

sensitive to the symmetry in the plane of the ring which might be affected by increasing the pressure. There is a growing evidence, however, that the emitting (π, π^*) triplet state in these systems steals its radiative power by mixing with a singlet state which has electric dipole polarization perpendicular to the molecular plane⁴⁻⁶ (i.e., not of the π, π^* type). If so, then the explanation given¹ for the observed effect on the lifetime seems improbable.

An attractive alternative explanation for the decrease of the observed lifetime at high pressures is the possibility of an increase in the rate constant of $T \rightarrow S_0$ radiationless process. Assuming all the radiationless processes to take place from the lowest triplet, one can calculate that a decrease of the lifetime by $\frac{1}{3}$ corresponds to a decrease in the yield by only $\frac{1}{3}$. The authors¹ mention that no change in the *relative intensity* at different pressures is observed. Due to changes in the absorption spectrum (thus the excitation spectrum), in the emission spectrum (thus the response of detection), and in the concentration of the emitting molecule (and thus the number of photons absorbed and emitted per unit time per unit volume), as the pressure increases, it would be impractical to relate the relative intensity to the absolute intensity (absolute quantum yields) accurately. Unfortunately, it is the latter quantity that is required to examine the rates of the radiationless processes. The fluorescence-phosphorescence intensity ratio, on the other hand, does not depend on the changes mentioned (as long as the energy of the two emissions are *not drastically* changed). This ratio is found to decrease as the pressure increases, thus indicating an increase in the rate of either $S_1 \rightarrow S_0$ or $S_1 \rightarrow T_1$ radiationless process. In either case this result points out to an *increase in radiationless processes as the pressure increases*.

The increase in radiationless processes at high pressure might be explained in the following way. The probability of the $T_1 \rightarrow S_0$ radiationless processes is shown⁷ to be proportional to the square of the vibrational overlap integral between the zero-point function of the triplet state and the nearby excited vibrational functions of the ground state. This overlap can be increased in two ways. The first is by increasing the energy spacing of some vibrational modes in the ground state. This was demonstrated previously⁷⁻⁹ by replacing deuterium by hydrogen atoms in $C_{10}D_8$ for which a lifetime decrease from 22 to 2.6 sec was observed.

Another way of increasing the overlap integral is by displacing the two potential curves with respect to one another.^{9a} This might be what is happening at high pressures. A strong spectroscopic indication for this being the case for the S_1 and S_0 states is the general observed increase of the half-bandwidth as the pressure increases.¹⁰ This points out that the nature of the corresponding transition is changing from a Franck-Condon allowed (slight change in geometry between ground

and excited state) to less-allowed (more change in geometry) transition as the pressure increases.

Therefore, we propose that there might be an increase in the radiationless processes ($T_1 \rightarrow S_0$, $S_1 \rightarrow T_1$, or $S_1 \rightarrow S_0$) in fluorescein and derivatives as the pressure increases and that this increase is probably¹ due to an increase in vibrational overlap mainly due to a change in the relative positions of the potential surfaces of the electronic states between which these transitions are taking place. It should be pointed out that a change in the relative position of the potential surfaces of the initial and final states has recently been proposed by Teller¹² to explain the increase of the rate of chemical reactions at high pressures.

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^{9a} This might also explain the general observation of decreasing the phosphorescence intensity upon an unsymmetric substitution of H atoms by methyl or other groups (or CH's by nitrogen atoms) in the aromatic system.

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¹¹ Two other effects should not be completely eliminated: (1) the increase of radiationless transitions due to an increase in the transfer efficiency of excitation energy into lattice (heat) energy, due to changes in the lattice structure, and (2) oxygen or other chemical effects.

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Crystal Spectrum of Copper Acetylacetonate

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RECENT papers^{1,2} concerning the crystal spectrum of copper acetylacetonate raised interesting questions and brought up conflicting opinions requiring further discussion. The purpose of this letter is to insert and interpret some new data bearing on this problem, to clarify the nature of some assumptions used in past papers, and to discuss some weak or controversial features of interpretation.