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K5
LIPS Studies of Primary Processes in The Photodissociation of C_2N_2 and C_4N_2

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The advent of tunable dye lasers has revived interest in the use of photoluminescence spectroscopy as a technique for characterizing the transient intermediates that occur in chemical processes. The spectral brightness of these lasers allows the selective excitation of free radicals such as CN, C_2, OH, etc., to an excited electron level from an individual quantum level in the lower state. The photons that result from the radiative decay of this excited state can be used to measure the number of free radicals originally present in the lower state. This technique called laser-induced photoluminescence spectroscopy (LIPS) has been used to study the primary photodissociation processes in C_2N_2 and C_4N_2.

The photon energy of the dissociation vacuum ultraviolet radiation was limited by a sapphire window to wavelengths greater than 1450 Å. Time dependent LIPS studies of the CN fragment produced from the photolysis of C_2N_2 have shown that roughly equal amounts of X state and A state radicals are produced in this wavelength region, which suggest that this is the principal primary process in the dissociation of C_2N_2. Similar studies have also been done for C_4N_2 and will be reported on.

A holographic grating monochromator has been used to discriminate between fluorescent radiation from the excited radical and scattered flash lamp light. This has permitted us to make LIPS measurements within 3 μs of the flash at a total of C_2N_2 or C_4N_2 pressure of 10 μm. These studies have shown conclusively that the X state radical is produced in high rotational levels as a result of the dissociation of either compound. The surprising thing about the observed rotational distributions is that they are Maxwellian with a rotational "temperature" of 1500 and 1400 K for C_2N_2 and C_4N_2 respectively. These observations can be explained in terms of a simple impulse model for photodissociation.

In both C_4N_2 and C_2N_2 most of the X state radicals are formed in the $v'' = 0$ level. A considerable fraction of the observed radicals, 30% for C_2N_2 and 15%, do, however, appear in the $v'' = 1$ level of the X state. These observations suggest that the C—N internuclear distance in the excited states of C_4N_2 and C_2N_2 responsible for the photodissociation is near the r_{CN} distance in the X state of CN.

K6
Collision-Induced Electronic Relaxation in Polyatomic Vapors

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Work in various laboratories has shown that the vapor fluorescence of a number of molecules is quenched by added gases. Every adduct so far tried is effective in quenching and the cross sections are often on the order of hard sphere. The quenching generally follows Stern–Volmer kinetics (not necessarily *simple* Stern–Volmer kinetics) and the fluorescence decay is found to be exponential.

These observations apply to formaldehyde [1], glyoxal [2, 3], propynal [4] and pyrimidine [5]. With the exception of formaldehyde, at least a significant component of the collision-induced S_1 decay is known to be triplet formation. The evidence in glyoxal is most compelling since the growth of triplet population accompanying singlet decay can be monitored directly by phosphorescence [3]. Sensitized biacetyl phosphorescence has been used to establish that collisions control the $S_1 \rightarrow T$ intersystem crossing in pyrimidine [5].

Cross sections for collision-induced triplet formation in pyrimidine, propynal and glyoxal seem not to be influenced by special heavy atom effects or oxygen