

## TRANSLATIONAL ENERGY DISTRIBUTION OF PHOTOFRAGMENTS

R. Bersohn

Department of Chemistry, Columbia University, New York, N.Y. 10027 (U.S.A.)

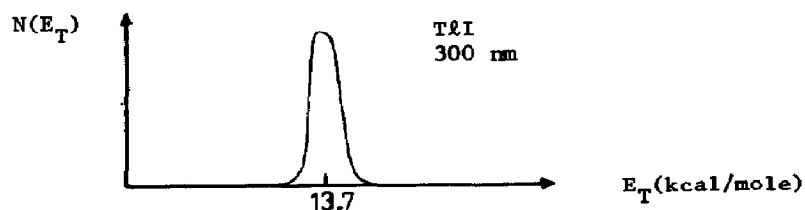
When a molecule absorbs a photon with energy  $\hbar\omega$  greater than the threshold for photodissociation  $D_0$ , the excess energy is partitioned among translational, rotational, vibrational, and electronic degrees of freedom, i.e.

$$\hbar\omega - D_0 = E_T + E_R + E_V + E_{el}$$

By photodissociating a molecular beam with a pulsed laser, one can measure the distribution of flight times of the fragments to a suitable detector and hence the distribution of  $E_T$ . We summarize here the results so far obtained with our collaborators M. Kawasaki, A. Freedman, and S.J. Lee.

Diatomic Molecules

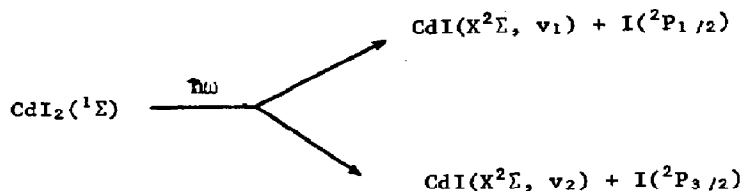
For a diatomic molecule the only internal degree of freedom is electronic so that the distribution of translational energies consists of a set of sharp peaks,  $\sim kT$  wide, each corresponding to a different final electronic state for the atoms. Photodissociation of TlI at 300 nm resulted in a translational energy distribution with a single sharp peak corresponding to an electronic energy of 0.96 eV. An accidental degeneracy arises from the fact that the energy of  $^2P_{3/2}Tl$  is only 0.02 eV different from that of  $^2P_{1/2}I$ .



### Triatomic Molecules

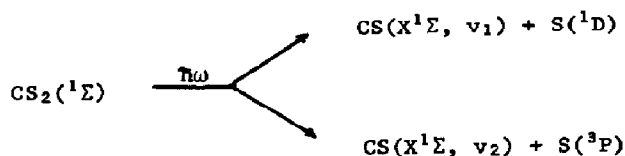
The linear triatomic is the most interesting system to investigate because the experimental results can be compared with the extensive theoretical developments of Jortner, Beswick, Freed and Band, S. Rice and others. Describable by only two coordinates the linear triatomic affords the simplest nontrivial model for the dynamics of dissociation.

$\text{CdI}_2$  when photodissociated at 280 and 300 nm resulted in a distribution with two peaks. One peak was maximized when the electric vector of the dye laser was parallel to the detection direction, the other when it was perpendicular. It appears that we obtain not one but two translational distributions

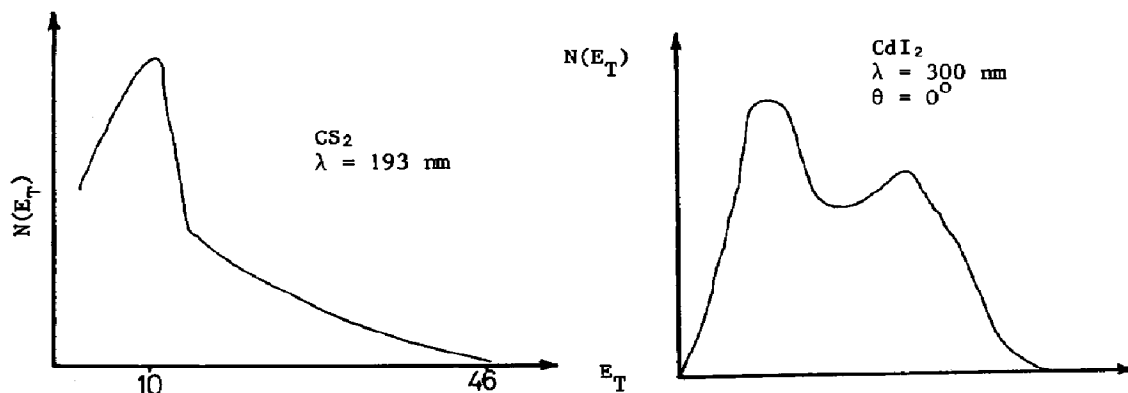


i.e. the distributions over  $v_1$  and  $v_2$  are superimposed and in practice cannot be readily separated.

$\text{CS}_2$  when photolyzed at 193 nm results in a translational energy distribution which is again clearly a sum of two distributions, one sharp and peaking at 12 kcal/mole and the other broad extending from 46 kcal/mole to at least 15 kcal/mole. We again have two processes



The angular distribution of the fragments has not been investigated but arguments will be given to show that both of these dissociations are predissociations from a strongly vibrational bent excited molecule. Thus the unknown rotational energy is important. The ideal linear triatomic has yet to be found.



### Polyatomic Molecules

$\text{Re}_2(\text{CO})_{10}$  when dissociated at 300 nm gave beautifully simple results. The Re-Re bond is stronger than the Re-C bonds but the electronic excitation involves promotion of an electron from a bonding to an antibonding orbital of the Re-Re bond. This is the bond that breaks and with strong anisotropy of  $\text{Re}(\text{CO})_5$  fragment distribution showing that dissociation takes place in less than a rotational period, i.e.  $< 2\text{ps}$ . The available energy,  $E_{\text{AVL}} = \hbar\omega - D_0 = 46 \text{ kcal/mole}$  is partitioned so that an average of 15 kcal/mole goes into translation and the balance into vibration. No rotation is excited because the repulsive force between the fragments during excitation acts along the line joining the centers of mass of the two fragments.

Aromatic halides photodissociate indirectly; aliphatic halides dissociate directly. What about aryl-alkyl halides such as benzyl halides? The aromatic part does the absorption but its energy must be transferred to the C-I bond to effect dissociation. When using 193 nm photons there is a striking difference between the translational energy distributions of iodobenzene and benzyl iodide. The former is flat and very broad extending from zero energy to the maximum available energy. The latter is sharp and peaked at low energies ( $\sim 5$  kcal/mole). The intervening  $\text{CH}_2$  group has severely limited the amount of energy which can be transferred from the phenyl ring to the C-I bond. For  $\text{C}_6\text{H}_5\text{I}$  we are forced to conclude that most of the vibrational energy of the ring is generated not by Franck-Condon factors but by the actual repulsive force acting during dissociation.

