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Effect of Pressure on the Optical Properties of Organic Phosphors*

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The effect of pressure to 54 kbar has been measured on absorption spectra, emission spectra, and decay rates of four organic phosphors. For fluorescein and dichlorofluorescein the decay rate increases with increasing pressure. The emission spectrum consists of two peaks which approach each other at high pressure. Thus there appears to be an increased mixing of triplet and excited singlet states at high pressure.

For acridine yellow and orange the absorption spectrum shows a dimer and monomer peak. The dimer peak decreases rapidly in intensity with increasing pressure. At high concentrations the component decay rates are largely independent of pressure. At lower concentrations the decay rate becomes slower at higher pressure. Evidently the emission can be associated with the dimer.

THE effect of pressure to 54 kbars has been measured on the absorption spectra, emission spectra, and decay rates of four organic phosphors. These include fluorescein, dichlorofluorescein, acridine orange, and acridine yellow. The formulas are shown in Fig. 1. The fluorescein and dichlorofluorescein were cp from Eastman Organic Chemicals Company. The acridine orange and acridine yellow were Matheson Coleman and Bell pure grade. The compounds were dissolved in boric acid glass.

The apparatus for absorption spectra studies has been previously described¹ as has the equipment for phosphor decay measurements.² The emission peaks were measured using a Steinheil Munchen spectrograph model 5063 with Royal X Pan film and the equipment arrangement used for decay studies. A Knorr-Albers micro-

photometer connected to a Speedomax recorder was used to measure film density.

Since the windows of the bomb subtend only a small solid angle for light emitted in the bomb, the emission spectra took from 30 min to 6 hr to give measurable density at any one pressure.

One point of interest can be noted from all the data. The runs were never quite reversible, indicating a permanent change in the structure of the boric acid matrix. This effect was not large enough to affect the interpretation of results.

Two energy diagrams which have application to many organic phosphors are presented in Fig. 2. The diagram in Fig. 2(a) was presented by Lewis^{3,4} for fluorescein, and the diagram in Fig. 2(b) is a simplified energy vs configurational coordinate diagram of Fig. 2(a). It illustrates one additional necessary condition for phos-

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¹ R. A. Fitch, T. E. Slykhouse, and H. G. Drickamer, *J. Opt. Soc. Am.* **47**, 1015 (1957).

² D. W. Gregg and H. G. Drickamer, *J. Appl. Phys.* **31**, 494 (1960).

³ G. N. Lewis, D. Lipkin, and T. Magel, *J. Am. Chem. Soc.* **63**, 3005 (1941).

⁴ G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.* **66**, 2100 (1944).

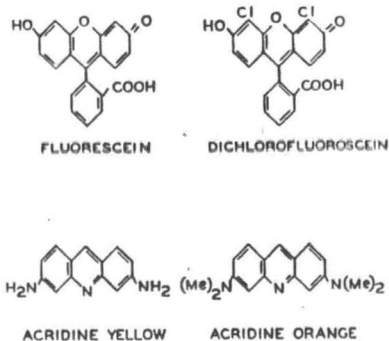


Fig. 1. Structural formulas.

phorescence in many organic phosphors, the crossing or close approach of the energy levels of the S_1 and T_1 states.

S and T represent singlet and triplet states, respectively. Transitions between states of the same multiplicity, $S_n \rightarrow S_m$ or $T_n \rightarrow T_m$, are spin allowed, but transitions between states of different multiplicity, $S \rightarrow T$ or $T \rightarrow S$, are spin forbidden. However, there are conditions under which spin-forbidden transitions can take place, but with considerably less probability than spin-allowed transitions. It is this sort of transition which is responsible for phosphorescence in organic compounds.

The excitation process involves a $S_0 \rightarrow S_1$ step followed by a rapid transition to the T_1 state, where the electron is trapped and released later as phosphorescence. The $S_0 \rightarrow S_1$ transition is spin allowed and appears as a strong peak in the absorption spectrum whereas the transition $S_0 \rightarrow T_1$ is spin forbidden and is usually not detected in the absorption spectrum. Since the transition, $S_1 \rightarrow S_0$, takes place in the order of 10^{-9} sec, it is necessary for the $S_1 \rightarrow T_1$ transition to be highly allowed or all the

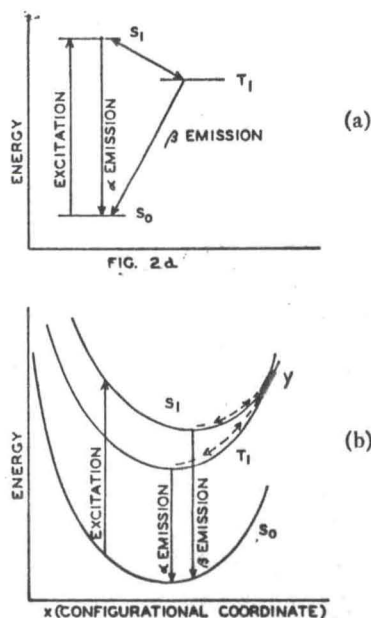


Fig. 2. Energy diagrams for organic phosphors.

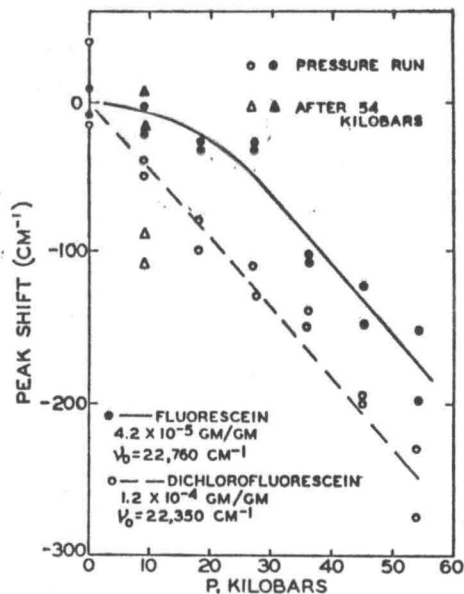


Fig. 3. Shift of absorption peak maxima vs pressure—fluorescein and dichlorofluorescein.

excited electrons will return to the ground state without being trapped. This transition is spin forbidden, so a possible explanation for its probability is presented with the aid of Fig. 2(b). The transition probability between two electronic states is inversely proportional to the square of the energy difference between them. If the S_1 and T_1 states have an energy crossing or position of close approach as illustrated at y the transition probability would be high at this point even between states with different spins.

After the electron is trapped in the T_1 state it can return to the ground state by several paths, two of which emit phosphorescence. The nonemitting paths, involving quenching of the phosphor, are minimized in glasses. The two emitting paths are: (1) the direct transition

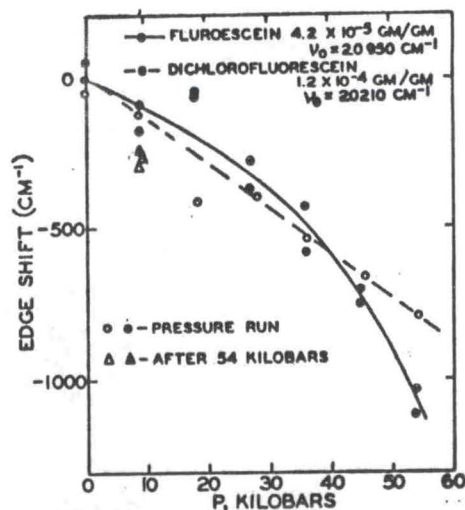


Fig. 4. Shift of low-energy edge of absorption peak vs pressure—fluorescein and dichlorofluorescein.

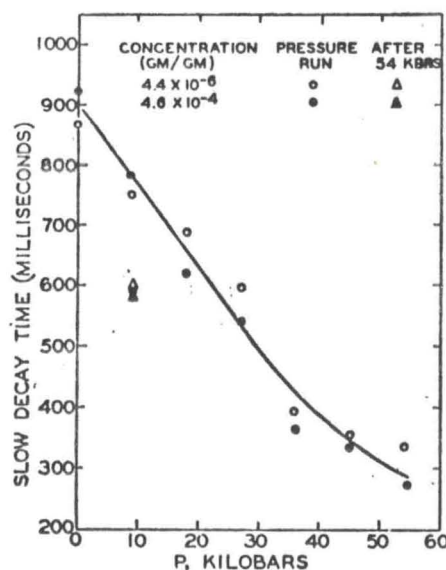


FIG. 5. Slow component decay time vs pressure for two concentrations—fluorescein in boric acid.

from the T_1 state to the S_0 state, called beta emission, and (2) the thermal re-excitation of the electron through point y to the S_1 state from where it then makes the radiative transition to the S_0 state, called alpha emission. The intensity of the alpha emission is quite temperature dependent, whereas that of the beta emission is not as much so. At room temperature, depending on the phosphor, one of these processes may be controlling or they may take place with nearly equal probability.

A spin-forbidden transition is totally forbidden if the spin and orbital momentum of the electron are completely separate. However, under the proper conditions there may be a certain amount of coupling between

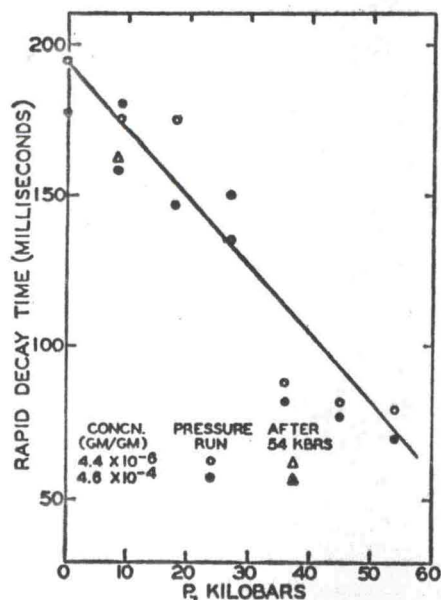


FIG. 6. Rapid component decay time vs pressure for two concentrations—fluorescein in boric acid.

them making the transition partially allowed. The coupling allows a state of spin a to mix with a state of spin b and the degree of mixing may be found from second-order perturbation theory and is given by⁵

$$\psi^1 = \psi_{(s=a)}^0 + \sum_j \int \psi_{(s=a)}^0 * [\sum_i \zeta_{ni} l_i s_i] \psi_{j(s=b)} d\tau / (E_a - E_j) \psi_{j(s=b)}. \quad (1)$$

The mixing coefficient may be abbreviated to $K\zeta_{ni}/\Delta E$, where k is in the order of unity. ζ_{ni} is the coupling coeffi-

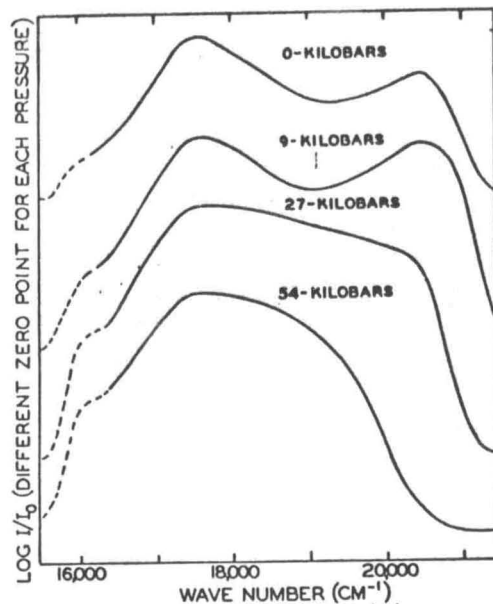


FIG. 7. Emission spectra of fluorescein in boric acid 4.6×10^{-4} g/g.

cient. In terms of oscillator strength we have⁵

$$f_{ab} = f^0 (K\zeta_{ni}/\Delta E)^2, \quad (2)$$

where f^0 is the oscillator strength of an allowed transition between states of the same multiplicity.

Forster⁶ shows that the oscillator strength is related to the decay time as follows: $1/\tau = Kf$, where K is a coefficient containing several terms which are not important for this argument. One then obtains

$$\tau = K'(\Delta E)^2. \quad (3)$$

The above discussion applies mainly to beta decay where the transition is from the T_1 state to the S_0 state.

If the model in Fig. 2 is valid and if the alpha, beta, and any monomolecular quenching decay processes are the only means by which the electron trapped in the triplet state returned to the ground state one would expect an exponential decay. The deviation from an

⁵ D. S. McClure, *Solid-State Physics* (Academic Press Inc., New York, 1959), Vol. 9, p. 400.

⁶ T. Forster, *Fluoreszenz organischer Verbindungen* (Vandenhoeck and Ruprecht, Göttingen, 1951).

TABLE I. Comparison of calculated and measured τ .

| Pressure | E | τ_1 (measured) | τ_1 (calc) | τ_2 (measured) | τ_2 (calc) |
|----------|-----------------------|---------------------|-----------------|---------------------|-----------------|
| atm | 2920 cm^{-1} | 900 msec | | 194 msec | |
| 54 kbar | 1600 cm^{-1} | 285 msec | (271 msec) | 70 msec | (58.3 msec) |

exponential decay is most likely due to different molecules having different interactions with the surroundings. This is discussed thoroughly by other authors,⁷⁻¹³ who propose representing the decay as a summation of exponentials. The reasons for representing the decay as a summation of exponentials are not important for the interpretation of the pressure data and thus will not be considered here. In this work they are represented as such mostly because it is a convenient method of characterizing them.

I. EFFECT OF PRESSURE ON FLUORESCIN AND DICHLOROFLUORESCIN PHOSPHORS

Fluorescein and dichlorofluorescein are discussed together because of their similar structural formulas and their similar characteristics under pressure. The results are presented and discussed in three parts: (1) the effect of pressure on the absorption spectra and decay rates of the two compounds, (2) the effect of pressure on the emission spectra of fluorescein, and (3) an interpretation of the results.

Figure 3 shows the shift of the absorption maxima with pressure. These correspond to the $S_0 \rightarrow S_1$ transition in Fig. 2. They both exhibit a single peak which shifts red with pressure, dichlorofluorescein shifting slightly more than fluorescein. However, the most important characteristic that they both exhibit is the large red shift of their low-energy edges. These shifts, presented in Fig. 4, are much larger than the shift of their respective peak maxima. They are important because they represent the shift of the lower edge of the S_1 state from whence the alpha emission takes place. This large shift of the red edge is not completely understood. It can not be explained by a simple broadening of the peak since there is no similar effect observed on its blue edge. It corresponds to a change of shape of the S_1 state as illustrated in Fig. 2(b).

Atmospheric decays were measured for both fluorescein and dichlorofluorescein each with concentrations ranging from 10^{-3} to 10^{-6} g/g. In both cases the decay was found to be independent of concentration. A filter with a transmission peak at $22\,720\text{ cm}^{-1}$ was used on the exciting light so as to excite only the first excited singlet

state, and a constant shutter speed of 54.6 rpm was maintained for all the decay measurements.

It was found that the decay of both fluorescein and dichlorofluorescein could be represented by a summation of two exponentials. The component decay times as a function of pressure are presented in Figs. 5 and 6 for fluorescein. The results for dichlorofluorescein were qualitatively similar although both fast and slow decay rates were 4-5 times faster at each pressure. The effect of pressure on the decay of two concentrations of fluorescein were measured and found to be the same, so pressure effects were measured for only one concentration of dichlorofluorescein.

In all cases both components showed shorter decay times at the higher pressures. At the same time the fraction the initial intensity due to the rapid decay increased with pressure, from 30% at 1 kbar to about 50% at 54 kbar. The question of how each path of decay, alpha and beta, is being affected by pressure will be discussed below. Measurements indicated that the total initial intensity of emission was substantially independent of pressure for both compounds.

The emission spectra of fluorescein at pressures from 0 to 54 kbar is presented in Fig. 7. The dotted portion of the curves in these and similar figures indicate regions where the film sensitivity changes rapidly so that the darkening density could not be established accurately. At atmospheric pressure there are two distinct peaks located at $17\,560$ and $20\,480\text{ cm}^{-1}$, representing beta and alpha emission, respectively.³⁻⁴ The red peak does not shift measurably with pressure. However, the blue peak shifts red roughly between 1200 and 1400 cm^{-1} in 54 kbar. Both the location and the shift of this peak corresponds closely with that of the low-energy edge of the absorption peak. This evidence helps to justify the assignment of this peak to alpha emission, the $S_1 \rightarrow S_0$ transition, because one would expect the emission peak to be located near the low-energy edge of the absorption peak for transitions between the same two states.³ It would thus shift with this edge. It is also noted that there does not appear to be a large change in the relative intensities of the two peaks. There may be a slight decrease in the relative intensity of the blue peak, but this is hard to verify with certainty.

The emission spectra of fluorescein in Fig. 7 shows how the relative positions of its S_1 and T_1 states are changing with pressure. This is important because the rate of beta decay depends on the amount of mixing that the T_1 state has with S states near it, or thus the amount of singlet character it assumes. This mixing is a function of the energy difference between the T_1 and

⁷ A. Baczynski and M. Czajkowski, Bull. Acad. polon. sci. VI, 653 (1958).

⁸ R. Bauer and M. Baczynski, Bull. Acad. polon. sci. VII, 113 (1958).

⁹ A. Jablonski, Acta Phys. Polon. XVI, 471 (1957).

¹⁰ A. Jablonski, Bull. Acad. polon. sci. VI, 589 (1958).

¹¹ M. Frackowiak, and J. Held, Acta Phys. Polon. XVIII, 93 (1959).

¹² M. Frackowiak and H. Walerys, Acta Phys. Polon. XIX, 199 (1960).

¹³ H. Walerys, Bull. Acad. polon. sci. VII, 47 (1959).

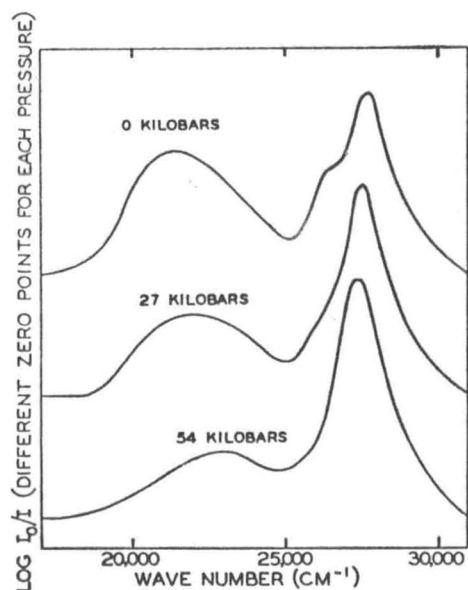


FIG. 8. Absorption spectra of acridine yellow in boric acid— 1.8×10^{-4} g/g.

S_1 states. Since the S_1 state is much closer to the T_1 state than any other S state it probably contributes effectively all of the singlet character present in the T_1 state. As shown in Eq. (5), the part of the decay time associated with this process is proportional to the square of the energy difference between the T_1 and S_1 states. The emission spectrum also shows that there is no large change in peak heights between the alpha and beta emission with pressure, indicating that the alpha emission process is also being enhanced by pressure. This means that the energy crossing, point y , is moving to lower energy along with the S_1 state.

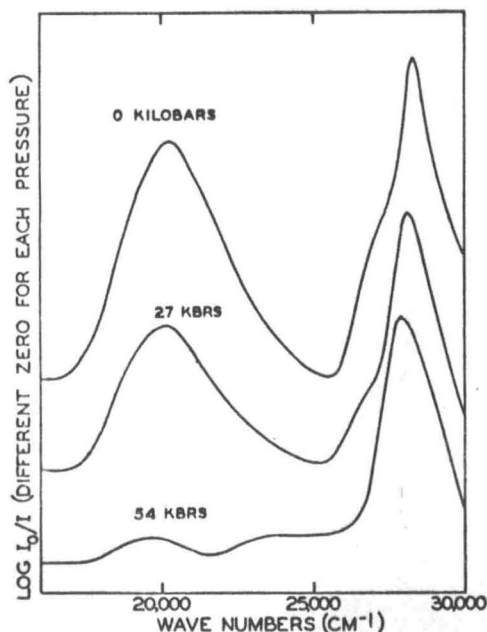


FIG. 9. Absorption spectra of acridine orange in boric acid— 5.4×10^{-4} g/g.

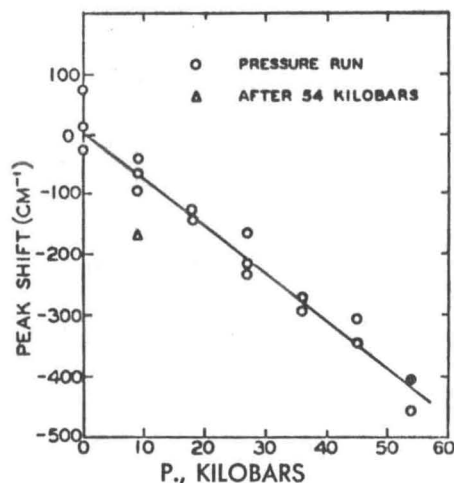


FIG. 10. Shift of monomer absorption peak at 27720 cm^{-1} vs pressure—acridine yellow in boric acid— 1.8×10^{-4} g/g.

A rough estimate can be made as to how much the change in the energy difference between the S_1 and T_1 states affected the decay rate of the phosphor. Since this energy difference can be related to the beta decay only, the decay will be assumed to be completely of the beta type. From Eq. (3) the following relationship would hold:

$$\frac{\tau(P=0)}{\tau(P=54 \text{ kbar})} = \frac{\Delta E(P=0)^2}{\Delta E(P=54 \text{ kbar})^2} \quad (4)$$

Using the ΔE 's measured from the emission spectra and the atmospheric τ_n 's, the τ_n 's at 54 kbar can be calculated and compared with the measured values. As seen in Table I, if the decay were all of the beta type, the change in the energy difference between the S_1 and

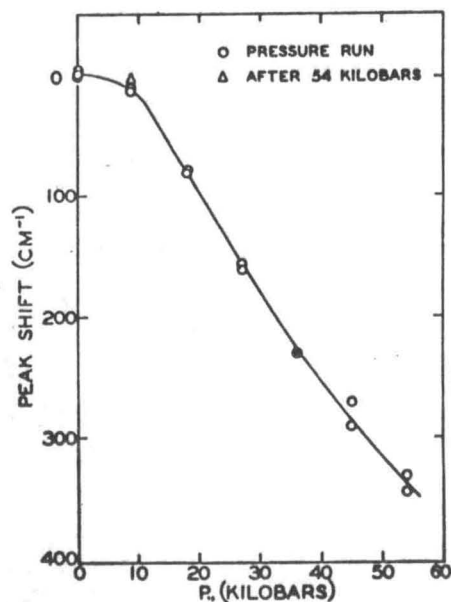


FIG. 11. Shift of monomer absorption peak at 28285 cm^{-1} vs pressure—acridine orange in boric acid— 5.4×10^{-4} g/g.

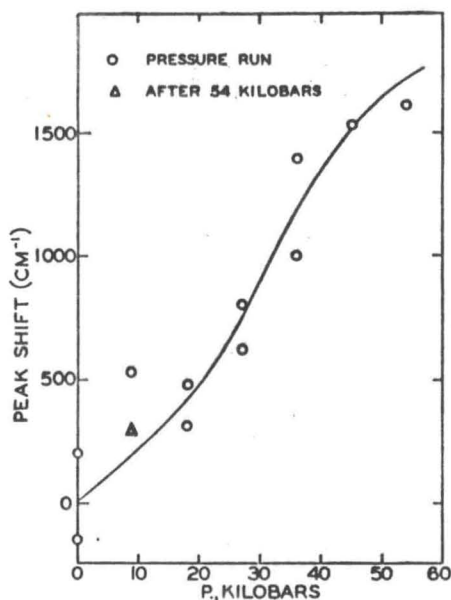


FIG. 12. Shift of dimer absorption peak at $21,700 \text{ cm}^{-1}$ vs pressure—acridine yellow in boric acid— $1.8 \times 10^{-4} \text{ g/g}$.

T_1 states with pressure would more than account for the decrease in decay times. However, there is a large portion of alpha decay, probably about 30 to 40% (estimated from emission spectra) so the change in the decay time cannot be entirely described in terms of beta decay.

II. EFFECT OF PRESSURE ON ACRIDINE YELLOW AND ACRIDINE ORANGE PHOSPHORS DISSOLVED IN BORIC ACID

Acridine yellow and acridine orange are discussed together because they have similar structural formulas and behave qualitatively the same under pressure.

Typical absorption spectra vs pressure are shown in Figs. 8 and 9. They both show two major peaks with a shoulder on the red side of the blue peak. Other workers

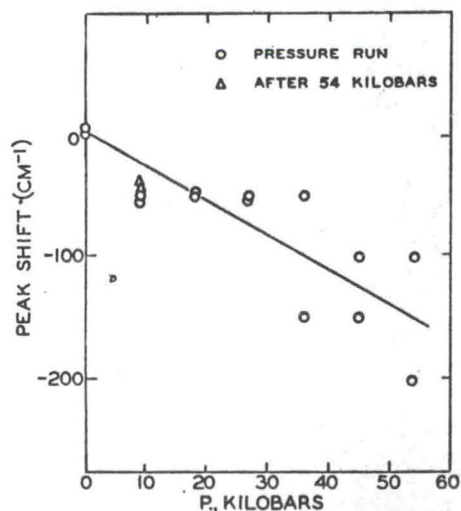


FIG. 13. Shift of dimer absorption peak at 20325 cm^{-1} vs pressure—acridine orange in boric acid— $5.4 \times 10^{-4} \text{ g/g}$.

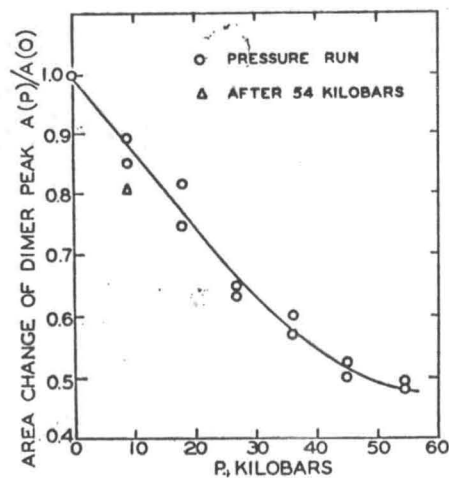


FIG. 14. Area change of dimer absorption peak vs pressure—acridine yellow in boric acid— $1.8 \times 10^{-4} \text{ g/g}$.

have found the red peak to be concentration dependent,¹⁴ the higher the concentration, the larger the red peak relative to the blue peak. This peak has been associated with the formation of a dimer, and the blue peak is associated with the monomer. As pressure is applied the dimer peak decreases in intensity, and so does the shoulder on the monomer peak. One would thus associate the shoulder with absorption in the dimer, perhaps the transition corresponding to the monomer peak, only shifted slightly red.

Figures 10–15 show for both compounds the shift in monomer and dimer peak maxima with pressure, and the change in area of their respective dimer absorption peaks with pressure. For both compounds the monomer absorption peak shifts red with pressure. But, their dimer absorption peak maxima shift in opposite directions. The dimer peak for acridine yellow shows a large blue shift, and that for acridine orange shows a small red shift. However, the red edge of the dimer peak shows

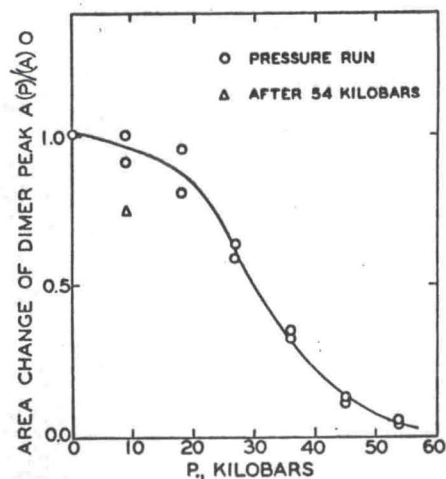


FIG. 15. Area change of dimer absorption peak vs pressure—acridine orange in boric acid— $5.4 \times 10^{-4} \text{ g/g}$.

¹⁴ V. Zanker, J. Phys. Chem. **200**, 250 (1952).

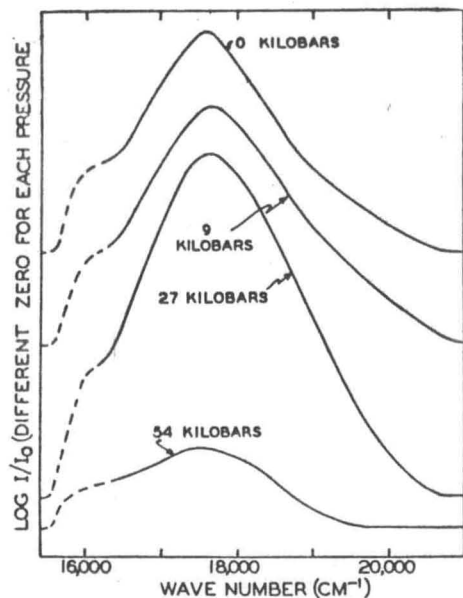


FIG. 16. Emission spectra of acridine orange in boric acid— 4.6×10^{-5} g/g.

no shift in either case. The dimer peak of acridine orange shows the larger decrease in area with pressure.

The emission spectra vs pressure for two concentrations of acridine orange are presented in Figs. 16 and 17. The acridine yellow spectra were similar. When making these measurements, no filter was used on the exciting light, so both monomer and dimer peaks were being excited. The shifts of the emission peaks with pressure were small and could not be accurately determined. There appears to be a concentration dependent peak on the red side of the strong peak in acridine orange. These peaks all decrease in intensity with pressure and

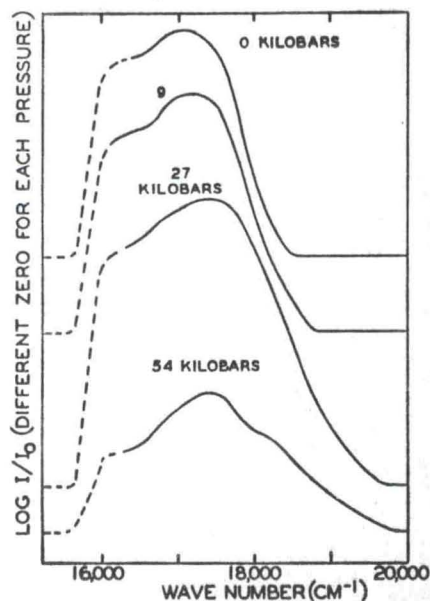


FIG. 17. Emission spectra of acridine orange in boric acid— 5.4×10^{-4} g/g.

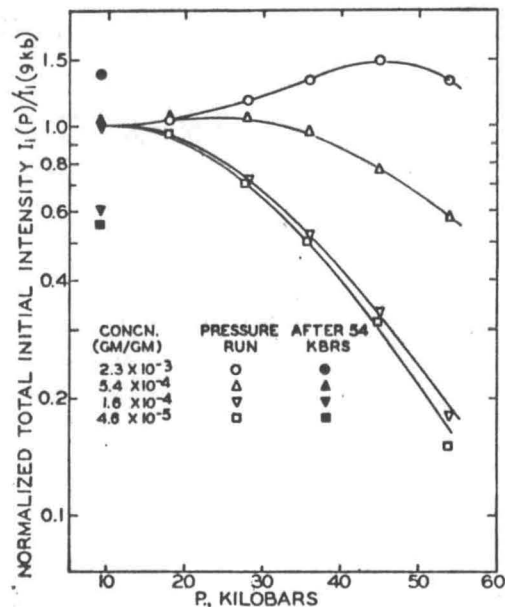


FIG. 18. Total initial emission intensity (normalized to 9 kbar) vs pressure—acridine orange in boric acid.

are located at the red edge of their respective dimer absorption peaks. This would tend to associate the emission with the dimer. The changes in the emission intensity with pressure for several concentrations of acridine orange are shown in Fig. 18. These were measured with a photomultiplier tube. Similar results were obtained for acridine yellow. The pressure effect on the intensity is strongly concentration dependent. This will be discussed in more detail below.

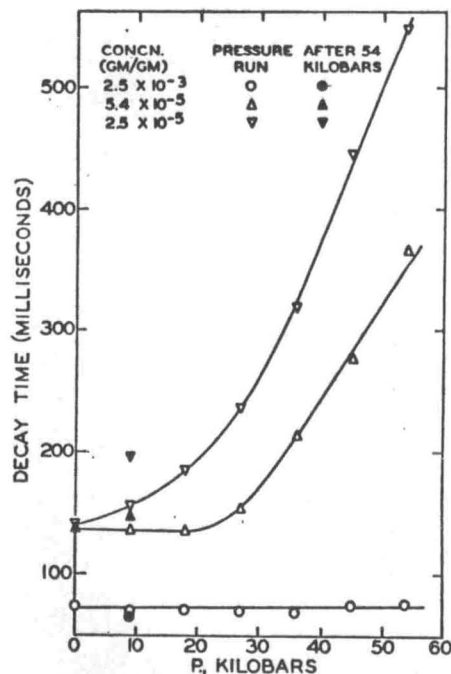


FIG. 19. Slow component decay time vs pressure for three concentrations—acridine yellow in boric acid.

It was found that concentration influenced the decay rate of the compounds and strongly influenced how they changed with pressure. During excitation a filter was used on the exciting light with a transmission peak at $27\,800\text{ cm}^{-1}$ so as to excite only the monomer peak. Attempts were made to measure the decays while exciting the dimer peaks, but the emission was not intense enough to obtain measurements. A constant shutter speed of 60 rpm was maintained for all decay measurements.

It was found that the decay of both acridine yellow and acridine orange could be represented by a summation of three exponentials. The effect of pressure on the decay of three concentrations of acridine yellow and four concentrations of acridine orange was measured, and typical component decay times are presented in Figs. 19–21. It is noted that at high concentrations there is little effect of pressure on the component decay times, but at low concentrations they increase with pressure. In all cases there was an increase in the fraction of initial intensity due to the fast decay with increasing pressure (from about 10%–20% of the total in 50 kbar). There was a corresponding decrease in the fractional contribution of the slowest exponential component.

In order to facilitate this discussion the following facts can be listed: (a) The dimer peak for both compounds is concentration dependent and decreases in intensity with pressure. (b) The shoulder on the low-energy side of the monomer peak also decreases with pressure, which associates it with the dimer. (c) The emission peaks were located at the low energy edge of the respective dimer absorption peaks which associates

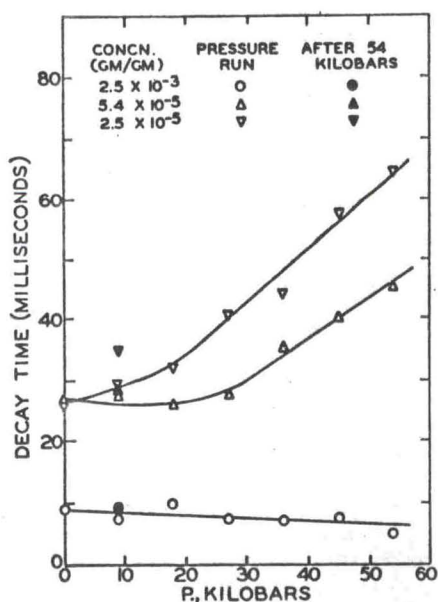


FIG. 20. Medium component decay time vs pressure for three concentrations—acridine yellow in boric acid.

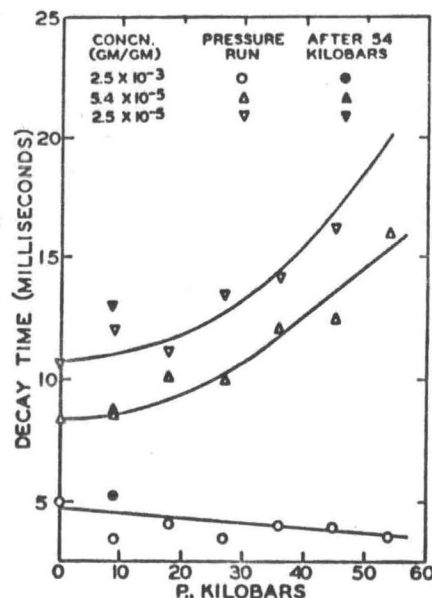


FIG. 21. Rapid component decay time vs pressure for three concentrations—acridine yellow in boric acid.

them with the dimer, while the excitation took place in both dimer and monomer peaks. (d) The effect of pressure on the emission intensity is concentration dependent; at the low concentrations there is a large decrease in intensity with pressure. (e) The effect of pressure on the decay times of the component decays is concentration dependent; at the low concentrations there is a large increase in the decay times with pressure. When measuring the decay times a filter with a transmission peak in the region of the monomer absorption peak was used on the exciting light.

From a, c, and d one would associate the emission with the dimer peak. When the emission spectra were measured both the monomer and the dimer peaks were excited, but when the decays were measured only the monomer peak was excited. In the case of the decays the excited electron could have been transferred to the dimer in either of two ways. The more likely is that the electron is excited at a monomer site where it is trapped in a T state associated with the monomer and then is transferred to the T state of the dimer. This transfer may take place in the form of an exciton.¹⁵ The less likely possibility is that the shoulder on the monomer peak which appears to be associated with the dimer site is excited and transfers its excited electron to the T state associated with the dimer peak. This second possibility is less likely because there is no strong line in the Hg exciting light in that region, and the filter on the exciting light is cutting off rapidly there.

The data indicate that the dimer is destroyed with pressure and that the excitation takes place in the

¹⁵ A. N. Terenin and V. L. Ermolaev, *Trans. Faraday Soc.* **52**, 1942 (1956).

monomer and is transferred to a dimer site before emission takes place. The decay data can be explained by assuming there is a critical dimer concentration; above this concentration there is sufficient dimer for the emission process, and below it the dimer concentra-

tion becomes the limiting factor in the transfer of an excited electron from the monomer to the dimer site.

ACKNOWLEDGMENT

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