

LETTERS TO THE EDITOR

ASTROPHYSICS

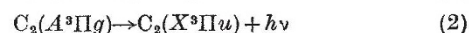
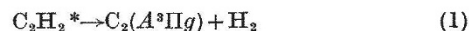
Origin of the $C(A^3\Pi_g) \rightarrow C_2(X^3\Pi_u)$ Emission in Comets

THE observation of the C_2 Swan bands ($A^3\Pi_g \rightarrow X^3\Pi_u$) in emission in the coma of comets was at one time taken as evidence that the ground state of C_2 was the $X^3\Pi_u$ state since this cometary emission is known to arise by means of a fluorescence process. However, Ballik and Ramsay¹ have shown that the ground state of C_2 is $x^1\Sigma^+_g$ and consequently the observation of the Swan bands would be consistent with the following: (1) C_2 is formed initially in the triplet system by decomposition (probably photodecomposition) of a hydrocarbon molecule. (2) The $^3\Pi_u \rightarrow ^1\Sigma^+_g$ transition does not occur to an appreciable extent prior to fluorescence excitation by solar radiation or in the time between successive excitations. The latter implies that C_2 experiences an insufficient number of collisions, or possibly no collisions, to effect the forbidden $^3\Pi_u \rightarrow ^1\Sigma^+_g$ transition. This is not an unreasonable requirement since it is known that the rotational and vibrational distribution of C_2 in cometary atmosphere corresponds to a temperature of about 2,500° K and that C_2 , therefore, must experience few if any collisions between the time of its formation near the nucleus and the time of its excitation farther out in the coma.

Thus, while the second requirement seems to be met, the first requirement of the specific formation of C_2 in the triplet system on photodissociation of a hydrocarbon molecule needs to be demonstrated. Any significant formation of C_2 in the singlet system must be excluded since appreciable concentrations of C_2 in the $x^1\Sigma^+_g$ ground state would eventually lead to population of upper singlet states ($b^1\Pi_u$, $c^1\Pi_g$, $d^1\Sigma^+_u$) and emission from these states (Fig. 1).

Recent work in our laboratory on the vacuum ultra-violet photolysis of CH_4 , C_2H_2 , C_2H_4 , and C_2H_6 suggests that photodissociation of methane and acetylene in the

vacuum ultra-violet at low pressures leads to the formation of C_2 in the $^3\Pi_g$ state. The emission from CH_4 was very weak and, since a secondary process for C_2 production from methane is required, the more interesting C_2H_2 system was investigated in detail. A weak emission consistent with the Swan bands of C_2 and the detection of molecular hydrogen formation was explained in terms of the decomposition of an electronically excited acetylene molecule².



Emission in the regions of other C_2 transitions (Fig. 1) was not observed. No emissions were observed from C_2H_4 and C_2H_6 .

On this basis we would suggest that the origin of the C_2 Swan bands in cometary emission spectra is the photodissociation of acetylene or an acetylene-type molecule leading to an eventual accumulation of C_2 in the $X^3\Pi_u$ state.

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¹ Ballik, E. A., and Ramsay, D. A., *J. Chem. Phys.*, **31**, 1138 (1959).

² Stief, L. J., DeCarlo, V. J., and Mataloni, R. J., *J. Chem. Phys.* (in the press).

PHYSICS

A Nitrogen-14 Triplet and Nitrogen-15 Doublet as a Standard for Electron Spin Resonance Hyperfine Splitting Determinations

THE results given here follow on from an earlier communication in which it was reported that treatment of certain methacrylate polymers with nitric oxide gas induced an electron spin resonance signal¹. It was later found that pure polymethyl methacrylate powder did not give a signal on treatment, and Law and Ebert² have suggested that the observed signal was due to traces of monomer in the polymer sample.

Methyl and *n*-butyl methacrylate monomers were treated with nitric oxide either by allowing the sample to stand in the presence of the gas for about an hour or, alternatively, by bubbling the gas through the monomer, the latter method being found to be the more satisfactory. The observed electron spin resonance absorption was investigated in the X-band region and the first derivative of the resulting signal (shown in Fig. 1) was found to consist of three evenly spaced peaks of equal intensities. It is suggested that the nitric oxide reacts with the carbon double bond ($C=C$) and as a result of this both an unpaired electron and a nitrogen nucleus become associated with the monomer. Similar results were obtained with nitrogen dioxide.

The *g*-value of the central peak was compared with that of diphenyl picryl hydrazyl (2-0036) and was found to be

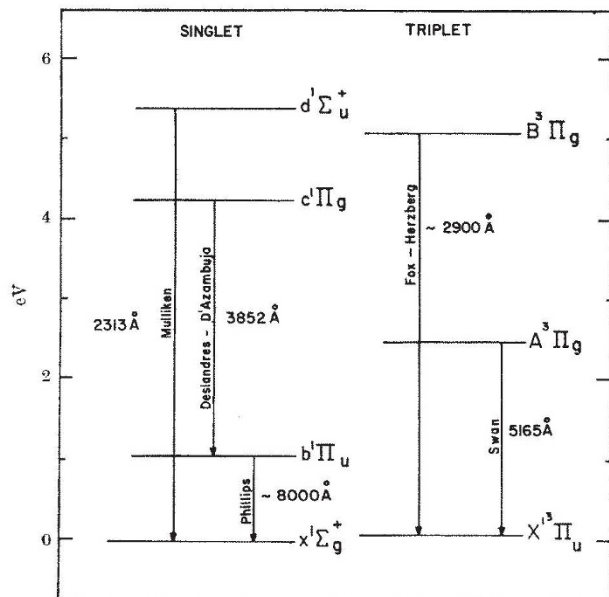


Fig. 1. Energy-level diagram of C_2 .