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; IPN_2=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 $A+N_2$ 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 Mulliken[7]—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 transitions[8] have been observed involving $^3\Delta_u$. According to Mulliken[9] the energy of $^3\Delta_u$ should be ~7.5 eV. On this basis Wilkinson[8] 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 Lichten[10] 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).

[1] C. Kenty, J. Chem. Phys. 35, 2267 (1961).
[2] C. Kenty, J. Chem. Phys. 23, 1555 (1955).
[3] C. Kenty, Report 16th Annual MIT Conference on Physical Electronics, 1956, p. 85.
[4] C. Kenty, Proc. 5th International Conference on Ionization Phenomena in Gases, 1961, p. 356.
[5] C. Kenty, J. Chem. Phys. 23, 1556 (1955).
[6] C. Kenty, Report 20th Annual MIT Conference on Physical Electronics 1960, p. 192.
[7] P. G. Wilkinson and R. S. Mulliken, J. Chem. Phys. 31, 674 (1959).
[8] P. G. Wilkinson, J. Chem. Phys. 32, 1061 (1960).
[9] R. S. Mulliken, The Threshold of Space (Pergamon Press, New York, 1957), p. 169.
[10] W. Lichten, J. Chem. Phys. 26, 306 (1957).

Proposed Effect of High Pressures on the Radiationless Processes*

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(Received June 11, 1962)

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 reported[1] 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 $\frac{1}{3}$). (2) The fluorescence and lowest absorption band red shift by a maximum value of ~1300 cm^{-1}. Relating the two observations, the authors[1] 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 ($\epsilon\approx10^4-10^5$ in boric acid[2]) indicates it to be due to a $S(\pi,\pi^*)\leftarrow S_0$ transition. McClure[3] 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