3}$ , from which  $\Delta\alpha_{zz} = 10^{-23} \text{ cm}^3$ , which represents quite a small increase of polarizability in the <sup>1</sup>nπ\* state compared with the ground state. This value of  $\Delta\alpha_{zz}$  predicts a crystal spectral shift of  $\Delta\mu F_z \sim 500 \text{ cm}^{-1}$  to higher energy than the gas, thereby accounting for a considerable fraction of what is observed.

### Relative Values of $|\Delta\mu|$ for Different States

According to eq 6 even if the molecule being excited by the light is in a polar lattice the measured  $|\Delta\mu|$  should differ from the unperturbed molecule  $|\Delta\mu|$  only to the extent that  $F\Delta\alpha$  is important. This means that very reliable relative values of  $|\Delta\mu|$  for different states can be obtained, especially in nonpolar host lattices. The uncertainties arising from  $|\cos \theta|$  and  $F_i$  are virtually removed in favorable cases if it can be assumed that there are relatively small changes in the molecular dimensions, charge distribution and polarization of the nearby host molecules for the states being compared. The effective fields appropriate to measurements for different states are not identical even in the uniform field ap-

(26) T. S. Lin, Ph.D. Thesis, The University of Pennsylvania, 1969; see also R. M. Hochstrasser and T. S. Lin, *Symp. Farad. Soc.*, 3, 100 (1969).

proximation because of the reaction field, but the uncertainty in  $(\Delta\mu_{01} - \Delta\mu_{02})$  should be less than  $\sim 0.03(\Delta\mu_{01} - \Delta\mu_{02})$ , as shown above.

A number of comparisons of this sort have been studied already. One is azulene in naphthalene,<sup>23</sup> where  $\Delta\mu_1/\Delta\mu_2 = 1.10 \pm 0.10$  (see Table I), while the theoretical prediction by Pariser<sup>27</sup> for this ratio is 0.75, much closer to what is observed than are the calculated values of  $\Delta\mu$  which are off by a factor of about two. Another example from aromatic chemistry is phenanthrene<sup>28</sup> in biphenyl (Table II), where  $\Delta\mu_S = 0.34 \pm 0.15$  D and  $\Delta\mu_T \approx 0$ . In this case  $\Delta\mu_S = \mu_S$  since the ground state is nonpolar.

Excited- and ground-state molecules have different equilibrium configurations, but whenever both states have equilibrium symmetry higher than  $C_1$  or  $C_s$  the observed value of  $|\Delta\mu|$  will correspond to the difference in the dipole moments for the equilibrium geometries. If the upper state reduces in symmetry to  $C_s$ , e.g., then the ground- and excited-state dipole moments may point in different directions. Corrections for this rotation would be needed for experiments on, e.g., oriented formaldehyde since  $\text{H}_2\text{CO}$  is known to undergo a  $C_{2v} \rightarrow C_s$  change on excitation to the  $n\pi^*$  states. For aromatic ketones such as benzophenone there is no spectral evidence to indicate that a  $C_2 \rightarrow C_1$  distortion occurs on excitation to the  $n\pi^*$  states: data for the singlet and triplet  $n\pi^*$  states of benzophenone<sup>29</sup> and *p*-dichlorobenzophenone<sup>20</sup> provide  $\Delta\mu_S/\Delta\mu_T$  values of 1.29 and 1.8, respectively, indicating that the dipole moment changes less on excitation of the triplet state, in contrast to what occurs with formaldehyde.<sup>30</sup> This could mean that in aromatic ketones the excited nonbonding electron has more tendency to drift away from oxygen when its spin is not changed, in accordance with Hund rule expectations.

Recent work on some vibrational levels of the first excited states of 2,3-diazanaphthalene<sup>31</sup> showed that the  $|\Delta\mu|$  values for different vibronic levels differed by less than 0.01 D, thereby showing that the levels most probably do not belong in different electronic states.

### Effect of Host Lattice on $|\Delta\mu|$

Anisotropic epr studies<sup>32</sup> have given the orientation of quinoxaline molecules in the durene host lattice, and we have studied the Stark effect in this system and also for quinoxaline in naphthalene.<sup>33</sup> Using an anisotropic Lorentz field we find  $|\Delta\mu| = 0.65 \pm 0.05$  D in the durene lattice and  $|\Delta\mu| = 0.61 \pm 0.05$  D in the naphthalene lattice. These results give some idea of the small uncertainties due to the anisotropy of the local field, as do the results in Table II.

Quinoxaline presents an interesting switch from usual expectations. It is found that  $\Delta\mu_T = 1.10 \pm$

(27) R. Pariser, *J. Chem. Phys.*, **25**, 1112 (1956); a quantum mechanical calculation for  $\pi$  electrons only.

(28) R. M. Hochstrasser and L. J. Noe, *Chem. Phys. Lett.*, **5**, 449 (1970).

(29) R. M. Hochstrasser and L. J. Noe, *J. Mol. Spectrosc.*, **38**, 175 (1971).

(30) A. D. Buckingham, D. A. Ramsey, and J. Tyrrell, *Can. J. Phys.*, **48**, 1242 (1970).

(31) R. M. Hochstrasser and D. A. Wiersma, *J. Chem. Phys.*, **56**, 528 (1972).

(32) J. S. Vincent and A. H. Maki, *J. Chem. Phys.*, **39**, 3088 (1963).

(33) J. W. Michaluk, Ph.D. Thesis, The University of Pennsylvania, 1972.

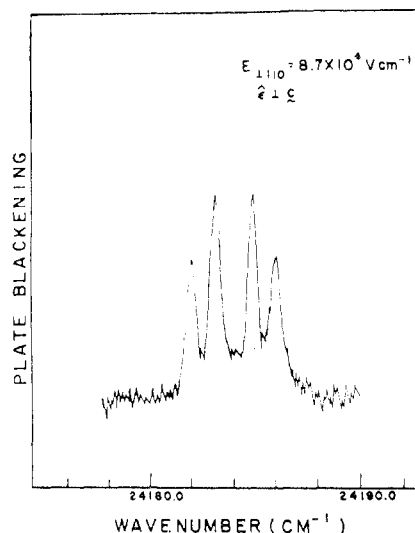


Figure 4. Absorption spectrum in polarized light of a benzophenone single crystal at 4.2 K. The electric field is perpendicular to the 110 crystal plane. The polarization of the light is  $\perp c$ . At zero field just a single line is observed at the center of this pattern, (reproduced from the *Journal of Chemical Physics*, with permission).

Table II

Host lattice (guest)	$\epsilon_\alpha$	$\Delta E$ , $\text{cm}^{-1}/10^5 \nu$	Uncor	Corrected for local field <sup>b</sup>	X-Ray data <sup>c</sup>
Azulene	$\epsilon_a$	1.45	0.401	0.472	0.438
in	$\epsilon_b$	0.77	0.212	0.225	0.210
naphthalene	$\epsilon_c$	3.22	0.891	0.853	0.874

<sup>a</sup> Experimental numbers are subject to uncertainties of  $\sim 0.02$ .

<sup>b</sup> Anisotropic Lorentz correction:  $F_\alpha = E_\alpha(n_\alpha^2 + 2)/3$ . <sup>c</sup> The data refer to the  $L$  axis of naphthalene.

0.08 D for the lowest  $\pi\pi^*$  triplet state, which is a greater change than for the  $n\pi^*$  singlet discussed above! Usually  $n \rightarrow \pi^*$  promotions are expected to give larger modifications of the charge distribution, but the explanation in this case is probably that  $\Delta\mu_T$  is in the opposite direction to  $\Delta\mu_S$ . The  $n \rightarrow \pi^*$  promotion shifts electrons out of the ring with the nitrogens, and the opposite occurs for  $\pi \rightarrow \pi^*$  excitation.

### The Stark Effect and Crystal Structure

There is an important relationship between the number of components into which a spectral line is split and the number of molecules per unit cell, and also between the energy distribution of these components and the relative dispositions of the molecules in a unit cell. There are also obvious effects of disorder on the number of components. Since optical spectra in the absence of external fields expose the number of molecules per asymmetric unit, it follows that in the electric field the total number of molecules in the unit cell can be directly counted by counting the splitting components for each asymmetric site. Of course the number of components depends on the field direction, and if this is chosen as a symmetry axis the number will be reduced. The four-line spectrum in Figure 4 is of a benzophenone crystal. Four is the maximum number of lines for any field direction, and there are three mutually perpendicular directions where only two lines are seen.

These results specify  $D_2$  symmetry for the group interchanging the molecules in the unit cell. The spacing of the levels in Figure 4 is due to the different projections of the molecules onto the direction perpendicular to the 110 face.<sup>29</sup> The ratio of the  $E_b$  to  $E_a$  splittings is  $3.21 \pm 0.03$ , whereas the ratio of the projections of the C=O bond onto the **b** and **a** axes is 3.21 from X-ray diffraction.<sup>34</sup>

### Isomerization in Excited States

One of the most powerful traditional uses of dipole moments in structural chemistry is as a device for distinguishing isomers, one of which is more polar than the other. It is fitting to end this summary with the analogous structural identification of excited-state isomers. When all *trans*-2,2'-bispyridine is used to form a dilute solid solution in a biphenyl host lattice, one can observe in the low-temperature spectra some rather sharp lines around 3200 Å that correspond to what appears to be two separate  $n\pi^*$  absorption systems.<sup>35</sup> Actually one of the systems shows a Stark splitting and the other does not, indicating that one system is due to polar molecules and the other is not.<sup>36</sup> These mixed crystals are prepared by Bridgman techniques from a melt and the relative amounts of oriented polar and nonpolar forms in the dilute mixed crystal are presumably determined by the crystal growth kinetics.

### Conclusions

Table I contains the complete list of data, as of November 1972, using the techniques described here

(34) E. B. Fleischer, N. Sung, and S. Hawkinson, *J. Phys. Chem.*, **72**, 4311 (1968).

(35) R. D. McAlpine, *J. Mol. Spectrosc.*, **38**, 441 (1971).

(36) R. M. Hochstrasser and A. H. Zewail, unpublished work.

(see ref 20–24, 26, 28, 29, 31, 33, 36–41). A trend at present is to probe higher order effects and investigate the influence of electric fields on dynamical processes in molecular solids. In this Account I have described how to extract from electric-field experiments various parameters relating to the anisotropy of the charge distributions of molecules and crystals. In so doing I left virtually no space to discuss the use of these parameters in interpreting the structure and behavior of excited states. Such a discussion will await a considerable enlargement of the scope of Table I and will require a pooling of information from numerous other sources of these excited-state parameters.<sup>42</sup>

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(37) R. M. Hochstrasser and T. S. Lin, *J. Chem. Phys.*, **49**, 4929 (1968).

(38) A. P. Marchetti, *J. Chem. Phys.*, **56**, 510 (1972).

(39) R. M. Hochstrasser and A. P. Marchetti, *J. Mol. Spectrosc.*, **35**, 335 (1970).

(40) D. A. Wiersma, *Chem. Phys. Lett.*, **16**, 517 (1972).

(41) R. M. Hochstrasser and A. H. Zewail, *Chem. Phys. Lett.*, **11**, 157 (1971).

(42) Note Added in Proof. We have recently studied the second-order Stark effect on the visible absorption spectra of *p*-benzoquinone using modulation techniques (R. M. Hochstrasser, L. W. Johnson, and H. P. Trommsdorff, *Chem. Phys. Lett.*, in press). These studies confirm the presence of at least two close lying electronic  $n\pi^*$  states being mixed by the field. Intensity changes, energy shifts (both positive and negative polarizabilities), and Stark induced spectra were observed. Stark modulation clearly provides a powerful new method for the study of the excited electronic states of molecules.

## Determination of Mechanistic Information from Nuclear Magnetic Resonance Line Shapes for Intramolecular Exchange

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The rates of chemical processes under equilibrium conditions can be obtained from temperature-dependent nmr line shapes. Activation parameters of varying degrees of accuracy have been presented in a continuously broadening stream of publications since

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the early work of Gutowsky and Holm.<sup>1</sup> More recently efficient computational techniques for the analysis of line shapes in complex spin systems have made it possible to extract quite detailed mechanistic information in certain cases, in addition to the conventional rate data.

One of the earliest kinetic studies was the elegant work of Whitesides and Mitchell<sup>2</sup> on  $(\text{CH}_3)_2\text{NPF}_4$

(1) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

(2) G. M. Whitesides and H. L. Mitchell, *J. Amer. Chem. Soc.*, **91**, 5384 (1969).