

stables are present during the discharge and continue to live on afterward, indeed for seconds.

A strong argument for a high concentration of energetic N_2 metastables is the marked lowering of the voltage gradient of a low-current discharge^{1,3}—several-fold—when a little N_2 is added to, say, 150 mm pure Xe. It is as if a small amount of Na vapor or other element having a low ionizing potential were added. Nitrogen atoms would not be very effective in lowering the gradient as their ionizing potential is rather high (IPN=14.48 V; IPN₂=15.5 V).

Another argument for the existence of a high concentration of long-lived N_2 metastables is the positive volt-ampere characteristic found for these diffuse discharges.⁴

The main function of the rare gas is to act as a buffer to keep the N_2 metastables away from the walls where the experiments show they are strongly destroyed. Calculations show that the time for a molecule to diffuse from the center to the wall of a 10-cm tube containing 150 mm Xe is calculated to be several seconds.

A type of Tesla discharge in A+N₂ which is known to dissociate N_2 strongly into normal and metastable N atoms,^{5,6} produces a very different afterglow than that of a weak diffuse dc or 60-cycle discharge; the latter afterglow contains, as the most prominent feature, a selection of the first positive bands but the former does not.

It is concluded that the long-lived N_2 metastables are efficiently produced by the mild discharge either by single electron impacts or by a two-stage process involving the metastable $N_2(^3\Sigma_u^+)$ in the discharge. The latter metastable appears to have too low an energy (6.167 eV) and too short a life— 2.6×10^{-2} sec according to Wilkinson and Mulliken⁷—to account for most of the present long afterglow results.

The process of King and Gatz does not account for the fact that only the BaII resonance lines appear in the afterglow.

No radiative transitions⁸ have been observed involving $^3\Delta_u$. According to Mulliken⁹ the energy of $^3\Delta_u$ should be ~ 7.5 eV. On this basis Wilkinson⁸ points out that there should be infrared transitions to $B^3\Pi_g$. Here the ν^3 factor would cause a small transition probability. Further as Lichten¹⁰ observes, if $^3\Delta_u$ were a little lower than 7.5 eV, it could not then radiate to $B^3\Pi_g$ and would have a very long life. In this case (indeed even at 7.5 eV) it would lie too low to account for the excitation of BaII in the manner indicated, and a more complicated explanation would have to be found. Higher vibration states of $^3\Delta_u$, on this view, could suffice provided they could have a sufficiently long life. $^3\Sigma_u^-$ (8.162 eV) presumably has much too short a life since it can radiate to $B^3\Pi_g$ (Y bands).

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Proposed Effect of High Pressures on the Radiationless Processes*

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PRESSURE effects on the emission properties of four organic molecules have recently been reported.¹ Two of the four studied molecules form dimers at ordinary pressures and increasing the pressure is found to destroy the dimer formation. The other two molecules, fluorescein and a dichloro derivative, show fluorescence and phosphorescence. For the latter compounds, it is reported¹ that as the pressure increases from 0 to 54 kb the following results are obtained: (1) The phosphorescence lifetime decreases from 0.9 to 0.285 sec (i.e., is shortened by $\frac{2}{3}$). (2) The fluorescence and lowest absorption band red shift by a maximum value of ~ 1300 cm^{-1} . Relating the two observations, the authors¹ attribute the decrease in the phosphorescence *observed lifetime* mainly to a decrease in its *natural lifetime*. This they attribute to an increase in the mixing between the lowest singlet and the emitting triplet state due to a decrease in their energy separation. Such interpretation, while possible, seems to be based on two serious assumptions. The first is that the lowest singlet state is the one that mixes with the emitting triplet, and the second is that the spin-orbit matrix elements between these two states must have been assumed to be constant as the pressure increases. The seriousness of these two assumptions can be indicated by the following facts. Since the phosphorescence has such a long-lived duration, it can safely be assigned to a $T(\pi, \pi^*) \rightarrow S_0$ transition. The high intensity of the low-energy absorption band ($\epsilon \approx 10^4 - 10^5$ in boric acid²) indicates it to be due to a $S(\pi, \pi^*) \leftarrow S_0$ transition. McClure³ has shown that in the aromatic systems the one- and two-center integrals of the spin-orbit matrix elements between $S(\pi, \pi^*)$ and $T(\pi, \pi^*)$ states vanish mainly because of the symmetry of these states with reference to the molecular plane. Therefore, *even* if these two states can couple together their matrix elements should be

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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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.