

experiment is readily obtainable through minor adjustments in the diatomic-like repulsive potential between the fragments. More interesting is the fact that the theory provides simple explicit criteria for the occurrence of fragment vibrational population inversions solely on the basis of known spectroscopic constants for the molecule and for the fragments and of the diatomic-like repulsive potential.

Model calculations indicate the possibility of generating large isotope effects in photodissociation processes by a suitable tailoring of the molecule. The absolute isotope effect is predicted to depend exponentially on the square root of the isotopic ratios of the reduced mass of the departing atom with respect to the remaining molecular fragment.

This research is supported, in part, by NSF grant MPS75-01549. K.F.F. is grateful to the Camille and Henry Dreyfus Foundation for a Teacher-Scholar Grant.

K4

*(Invited Lecture)*

#### **Infrared Laser Enhanced Reaction Dynamics**

W. BRAUN

*National Bureau of Standards, Physical Chemistry Division, Washington, D.C. 20234 (U.S.A.)*

To date considerable kinetic information has been derived on state selected chemical reactions [1, 2] by Polanyi and co-workers employing the "arrested relaxation infrared chemiluminescence method" which probes vibrational and rotational energy distributions in reaction products formed in fast reactions (*e.g.* reactions of the exchange type  $A + BC \rightarrow AB + C$ ). Information about the details of the potential surfaces characterizing reaction systems can in principle be obtained through trajectory computations.

Now that infrared lasers are available, which are either continuously tunable, or which emit discrete emissions that can be matched to specific infrared molecular absorptions employing a magnetic or electric field, the unique possibility of producing high concentrations of diatomic and multi-atomic reactants in specific vibrational states and measuring the specific

effect of vibrational energy on reaction kinetics becomes possible. A brief description of the methodology will be presented *i.e.* available laser systems and techniques for performing infrared "laser enhanced reaction dynamics" measurements. Either real-time kinetic measurements, or depth of modulation measurements can be made; the former is suitable to measuring reactions rapid compared to vibrational relaxation times, the latter must be employed if reaction rates are very slow compared to vibrational relaxation times. From these types of experiments two kinds of information can be obtained. The specific effect of vibrational energy on increasing (or possibly decreasing) the absolute reaction rate can be determined [3]. Can these state selected reactions be described by an Arrhenius formulation and if so does the energy of activation or the pre-exponential (or both) change if vibrational energy is added to one of the reactants? [4]. Several phenomenological formulations will be discussed and compared with recent data. A second kind of information that can be derived is similar to that obtained from the "arrested relaxation infrared chemiluminescence method". The distribution of energy in product molecules can be probed either by measuring the visible or u.v. emission from specific chemiluminescence reactions [5, 6] or product molecules can be probed during various stages of relaxation by using continuously tunable dye lasers. The effect of reactant vibrational energy on the distribution of energy in reaction products is clearly discernible and the results of several chemiluminescent reaction systems will be discussed. Implications of present results on theory of chemical reactions will be presented and suggestions for future experiments will be briefly outlined.

- 1 L. J. Kirsch and J. C. Polanyi, *J. Chem. Phys.*, 57 (1972) 4498.
- 2 D. J. Douglas, J. C. Polanyi, and J. J. Sloan, *J. Chem. Phys.*, 59 (1973) 6679.
- 3 M. J. Kurylo, W. Braun, A. Kaldor, S. M. Freund, and R. P. Wayne, *J. Photochem.*, 3 (1974) 71.
- 4 M. J. Kurylo, W. Braun, C. Nguyen Xuan, and A. Kaldor, *J. Chem. Phys.*, 62 (1975) 2065.

- 5 W. Braun, M. J. Kurylo, A. Kaldor, and R. P. Wayne, *J. Chem. Phys.*, 61 (1974) 461.
- 6 A. Kaldor, W. Braun, and M. J. Kurylo, *J. Chem. Phys.*, 61 (1974) 2496.

### K5

#### LIPS Studies of Primary Processes in The Photodissociation of $C_2N_2$ and $C_4N_2$

M. J. SABETY-DZVONIK, R. J. CODY and W. M. JACKSON\*

*Astrochemistry Brand, Goddard Space Flight Center NASA, Greenbelt, Md. 20770 (U.S.A.) and \*Howard University Department of Chemistry, Washington, D.C. 20059 (U.S.A.)*

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  $\mu$ s of the flash at a total of  $C_2N_2$  or  $C_4N_2$  pressure of 10  $\mu$ m. 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

A. E. W. KNIGHT and C. PARMENTER  
*Chemistry Department, Indiana University, Bloomington, Ind., (U.S.A.)*

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