

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

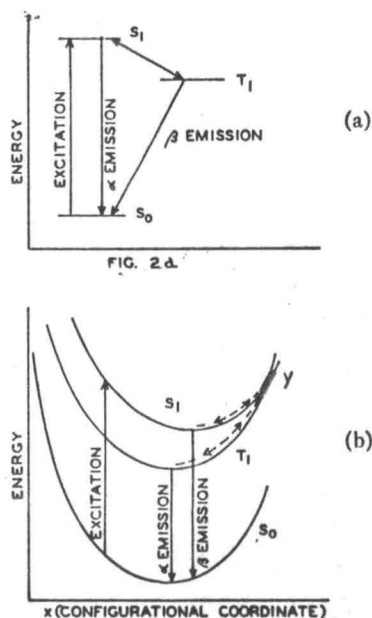


Fig. 2. Energy diagrams for organic phosphors.

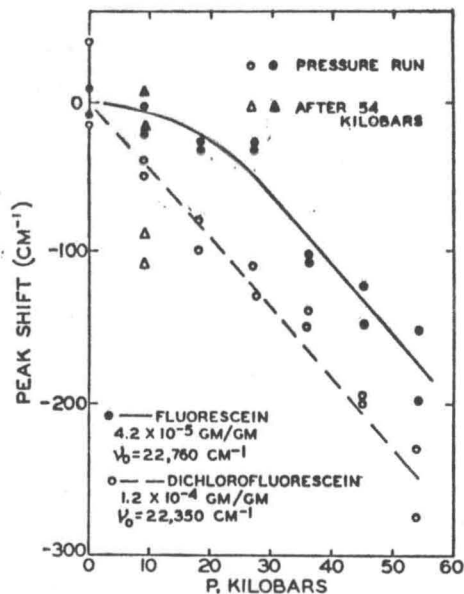


Fig. 3. Shift of absorption peak maxima vs pressure—fluorescein and dichlorofluorescein.

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

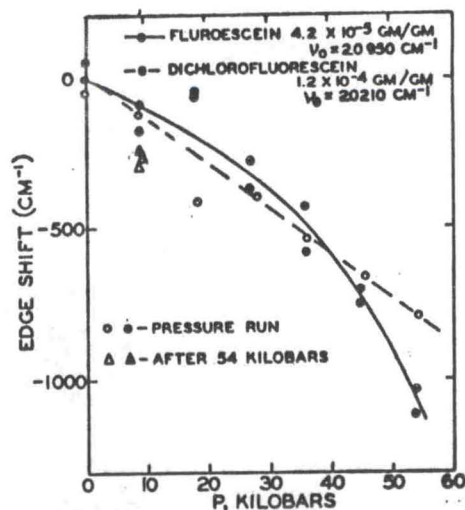


Fig. 4. Shift of low-energy edge of absorption peak vs pressure—fluorescein and dichlorofluorescein.