

## VIBRONIC EFFECTS IN THE PHOTODISSOCIATION OF CYANOGEN

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Several years ago we reported the first use of a tunable dye laser to excite, and thus detect, the ground state fragments produced by a photochemical reaction [1]. With this method we were able to characterize the initial vibrational and rotational distribution of CN ( $X^2\Sigma$ ) radicals produced by the photolysis of a number of compounds.

All of that work was done using the broadband output of a VUV flashlamp. Naturally, the use of such an excitation source made it difficult to unambiguously assign the state of the parent molecules from which the dissociation products were formed. In some cases we were able to convolute the lamp emission spectrum with the parent molecule absorption spectrum so as to show that a single state was primarily excited. The results of this work showed that it would be extremely desirable to study photodissociation dynamics as a function of the wavelength of the incident light, where one could observe the effect of the structure of the upper potential curve upon the dynamics of the process. If the range of tunability were wide enough one could also study photodissociation from different excited states. In pursuit of these goals we have constructed a tunable VUV photofragment monochromator and report here on the first results obtained with this instrument.

The details of the experimental apparatus were recently published [2]. The photolysis light source is a VUV argon flashlamp whose electrodes form the entrance slit of a holographic grating monochromator. The dispersed light irradiates the gas under study and ground state fragments are detected using laser induced fluorescence techniques.

We have been able to measure rotationally resolved excitation spectra of CN ( $X^2\Sigma^+$ ) radicals formed by the photodissociation of cyanogen, under collisionless conditions. From these spectra we constructed the collisionless rotational and vibrational distributions of radical fragments. As had been previously observed using the broadband flashlamp

excitation source the distributions were Boltzman in nature and we could unambiguously assign a temperature to each [1]. Table I shows the measured rotational and vibrational temperatures as functions of the incident photon wavelength. Clearly both temperatures increase as the vibronic energy of the excited state increases.

The primary rotational distributions may be used to derive a translational distribution for individual vibrational levels of the CN radical fragments. Correlation arguments suggest that cyanogen photodissociation yields one ground state and one ( $A^2\Pi$ ) CN radical. This is supported by our observation of quenched products from the A state radical when nitrogen is mixed with the cyanogen and laser gain measurements. [3]. Both in earlier work and here no quenching from the  $A v'' = 1$  to the  $X v'' = 5$  level was seen. This means that almost all of the CN ( $A^2\Pi$ ) radicals are formed in the  $v'' = 0$  level. From conservation of angular momentum arguments we conclude that the two CN fragments carry off the same rotational energy.

Considering these points the observed rotational distributions may be used to construct an exact energy balance for each rotational state, and thus build up a translational energy distribution of products. Note, that the above assumptions when coupled with the fact that the observed rotational distribution is Boltzman like, leads to the conclusion that the translational distribution has to be non-Boltzman in character. The translational energy distribution is fixed by the requirement of energy conservation. Table II shows how energy is partitioned among the various degrees of freedom for the most probable rotational state at each photolysis wavelength. This table also shows that the translational energy of the fragments increases as the vibronic energy of the excited state is increased.

We conclude from our results that the rotational energy of the radical fragments increases as more vibrational energy is placed into the vibrational stretching mode of the excited parent molecule. This indicates that redistribution of the energy occurs on a time scale that is rapid compared to the predissociation process. Similar behavior has been seen in multiphoton infrared photolysis of molecules.

Finally, while a Boltzman like distribution has been observed for the rotational states, this implies that the translational energy distribution must be non-Boltzman in character. Evidently, the recoil energy of the fragments is fixed by the specification of the internal energy. The internal energy distribution itself, appears to be random.

1. R.J. Cody, M.J. Sabety-Dzvonik and W.M. Jackson, *J. Chem. Phys.* 66(5), 2145 (1977).
2. G.E. Miller, W.M. Jackson and J.B. Halpern. To be published in *Applied Optics*.
3. M.J. Berry, Molecular Energy Transfer, pp 114, J. Jortner and R.D. Levine editors. (Wiley, New York 1976).

TABLE I  
Vibrational and Rotational Temperatures of CN ( $X^2\Sigma$ ) Radicals  
Produced from the Photolysis of Cyanogen.

Photolyzing Wavelength	T vibrational	T Rotational
164 ± 2 nm	2100 ± 500 K	570 ± 70 K
159 ± 2 nm	2600 ± 500 K	1200 ± 200 K
154 ± 2 nm	4300 ± 300 K	1510 ± 120 K

TABLE II

Product Energy Distribution as a Function of Vibronic Energy  
in the Excited State.

$\lambda_{\max}$ (nm)	$E_{\text{avail}}$	$E_{\text{rot.}}$		$E_{\text{vib.}}$		$E_{\text{elec.}}$		$E_{\text{trans.}}$
		X	A	X	A	X	A	
164.0	15,640	209	209	1035	906	0	9242	2080
158.7	17,675	432	432	1035	906	0	9242	2879
153.6	19,767	550	550	1035	906	0	9242	3807

All energies are in  $\text{cm}^{-1}$ . The translational energy is the energy per fragment.  $E_{\text{avail}}$  is the difference between the photon's energy and the energy necessary for dissociation.