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A. P. Marchetti [a] & M. Scozzafava [a]

[a] Research Laboratories, Eastman Kodak Company, Rochester, New York, 14650

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Crystal Field Induced Dipole Moments

The Stark Spectrum of Naphthacene in Benzophenone

A. P. MARCHETTI and M. SCOZZAFAVA

Research Laboratories, Eastman Kodak Company, Rochester, New York 14650

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In the polar host crystal benzophenone, the nonpolar guest naphthacene exhibits different dipole moments in its ground and first excited state. The dipole moment changes upon excitation for three guest sites are 1.2, 0.35, and 0.61D, as measured by low-temperature Stark techniques. The dipole moments are attributed to the polarizability of the guest in the electrostatic crystal field of the host, which is estimated to be $\sim 10^7$ V/cm.

INTRODUCTION

In a molecular crystal composed of polar molecules, an internal electric field can arise from the array of dipoles that constitute the crystal. This crystal field will act on a guest molecule in the crystal to shift its energy levels, to induce a dipole moment, and to alter intensity in various transitions. Previous work on such crystals has indicated that the crystal field can be large enough ($\sim 10^7$ V/cm) to contribute to the crystal shift.[1–3] For azulene as a guest in benzophenone, the polarizability change ($\Delta\alpha$) has been observed as a contribution to the dipole moment change ($\Delta\mu$) upon excitation.[4]

The general purpose of this work is to probe experimentally the effects of a crystal internal electric field on the spectrum of a nonpolar guest molecule. Our intent here is to measure the change in the induced dipole moment on excitation and use it to estimate the magnitude of the crystal field. We have accomplished this through the use of low-temperature Stark modulation techniques.

EXPERIMENTAL

Naphthacene-doped benzophenone crystals ($\sim 2 \times 10^{-6}$ *M*) were grown from enthanol or *n*-butanol by slow evaporation. The crystal faces and directions were identified from the external morphology.

The crystals used for Stark measurements were cut into rectangular slabs typically 1 × 7 × 10 mm. These crystals were placed between tin oxide-coated quartz disks and immersed in liquid helium. Electrical contact was made from the tin oxide electrodes to appropriate ac and dc high-voltage power supplies. The Stark spectra were obtained through field-modulation techniques,[5] although some direct absorption and emission dc Stark spectra were recorded for illustration.

The spectra were taken on a 1 m Jarrel-Ash spectrometer, mainly in first order, although some measurements were made in second order. The spectra were recorded using a cooled I.T.T. FW130 photomultiplier. The photomultiplier output was fed to a PAR model 124A lock-in amplifier for modulated Stark measurements and to an electrometer for dc measurements.

Spectra were also photographed on Kodak spectroscopic plates, type IaF. Wavelength calibration was provided by a hollow cathode ion arc lamp.

RESULTS

The absorption spectrum of naphthacene ($^1B_{2u} \leftarrow {}^1A_{1g}$ transition[6]) in benzophenone is shown in Figure 1 for crystals grown from ethanol. This transition is polarized along the short in-plane molecular axis (M). There are four site origins (O_1, O_2, O_3, and O_4), identified by the coincidence of absorption and emission (not shown) lines; and there are four separate vibrational progressions built on these origins. The same site origins were found with crystals grown from *n*-butanol but the spectrum built on O_1 was much more intense than the other spectra.

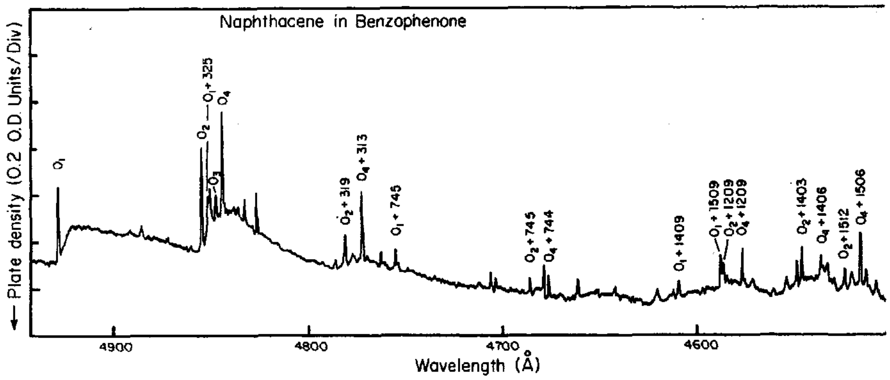

FIGURE 1 The unpolarized absorption spectrum of naphthacene in benzophenone at 4.2°K. The four site origins were identified by coincidence of absorption and emission (not shown) lines.

The vibrational analysis is given in Table I. The excited-state vibrational frequencies observed in this work are nearly the same as the values found by others,[6] but significant site-to-site variation of the vibrational frequency is observed. Furthermore, the spectrum built on O_2 contains a prominent low-frequency vibration of about 18 cm^{-1}, which also appears in combination with at least one other vibration and is observed in the emission spectrum. These variations in lattice and vibronic spectra must represent differences in the site-to-site host environment.

TABLE I

The vibrational analysis of the $^1B_{2u} \leftarrow {}^1A_{1g}$ absorption of naphthacene in benzophenone at 4·2°K

Intensity	Wavelength (Å)	Wavenumber (cm^{-1})[a]	Analysis
s	4929.8	20,279	O_1
w	4887.0	20,457	$O_1 + 178$
s	4855.5	20,589	O_2
sh	4852.1	20,604	$O_1 + 325$
m	4851.3	20,607	$O_2 + 18$
w	4847.9	20,622	O_3
vs	4844.8	20,635	O_4
w	4833.1	20,685	$O_1 + 406$
m	4826.9	20,711	$O_1 + 432$
m	4781.5	20,908	$O_2 + 319$
w	4777.4	20,926	$O_2 + 319 + 18$
s	4772.4	20,948	$O_4 + 313$
w	4762.8	20,990	$O_2 + 401$
w	4755.1	21,024	$O_1 + 745$
w	4706.1	21,243	$O_4 + 608$
w	4703.4	21,255	—
w	4686.0	21,334	$O_2 + 745$
m	4678.4	21,369	$O_3 + 747$
m	4676.2	21,379	$O_4 + 744$
w	4661.8	21,445	$O_1 + 1166$
w	4609.6	21,688	$O_1 + 1409$
m	4588.3	21,788	$O_1 + 1509$
w	4586.5	21,797	$O_2 + 1208$
w	4584.9	21,805	$O_1 + 325 + 1201$
m	4576.7	21,844	$O_4 + 1209$
w	4554[illegible]	21,950	$O_2 + 1361$
m	[illegible]	21,980	$O_4 + 1345$
m	[illegible]	21,992	$O_2 + 1403$
[illegible]	4535.7	22,041	$O_4 + 1406$
	4532.9	22,055	—
	4523.5	22,101	$O_2 + 1512$
w	4520.1	22,117	$O_2 + 319 + 1208$
s	4515.3	22,141	$O_4 + 1506$
w	4512.1	22,156	$O_4 + 313 + 1209$

[a] Vacuum wavenumbers.

s = strong, m = medium, w = weak, sh = shoulder, v = very

TABLE II

Polarization ratios and calculated direction cosines for the short in-plane (M) axis and the long in-plane axis (L) of napthacene in benzophenone

	O_1	O_2	O_4
I_a/I_b	0.093	0.48	2.20
I_{a+b}/I_c	4.98	2.86	1.09
$\lvert\cos\theta_{Ma}\rvert$	0.27	0.49	0.61
$\lvert\cos\theta_{Mb}\rvert$	0.89	0.71	0.41
$\lvert\cos\theta_{Mc}\rvert$	0.38	0.51	0.68
$\lvert\cos\theta_{La}\rvert$	(+)0.96[a]	(+)0.82	(+)0.56
$\lvert\cos\theta_{Lb}\rvert$	(+)0.29	(+)0.57	(+)0.83
$\lvert\cos\theta_{Lc}\rvert$	~0	~0	~0

[a] The signs of cos θ_L were chosen so that the long axis of naphthacene was approximately parallel to the line joining the centers of the two phenyl rings of the absent benzophenone with the projection on **a** chosen positive (see text).

Polarization data for the three most prominent origins (O_1, O_2, and O_4) are given in Table II along with the absolute values of the direction cosines for the short in-plane axis (M) of naphthacene derived from these data by using the "oriented gas" assumption.[2] This assumption should be satisfactory, as it correctly predicts the polarization observed for naphthacene in other hosts where the guest orientation is obvious from packing consideration;[6] moreover, since the molecular transition is strong, its direction should not be influenced appreciably by the crystal field.[7] If the naphthacene substitutes for one benzophenone molecule in the host crystal, then on the basis of the crystal structure,[8] it seems most likely that the long axis (L) of naphthacene will lie in the **ab** plane of the crystal, which is the approximate molecular plane of benzophenone.[8] Using this assumption and the orthogonal property of direction cosines, approximate absolute values of the direction cosines for the long axis can be obtained. These are also given in Table II.

Stark data for the three most intense origins (O_1, O_2, and O_4) are given in Table III and displayed in Figure 2. It is interesting that Stark splittings are observed for a field along only a single crystal direction for O_2 and O_4. No Stark modulation signals were observed with the applied field ($\mathscr{E}$) parallel to **c** for O_2 and O_4 and only a very weak signal was observed for O_1. The total change in induced moment for each origin is also given in Table III. The method of calculating the dipole moment change from the splitting

TABLE III

Stark data for the three strongest site origins of naphthacene in benzophenone: splitting (cm^{-1}) at 10^5 V/cm applied and the total induced dipole moment change (D)

	O_1	O_2	O_4
$\mathscr{E}\parallel a$	4.47	1.95	<0.5
$\mathscr{E}\parallel b$	4.34	N.S.[a]	2.98
$\mathscr{E}\parallel c$	< 0.5	N.S.	N.S.
$\lvert\Delta\mu\rvert$	1.20	0.35	0.61

[a] No signal observed.

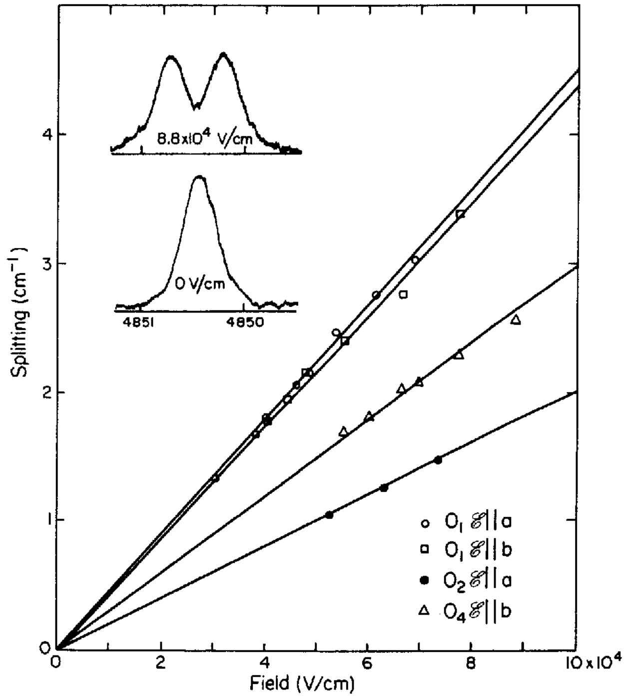

FIGURE 2 The absorption Stark splittings of the three strongest site origins as a function of applied external field. The insert shows the emission from Origin 4 (O_4) at zero field and at a dc applied field parallel to **b** of 8.8×10^4 V/cm.

is outlined elsewhere, as well as the methods for estimating the applied field at the molecule.[1–5,9]

DISCUSSION

The observed dipole moment change for naphthacene in benzophenone is attributed to the influence of an electrostatic crystal field. A lower limit to the magnitude of this field **F** is $|\mathbf{F}| \geq |\Delta\boldsymbol{\mu}|/|\Delta\alpha_{\max}|$, where $\Delta\alpha_{\max}$ is the largest component of the polarizability change. Experimental values of this polarizability change have been reported by several workers.[10–12] Using Liptay's values[10] $\Delta\alpha_{MM} = 15 \pm 6$ Å^3, $\Delta\alpha_{LL} + \Delta\alpha_{NN} = 59 \pm 6$ Å^3 ($= \Delta\alpha_{\max}$), one concludes that the effective crystal field strengths are at least 6×10^6, 2×10^6, and 3×10^6 V/cm for the sites represented by origins O_1, O_2, and O_4.

An examination of the crystal structure of benzophenone indicates that certain orientations of the guest, naphthacene, consistent with those inferred from the polarization data, are most likely on the basis of crystal packing. It is probable that the naphthacene substitutes for a benzophenone molecule so that the long axis of naphthacene is more or less parallel to a line that would have joined the centers of the phenyl rings of the absent benzophenone. This further assumption about the orientation in the **ab** plane can be used to assign signs to the direction cosines derived for the naphthacene long axis (Table II). For each site, one can analyze $\Delta\boldsymbol{\mu}$ into components parallel and perpendicular to the molecular long axis (L) in the **ab** plane. If an upper limit is set on the out-of-plane polarizability change, $\Delta\alpha_{NN} \leq \Delta\alpha_{MM}$, then the crystal field can be lower bounded parallel to $L(F_{\|} \geq \Delta\mu_{\|}/59)$ and perpendicular to $L(F_{\perp} \geq \Delta\mu_{\perp}/15)$. The vector sum of these values gives a more appropriate lower bound to the crystal field. The resultant lower bounds are 12×10^6, 5×10^6, and 6×10^6 V/cm for sites 1, 2, and 4, each about twice the lower limit computed above, and of the same order of magnitude as the values obtained by summing the field contributions from the surrounding permanent dipoles.[3] If, on the other hand, the value $\Delta\alpha_{LL} = 4.5$ Å^3 given in reference 12 is used with the assumption that $\Delta\alpha_{LL} \simeq 4\Delta\alpha_{MM}$, the crystal field must be huge, $\sim 2 \times 10^8$ V/cm—comparable to the classical ionization field of a hydrogen atom.[13] Fields this large should produce much larger crystal-field Stark shifts (on the order of 5000 cm^{-1}) than are observed in the spectrum of azulene in benzophenone.[2] Thus, it appears that the values of Liptay *et al.* are preferable.

These experimental values of crystal fields differ enough from site to site to raise questions about the uniformity of this field. To estimate the spatial variation of the crystal field, we have calculated its value at several points about an "absent" benzophenone molecule by summing contributions from molecular dipole moments out to 50 Å.[1,3]

The results of this calculation indicate that the field is nonuniform in magnitude (factor of 4 or 5) and direction ($\pm 60°$). Thus, the observed field effects at a guest molecule are really due to some kind of average of this field over the molecule and may be poorly correlated with the field calculated at any single point.

Finally, using the experimental value of the electric field at each site and the experimental value of the polarizability change of naphthacene on excitation, we find that the second-order Stark energies, $\Delta W = \frac{1}{2}\mathbf{F} \cdot \Delta\boldsymbol{\mu}$, are on the order of 25–150 cm^{-1}. Thus, the differences from site to site in the second-order Stark energy must make a sizable contribution to the site splittings, which are on the order of several hundred cm^{-1}.

Qualitatively, this discussion has concentrated on the contribution to the crystal field due to the permanent dipole moment of the host molecule because this contribution should be dominant in favorable cases. The experimental results represent the full electrostatic field in the crystal whatever its source. Higher multipole moments may make a sizable contribution. For example, a point quadrupole representing the quadrupole moment of benzene ($q_{LL} = q_{MM} = 2.8 \times 10^{-26}$ esu cm^2 and $q_{NN} = 5.6 \times 10^{-26}$ esu cm^2)[14] can give rise to an electric field as large as 3×10^6 V/cm at a distance of 5 Å.[15] This is a sizable field at a distance on the order of molecular spacing. It and the contribution of higher multipole moments should then influence induced moments and could make a major contribution to multiple site effects observed[16–19] in nonpolar crystals.

In this treatment we have used *point* multipoles to *estimate* the crystal electric field. There are, of course, serious errors involved in this procedure, particularly for small distances.[20] Perhaps in the near future this problem may be circumvented as molecular wave functions of sufficient quality to calculate electrostatic interactions directly become available.[21–23] A clearer picture of the crystal field and its contribution from individual molecular multipole moments should then be available!

CONCLUSIONS

From the investigation we have concluded:

1) Naphthacene in benzophenone has induced dipole moments which change by 1.2, 0.35, and 0.61D for the three most prominent sites on excitation to the $^1B_{2u}$ state.
2) The crystal field acting on one guest naphthacene molecule is $\geq 6 \times 10^6$ V/cm.
3) The site-to-site differences in the second-order Stark energy can contribute significantly to the site splitting.

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