

where subscripts s and u indicate substituted and unsubstituted phenol. Previous investigations^{13,14} have shown that ΔH_3° may be expressed as the sum of two terms representing solute-solvent interactions (ΔH_{ext}) and "internal" effects. These considerations have led to the equation

$$\Delta H_3^\circ = \Delta H_{\text{int}} + \beta \Delta S_3^\circ \quad (\beta = 280^\circ) \quad (4)$$

for reactions of type 3. Experimental enthalpy and entropy changes are represented by ΔH_3° and ΔS_3° while ΔH_{int} represents the part of the total ΔH_3° that is associated with breaking and forming O-H bonds as affected by resonance, inductive effects, etc. Combination of 4 with $\Delta F_3^\circ = \Delta H_3^\circ - T\Delta S_3^\circ$ leads to

$$\frac{\Delta F_3^\circ}{\Delta H_{\text{int}}} = 1 + \frac{(\beta - T)\Delta S_3^\circ}{\Delta H_{\text{int}}} \quad (5)$$

and then, because $\frac{(\beta - T)\Delta S_3^\circ}{\Delta H_{\text{int}}} \ll 1$, to

$$\Delta F_3^\circ \cong \Delta H_{\text{int}} \quad (6)$$

Values of ΔH_3° and ΔS_3° used in eq. 4 have been calculated from the values of $\Delta H_{\text{ion}}^\circ$ and $\Delta S_{\text{ion}}^\circ$ in Table II and are listed in Table III along with values of ΔH_{int} and ΔF_3° ($\Delta \Delta F^\circ$).

TABLE III
THERMODYNAMICS OF PROTON TRANSFER (REACTION 3) FOR
SUBSTITUTED PHENOLS

HA _s	ΔS° ^a	ΔH_3° ^a	$\Delta H_{\text{int}}^\circ$ ^a	ΔF_3° ^a
2,4,6-Trimethylphenol	-4.8	-0.21	+1.13	+1.21
3,4,5-Trimethylphenol	-1.1	+0.03	+0.34	+0.34
2,4,5-Trimethylphenol	-0.1	+0.75	+0.78	+0.77
2,3,5-Trimethylphenol	-1.9	+0.35	+0.88	-0.81
<i>m</i> -Cyanophenol	+5.0	-0.45	-1.85	-1.95
<i>p</i> -Cyanophenol	+6.8	-0.73	-2.63	-2.77
<i>m</i> -HOC ₆ H ₄ N(CH ₃) ₃ ⁺	+10.2	+0.44	-2.42	-2.65
<i>p</i> -HOC ₆ H ₄ N(CH ₃) ₃ ⁺	+6.9	-0.19	-2.12	-2.25

^a ΔH and ΔF° in kcal./mole, ΔS° in cal./deg. mole.

The physical meaning of eq. 4, with β close to T , is that the effects of solute-solvent interactions on

(13) L. G. Hepler and W. F. O'Hara, *J. Phys. Chem.*, **65**, 811 (1961).

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ΔH_3° and $T\Delta S_3^\circ$ are nearly equal and hence contribute so little to ΔF_3° that $\Delta F_3^\circ \cong \Delta H_{\text{int}}$.

A traditional explanation of the cyanophenols as compared to phenol and each other is that both are stronger acids than phenol because of the electron-withdrawing effect of the cyano group (partly due to resonance) and that *p*-cyanophenol is a stronger acid than *m*-cyanophenol because of resonance stabilization of the anion of *p*-cyanophenol. It can be seen that this explanation is in accord with the pK values. Since experimental ΔH° values include contributions from the solute-solvent interactions, it should not be surprising that ΔH_3° values are not simply related to either the pK values or the traditional explanation. Although the contribution of $\Delta H_{\text{external}}$ to ΔH_3° is important, eq. 4-6 and the accompanying discussion show that the net effect of solute-solvent interactions on ΔF_3° and thence ΔpK is small so that ΔH_{int} (to which resonance and inductive arguments apply) largely determines acidity.

Similar arguments apply to the other phenols.^{13,15} For instance, both HOC₆H₄N(CH₃)₃⁺ compounds are stronger acids than phenol. A simple explanation is that the positively charged substituent makes it "easier" to remove a proton from these compounds than from phenol. On the basis, the *m*-compound should be a stronger acid than the *p*-compound because the *m*-substituent is closer to the phenolic hydrogen than is the *p*-substituent. This explanation is supported by the pK and ΔH_{int} values, but the ΔH_3° and ΔS_3° values (which are affected importantly by solute-solvent interactions) are not simply related to the above explanation.

Acknowledgment.—Except for preliminary experiments on the HOC₆H₄N(CH₃)₃⁺Cl⁻ compounds, which were supported by the National Science Foundation, this research has been supported by a grant from the National Institute of Health. We are grateful to F. Millero and Dr. J. C. Ahluwalia for help with some of the calorimetric experiments and to F. Garneau and D. Turecek for help with determinations of some of the pK values. We thank Dr. Joseph Epstein for interesting us in the HOC₆H₄N(CH₃)₃⁺Cl⁻ compounds.

(15) L. P. Fernandez and L. G. Hepler, *ibid.*, **81**, 1783 (1959).

[CONTRIBUTION FROM THE INTERNATIONAL BUSINESS MACHINES CORP., THOMAS J. WATSON RESEARCH CENTER, YORKTOWN HEIGHTS, N. Y.]

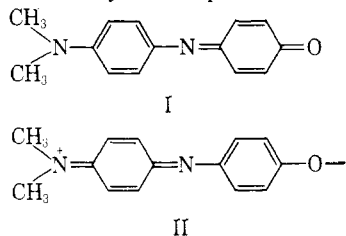
Stark Effect of Phenol Blue (Electrochromism)

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The effect of an external electric field on the absorption spectrum of phenol blue in an inert, transparent rigid matrix of high dielectric strength (polystyrene) has been studied. A net band shift to the red is observed. The results may be explained by assuming that a Stark shift occurs. A shift of 12 cm.⁻¹ at 9×10^5 v./cm. is observed on the band edge at 6500 Å., and this corresponds to an actual shift of 15 cm.⁻¹ when an intensity change correction is applied. A method for treating data to determine true band shifts in the presence of a simultaneous change in intensity is derived.

Phenol blue (I) has been of interest for some time because of the sensitivity of the position of its absorption



maximum to the polarity of a solvent. Brooker¹ found the maximum to be at 5520 Å. in cyclohexane and 6680 Å. in water. He rationalized this effect as due to a lowering of energy of the charged resonance forms, II, in a more polar solvent resulting in increased resonance stabilization of the molecule. Bayliss and McRae² and Platt³ have used this concept of solvent-

(1) L. G. S. Brooker and R. H. Sprague, *J. Am. Chem. Soc.*, **63**, 3214 (1941).

(2) N. S. Bayliss and E. G. McRae, *J. Phys. Chem.*, **58**, 1002 (1954).

(3) J. R. Platt, *J. Chem. Phys.*, **25**, 80 (1956).

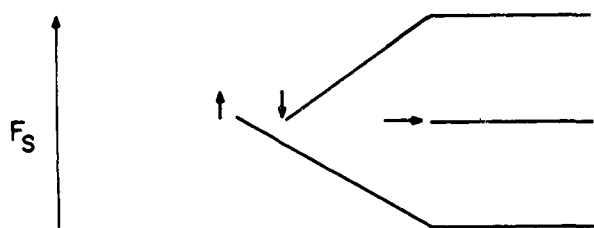


Fig. 1.—Random dipoles in a unidirectional field.

solute dipole interactions to account for general solvent effects in spectra. Brooker was unable to correlate his data with a macroscopic solvent property (the dielectric constant), and later measurements by LeRosen and Reid⁴ showed that the effect of solvent could not be correlated with the index of refraction of the solvent.

A general theory of solvent effects on electronic spectra has been worked out by Ooshika,⁵ Longuet-Higgins,⁶ and McRae⁷ by means of perturbation theory. (Here the solvent field interaction with the solute dipoles is taken as the perturbation.) McRae⁷ was able to fit the existing data for phenol blue in relatively nonpolar solvents by an equation involving only first-order corrections; he estimated the excited state dipole moment to be between 7.5 and 9.1 D., an increase of about 2.5 D. from the reported ground state⁸ value of 5.80 D. Recently, Kosower⁹ has shown that the solvent effects on the position of the maximum in phenol blue correlate with Z ,¹⁰ a universal solvent parameter, and he estimated the dipole moment in the first excited state of phenol blue to be at least 10.2 D. in polar solvents. Figure 1 shows schematically how the energy of a molecular level with fixed dipole moment varies with orientation when an external electric field is applied.

The effect of an electric field on an isolated, rigidly held dye molecule (methyl red) has been recently reported.¹¹ In that study, an electrochromic shift of the absorption spectrum was observed and the hypothesis offered that the shift was due to changes in electronic polarizability between the ground and excited state. Work by Labhart¹² shows, however, that this cannot be the only important effect and that changes in dipole moment and in transition moment must be taken into account, including changes due to the action of the static electric field in displacing the nuclei (before the absorption act). Accordingly, we can write the expression for the energy of a given state, as perturbed by an external field, only if the description of the state specifies nuclear as well as electronic coordinates.

It appears that a semiclassical treatment of the excited state is sufficient, and hence one can predict that the absorption band of a given molecule can be discussed in terms of changes in the whole band. In addition, one must average over all the orientations of the molecule relative to the polarization vector of the incident light. Such a treatment predicts a change in center frequency, a change in integrated intensity (*i.e.*, oscillator strength), and a broadening of the

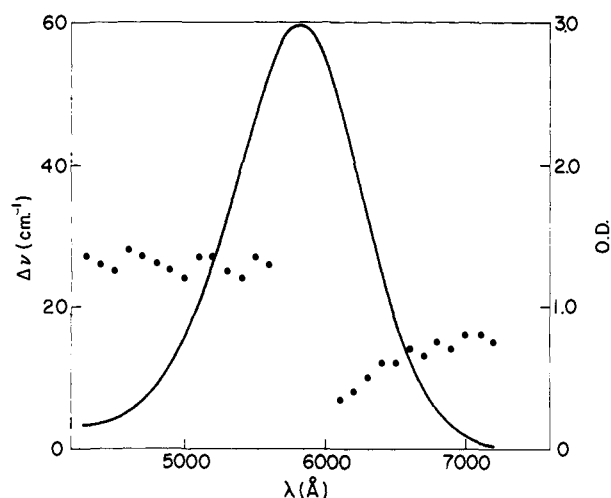


Fig. 2.—The observed shifts along the band edge. The dots are the displacements in cm^{-1} (left scale). The solid line shows the absorption band in O.D. (right scale).

observed absorption band, all three changes being proportional to the square of the applied electric field.

It appears that the broadening effect is difficult to determine experimentally because it involves the second moment of the absorption line, and hence is subject to errors due largely to uncertain contributions from the wings of the line. We show in Appendix I an approximate method treating the data obtained at 100 Å. intervals along the absorption band of phenol blue.

In Appendix II we indicate a method for checking the approximate method as well as deriving the mean shift and the mean change in intensity of the band.

Experimental

Phenol Blue.—Phenol blue was prepared by the method of Fieser¹³; after recrystallization from ethyl acetate it melted at 159–160°.

Polystyrene.—Lustrex (clear polystyrene) was used as such in the majority of the experiments. Purification by precipitation from benzene with methanol and drying at 60° did not alter any results.

Preparation of Samples.—Ten grains of polystyrene was dissolved in approximately 200 ml. of benzene and the requisite amount of phenol blue (0.05 to 0.15 g.) dissolved in benzene was added. The solution was poured into large Petri dishes and allowed to evaporate. The resultant polymeric mass was pressed into thin films by heat molding at 160°. The spectrum of phenol blue (~ 0.02 molal) in a thin film (0.065 mm.) of polystyrene is shown in Fig. 2 (solid line).

Electrodes.—Transparent electrodes were made by coating ordinary 2×3 in. microscope slides with a conducting film of tin oxide following the method of Gomer.¹⁴ Contacts for the connecting wires were made with du Pont colloidal silver paint. The size of the cell was such that it could be placed in the light path of a Cary spectrophotometer. In the experiments reported here, the sample was placed at right angles to the light path.

Instruments.—A Cary Model 14 spectrophotometer was used for the optical measurements. A Sorenson Model 230-6P high voltage d.c. power supply was used with a constant voltage transformer on the power line side.

Low Temperature Cell.—A cell of the type described by Wagner and Hornig¹⁵ was equipped with quartz windows. The sample was placed between tin oxide coated quartz plates and electrical connections were made with colloidal silver paint.

Results

A. The Effect of a Constant Applied Field Over the Total Band.—A typical spectrum of phenol blue in polystyrene is shown in Fig. 2 (solid line). The change in optical density, $\Delta\text{O.D.}$, caused by the application of a constant field was determined by a point-by-point method at intervals of 100 Å. These are pre-

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(5) Y. Ooshika, *J. Phys. Soc. Japan*, **9**, 594 (1954).

(6) H. C. Longuet-Higgins and J. A. Pople, *J. Chem. Phys.*, **27**, 192 (1957).

(7) E. G. McRae, *J. Phys. Chem.*, **61**, 562 (1957).

(8) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, p. 348.

(9) E. M. Kosower, *J. Am. Chem. Soc.*, **80**, 3261 (1958).

(10) E. M. Kosower, *ibid.*, **80**, 3253 (1958).

(11) J. Kumamoto, J. C. Powers, Jr., and W. R. Heller, *J. Chem. Phys.*, **36**, 2893 (1962).

(12) H. Labhart, *Helv. Chim. Acta*, **44**, 457 (1961).

TABLE I
THE EFFECT OF A CONSTANT APPLIED FIELD AT DIFFERENT WAVE LENGTHS

The film is 0.08 mm. thick, the applied field 7 kv., and the actual field $\sim 9 \times 10^5$ v./cm. The concentration of phenol blue was 0.050 g. in 10 g. of polystyrene (0.02 molal).

λ , Å.	ν , cm. ⁻¹	O.D.			λ' , Å.	ν' , cm. ⁻¹	$\Delta\nu'$, cm. ⁻¹ (obsd.)	$\Delta\nu$ (cor. for intens. loss)
		(obsd. without field)	(corr. for background)	Δ O.D. (obsd. due to field)				
7500	13333.3	-0.033	0.000	0.000				
7300	13699.0	- .005	.025	.002				
7200	13888.9	+ .021	.049	.002	7208.0	13873.5	15.4	
7100	14084.5	+ .053	.080	.004	7108.0	14068.7	15.8	
7000	14285.7	.105	.131	.005	7008.0	14269.4	16.3	
6900	14492.8	.177	.201	.008	6906.5	14479.1	13.7	
6800	14705.9	.285	.307	.009	6807.0	14690.8	15.1	
6700	14925.4	.435	.455	.012	6706.0	14912.0	13.4	
6600	15151.5	.638	.658	.015	6606.0	15137.8	13.7	
6500	15384.6	.906	.922	.017	6505.0	15372.8	11.8	
6400	15625.0	1.235	1.248	.018	6405.0	15612.8	12.2	
6300	15873.0	1.625	1.635	.018	6304.0	15862.9	10.1	
6200	16129.0	2.025	2.032	.013	6203.0	16121.2	7.8	
6100	16393.4	2.420	2.425	.009	6102.5	16386.7	6.7	
6000	16666.7	2.743	2.746	.002	6001.0	16663.9	2.8	
5900		2.939	2.940	— .005				
5800		2.985	2.983	— .017				
5700	17543.9	2.870	2.864	— .022	5712.0	17507.0	36.9	
5600	17857.1	2.632	2.622	— .024	5608.0	17831.7	25.4	
5500	18181.8	2.320	2.307	— .026	5508.0	18155.4	26.4	
5400	18518.5	1.995	1.979	— .024	5407.0	18494.5	24.0	
5300	18867.9	1.647	1.629	— .023	5307.0	18843.0	24.9	
5200	19230.8	1.325	1.303	— .022	5207.0	19204.9	25.9	
5100	19607.8	1.042	1.016	— .017	5107.0	19581.0	26.8	
5000	20000.0	0.808	0.779	— .013	5006.0	19976.0	24.0	
4900	20408.2	.615	.580	— .009	4906.0	20383.2	25.0	
4800	20833.3	.465	.425	— .007	4806.0	20807.3	26.0	
4700	21276.6	.352	.306	— .006	4706.0	21249.5	27.1	
4600	21739.1	.271	.219	— .004	4606.0	21710.8	28.3	
4500	22222.2	.216	.157	— .002	4505.0	22197.6	24.6	
4400	22727.3	.183	.116	— .001	4405.0	22701.5	25.8	
4300	23255.8	.171	.097	.000				
4200		.183	.102					
4100		.235	.148					
4000		.343	.248					

sented in Table I, under Δ O.D. observed. These data were analyzed by means of the "moment method" described in Appendix II. We find a loss of intensity or negative gain of 0.0044 for an applied field of 9×10^5 v./cm. The mean frequency shift is 15.8 cm.⁻¹ to the red for the same applied field. Broadening was calculated as 23,000 (cm.⁻¹)²; however, it is doubtful whether this quantity, B , has even an order-of-magnitude significance because of the uncertainties mentioned earlier.

An alternative method of analyzing for frequency shift is described in Appendix I. In this method we calculate the apparent shift at each point where the changes in O.D. were observed using the slope of the curve at that wave length and a similar triangle approximation. The values λ' , ν' , and $\Delta\nu'$, thus derived, are listed in Table I, columns six, seven, and eight, and these apparent shifts are shown in Fig. 2 (dots).

The final column in Table I was calculated by allowing for the effects of a uniform change in intensity. These corrected shifts, $\Delta\nu$, are plotted in Fig. 3 (circles). The formula relating the corrected and apparent shifts is

$$\Delta\nu_{\text{corr}} = \Delta\nu' \left(1 - \frac{\Delta f/f}{\Delta\text{O.D./O.D.}} \right)$$

The oscillator strength, f , is obtained by integrating the absorption curve over the frequency range.

The average frequency shift is 17 ± 2 cm.⁻¹, in satisfactory agreement with that derived by the mo-

TABLE II

DEPENDENCE OF THE SHIFT ON APPLIED FIELD

The film had a thickness of 0.05 mm. and the concentration of phenol blue was 0.066 molal (0.150 g. in 10 g. of polystyrene).

A. Measurements made at 6500 Å. B. Measurements made at 5100 Å.

Ap- plied field, kv.	A.			Ap- plied field, kv.	B.		
	O.D. obsd.	λ , Å.	ν , cm. ⁻¹		O.D. obsd.	λ , Å.	ν , cm. ⁻¹
0	1.902		15384.6	8	1.820	5124.3	19514.9
1	1.905	6500.7	15383.0	7	1.843	5119.7	19532.4
2	1.914	6502.2	15379.4	6	1.863	5115.6	19548.0
3	1.922	6503.5	15376.3	5	1.886	5111.0	19565.4
4	1.934	6505.5	15371.6	4	1.905	5107.1	19580.6
5	1.954	6508.9	15363.7	3	1.916	5104.9	19589.0
6	1.979	6513.0	15353.9	2	1.926	5102.8	19597.1
7	2.005	6517.3	15343.6	1	1.932	5101.6	19601.7
6	1.980	6513.2	15353.5	0	1.940		19607.8
5	1.958	6509.5	15362.1				
4	1.937	6506.0	15370.4				
3	1.922	6503.5	15376.3				
2	1.912	6501.8	15380.2				
1	1.902	6500.2	15384.2				
0	1.900						

ment method. A general derivation of the relation between the moment and point-wise methods of analysis has been carried out¹⁶ and applied to these

(16) W. E. Donath, to be submitted for publication.

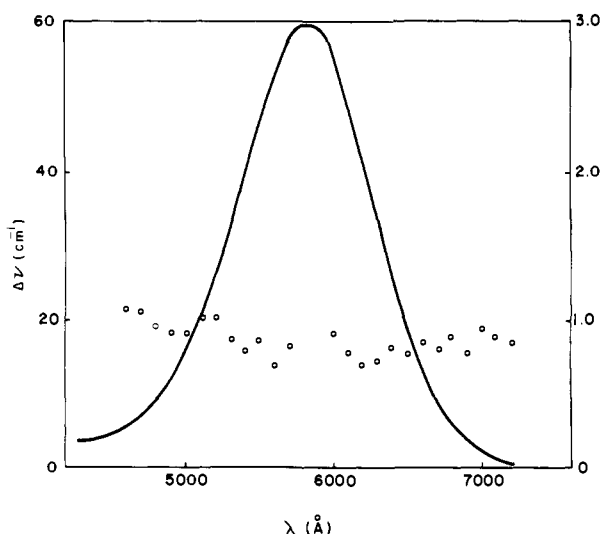


Fig. 3.—Intensity change correction

$$\Delta\nu = \Delta\nu' \left(1 - \frac{\Delta f/f}{\Delta O.D./O.D.} \right)$$

The circles are the displacements in cm^{-1} (left scale). The solid line shows the absorption band in O.D. (right scale).

data, with no significant changes in the numerical values.

B. Electric Field Dependence of the Shift.—The changes in optical density at a fixed wave length, 6500 Å., on the band edge were studied with varying applied fields. Corresponding measurements were made on the opposite band edge at 5100 Å. A representative sample using a more concentrated film (0.066 molal) is shown in Fig. 4 and the data are given in Table II. These results are plotted in Fig. 5 with a linear and a quadratic field dependence. It is clear that an adequate fit with the quadratic field dependence is found. Additional studies were carried out on films containing 0.02 molal phenol blue as well as the pure material melted into a sandwich between mylar sheets. The results were essentially the same as described above.

C. Measurements Made at Low Temperature.—The apparent shift measured with liquid nitrogen in the cell was dependent on the square of the applied field and of the same magnitude as that at room temperature. Since the band shifts as the temperature decreases, it was difficult to compare equivalent points on the spectrum, but the shift is approximately the same with liquid nitrogen as at room temperature.

Discussion

It is clear from the data observed that band broadening makes no significant contribution. The presence of both a band shift to the red and a band broadening should make the observed shift appear smaller on the blue edge and larger on the red edge. In fact, just the reverse is shown in Fig. 2. When the small loss in intensity is taken into account (eq. 10, Appendix I) there is satisfactory agreement among all the points for a simple band translation, Fig. 3.

Since the derivation shown in Appendix I contains a simplifying assumption about the intensity effect and neglects higher terms in expansions, a more rigorous derivation was made (Appendix II) and was used in a machine calculation and found to agree with the values given in Table I.

Conclusion

The results of this study show that the major effect of an external electric field on a rigidly held matrix iso-

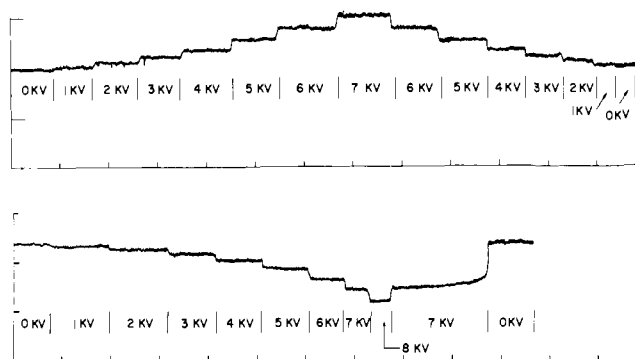


Fig. 4a (upper curve).—The effect of varying field at 6500 Å. The time scan is from right to left at 1 min./div. The vertical scale is in 0.1 optical density unit/div.

Fig. 4b (lower curve).—The effect of varying field at 5100 Å. The time scan is from right to left at 1 min./div. The vertical scale is in 0.1 optical density unit/div.

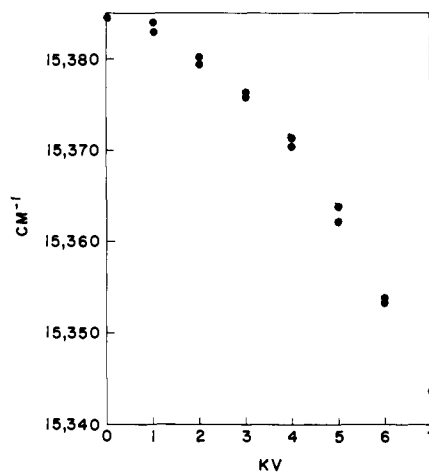


Fig. 5a.—Field dependence at 6500 Å. plotted with linear field.

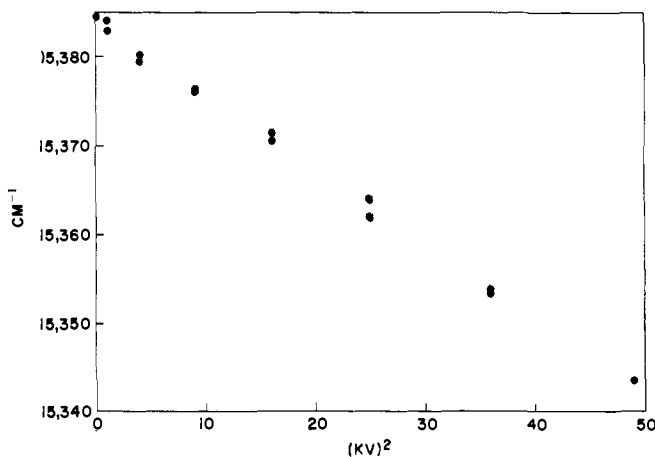


Fig. 5b.—Field dependence at 6500 Å. plotted with the square of the field.

lated molecule of phenol blue is a band shift to the red. The absence of any temperature effect on the shift makes it seem unlikely that these molecules are being reoriented in the matrix by the field. (Such an orientation change could in principle give rise to the observed effect.)

The failure to detect any systematic trend in the shifts along the band edges in Fig. 3 indicates that the expected band broadening is difficult to observe. This would be the case if the broadening is small relative to the band width.

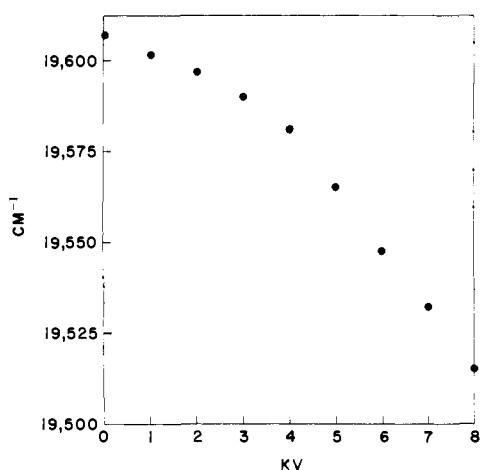


Fig. 5c.—Field dependence at 5100 Å, plotted with linear field.

It appears that the general explanation for the solvent sensitivity of phenol blue in terms of a solute-dipole solvent-field interaction¹⁷ is not complete and should include a contribution from the second-order term. This quadratic field dependent effect can be rationalized as arising from a mixing of excited states induced by the external electric field. This sort of behavior has been known for a long time in atomic spectra and is the classical Stark effect.¹⁵

Acknowledgments.—We wish to thank Dr. H. L. Friedman and Dr. W. L. Peticolas for encouragement and critical discussions and Dr. W. E. Bron for his cooperation in performing the experiments.

Appendix I

A broad band which has shifted an amount $\Delta\nu$ may be described in terms of its extinction coefficient $\epsilon(\nu)$ as

$$\epsilon(\nu + \Delta\nu) = \epsilon(\nu) + (\partial\epsilon/\partial\nu)\Delta\nu + (\partial^2\epsilon/\partial\nu^2)\Delta\nu^2 \quad (1)$$

If we assume that a uniform change in intensity occurs, we can relate the new extinction coefficient $\epsilon'(\nu)$ with

$$\epsilon'(\nu) = (1 + G)\epsilon(\nu) \quad (2)$$

where G is defined in terms of the oscillator strength of the band f as

$$G = \Delta f/f \quad (3)$$

and it follows that

$$\epsilon'(\nu) - \epsilon(\nu) = \int_{\nu} \Delta\epsilon(\nu)d\nu = G \int_{\nu} \epsilon(\nu)d\nu \quad (4)$$

Using expressions 1 and 2 to allow for a shift $\Delta\nu$ and a simultaneous change in intensity G we have

$$\epsilon'(\nu + \Delta\nu) = (1 + G)[\epsilon(\nu) + (\partial\epsilon/\partial\nu)\Delta\nu + \dots] \quad (5)$$

For small shifts and small changes in intensity we may neglect the higher terms.

$$\Delta'\epsilon(\nu) = \epsilon'(\nu + \Delta\nu) - \epsilon(\nu) = G\epsilon(\nu) + (\partial\epsilon/\partial\nu)\Delta\nu \quad (6)$$

Rearranging terms gives

$$[\Delta'\epsilon - G\epsilon(\nu)] \frac{1}{\partial\epsilon/\partial\nu} = \Delta\nu \quad (7)$$

In terms of an actual observed shift of the band $\Delta\nu'$ we may write

(17) For a recent review, see A. I. Kiprianov, *Russ. Chem. Rev.*, **29**, 618 (1960).

(18) E. U. Condon and G. H. Shortley, "The Theory of Atomic Spectra," Cambridge Univ. Press, Cambridge, 1957, Chapter XVII, pp. 397-417.

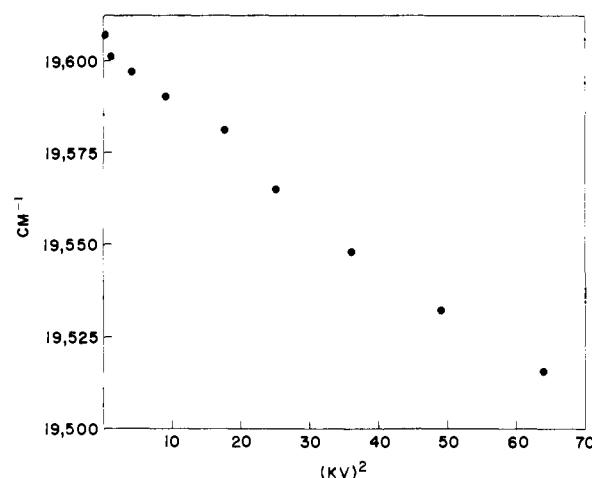


Fig. 5d.—Field dependence at 5100 Å, plotted with the square of the field.

$$\Delta\nu' = \frac{\Delta\epsilon}{\partial\epsilon/\partial\nu}, \quad \frac{\nabla\epsilon}{\Delta\nu'} = \partial\epsilon/\partial\nu \quad (8)$$

Substituting in eq. 7 we can relate the experimentally determined shift to the actual shift

$$\Delta\nu(\Delta\epsilon/\Delta\nu') = \Delta\epsilon - G\epsilon(\nu) \quad (9)$$

and

$$\frac{\Delta\nu}{\Delta\nu'} = 1 - \frac{G\epsilon(\nu)}{\Delta\epsilon} \quad (10)$$

$$\Delta\nu = \Delta\nu' \left(1 - \frac{\Delta f/f}{\Delta\epsilon/\epsilon} \right)$$

and $\Delta\epsilon/\epsilon = \Delta\text{O.D.}/\text{O.D.}$, where O.D. is the observed optical density.

Appendix II

Deduction of change in a single broad optical absorption band due to external influence (stress, electric field, etc.) is given. If we assume that the band absorption can be represented as an extinction or absorption coefficient which vanishes sufficiently rapidly at infinity that the first and second moments exist, we may make the following definitions:

Define

$$\phi \equiv \int_{-\infty}^{\infty} \epsilon(\nu)d\nu \quad (1)$$

$$\langle\nu_0\rangle \equiv \int \nu\epsilon(\nu)d\nu/\phi \quad (2)$$

$$\langle w^2(0)\rangle \equiv 4 \int (\nu - \langle\nu_0\rangle)^2 \epsilon(\nu)d\nu/\phi \quad (3)$$

Define the *intensity change* by

$$\frac{\int [\epsilon(\nu, F) - \epsilon(\nu, 0)]d\nu}{\phi} \equiv G \quad (4)$$

Define *mean frequency shift* by

$$\Delta(\nu) \equiv \frac{\int \epsilon(\nu, F)(\nu - \langle\nu_0\rangle)d\nu}{\phi(1 + G)} \quad (5)$$

Define *mean broadening* by

$$B = \langle w^2(F)\rangle - \langle w^2(0)\rangle = \frac{4 \int \epsilon(\nu, F)(\nu - \langle\nu_0\rangle - \Delta(\nu))^2 d\nu}{(1 + G)\phi} - \langle w^2(0)\rangle \quad (6)$$

Equations 1, 2, and 5 may be manipulated to give

$$\Delta(\nu) = \frac{\int \Delta\epsilon(\nu, F)(\nu - \langle\nu_0\rangle)d\nu}{(1 + G)\phi} \quad (7)$$

where

$$\Delta\epsilon(\nu, F) = \epsilon(\nu, F) - \epsilon(\nu) \quad (8)$$