

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 transition 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 dissociation; 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 $\text{H}^+ + \text{D}$ or $\text{D}^+ + \text{H}$ 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 CH_3CN

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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 photodetachment 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 threshold 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 $\text{CH}_3 + \text{CN}$ 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 $\nu' = 16$.

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 disappearance 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 prominent 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 $\text{C} + \text{CN}$, with some of the carbon atoms migrating from the site of their photoproduction but others recombining to form the more stable CNC isomer.

Another recent series of experiments in this laboratory has been concerned with the products of the interaction of excited argon atoms with methyl cyanide. The sampling configuration used for these experiments has been described in a previous publication [8] reporting the appearance of prominent absorptions of HC_2 in the infrared spectrum of the products of the interaction of excited argon atoms with acetylene. In a study of the interaction of excited argon atoms with methane [9], a very prominent absorption of CH_3 resulted, with a significant reduction in the intensities of secondary photolysis product absorptions, compared with the 1216 Å photolysis study of matrix-isolated CH_3 [10]. Thus, it was expected that secondary photodecomposition would play a less important role in the studies of the interaction of excited argon atoms with methyl cyanide than in the studies of its photolysis at 1216 Å. The observations were consistent with this expectation; in typical excited argon atom studies the violet bands of CN and the infrared and ultraviolet absorptions of both CCN and CNC were weak. A number of infrared and ultraviolet absorptions of hydrogen-containing products which were relatively weak in the 1216 Å photolysis studies were very prominent in the excited argon atom studies. This result is not inconsistent with the observation of the CN violet bands by Stedman and Setser [3], since the CN bands are intrinsically strong and some CN is produced, but it does indicate that the major photolysis process for methyl cyanide in the 1050 - 1100 Å spectral region (corresponding to 11.5 and 11.7 eV metastable argon atoms) involves H atom detachment.

In addition to a small concentration of CH_3NC , some five different hydrogen-containing products resulted from the interaction of excited argon atoms with methyl cyanide. Of these products, two appeared in several times greater concentrations in the excited argon atom studies than in the 1216 Å photolysis studies. One group of infrared absorptions (Group A), at 437, 868 and 1917 cm^{-1} , and an ultraviolet absorption at 2645 Å disappeared when the sample was exposed to filtered mercury-arc radiation of wavelength longer than 3450 Å. A second group of infrared absorptions (Group B), at 690, 872, 1000, 1124, and 2040 cm^{-1} , and a progression between about 3060 and 2500 Å with band separations of approximately 1000 cm^{-1} disappeared on exposure of the deposit to the full light of a medium-pressure mercury arc. Infrared absorptions with Group B photolysis behavior appeared at 421, 648, 800, 921, 1998, 2017, and 2246 cm^{-1} in studies of the interaction of excited argon atoms with CD_3CN . In a previous study of the reaction of NH (produced by the photolysis of HN_3) with C_2H_2 in an argon matrix, Jacox and Milligan [11] observed a similar pattern of infrared absorptions and tentatively assigned them to the previously unreported species ketenimine, $\text{H}_2\text{C}=\text{C}=\text{NH}$. Three other groups of infrared absorptions, distinguished by whether they slowly disappeared, remained constant in intensity, or grew in intensity on prolonged mercury-arc irradiation of the sample, had similar relative intensities in the 1216 Å photolysis and excited argon atom studies.

Experiments utilizing $^{13}\text{CH}_3\text{CN}$, $\text{CH}_3^{13}\text{CN}$ and CH_3^{15}N have provided further support for the assignment of the Group B absorptions to ketenimine. Although the infrared spectra show only five of the expected twelve fundamental absorptions, precluding a definitive normal coordinate analysis, reasonable assignments for all five of these absorptions are possible. Comparison with the behavior of the isoelectronic species allene and ketene on isotopic substitution is helpful in making these assignments.

The cage recombination of the H atom with CH_2CN to form ketenimine is analogous to the cage recombination of H atoms with CN to produce HNC (as well as to re-form HCN), observed in studies of the 1216 Å photolysis of HCN in argon and nitrogen matrices [12]. As in the earlier studies, it would be expected that a significant fraction of the H atoms should be able to diffuse from the site of their production, leading to the stabilization of CH_2CN . The relatively high yields of ketenimine and of the species responsible for the Group A absorptions in the excited argon atom studies suggests that both products result from a primary decomposition process. Unfortunately, the isotopic data for the Group A absorptions do not suffice for a definitive identification of the species which contributes them. The 1917 cm^{-1} peak behaves appropriately for assign-

ment to a CN stretching vibration which is somewhat coupled to vibrations of other parts of the molecule. Although the 868 cm^{-1} peak cannot be attributed to a pure out-of-plane wagging motion of a CH_2 group, the observed isotopic substitution dependence of this peak could be rationalized in terms of the expected mixing of this vibration with the out-of-plane bending fundamental of the CCN chain. The appearance of this absorption at a frequency significantly higher than that of the out-of-plane deformation fundamental of CH_3 [9, 10] is not inconsistent with such an assignment, in view of the expected interaction of the unpaired electron of CH_2CN with the π electrons on the CN group. The closely related H_2CF free radical has also recently been observed in this laboratory to photodecompose on exposure of the sample to the full light of a medium-pressure mercury arc.

In summary, H atom detachment has been found to predominate both on 1216 \AA photolysis of CH_3CN isolated in an argon matrix and on collisional interaction of CH_3CN with $11.5 - 11.7\text{ eV}$ excited argon atoms, followed by the trapping of the products in solid argon at 14 K . Secondary photodecomposition processes play a much more important role in the 1216 \AA photolysis studies than in the excited argon atom studies. A major product in the excited argon atom studies is ketenimine, $\text{CH}_2=\text{C}=\text{NH}$, previously identified in matrix isolation studies of the reaction of NH with C_2H_2 . A partial vibrational assignment for ketenimine is possible, utilizing the detailed isotopic data obtained in these experiments. A band system between 3060 and 2500 \AA may also be contributed by ketenimine. Present data permit only a tentative identification of CH_2CN .

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PHOTOCHEMICAL REACTIONS OF NITROMETHANE IN NON-AQUEOUS SOLUTIONS

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Investigations on photochemical properties of nitromethane have been carried out for many years and have been mainly concerned with the photolysis of nitromethane in the gaseous and liquid phases and in frozen matrices [1, 2]. The dissociation of the C—N bond into free radicals CH_3 and NO_2 has been assumed as the most probable primary process of nitromethane photolysis. This abstract presents results of photochemical studies on nitromethane in benzene, cyclohexane and isopropanol solutions irradiated with wavelengths of 254 nm , longer than 290 nm and 313 nm . Nitroalkanes show two absorption bands at about 200 nm and 270 nm . However, we have shown after a precise examination of the nitromethane spectrum that an additional band at 330 nm can be