

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 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 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).