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Confirmation of the Anomalous Fluorescence of Azulene*

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The light emission properties of the azulene molecule and several alkyl-substituted azulenes have been studied. In confirmation of recent results of Beer and Longuet-Higgins, it is found that anomalous ($S'' \rightarrow S$) fluorescence occurs in azulene, with $\bar{\nu}_{\max}$ at 26 802 cm^{-1} (rigid glass solution in EPA at 77°K). Red-shifts for this fluorescence are found in several alkyl-substituted azulenes, in qualitative agreement with substitution theory. The absence of normal ($S' \rightarrow S$) fluorescence and the absence of any phosphorescence ($T \rightarrow S$) emission to 11 000 Å, the apparatus limit, are also confirmed. The emission observations are discussed, and alternative interpretations are given.

I. INTRODUCTION

QUANTUM mechanical theory has permitted the accurate prediction of the location of electronic energy levels in molecules, and of the probability and polarization of radiative transitions between the ground and excited states. In the case of radiationless transitions, the theory is relatively undeveloped and no predictions can be made concerning these at present. Nevertheless, as a result of the study by many workers of a large number of molecules under excitation, the conclusion has been drawn that normal ($S' \rightarrow S$) fluorescence is unique in general. In previous cases, no excited singlet states (S'' , S''' , etc.) had been observed to emit light upon excitation, the same being true for triplet states (T' , T'' , etc.) higher than the lowest triplet state (T). This empirical evidence is summarized in the rule¹: *The emitting electronic level of a given multiplicity is the lowest excited level of that multiplicity.* This observation is the result of the extremely high probability of radiationless transition between excited states, the excess energy being converted to vibrational energy, carried off by collisions with neighboring molecules.

Recently, two exceptions to the common behavior have been noted. In the case of the *naphthalene* molecule, triplet-singlet emission has been reported² in the visible region, at 18 500 cm^{-1} , whereas it is fairly certain that the lowest triplet level³ is at 10 250 cm^{-1} . Evidently, the radiationless ($T' \rightarrow T$) transition does not take place readily to the rather low-lying lowest triplet, so that the triplet level at 18 500 cm^{-1} yields what is evidently the anomalous ($T' \rightarrow S$) phosphorescence emission. In the case of the *azulene* molecule, Beer and Longuet-Higgins⁴ have made the discovery that the second excited singlet level emits light upon excitation, producing the anomalous ($S'' \rightarrow S$) fluorescence (see Figs. 1 and 2). Moreover, these authors found that normal ($S' \rightarrow S$) fluorescence cannot be obtained by

normal excitation. Previous authors⁵ have emphasized the spectral similarity of azulene and naphthalene. Evidently, this similarity does not extend to their emission properties, since naphthalene exhibits a unique normal ($S' \rightarrow S$) fluorescence (see Fig. 2).

The observations of Beer and Longuet-Higgins are important and deserve confirmation. We undertook the present work since we had instruments of higher speed and higher resolving power available, as well as a much more powerful light source. There is always a possibility that a single observation could be due to impurities in the sample, so that we endeavored to procure a highly purified sample from a different source than the sample used by Beer and Longuet-Higgins. In addition, using several substituted azulenes, we endeavored to make use of substitution effects to establish the authenticity of the emission. All of the observations made by Beer and Longuet-Higgins were confirmed in our work.

II. EXPERIMENTAL

The azulene used in our work was a chromatogrammed sample obtained from Dr. A. G. Anderson and used without further purification. The two different trimethylazulenes (see Table I) used in our work were obtained from Dr. Werner Herz in the form of trinitrobenzene complexes. These complexes were decomposed upon chromatography on an alumina column, and the pure azulenes obtained in the eluate. The sample of guaiazulene was obtained commercially.⁶ The sample was converted to its trinitrobenzene complex, which was then recrystallized from ethanol until the melting point was increased to a constant value of 147°C. The purified complex was then dissolved in isopentane and passed over an alumina column. The trinitrobenzene was preferentially adsorbed, and the purified guaiazulene passed through the column with the isopentane eluate, as in the case of the other azulenes.

The isopentane solutions of the azulenes were diluted with ethyl ether and ethanol to make standard EPA solvent (5 parts isopentane, 5 parts ethyl ether, and

* Work done under a contract between the Office of Naval Research, U. S. Navy, and the Florida State University.

¹ M. Kasha, Discussions Faraday Soc. No. 9, 14 (1950).

² C. Reid, J. Chem. Phys. **20**, 1214 (1952).

³ McGlynn, Padhye, and Kasha, J. Chem. Phys. **23**, 593 (1955).

⁴ M. Beer and H. C. Longuet-Higgins, J. Chem. Phys. **23**, 1390 (1955).

⁵ Mann, Platt, and Kleven, J. Chem. Phys. **17**, 481 (1949).

⁶ Aldrich Chemical Company, 3747 North Booth Street, Milwaukee 12, Wisconsin.

2 parts ethyl alcohol, by volume). These dilute solutions of the azulenes were a pale blue, and were supercooled to 77° using liquid nitrogen, a rigid glass solution of each azulene being produced as a result.

For excitation of the fluorescence, the 1 K.W. high pressure watercooled mercury arc (AH6) was used. The light of this arc, after filtering, was focused by means of an $f/1.5$ quartz condensing lens onto the sample immersed in the coolant in a quartz optical Dewar. The filter used gave a fairly narrow band of light with a maximum at 3100 Å. The filter train used in exciting the UV band of the azulenes consisted of a 5 cm path of aqueous nickel sulfate, 200 g/l; a 3 mm

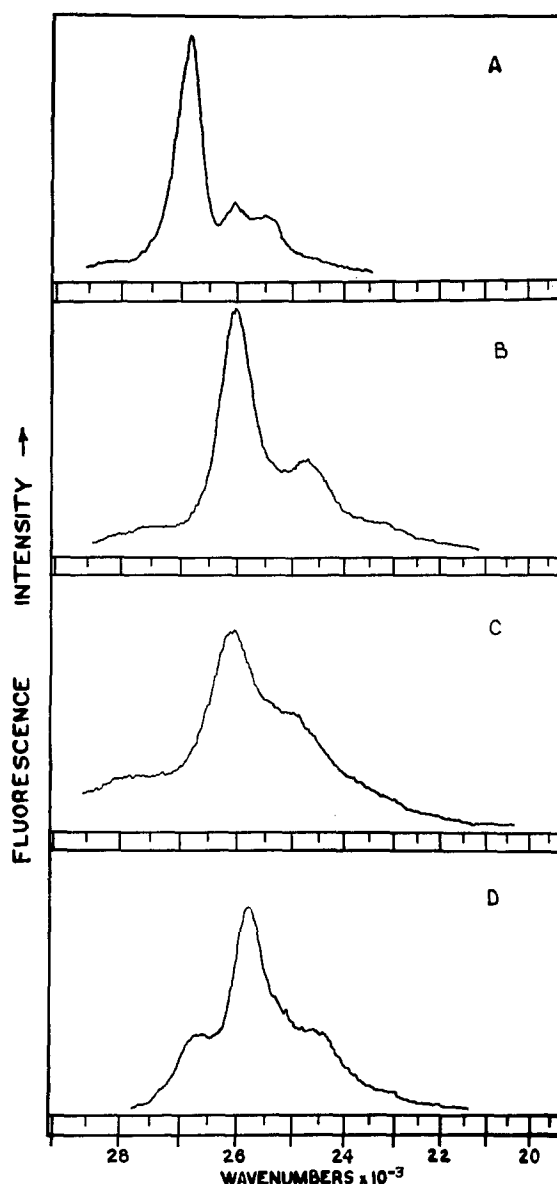


FIG. 1. Anomalous ($S'' \rightarrow S$) fluorescence spectra of azulenes in rigid glass solution (EPA) at 77°K. Curve A, azulene; Curve B, 2,4,8-trimethylazulene; Curve C, 2,4,5-trimethylazulene; and Curve D, 1,4-dimethyl-7-isopropylazulene (guaiazulene).

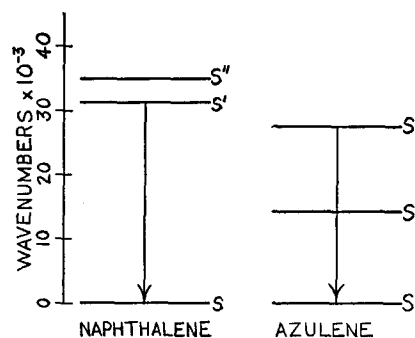


FIG. 2. Diagram comparing the unique fluorescence observed for naphthalene and azulene, upon excitation in the $S'' \leftarrow S$ absorption band. Zero-point vibrational levels for the three lowest singlet states are indicated by S , S' , S'' .

path of Corning Glass No. 9863; and a 1 cm path of aqueous potassium chromate, 0.2 g/l.

To record the fluorescence spectra, the Beckman Automatic Recording Spectrophotometer, Model DK-1, was used. A photomultiplier-recording spectrophotometer is ideal for such studies because its inherently high speed permits well-resolved continuous tracings of fluorescence spectra to be obtained rapidly.

In the search for phosphorescence in the azulenes studied, the Steinheil Universal Spectrograph, Model GH, was used. This instrument has collimator and camera apertures of approximately $f/3$, yet gives medium dispersion with its three large coated glass prisms. Eastman Kodak $I-L$ and $Z-3$ spectrographic plates were used in the search for infrared phosphorescence. Both types of plates were hypersensitized by the standard alcoholic ammonia procedure recommended by the plate manufacturer. The $AH-6$ arc was used to excite the visible absorption band in this work. The filter train consisted of a 5 cm path of aqueous copper

TABLE I. Frequencies and substitution red shifts of the anomalous ($S'' \rightarrow S$) fluorescence of azulenes.

Formula	Code	Name	Frequency $\bar{\nu}_{\max}, \text{cm}^{-1}$	Red Shift $\Delta\bar{\nu}$
	A	azulene	26 802	0
	B	2,4,8-trimethylazulene	26 102	700
	C	2,4,5-trimethylazulene	25 967	835
	D	1,4-dimethyl-7-isopropyl- azulene (guaiazulene)	25 700	1102

sulfate, 300 g/l; various Corning filters were tried which have transmissions at 5000 Å.

III. DISCUSSION

(a) The Anomalous ($S'' \rightarrow S$) Fluorescence

The fluorescence observations of Beer and Longuet-Higgins⁴ were confirmed in our work. The recording spectrophotometer tracings (Beckman Recording Spectrophotometer Model DK-1) are presented in Fig. 1. The result for azulene itself is very similar to that previously reported, except that the fine structure is somewhat better resolved. The frequencies and other data are given in Table I.

A comparison of the anomalous ($S'' \rightarrow S$) fluorescence of azulene (Curve A, Fig. 1) and the *ultraviolet* ($S'' \leftarrow S$) absorption curve of azulene⁷ indicates the usual approximate relationship between absorption and fluorescence. The absorption curve at room temperature has a first vibrational peak (weak) at approximately 27 800 cm^{-1} . In the emission curve in EPA glass solution at 77°K there is a weak first peak at about 28 200 cm^{-1} . Unfortunately, the absorption curve in EPA glass solution at 77°K is not available for comparison, but it is expected to be shifted to higher frequencies compared with the room temperature absorption curve (This is the normal frequency relationship found in low temperature glass solution spectroscopy); this would bring the absorption and fluorescence curves into close frequency correspondence.

In Table I are given the $\bar{\nu}_{\text{max}}$ values, i.e., the frequencies of the strongest band of the emissions. The weak long wavelength band seems to be real; it was noted also by Beer and Longuet-Higgins⁴ and apparently is enhanced by 1,4,7-trisubstitution (see Curve D).

The effect of alkyl substitution on the ultraviolet ($S'' \leftarrow S$) absorption⁷ of azulene is to cause a red-shift, dependent on the number and position of the substituted groups. It is evident that the substitution red-shift also is observed in the comparison of the anomalous ($S'' \rightarrow S$) fluorescence of azulene and that of substituted azulenes (see Table I, and Fig. 1). This lends additional support to the establishment of the fluorescence as an authentic azulene fluorescence, and makes it extremely improbable that an impurity is responsible.⁸

The comparison of the singlet energy level schemes of azulene and naphthalene (see Fig. 2) indicates the much wider spacing between the zero-point levels of the first two excited singlet states of azulene compared with the analogous spacing in naphthalene. This is in conformity

with the interpretation of Beer and Longuet-Higgins⁴ that the anomalous fluorescence occurs because internal conversion fails to take place between the S'' and S' levels on account of their wide separation. However, this separation itself is not unique, since such separations can be found in numerous other molecules. Thus, this may be a necessary but not a sufficient condition to explain the anomalous fluorescence. It seems necessary to learn where all of the triplet levels lie before the mechanism of the anomalous fluorescence can be deduced unequivocally. If any excited triplet levels lie within 3000 cm^{-1} of the second excited singlet (S'') level, it is likely that no ($S'' \rightarrow S$) fluorescence would be observable, since *inter-system crossing* to the triplet manifold would then become highly probable. The relatively high quantum yield of the azulene anomalous ($S'' \rightarrow S$) fluorescence suggests that no triplet levels lie in the S'' level vicinity. Future triplet-triplet absorption studies will settle this point.

(b) The Absence of Normal ($S' \rightarrow S$) Fluorescence

In agreement with Beer and Longuet-Higgins,⁴ no fluorescence could be found corresponding to the visible absorption band. Their interpretation of this result is that the ground and first excited singlet states must cross, so that excitation results in conversion of electronic excitation to vibrational energy of the ground state. While such a process is always possible, the fact that most molecules with visible or even infrared absorption bands possess either fluorescence ($S' \rightarrow S$) emission or phosphorescence ($T \rightarrow S$) emission, or both, argues against the interpretation given. In other words, applying the energy-spacing arguments given by Beer and Longuet-Higgins in explaining the anomalous ($S'' \rightarrow S$) fluorescence (the S'' and S' levels being approximately 13 000 cm^{-1} apart, measured as 0,0-differences), the fact that the S' and S levels are separated by 14 000 cm^{-1} , for 0,0-differences, would argue against a radiationless transition between the latter pair.

An alternative explanation of the failure to obtain normal ($S' \rightarrow S$) fluorescence is that an excited triplet level lies just below the S' level, or possibly at nearly the same energy as the S' level (zero point energies in each case). Such a possibility can be checked by triplet-triplet absorption studies. The discussion below indicates why it is unlikely that the lowest triplet is involved here. The consequences of this interpretation, if true, is that light absorbed in the visible absorption band would be converted completely to lowest triplet state excitation.

(c) The Nonobservation of the Phosphorescence ($T \rightarrow S$) Emission

In agreement with Beer and Longuet-Higgins,⁴ no phosphorescence could be observed (see experimental part). It seemed possible that our superior equipment

⁷ See Maxwell Gordon, Chem. Rev. **50**, 127 (1952).

⁸ One of the referees of this paper raised the question of interpretation of the emission as possibly due to "a $T' \rightarrow T$ emission, arising from a high population of the T state." Since essentially monochromatic excitation was used, this interpretation would require an exact coincidence of the $S'' \leftarrow S$ and $T' \leftarrow T$ absorption frequencies. This seems rather improbable in view of the uniform behavior of the four azulenes studied. Moreover, saturation of a triplet state cannot be achieved by the light intensities used, according to our experience.

would reveal emission where theirs failed to do so. No emission was detected, out to about 11 000 Å, the wavelength limit of our equipment and plates.

The interpretation given by Beer and Longuet-Higgins for the failure to observe phosphorescence is that the lowest triplet level lies *above* the lowest excited singlet level, and that radiationless transition between these effectively quenches phosphorescence.

We prefer to interpret the failure to observe phosphorescence in the azulenes studied as simply a matter of wavelength difficulties. We believe it rather likely that the *lowest* triplet, corresponding to the visible ($S' \leftarrow S$) absorption band, may lie in the infrared at wavelengths longer than 12 000 Å.

It is evident that much of the discussion of the observed results on azulene emissions hinges on the role of the lowest several triplet states of azulene.

None of these have been found thus far, but it is highly desirable that information on this point should be actively sought.

IV. ACKNOWLEDGMENTS

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Spectroscopic Properties of Organic Photoconductors. II. Specular Reflection Spectra of Cationic Dye Films

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The specular reflectivity of solid dye films has been measured at 12° incidence, by means of a new device attached to the Beckman Quartz Spectrophotometer. The observed spectra are in general agreement with the results of dispersion theory.

THE brilliant metallic reflection colors of solid dyestuffs have been known for nearly a century. Christiansen, Kundt, Pfüger, and other early workers established their origin in the strong fluctuations in refractive index, associated with intense absorption bands. Pfüger¹ confirmed the Helmholtz theory of "anomalous" dispersion by comparing directly measured refractive indices and extinction coefficients of solid fuchsin and cyanine with values computed from Brewster's angle of reflection polarization. From these data, Wood² later computed a reflection spectrum for cyanine. Curiously, however, it appears that, with one exception,^{3,4} the specular reflection spectra of solid dyes have never been measured directly.

In the course of absorption measurements on solid films of some photoconductive dyes⁵ it became necessary to correct for the strong variation in reflectivity which

accompanies and distorts each absorption band. A simple device was built, which permits one to make concurrent transmission and specular reflection measurements on identical samples. The results are presented in the present communication.

EXPERIMENTAL

In order to obtain films of reproducible structural and photoelectric properties, it was necessary to deposit them inside evacuated 1×1 cm square Pyrex cuvettes. The details concerning sample preparation have already been presented (I). Reflection measurements were carried out in a device attached to the Beckman quartz spectrophotometer (Fig. 1). Monochromatic light from the exit slit, approximately collimated by a small quartz lens, is reflected from the aluminized first face of a 102° isosceles prism⁶ onto the sample cell, striking the latter at 12° from normal incidence. The light reflected from the dye on the inside of face "B" (Fig. 2) is returned to the aluminized second leg of the prism, and thence transmitted to the photometer. Unwanted light, reflected from the clear "front" window ("F") of the cell, falls on a blackened

* This work was supported by the Charles F. Kettering Foundation.

¹ A. Pfüger, *Wied. Ann.* **56**, 412 (1895); **65**, 173, 214, 225 (1898).

² R. W. Wood, *Physical Optics* (The MacMillan Company, New York, 1934), third edition, p. 512.

³ W. H. Taylor, *Z. Krist.* **91**, 450 (1935); *J. Soc. Chem. Ind.* **13**, 732 (1935).

⁴ Scott Anderson, *J. Opt. Soc. Am.* **39**, 49 (1949).

⁵ J. W. Weigl, *J. Chem. Phys.* **24**, 364 (1956)—hereafter referred to as "I."

⁶ Made to order by the Wm. Buchele Optical Company, 1309 Milburn Avenue, Toledo, Ohio.