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EMISSION SPECTRA OF THE CN RADICAL PRODUCED BY THE REACTION OF METASTABLE ARGON ATOMS WITH CH_3CN AND HCN

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The CN violet and red emission spectra have been observed by the dissociative excitation of CH_3CN and HCN by collision with Ar ($^3P_{0,2}$) atoms formed by a microwave discharge. In the violet bands the relative populations in higher vibrational levels ($v' \geq 11$) for the $B\,^2\Sigma$ state resulting from HCN are much larger than the corresponding populations resulting from CH_3CN. Vibrational structure with maximum intensity at $v' = 6$ or 7 has been observed in the red bands.

The violet and red emission bands of the CN radical ($B\,^2\Sigma - X\,^2\Sigma$ and $A\,^2\Pi - X\,^2\Sigma$, respectively) have been observed in the following processes: a) reactions of active nitrogen atoms with a number of organic compounds,[1-5] b) photodissociation of cyanides,[6,7] and c) energy transfer reactions from metastable argon atoms to a number of cyanides.[8,9] For processes a) and b) the mechanism of production of the excited CN radicals and their initial energy distributions among the vibrational and rotational degrees of freedom have been investigated in detail, whereas for process c) no systematic study seems to have been made except for a study of Setser and Stedman,[8] who observed the violet and red emissions and determined the dissociation energies of cyanides. In a more recent report, Setser et al.[9] also measured the rotational relaxation of $CN(B\,^2\Sigma)$ formed by interaction of metastable argon with BrCN.

The present study has been undertaken to investigate process c) in some detail. Emission spectra have been observed by mixing acetonitrile or hydrogen cyanide into an argon afterglow produced by a microwave discharge. The relative intensities of the vibrational structures of the

spectra can be used to estimate the initial energy distributions of the CN fragment, since the radiative lifetime of the CN $B\,^2\Sigma$ state (85 ns)[10] is less than the mean time between collisions[9] at the pressure of below 0.3 Torr.

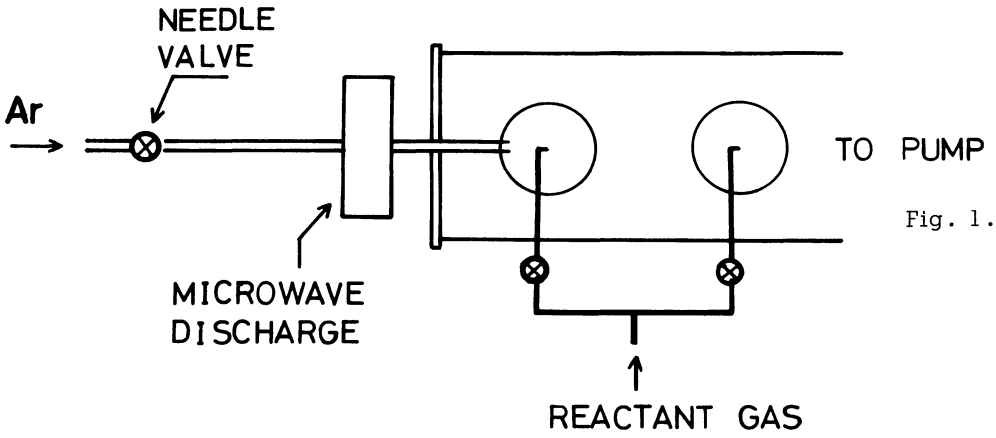

Fig. 1. Schematic design of the apparatus.

Experimental and Results

Experimental arrangements are shown in Fig. 1. Metastable $Ar(^3P_{0,2})$ atoms were produced by a 2450 MHz microwave discharge with the input power varied from about 0.1 to 1 kW. Except when the dependence on the discharge power was studied, spectroscopic measurements were made with the input power at about 0.5 kW. The discharge section was made of a 15 mm i.d. quartz tube, and the product was admitted into a reaction chamber made of a 100 mm i.d. stainless steel tube. The chamber was evacuated by a 500 ℓ/s mechanical pump.

The reactant gas was injected into the reaction chamber through a 0.4 mm i.d. stainless steel tube at either 14 cm or 26 cm downstream from the discharge section, and emission was observed through a quartz window provided in each reaction region. Most observations were made at the former position.

The pressure of the system was measured near the top of the injection tube with a Pirani gauge calibrated against a McLeod gauge. The purity of the gases was greater than 99%, and no impurity effect was observed. The measurements of the spectra were made by means of a Czerny-Turner scanning monochromator and a photomultiplier with the aid of a lock-in amplifier.

That the argon metastable species were produced in sufficient density by the discharge was confirmed by a measurement of the nitrogen second positive bands. When nitrogen gas of about 0.05 Torr was introduced into the argon afterglow through the injection tube, strong N_2 $C\,^3\pi - B\,^3\pi$

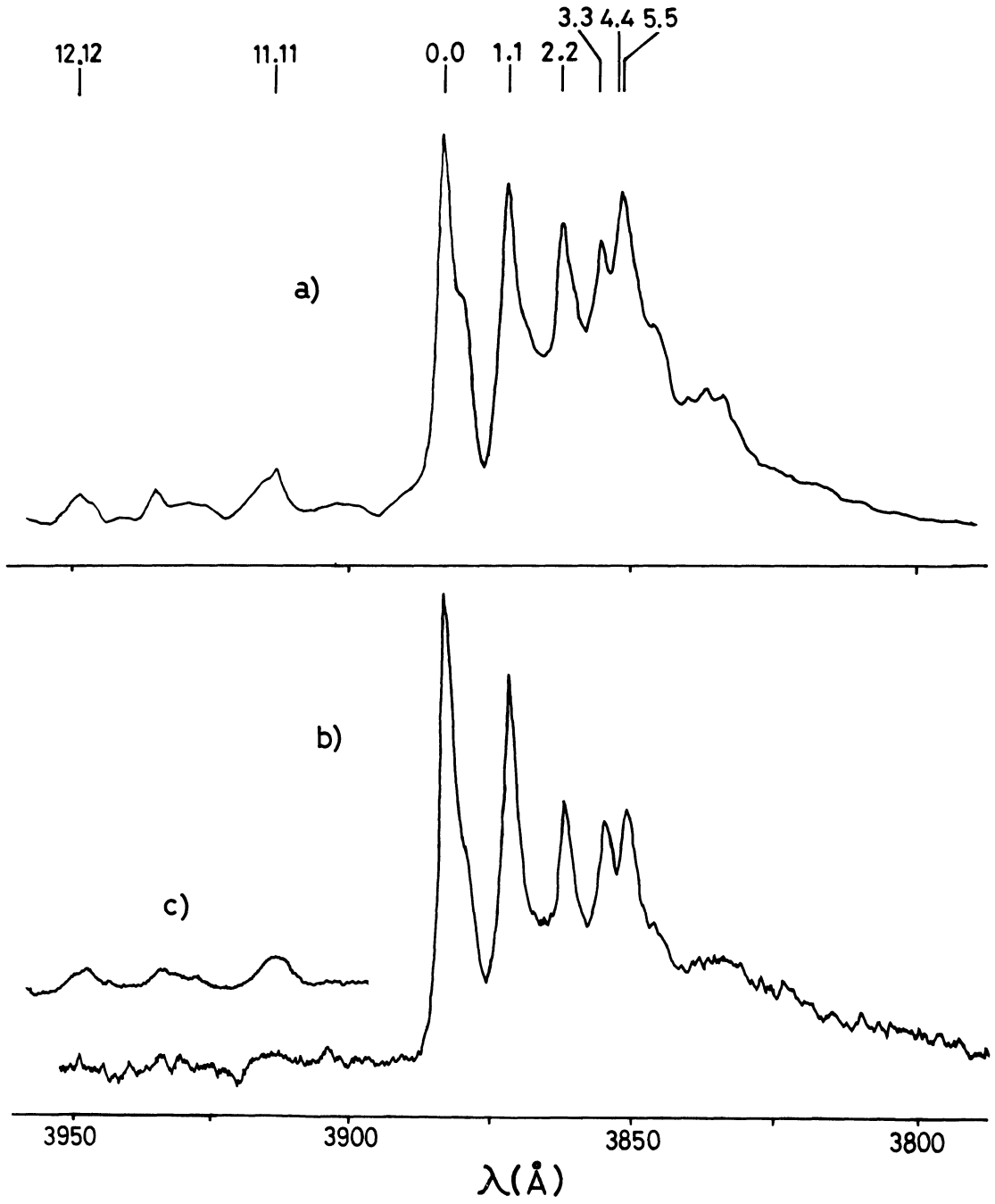

Fig. 2. CN violet band emission from Ar($^3P_{0,2}$) atoms with HCN (a) and with CH_3CN (b), (c) recorded with slit widths of 140 μ in (a), (b) and 200 μ in (c).

bands from the vibrational levels $v' \leq 2$ with unresolved rotational structure were observed. According to previous studies,[11-13] this spectrum is characteristic of the collision of N_2 with metastable argon species.

The CN violet and red bands observed at pressures of 0.3, 0.02 and 0.03 Torr for argon,

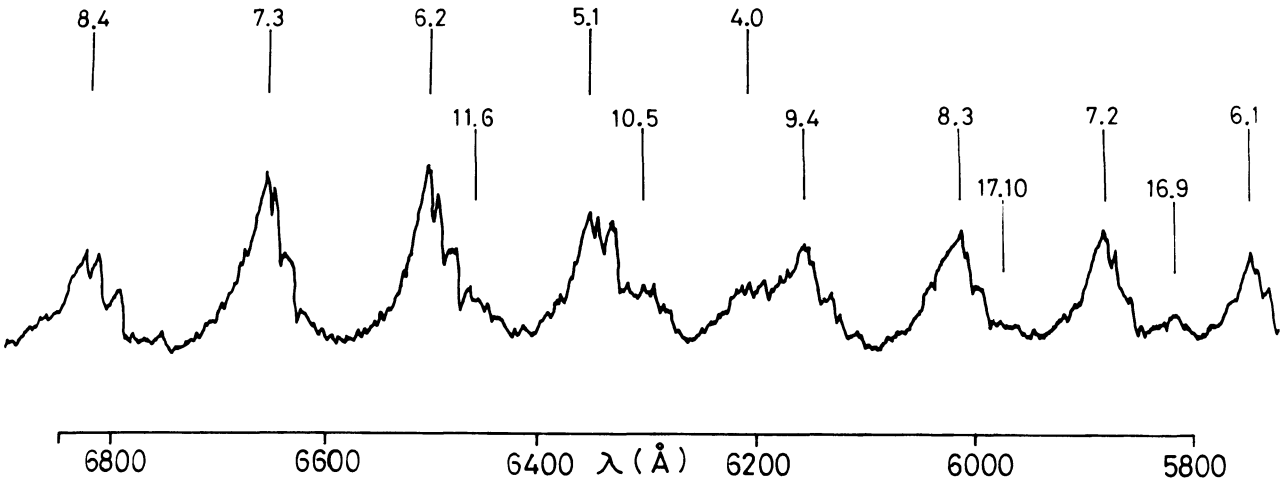

Fig. 3. CN red band emission from Ar($^3P_{0,2}$) atoms with HCN.

CH_3CN and HCN, respectively, and with spectral resolution of about 2 Å are shown in Figs. 2 and 3. For CH_3CN an intense emission band for the CH radical ($A\,^2\Delta - X\,^2\Pi$) was observed at 4315 Å besides the CN bands. The dependence of the band intensities on the argon pressure was examined with the discharge power held constant (0.5 kW). As shown in Fig. 4, the violet and red bands, much like the N_2 second positive band, first increase in intensity nearly linearly with the argon pressure and then start to decrease, whereas the CH band starts to appear at about 0.2 Torr and rises steeply from about 0.4 Torr. Similar trends were observed when the discharge power was varied and the argon pressure was held at 0.3 Torr. In all cases, no significant differences were observed in the relative intensities of the vibrational structures. The above findings support the view that the $B\,^2\Sigma$ and $A\,^2\Pi$ states of the CN radical are produced in a primary collision process with metastable argon atoms, but not the $A\,^2\Delta$ state of the CH radical.

The violet band resulting from HCN (Fig. 2a) has much stronger vibrational structures corresponding to $v' \geq 11$ than that resulting from CH_3CN (Fig. 2b and 2c). This difference may be accounted for by the following reasoning. For both cyanides the maximum energies to be transmitted to the CN radical are estimated to be nearly equal (about 6.3 eV) from the difference between the excitation energy of argon and the dissociation energies of the cyanides[14] (5.2 eV for HCN and 5.3 eV for CH_3CN). In the case of CH_3CN, however, a fraction of this energy can be transmitted to the internal energy of the CH_3 radical, and this makes the excitation to higher vibrational levels less probable. The band envelopes in the region 3840-3800 Å were compared with the theoretical envelopes calculated with an effective rotational temperature. For both

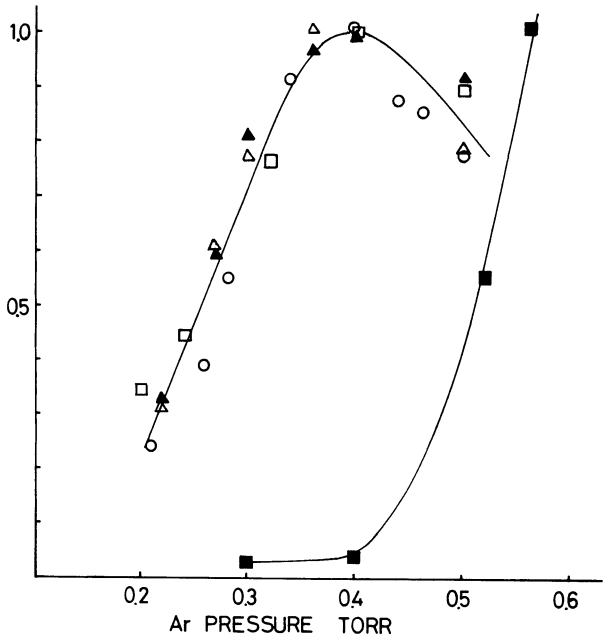

Fig. 4. Dependence of band intensities on the pressure of argon gas. ○: N_2 second positive band, △: CN red band from HCN, ▲: CN violet band from HCN, □: CN violet band from CH_3CN, ■: CH 4315 Å band from CH_3CN.

HCN and CH_3CN the estimated rotational temperatures are found to be significantly higher than the room temperature.[15]

The red band spectra, shown in Fig. 3, resulting from HCN and CH_3CN are similar to each other but are distinctly different from that observed by Mele and Okabe[6] in the photodissociation of HCN, where the emission spectrum was weak and composed mainly of the transitions from higher vibrational levels, $v' \geq 10$. They interpreted their result as indicating that the upper states of the molecule formed by light absorption interact with the potential energy curve leading to CN $B\,^2\Sigma$ but not with the curve yielding CN $A\,^2\pi$. The $B\,^2\Sigma$ state thus formed then crosses over to the $A\,^2\pi$ state since the potential energy curves of the two states cross at low vibrational levels of the B state ($v' = 0$ of the $B\,^2\Sigma$ corresponds to $v' = 10$ of the $A\,^2\pi$ state). Another interpretation in terms of the perturbation between the rotational levels of the A and B states has been made by Jackson and Faris.[7] In contrast to the photodissociation results, the present experiment shows that the CN $A\,^2\pi$ state is formed directly from HCN and CH_3CN by the impact of the metastable argon atom. A further study is being undertaken to elucidate the mechanism of production of the $A\,^2\pi$ state.

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