Spectroscopic Properties of Organic Photoconductors. I. Absorption Spectra of Cationic Dye Films

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only tentatively suggested.

$$CH_3 + O_2 \rightarrow CH_3O_2$$
$$CH_3 + O_2 \rightarrow H_2CO + OH$$
$$CH_3 + O_2 \rightarrow CH_2 + HO_2$$
$$CH_3O_2 + CH_3 \rightarrow CH_3O_2CH_3$$
$$CH_3O_2 + RH \rightarrow CH_3O_2H + R$$
$$CH_3O_2CH_3 \rightarrow 2CH_3O$$
$$CH_3O_2H \rightarrow CH_3O + OH$$
$$CH_3O \rightarrow H_2CO + H$$
$$CH_3O + RH \rightarrow CH_3OH + R$$
$$H + O_2 \rightarrow HO_2$$
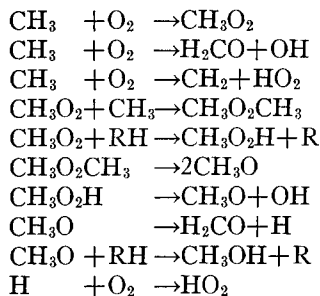
The CHO radical, if present, might be formed by either

$$H_2CO + O_2 \rightarrow HO_2 + CHO$$

or perhaps

$$CH_3 + O_2 \rightarrow CHO + H_2O.$$
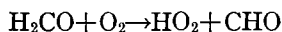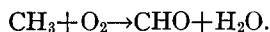
It would be removed by two fast reactions:

$$CHO + O_2 \rightarrow HO_2 + CO,$$
$$CH_3 + CHO \rightarrow CH_3CHO.$$
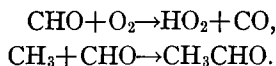
CO, CO_2, and H_2O were naturally to be expected as products. H_2O_2 could be formed from HO_2 and a H atom or by the combination of two OH radicals. Ketene could come from the reaction[14]

$$CH_2 + CO \rightarrow CH_2CO.$$
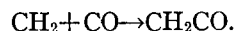
Acetylene and methyl ketene or acrolein (mass 56) cannot be accounted for as easily and were probably secondary products produced after several reaction steps. $CH_3O_2CH_3$ and CH_3O_2H are very unstable with respect to O—O bond scission even at room temperatures. At 1000°C their lifetime will be less than 10^{-6} sec. With a flow rate of only 5000 cm/sec in the reactor, their absence from the products was not surprising. Their decomposition would account for the CH_3O and OH radicals.

Although most of the radicals reported here were detected by Eltenton[1] in the $CH_4 - O_2$ flame, the present method has the advantage that, because of the low concentration of reactants, the concentration of intermediates relative to final products is much higher than in low-pressure flames. For this reason their detection is easier and the whole mass spectrum is less complicated.

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Spectroscopic Properties of Organic Photoconductors. I. Absorption Spectra of Cationic Dye Films

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The absorption spectra of solid films of six photoconductive dyes are reported. The transitions in the solid state correspond to those of the "isolated" cations in solution. However, the longest-wavelength singlet-singlet absorption band is split into components separated by 1000 cm^{-1} or more. Other bands are unaffected, except for a general decrease of oscillator strength. The results are interpreted in terms of light absorption by a single molecule, followed by exciton motion in the lowest excited state.

THE electronic energy levels of organic crystals generally are nearly identical with those of the individual molecules, and the molecules act in various ways as though they were isolated. In a number of highly conjugated solids, however, there is sufficient interaction among neighbors to permit excited electrons to migrate through a "conduction band"—a communal energy level extending through large regions of the lattice. These are the organic semi- and photoconductors. The best known of these are, at present, the photoconductive films of cationic dyes, which have recently been investigated in detail by Vartanian[1] and Nelson.[2] These systems are of special interest because their solid-state behavior is largely determined by well-known properties of their isolated components.

The present series of papers on the absorption, reflection, and action spectra[3] of certain of these photoconductive dye films (referred to, below, as I,

[1] A. T. Vartanian (a) Acta Physicochim. U.R.S.S. 22, 201 (1947); (b) J. Phys. Chem. U.S.S.R. 20, 1065 (1946); (c) 22, 769 (1948); (d) 24, 1361 (1950); (e) Bull. Acad. Sci. U.S.S.R. (Phys. Ser.) 16, 169 (1952).
[2] R. C. Nelson (a) J. Chem. Phys. 19, 798 (1951); (b) 20, 1327 (1952); (c) 22, 885–95 (1954).
[3] An excitation, or action spectrum of photoconduction is the relationship between the wavelength of incident light and the photocurrent produced.

II, and III, respectively) is primarily concerned with the relationship between the molecular and crystal energy levels. It will be shown that the primary photoexcitation of carriers is practically equivalent to the excitation of individual dye molecules to well-known singlet levels, followed by electron ejection into the lattice. Much is known about the spectroscopy and photochemistry of "isolated" dye molecules in dilute solution; this information may now be applied to the behavior of these substances in the solid state.

While Holmes,[4] Vartanian,[5] and others[6,7] have already published absorption spectra of solid dyes, it was desirable to reinvestigate selected *cationic* dye films, prepared under conditions yielding photoconductive samples, and corrected for reflectivity. We have also compared the oscillator strength in the solid and dissolved dyes, measured the effect of temperature changes and of variations in the anions upon film spectra, and correlated the absorption and excitation spectra[3] of photoconductivity (III).

EXPERIMENTAL

The triphenylmethane dyes, crystal violet (XlV), malachite green (Mkg), and basic fuchsin (Bfs), were purified by the method of Lewis, Magel, and Lipkin,[8] vacuum-dried and redissolved in absolute alcohol or methanol. Trypaflavine (Tryp), methylene blue (MeBlu) and rhodamine B (Rdm) were subjected to vacuum sublimation. Pinacyanole (Pin) (Eastman) was used without purification. The solution spectra of all dyes, before and after film formation, were in satisfactory agreement with the best data in the literature.

The photoconductivity of cationic dyes is sensitive to oxygen and perhaps to traces of solvent and water vapor. Therefore, in order to make these films comparable to those used for the measurement of action spectra (III) and the kinetics of photoconduction,[2] the dye was deposited from concentrated alcohol solution, under nitrogen, on one clear face of a 1 cm ×1 cm square Pyrex absorption cell which had been attached to a vacuum line. The system was evacuated for two hours or more. At the end of this time, certain of the samples were sublimed to the opposite face of the cell by gentle application of a soft microflame to the lower face originally bearing the dye. The upper face was cooled, usually by silicone grease contact with a liquid nitrogen-cooled copper block. Finally the cell was sealed. All these operations were carried out in subdued light, in order to avoid possible photodecomposition. Films of these dyes, prepared in this manner, are photoconductive.

All dyes described, except crystal violet, could be sublimed without appreciable decomposition. Methylene blue was found to leave a brownish film upon the heated surface; for this reason, it was initially deposited on the vertical sides of the cell, where the residue could not obstruct the optical path.

Because of the errors inherent in the photometry of samples of nonuniform optical density, a great effort was made to produce films as homogeneous and "glassy" in appearance as possible. Samples showing visible microcrystalline structure, or appreciable variation in transmissivity across the window area of the cell, were rejected.

X-ray diffraction patterns[9] of powdered and intact films of crystal violet, pinacyanole, and rhodamine B showed lines as sharp as those of the crystalline dyes, and those of metallic copper. From this we concluded the films to be polycrystalline, with domain sizes of the order of 1000 Å or more.[10]

All spectral measurements were carried out with a Beckman Quartz Spectrophotometer. Pyrex sample cells were used to simplify the glass blowing, even though this limited the observable region to wavelengths greater than 3200 Å. For transmission measurements at about 77°K the usual cell compartment was replaced by a special attachment,[11] in which evacuated standard and sample cells were immersed in liquid nitrogen, and alternately rotated in and out of the optical path. The light reaching the phototube could be polarized, when desired, by insertion of a small sheet of Polaroid in the entrance window of the phototube compartment.

The reflectivity of each film was compared to that of a standard aluminum surface enclosed in a matching cell, by means of another attachment to the Beckman spectrophotometer. Absorption spectra were then computed from transmission and specular reflection measurements, with full correction for multiple reflection effects (II).

The ratio of the extinction coefficients of the solid and dissolved dye was determined by comparing the optical density of a measured area of film with that of the same quantity of dye in solution. After the cell had been opened, excess dye around the edges of the window and adjacent sides was removed by means of pipe cleaners moistened with a nonpolar, volatile solvent, such as chloroform, which would not disturb the uniform film over the window. The remaining area was then estimated, with an error of about ±15% by means of a transparent millimeter scale. The dye was

[4] W. C. Holmes and A. R. Peterson, J. Phys. Chem. **36**, 1248 (1932).

[5] A. T. Vartanian, J. Tech. Phys. U.S.S.R. **20**, 847 (1950); Chem. Abstracts **44**, 9799d.

[6] W. E. Speas, Phys. Rev. **31**, 569 (1928).

[7] (a) S. E. Sheppard, Revs. Modern Phys. **14**, 303 (1942); (b) S. E. Sheppard and G. E. Geddes, J. Am. Chem. Soc. **66**, 2003 (1944). (c) S. E. Sheppard and P. T. Newsome, *ibid.* **64**, 2937 (1942).

[8] Lewis, Magel, and Lipkin, J. Am. Chem. Soc. **64**, 1774 (1942).

[9] Run in collaboration with Professor C. H. Shaw of this Department.

[10] C. W. Bunn, *Chemical Crystallography* (Oxford University Press, London, 1946), p. 366.

[11] Patterned after the design of G. D. Dorough and K. T. Shen, J. Am. Chem. Soc. **72**, 3939 (1950).

TABLE I. Extinction coefficients and oscillator strengths.

Dye	Film		Band	λ_m A.	$\bar{\nu}_m$ cm⁻¹	β_m	$\epsilon_m \times 10^{-4}$	f	f_f/f_s	$\Delta\bar{\nu}$ cm⁻¹	$\Delta\bar{\nu}_f/\Delta\bar{\nu}_s$
Rdm	1	Sol'n	1, tot.	5480	18 250	...	11.0	0.73	...	1540	...
		Film	1, tot.	5750	17 400	1.64	2.13	0.22	0.30	2400	1.56
			1, lg.-λ	5750	17 400	1.64	2.13	0.12	...	1320	0.86
			1, sh.-λ	5360	18 650	1.02	1.32	0.10	...	1740	1.13
Rdm	2	Sol'n	1, tot.	5480	18 250	...	11.0	0.73	...	1540	...
		Film	1, tot.	5750	17 400	1.86	2.65	0.26	0.36	2280	1.48
			1, lg.-λ	5750	17 400	1.86	2.65	0.14	...	1240	0.80
			1, sh.-λ	5360	18 650	1.15	1.64	0.12	...	1670	1.08
Mkg	3	Sol'n	1, tot.	6180	16 200	...	9.55	0.73	...	1760	...
		Film	1, tot.	6670	15 000	0.606	2.58	0.40	0.55	3540	2.03
			1, lg.-λ	6670	15 000	0.606	2.58	0.22	...	2010	1.15
			1, sh.-λ	6030	16 600	0.445	1.90	0.17	...	2090	1.20
		Sol'n	2	4260	23 500	...	1.85	0.25	...	3100	...
		Film	2	4360	22 900	0.200	0.85	0.14	0.56	3860	1.24
		Sol'n	3	3150	31 700	...	1.88	0.22*	...	2700*	...
		Film	3	3250	30 800	0.235	1.00	0.13*	0.50*	2960*	0.94*
Mkg	4	Sol'n	1, tot.	6180	16 200	...	9.55	0.73	...	1760	...
		Film	1, tot.	6700	14 900	0.397	3.33	0.51	0.705	3520	2.05
			1, lg.-λ	6700	14 900	0.397	3.33	0.25	...	1720	1.00
			1, sh.-λ	6100	16 400	0.302	2.58	0.26	...	2360	1.36
		Sol'n	2	4260	23 500	...	1.85	0.25	...	3120	...
		Film	2	4390	22 800	0.128	1.07	0.16	0.735	3520	1.26
		Sol'n	3	3150	31 700	...	1.88	0.22	...	2700*	...
		Film	3	3240	30 900	0.148	1.24	0.15*	0.68*	2800*	1.03*
Mkg	5	Sol'n	1, tot.	6180	16 200	...	9.55	0.73	...	1760	...
		Film	1, tot.	6590	15 200	0.630	3.45	0.55	0.75	3660	2.08
			1, lg.-λ	6590	15 200	0.630	3.45	0.29	...	1960	1.11
			1, sh.-λ	5920	16 900	0.475	2.61	0.26	...	2260	1.28
		Sol'n	2	4260	23 500	...	1.85	0.25	...	3100	...
		Film	2	4350	23 000	0.250	1.27	0.21	0.84	3880	1.25
		Sol'n	3	3150	31 700	...	1.88	0.22*	...	2700*	...
		Film	3	3240	30 900	0.310	1.70	0.19*	0.86*	2600*	0.96*
Mkg	6	Sol'n	1, tot.	6180	16 200	...	9.55	0.73	...	1760	...
		Film	1, tot.	6590	15 200	0.738	2.92	0.49	0.67	3900	2.22
			1, lg.-λ	6590	15 200	0.738	2.92	0.27	...	2200	1.25
			1, sh.-λ	5950	16 800	0.525	2.08	0.22	...	2380	1.35
		Sol'n	2	4260	23 500	...	1.85	0.25	...	3100	...
		Film	2	4350	23 000	0.300	1.23	0.21	0.84	3930	1.27
		Sol'n	3	3150	31 700	...	1.88	0.22*	...	2700*	...
		Film	3	3230	31 000	0.350	1.40	0.17*	0.77*	2900*	1.07*
XIV	7	Sol'n	1	5860	17 030	...	10.6	1.12	...	2440	...
		Film	1	5920	16 900	0.490	3.3	0.67	0.63	4700	1.95
XIV	8	Sol'n	1	5860	17 030	...	10.6	1.12	...	2440	...
		Film	1	5990	16 700	0.450	2.5	0.52	0.46	4800	1.95
Tryp	9	Sol'n	1	4600	21 700	...	5.48	0.53	...	2230	...
		Film	1	4560	21 900	0.960	2.20	0.45	0.80	4710	2.00
Pin.	10	Sol'n	1, lg.-λ	6060	16 500	...	15.8				
			1, sh.-λ	5630	17 775	...	7.30				
			1, tot.					1.10	...	1600	...
		Film	1, tot.	5850	17 100	0.240	2.60	0.63	0.57	5600	3.50
MeBlu	11	Sol'n	1	6550	15 280	...	9.00	0.63	...	1620	...
		Film	1	6670	15 000	0.660	2.2	0.24	0.40	2400	1.5

* Based on the long-λ half of band 3; lg.-long, sh.-short-λ components; λ_m-wavelength at absorption maximum; f-oscillator strength. ϵ_m-extinction coefficient and band width, $\Delta\bar{\nu}$ =area under peak/ϵ_m =f/(4.32 ×10⁻⁹ ϵ_m).

dissolved in an appropriate solvent, diluted to known volume, and its absorption spectrum was measured. The ratio of extinction coefficients could then be calculated from the relation[12]:

$$\epsilon_f/\epsilon_s = (\beta_f/\beta_s)(V_s/A_f).$$

The extinction coefficients of methylene blue were found in the literature,[7b] while those of crystal violet[13]

in methanol, of pinacyanole in acetone,[14] of rhodamine B and trypaflavine[15] in methanol containing $\sim$1.0N sodium iodide (to quench fluorescence), and of malachite green in acidic methanol[16] were determined by measur-

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[12] ϵ=decadic molal extinction coefficient (liters/mole cm), β=absorbancy= $-\log_{10}I/I_0$, A_f=area of film (cm²) dissolved in total volume V_s (cm³) of solution.
[13] Commercial chloride, partially hydrated (effective mole wt. 432.5) in ethanol: ϵ_m=10.7×10⁴ at λ5890 A. Purified oxalate in methanol: ϵ_m=10.1×10⁴. Lewis et al.[8] cited "rough" value of 8.1×10⁴ for the chloride in ethanol.

[14] Our curves for pinacyanole in c.p. acetone resemble those for ethanol of Sheppard and Geddes, J. Am. Chem. Soc. 66, 1995 (1944), but are in decided disagreement with data for acetone, reported by Korrin, Klevens, and Harkins, J. Chem. Phys. 14, 480 (1946).
[15] National Aniline Division; corrected for 8.0% moisture and assumed to be half diaminoacridine hydrochloride; effective mole wt.=312.
[16] Malachite green fades rapidly in dilute methanol solution, apparently by reacting with traces of base in the solvent. Addition of conc. HCl to make the solution $\sim$10⁻³N preventing fading. Our data are in close agreement with those of Tolbert, Branch, and Berlenbach, J. Am. Chem. Soc. 67, 887 (1945).

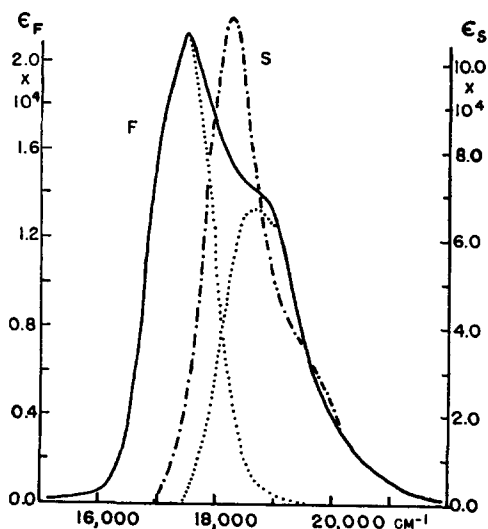FIG. 1. Absorption spectra of Rhodamine B sublimed film (F) and dilute solution (S) in methanol containing $1.5N$ NaI. Note separate ordinates for film and solution.

ing the spectra of known concentrations of dye (all $\sim5\times10^{-6}$M).

RESULTS

(a) Splitting of the Long-Wavelength Bands

Figures 1–6 and Table I compare the molal extinction coefficients of cationic dyes as solid films and in solution. The most obvious difference is the broadening of the first (i.e., longest-wavelength) absorption bands in the solid. This has already been noted by Holmes[4] and Vartanian.[5] However, in the region of each absorption band, the reflectivity increases greatly with increasing wavelength—sometimes varying from 5–40% of incident light—sufficiently to cause serious distortion of the transmission curves (II). Since the previous workers did not correct for reflection losses, they were
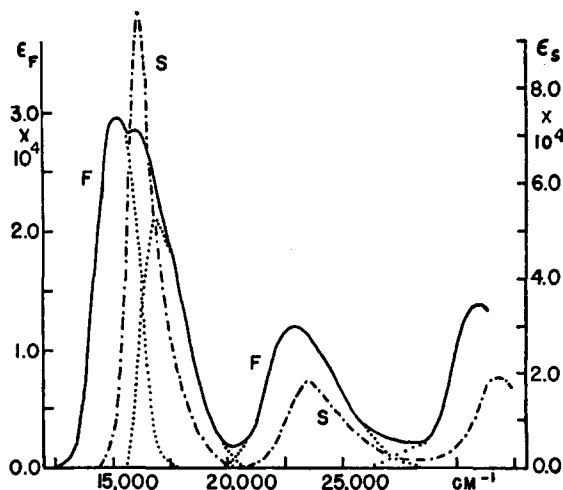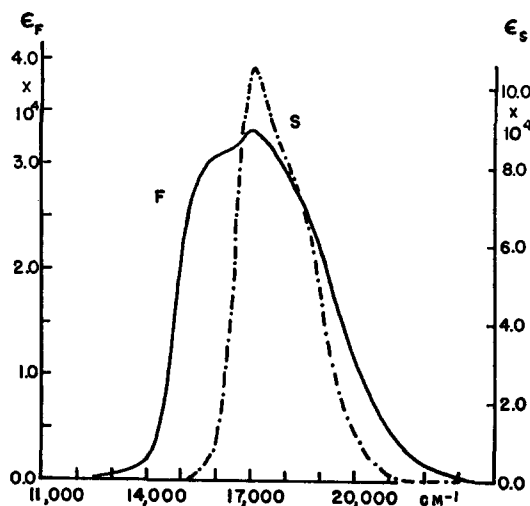

FIG. 3. Absorption spectra of Crystal Violet film, deposited from solution, and dilute methanol solution.

not able to interpret the shoulders which were already apparent on some of their spectra, and which are more quantitatively shown in the present results.

The first absorption band in rhodamine B films (including the shoulder) appears about twice as broad as the solution peak. However, it may be subdivided into two components of approximately equal area, each having about the same band width as the entire solution peak, and more or less symmetrically spaced to the longer- and shorter-wavelength sides of it. (In each case, the longer-wave component of the film band was arbitrarily assumed to coincide at the peak with the total film absorption curve, and to be symmetrical about λ_m.)

In malachite green films, three regions of absorption could be observed, corresponding to transitions from the ground to nondegenerate excited singlet levels, having, respectively, "x," "y," and "y'" oriented

FIG. 2. Absorption spectra of Malachite Green sublimed film and solution in methanol containing $10^{-3}N$ HCl.
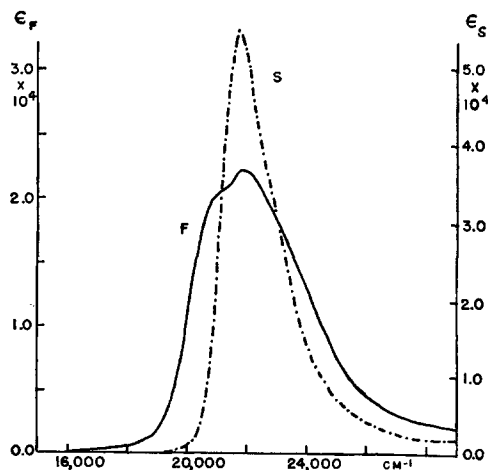

FIG. 4. Absorption spectra of Trypaflavine sublimed film and solution in methanol containing $1.0N$ NaI.
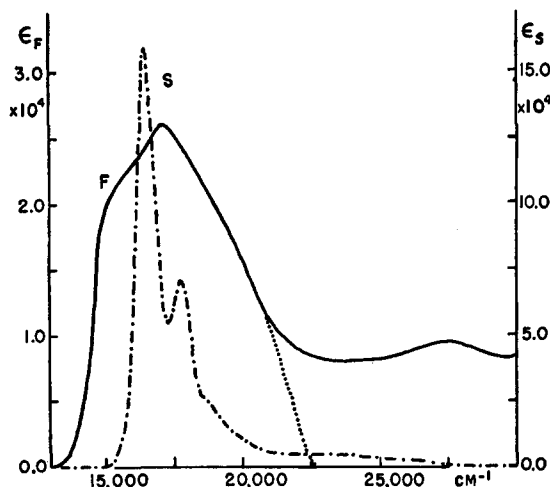
FIG. 5. Absorption spectra of Pinacyanole sublimed film and solution in acetone.

transition moments.[17] The first film peak, which was just twice as broad as the corresponding "x" band in solution, could again be resolved into two components of approximately equal band width and oscillator strength, located to either side of the solution peak. These components were, on the average, about 1.25 times as broad as the solution peak. However, the second film band *as a whole* was broadened only as much as the components of the first ($\Delta\bar{\nu}_f/\Delta\bar{\nu}_s = 1.25$), and the third one hardly at all. Thus the shape of each *component* of film band 1 matched that of the entire second and third film bands, as well as, approximately, that of the solution peaks. The second and third bands showed no shoulders.

The ratio of oscillator strengths in the film and solution bands, f_f/f_s, was roughly the same for bands 1, 2, and 3—provided that the *entire* band was considered each time. This shows that both components arise from solution band 1, rather than from a new, unrelated level.

A similar splitting is undoubtedly responsible for the broadening and shoulders observed in the longest-wavelength bands of crystal violet, trypaflavine, and other ionic dyes, described here and in the literature.[4,5] On the other hand, the *higher-energy* bands of several other triphenylmethane and acridine dyes[5] appear, like those of malachite green, not to be broadened. It follows that the splitting affects the first excited singlet level, and not the ground state.

The calculated separation between the components of film band 1 was a fairly sensitive function of the graphical procedure used to resolve them and hence is not accurately known. It was approximately 1200 cm^{-1} in rhodamine and 1600 cm^{-1} in malachite green—

comparable to the width of the solution peaks. That the broadening and splitting was not due to vibrational structure was shown by the fact that the film transmission curves were not affected, within the error due to multiple reflection corrections, by cooling the samples to 77°K. (See, e.g., Fig. 7.) This is consistent with the old observation of Speas[6] that a rhodamine B film on a glass slide showed essentially the same absorption at 20°C and at −70°C.

The films were sufficiently homogeneous to show no dichroism, even though the individual molecules retained their "x" and "y" bands, and though, in addition, the work of Davydov[18] might lead one to expect the two components of the first peak to show different polarizations, depending on molecular orientation within the lattice. While such uniformity was here desirable for accurate photometry, a great deal could be learned by a study of oriented films or single crystals.[6,19]

(b) Oscillator Strength

The oscillator strength, f, of the "optical" electrons[20] is a measure of the total probability of a transition, and hence proportional to the integrated absorption in a given band.

$$f = 1000 \log_e 10 (mc^2/N_A\pi e^2) \int \gamma\epsilon d\bar{\nu} = 4.32 \times 10^{-9} \int \gamma\epsilon d\bar{\nu}.$$

The constants e, m, c, and N_A have their customary significance, ϵ is the decadic molal extinction coefficient
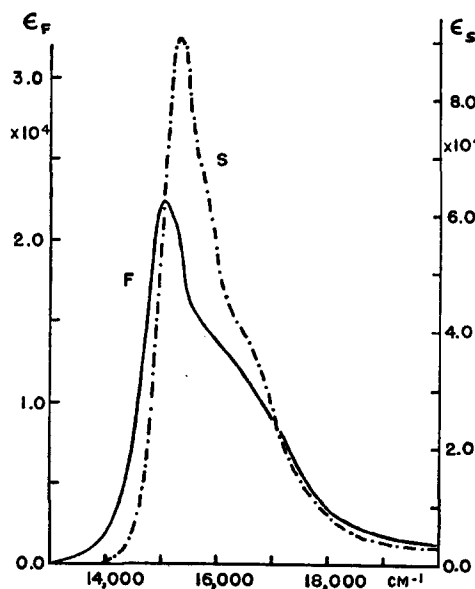

FIG. 6. Absorption spectra of Methylene Blue sublimed film and solution in ethanol.

[17] (a) P. P. Feofilov, Doklady Akad. Nauk. S.S.S.R. **57**, 447 (1947); (b) P. P. Feofilov and I. G. Faerman, *ibid.* **87**, 931 (1952); Chemical Abstracts **47**, 4204g. (c) C. Looney and W. T. Simpson, J. Am. Chem. Soc. **76**, 6293 (1954).

[18] A. S. Davydov (a) Bull. Acad. Sci. U.S.S.R. (Phys. Ser.) **12**, 664 (1948); (b) J. Exptl. Theoret. Phys. U.S.S.R. **18**, 210 (1948); (c) *ibid.* **21**, 673 (1951). (Translated by M. Kasha.)
[19] S. Anderson, J. Opt. Soc. Am. **39**, 49 (1949).
[20] R. Ladenburg and F. Reiche, Naturwiss. **11**, 584 (1923).

(liters/mole cm), $\bar{\nu}$ is expressed in cm^{-1}, and f is dimensionless. The Lorentz-Lorenz factor, $\gamma(\leq 1.0)$, which corrects for the influence of the refractive index of the surroundings, is assumed to be unity.[21,22]

Surprisingly few reliable measurements of absolute molal extinction coefficients and oscillator strengths of dissolved dyes have appeared in the literature, so that even the solution oscillator strengths, listed in Table I, are of some novelty. The two bands among these, having oscillator strengths in excess of unity (crystal violet, pinacyanole), almost certainly each correspond to two distinct transitions.[17,23] The maximum extinction coefficients of the film bands were much lower than those of the corresponding solution peaks; and in spite of the increased band width, the oscillator strengths in the solid appeared to be reduced by 20–70%. While the several bands of any given film (e.g., of malachite green) showed roughly the same reduction in intensity, there was considerable variation in the ratio, f_f/f_s, from sample to sample—probably largely due to errors in the measurement of the effective area of film dissolved (Table I). To determine whether the reductions in oscillator strength were real, it was necessary to rule
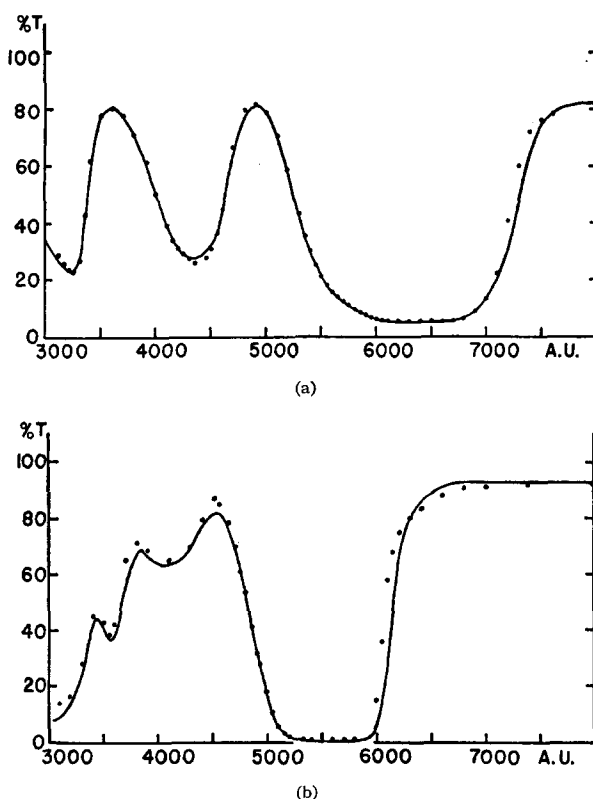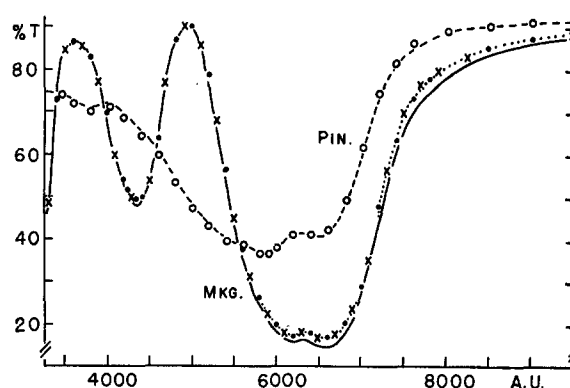

FIG. 8. Transmission of Malachite Green (Mkg) and Pinacyanole (Pin) films in polarized and natural light. Mkg: solid line—natural light; ●—horizontally, ✕—vertically polarized light. Pin: broken line—natural light; ○—horizontally polarized light.

out certain photometric errors which may be encountered in the study of ordered systems—errors due to irregular sample thickness[24] or to preferential orientation of molecules.[25,26]

Microscopic examination showed *sublimed* films of malachite green, rhodamine B, pinacyanole, and trypaflavine to be very homogeneous, with only a few scattered crystals of the order of 5–25μ over an otherwise uniform background. These films darkened uniformly between crossed polarizers and showed no microscopic dichroism in either reflection or transmission. The extinction coefficients were approximately independent of film thickness (Table I) and of the polarization of the light (Fig. 8). These films may therefore be considered sufficiently uniform for accurate photometry.[27]

Films deposited from solution, while still smooth to the naked eye, showed 1–50μ microcrystals, distributed over a lighter background. The larger crystals showed residual reflection and transmission between crossed polarizers, indicating strong birefringence. For this reason, the apparent decrease in oscillator strength of crystal violet films deposited *from solution* may be largely due to false transmission through the clear areas between microcrystals. In a similar way, alcohol-deposited microcrystalline deposits of rhodamine and malachite green displayed greater apparent reductions of oscillator strength than sublimed films.

Originally homogeneous light blue films of methylene blue gradually faded when stored, evacuated and darkened, over a period of weeks—apparently due to re-orientation[19] or reaggregation. The blue color reappeared instantaneously upon solution of such

(a)

(b)

FIG. 7. Temperature effects on the spectra of films of (a) Malachite Green and (b) Rhodamine B. Solid line: 298°K, dots: 77°K.

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[27] We are indebted to Dr. H. Pincus of the Geology Department and to Dr. R. Speiser of the Department of Metallurgy for the use of a 200✕(0.5 N.A.) petrographic microscope and a 500✕ (0.4 N.A.) Bausch & Lomb Metallograph.

TABLE II. Peak extinction coefficients of a crystal violet film.

Assume randomly oriented molecules, film density = 1.17 g/cc*
Molecular weight of anhydrous chloride = 408 g/mole
Concentration, $c = 2.87$ moles/liter, $cN_A = 17.3 \times 10^{20}$ molecules/cc
Molecular volume = $580A^3$, geometrical crossection = $70A^2$, mean molecular dimension (assuming cubes), $a = 8.35$ A
Film extinction coefficients, to log. base 10:
$\epsilon \approx 3.0 \times 10^4$ liters/mole cm. (or cm²/m. mole)
$\epsilon c \approx 8.65 \times 10^4$ cm⁻¹
$\epsilon c a \approx 7.2 \times 10^{-3}$, or 0.72% per molecule
$\epsilon c / N_A \approx 0.50A^2$ per molecule (optical cross section)
Film extinction coefficient in "natural units", to log. base e:
$\kappa_0 \approx 0.405$ per $\lambda/4\pi$ of thickness, at $\lambda_m = 5950$ A.
Film thickness—for film transmitting 10% at peak: 1180 A, or 140 molecules.

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* C. Stora and G. van Eller, Compt. rend. 229, 766 (1949) found 1.17 g/cc for crystals of crystal violet; this has been roughly confirmed by unpublished measurements on *films* of methyl violet.

bleached films, indicating that here, too, the loss of color had been due to the inhomogeneity of the deposits. The film whose spectrum appears in Fig. 6 had not yet undergone this process to a measurable extent; nonetheless, the tabulated oscillator strength may be too low on this account.

(c) Anion Effects on Film Spectra

In view of the striking differences in electrical behavior among various salts of crystal violet,[2b] the absorption spectra of the fluoride, chloride, iodide, sulfate, and oxalate of this dye were compared. Although these films were not especially uniform, and the spectra were not corrected for reflection, at least qualitatively, the curves for all derivatives were alike. Since the oxalates and sulfates of crystal and methyl violet are semiconductors with trap depths of the order of 0.4 ev (equivalent to 3200 cm⁻¹)[2b] we looked for electronic absorption bands in the near infrared which might cause optical freeing of the trapped carriers. Thick photoconductive films of the chlorides, sulfates, and oxalates were prepared in an evacuated cell with silver chloride windows, and their infrared absorption was measured by means of a Beckman IR-3 spectrophotometer.[28] The spectra showed only the various vibrational bands appropriate to the dye cations and associated anions. No electronic bands were found beyond the absorption edge of the lowest singlet-singlet band of the dye.

DISCUSSION

It has been shown that the absorption of visible or near-ultraviolet light by solid cationic dyes causes excitation of individual cations from the ground state (S) to the well-known excited singlet states (S', S'',

S''', depending on wavelength) characteristic of the "isolated" molecules. Since excited states higher than the first are neither broadened nor split in the crystal, they must be so short-lived that their "natural" band width obscures any interaction effects. The S' state, on the other hand, would be expected to have a sufficiently long lifetime to permit interactions between the initially excited cations and their neighbors. This is consistent with the observation that in isolated molecules, as well, all highest states of a given multiplicity are quickly degraded to the lowest excited level of the series ($\tau < 10^{-13}$ sec), so that luminescence is observed only from the latter.[29,30]

Davydov[18] has shown that in crystals of aromatic hydrocarbons interaction between neighboring molecules of different orientations can lead to a splitting of transitions between molecular energy levels, even though these levels be nondegenerate. In condensed hydrocarbons this effect leads to a band separation of the order of 100 cm⁻¹. If the much greater splitting observed in these ionic dyes is attributed to the "Davydov effect," the energy of interaction, ΔE, of neighboring molecules in the first excited state must be of the order of the observed splitting, i.e., about 1200 cm⁻¹. The excitation can remain localized on the absorbing molecule for only about $\hbar/\Delta E \cong 5 \times 10^{-15}$ second before moving on to a neighbor.[31] It then travels through the lattice by this mechanism, as a "fast exciton," having an energy equal to that of the S' level and—judging by the low luminescence yield—a lifetime of the order of 10^{-10} sec. It finally interacts with some molecule and is degraded thermally, by luminescence, or by carrier excitation. The large observed splitting is consistent with the expectation[18] that the molecular interaction should be strongest for transitions, such as those having great transition moments.

We thus have a rather detailed outline of the sequence of steps from the absorption of a photon to the excitation of carriers. This mechanism implies that the weak luminescence of these systems be completely depolarized. Experiments on this question are now underway. No interpretation can as yet be given to the observed decrease in the oscillator strength of dye cations assembled into a lattice. The phenomenon may be related to the well-known decrease in the dipole strength of dye dimers in aqueous solution.[7b,32]

[28] We are indebted to Professor R. A. Oetjen of this Department for the use of this instrument.

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