INFRARED PHOTODISSOCIATION OF DIATOMIC IONS INITIALLY FORMED IN HIGH VIBRATIONAL LEVELS

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When an ionic beam is accelerated to high energies, the thermal energy spread of the ions in the beam is roughly kept constant while their velocity spread is reduced drastically. This effect permits one to determine the discrete velocities of fragments resulting from a predissociative [1] or a photodissociative [2] process. Normally, these latter phenomena produce fragments whose velocity differences cannot be isolated from their thermal spread, but with the contraction in velocity distribution afforded by the acceleration process even small velocity differences can be resolved. This technique is already well established under the name of translational spectroscopy. It requires good energy and angular resolutions. In the case of photodissociation one can refer to a review article [1].

All previous fast-ion photodissociation experiments either in merged or crossed beam configuration have been carried out with visible lasers. However, we recognize that

TABLE 1

v ($J = 0$)	Fraction of H_2^+	$D_e - E_v$ (eV)	W (eV) (λ_1)	σ (10^{-17} cm^2)	
				$\lambda_1 = 9.6$ μm	$\lambda_2 = 10.6$ μm
0.14	0.986	2.65 >> 0.17			
15	0.005	0.1049	0.011	0.257	0.074
16	0.604	0.0533	0.063	2.660	3.149
17	0.003	0.0191	0.097	1.003	0.757
18	0.002	0.0029	0.113	0.195	0.157

$D_e - E_v$ gives the energy position of the rovibronic level with respect to the dissociation limit.
W is the kinetic energy of the photofragments.
σ is the photodissociation cross section for the two main lines of CO_2 lasers.

molecular ions can be formed in high vibrational levels by photoionisation or by electron bombardment. These vibrational levels can then be photodissociated by an IR laser. In Table 1 we have reported the relative populations of the high vibrational levels of H_2^+ formed in an electron impact ion source. These population densities are at least ten times smaller than the corresponding ones probed by Los, Durup and Carrington [1, 2] in their photodissociation experiment. But this is largely compensated for by the higher photon densities of the CO_2 laser, so that for an equivalent amount of power, the signal obtained via an IR laser is actually higher than that of a visible laser.

The IR photodissociation experiment implies, however, a greater angular resolution and a defined zero scattering angle. We have calculated the photodissociation cross section for the vibrational levels 15, 16, 17 and 18 of H_2^+, following Dunn's [3] treatment, for the CO_2 laser lines. Given the good overlapping of the ground state wave func-

tions with the continuum, the photodissociation cross sections are relatively high and the experiment is feasible (see Table 1). The kinetics of the dissociation process has been described in terms of partial collision dynamics. Seen in this light, the dissociative transi- tion occurs at a highly localized internuclear distance corresponding to the primary peak of the Airy function which is also characteristic of the particular vibrational level involved. This helps to define the rotation angle of the internuclear axis during the disso- ciation; therefore from the angular distribution of the fragments (or laser polarisation) one can determine the symmetry of the transition [4].

In such experiments, the "collision energy" is of course smaller than the laser energy, the exact relationship being defined by $h\nu = E_v + W$. W can vary between 0.1 and 0.01 eV. So in the case of HD^+, whose two asymptotic dissociative limits are separated by only 0.003 eV, one can probe the relative branching ratios in $H^+ + D$ or $D^+ + H$ as a function of the collision energy, whose value is comparable with the isotope energy shift. This enables one to probe the adiabatic and diabatic correlation diagrams.

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THE INTERACTION OF 1216 Å PHOTONS AND OF EXCITED ARGON ATOMS WITH CH₃CN

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There have been relatively few studies of the photodecomposition of methyl cyanide. Experiments in the laboratory of Steacie [1] have established that photodetach- ment of a hydrogen atom is the predominant process at 1849 Å but that rupture of the C—C bond, a higher energy process, also occurs. Okabe and Dibeler [2] reported a thres- hold of 1455 Å for the appearance of the B–X fluorescence ("violet bands") of CN on photolysis of methyl cyanide. However, at 1216 Å this fluorescence was only about 3% as intense for methyl cyanide as for cyanogen chloride, suggesting that the formation of $CH_3 + CN$ is not the predominant photodecomposition process even at this wavelength. In studies of the interaction of methyl cyanide with metastable argon atoms (11.5 - 11.7 eV), Setser and Stedman [3] also observed the violet bands of CN, with the upper limit $v' = 16$.

Recent studies in this laboratory [4] of the 1216 Å photolysis of methyl cyanide isolated in solid argon at 14 K have provided abundant evidence for the importance of H atom stripping; secondary photolysis leading to complete loss of the H atoms of the parent molecule plays an important role. Comparison of the visible–ultra-violet spectrum of the photolyzed sample deposit with the spectra reported by Merer and Travis for the two C_2N isomers demonstrated that extensive skeletal rearrangement also occurred; two band systems of CNC [5] were prominent, but only weak CCN [6] absorptions were present. The two infrared-active vibrational fundamentals of ground state CNC were also identified. The predominance of CNC in these experiments is consistent with the predissociation of CCN noted by Merer and Travis [6] and with the gradual disap- pearance of CCN during the argon-matrix study of its fluorescence spectrum, recently reported by Bondybey and English [7]. Because the violet bands of CN were very promi- nent but the Mulliken bands of ground state C_2 was undetectably weak in the 1216 Å photolysis studies, it is inferred that the predissociation of CCN leads to the formation of C + CN, with some of the carbon atoms migrating from the site of their photoproduction but others recombining to form the more stable CNC isomer.