Predissociation in Fluorescence Emission Spectra: Fluorescence of Acetone Vapour

THE fluorescence of acetone was first observed by Gelbke¹. It was also observed independently in the vapour by Mr. C. W. Woolgar of King's College, London, who kindly directed our attention to its existence. Recently, Damon and Daniels², in a paper on the photochemical decomposition of acetone, have described the visible fluorescence of acetone vapour as a greenish emission consisting of two diffuse bands, one extending from $\lambda\lambda$ 4100 to 4820 Å., the other from 4990 Å. to the limit of the sensitivity of the plate (5210 Å.). They record that the intensity is reduced and the colour of the fluorescence changed to blue by the addition of oxygen or air, but that the bright green fluorescence is restored after a period of illumination. These changes are readily explained by the specific quenching action of oxygen due to photochemical oxidation, which is known to occur. The excited molecules of acetone upon reaction lose their power to fluoresce, while the blue fluorescence is the product of a transient intermediate compound present during the process of oxidation.

We have ourselves been engaged in the study of this fluorescence during the past six months, and in view of the publication of the work of Damon and Daniels, feel we may be permitted to give this preliminary account of a result which we believe to be of fundamental importance to photochemical theory.

Using as exciting radiation the mercury line at λ 3340 Å., we have obtained a series of photographs of the fluorescence spectrum of acetone, of particular interest. From these it is apparent that the visible fluorescence is accompanied by a very considerable emission in the ultra-violet, the wave-lengths extending down to that of the exciting line. There is this striking difference between the visible and ultra-violet fluorescence, however; whereas the former consists of diffuse bands, the latter consists of a series of fine and sharp lines. The phenomenon of pre-dissociation (of which diffuse bands associated with photochemical decomposition are a manifestation) has previously been mainly associated with absorption spectra. We have here the first recorded example of its existence in the reverse process of fluorescence. Whereas in the case of absorption, the condition of predissociation represents a transition from a stable lower to an unstable upper level, predissociation in fluorescence represents the reverse, a transition from an upper excited level to a lower unstable level. These facts can be readily interpreted in terms of a Franck-Condon potential energy diagram.

The analysis of this fluorescence led us to infer, first the existence of a hitherto unsuspected region of absorption by acetone in the near infra-red, and secondly a region of discrete structure in the ultra-violet absorption band of acetone, which has previously been supposed to be continuous. Both these predictions have been verified: using specially purified liquid acetone, we have obtained photographs of a series of diffuse infra-red bands extending from $\lambda\lambda$ 7205 Å. to the limit of sensitivity of our plates (about 11000 Å.), while with a column of acetone vapour at low pressure we have obtained photographs of the expected discrete structure of the ultra-violet band.

The unstable infra-red level may well be the initial stage reached in the homogeneous thermal decomposition of acetone described by Hinshelwood and

Hutchinson³. Molecular activation (68.5 kcal. in this case) then represents the total energy which must, on the average, be introduced into the various degrees of freedom of the molecule to ensure the reaching of our unstable level; decomposition then follows. A full account of this work will be published when collateral experiments on the photochemical decomposition now in progress have been completed.

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¹ Gelbke, *Jahrbuch der Radioaktivität*, 10, 1; 1913.

² Damon and Daniels, *J. Amer. Chem. Soc.*, 55, 2363; 1933.

³ Hinshelwood and Hutchinson, *Proc. Roy. Soc., A*, 113, 221; 1926.

Fine Structure and Predissociation in the Spectrum of Calcium Hydride

IN 1925 Mulliken¹ reported a band system, emitted by the CaH molecule, and having a very unusual structure. It is composed of singlet *P* and *R* branches, which are abruptly cut off at *P* ($11\frac{1}{2}$) and *R* ($9\frac{1}{2}$). It was generally assumed that this band, shortly named the *C*-band, corresponds to a ${}^2\Sigma^* \rightarrow {}^2\Sigma$ transition, and that the non-appearance of doublet components in the series was caused by some peculiar unstable conditions in the activated ${}^2\Sigma^*$ state. Later on², we were able to show that ${}^2\Sigma^*$ suffers from predissociation into the continuous region of an activated ${}^2\Sigma$ level, causing the remarkable cut-off in the series at low pressure in the source of light.

FIG. 1.

However, the singlet structure of the *C*-band is incompatible with the general theory on band structure as well as with Kronig's rules of predissociation. According to these rules, either both or none of the doublet components (F_1 , F_2) in ${}^2\Sigma^*$ should be missing, having identical symmetry properties in ψ . We considered these arguments of such weight that we undertook a new investigation of the spectrum, using very high dispersion (0.58 Å./mm.). The band lines were resolved into doublets, as shown in Fig. 1, which gives the region around the head of the *P*-branch at λ 3534. Our analysis indicates that ${}^2\Sigma^*$ forms very narrow rotational doublets [$F_1 - F_2 = 0.011(K + \frac{1}{2})$], with their centres represented by the formula:

$$T(K) = 28353.04 + 4.792 K(K+1) - 8.9 \times 10^{-4} [K(K+1)]^2 - 2.22K.$$

This expression contains a large term, linear in *K* and previously attributed to the interaction between the electronic spin and the rotation of the molecule. According to our new results, this term must now be identified with an *l*-uncoupling effect, ${}^2\Sigma^*$ forming a typical case *d*.