June, 1977] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 50 (6), 1449—1452 (1977) 1449

Formation of CN($B^2\Sigma^+$) in the Reaction of Acetonitrile with Metastable Ar($^3P_{2,0}$) Atoms

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(Received January 7, 1977)

A flowing-afterglow method was applied to the formation of CN($B^2\Sigma^+$) from CH_3CN by impact of metastable argon atoms, Ar($^3P_{2,0}$). Emission spectra of CN $B^2\Sigma^+$-$X^2\Sigma^+$ (violet band) were analyzed to estimate the energies distributed to the vibrational and rotational motions of CN($B^2\Sigma^+$). In comparison with the CN($B^2\Sigma^+$) produced from HCN under similar experimental conditions, relative populations in excited vibrational states are smaller. The effective rotational temperatures range from 5000±1000 K ($v=0$—2) to 2000±1500 K ($v=5$—10). An intensity anomaly caused by the rotational perturbation with $A^2\Pi$ is used for estimating the ratio of the formation rates of CN $B^2\Sigma^+$ and $A^2\Pi$, F_B/F_A, to be 0.19±0.05.

Metastable argon atoms, Ar($^3P_{2,0}$), are known to react with cyanides (XCN, X=H, Cl, Br, I, CN, and CH_3) and produce CN radicals in electronically excited states. Studies on light emission from the CN radicals thus formed have been reported.[1—6] The vibrational and rotational distributions of the CN($A^2\Pi$) and CN($B^2\Sigma^+$) radicals produced by photodissociation[7,8] and electron impact[9,10] have also been studied in detail. A comparison of the results shows that the distributions resulting from the metastable reactions extend more broadly among different internal states and that the production of CN($A^2\Pi$) is more favored than that in the other reactions.

The emission from CN($B^2\Sigma^+$) formed in the reaction of metastable argon atoms with CH_3CN has previously been studied; spectra were reported in Refs. 1 and 5, and an analysis of a vibrational distribution was made on a spectrum taken with medium resolution,[3] where no rotational structure was observed. In the present paper a detailed analysis of the CN violet emission from acetonitrile based on a spectrum taken with higher resolution is presented. Rotational and vibrational distributions are obtained by a band envelope analysis for $\Delta v=0$ and -1 sequences. In addition, quantitative information on the formation rate to the CN $A^2\Pi$ and $B^2\Sigma^+$ states is obtained by an analysis of anomalies in the rotational distribution caused by the rotational perturbation between the two states.

Experimental

A flowing afterglow apparatus[1] was used. The flow tube was evacuated by a mechanical booster pump (500 l/s). Argon gas (99.99% nominal purity) was admitted into the flow tube after passing through a liquid nitrogen trap and is subjected to microwave discharge (2450 MHz, 500 W). Ionic species generated in the discharge section were collected on grids, and neutral atoms were led into the reaction zone. Acetonitrile (extra pure) was introduced into the flow about 15 cm downstream from the discharge section. The time of flight of argon atoms from the discharge section to the reaction zone was estimated to be of the order of 1 ms. The flame in the reaction region was observed through a quartz window and focused by a lens on a Spex 1704 monochromator. A photomultiplier (HTV R585) and a photon counting unit were used. The CN violet system ($B^2\Sigma^+$-$X^2\Sigma^+$) was observed for $\Delta v=+1$, 0, and -1 sequences.

The pressures of argon and the sample were monitored at the reaction zone by a Pirani gauge, which was calibrated against a McLeod gauge. Typical pressures were 0.3 and 0.01 Torr for argon and acetonitrile, respectively.

The effect of the light generated in the discharge section was checked by a time-of-flight experiment[13] and was found to be negligible.

Vibrational and Rotational Distributions

Provided the CN($B^2\Sigma^+$) formed has thermal velocity, the effect of collisional relaxation on the rotational distribution can be ignored, since the mean time between effective collisions (200 ns, as estimated from the cross section of rotationally inelastic collision, 85 Å^2)[4] is appreciably longer than the radiative lifetime of CN($B^2\Sigma^+$) (60 ns[14]). It is not known, however, whether the CN($B^2\Sigma^+$) produced is thermal. Therefore, the effect of collisional relaxation was tested by taking spectra at different argon pressures (Fig. 1). Since the spectra were essentially pressure-independent, the effect of rotational relaxation was ignored in the present analysis of relative intensities.

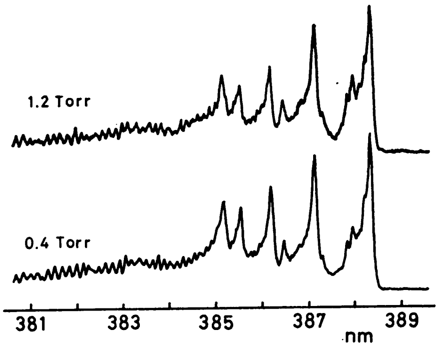

Fig. 1. Check of dependence of the spectra on argon pressure, CN $B^2\Sigma^+$-$X^2\Sigma^+$ 0-0 sequence. No appreciable collisional relaxation with argon is observed.

The CN $B^2\Sigma^+$-$X^2\Sigma^+$ $\Delta v=0$ and -1 sequences were used for analysis. Since transitions from different vibrational states, especially from higher vibrational states, were heavily overlapped by one another in these sequences, their band envelopes were analyzed by simulation. Relative vibrational populations and effective rotational temperatures were taken as parameters. The intensity of a transition is given by

$$I^{v'N'}_{v''N''} \propto P_{v'N'} q_{v'v''} \nu^3 S_{N'N''} R_{v'N'}/Q_{v'}, \qquad (1)$$

where $P_{v'N'}$ is the population in the level v' and N', ν is the transition frequency, $q_{v'v''}$ is the Franck-Condon factor, $S_{N'N''}$ is the rotational line-strength, $Q_{v'}$ is the rotational state sum, and $R_{v'N'}$ is the rotational distribution, which is assumed to follow the Boltzmann statistics. The intensities were superposed to obtain a band envelope. Molecular constants[15,16] and the Franck-Condon factors[17] were taken from the literature. Rotational line-strengths were calculated according to Mulliken's formulas.[18]

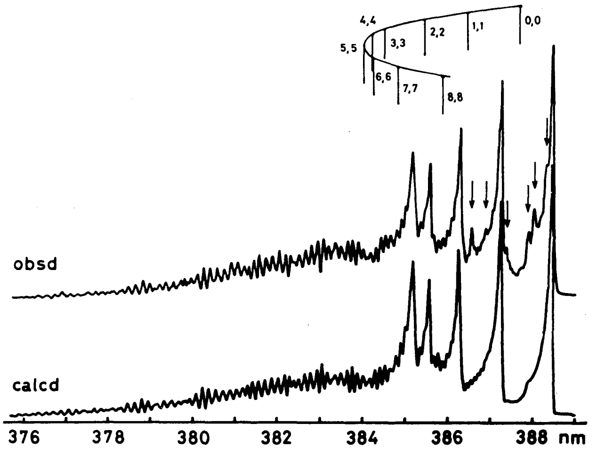

Fig. 2. Observed and simulated spectra of the CN $B^2\Sigma^+$-$X^2\Sigma^+$ 0-0 sequence. Those lines in the observed spectrum for which rotational perturbations with the $A^2\Pi$ state are known (indicated by arrows) are enhanced.

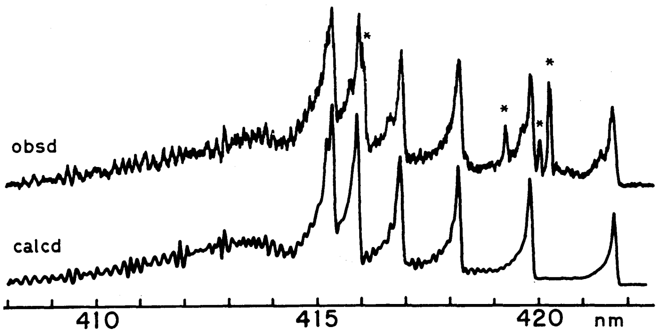

Fig. 3. Observed and simulated spectra of the CN $B^2\Sigma^+$-$X^2\Sigma^+$ 0-1 sequence. Asterisks indicate argon stray lines.

Simulated spectra are shown in Figs. 2 and 3 for the $\Delta v=0$ and -1 sequences, respectively. The observed and simulated spectra agree well except in the region where the intensities of the observed spectra are enhanced by the rotational perturbation with the $A^2\Pi$ state. The parameters used are listed in Table 1. The available energy, which is calculated from the argon metastable energies (11.55 and 11.72 eV[19]) and the C–C bond dissociation energy (5.2[20] or 5.32 eV[21]), is such that CN radicals can be excited up to $v'=14$ in the $B^2\Sigma^+$ state. Nevertheless, levels higher than $v'=11$, which are expected to appear as tail bands, were not observed.

Excess energy is defined as $E_{\text{excess}} = E_{\text{Ar}(^3\text{P}_{2,0})} - D_0 - E_{\text{CN(B)}}$, where $E_{\text{Ar}(^3\text{P}_{2,0})}$ is the excitation energies of Ar(^{3}P$_{2,0}$), D_0 is the dissociation energies for H–CN and CH$_3$–CN, and $E_{\text{CN(B)}}$ is the electronic excitation energy of the CN($B^2\Sigma^+$). Then, excess energies for HCN and CH$_3$CN are nearly equal, since the dissociation energies, D_0, for H–CN (5.2[22] or 5.5 eV[20]) and CH$_3$CN (5.2[20] or 5.32 eV[21]) are nearly equal. The excess energy is distributed to vibration and rotation of CN($B^2\Sigma^+$) and the translational motions of the fragments. For CH$_3$CN, energy is also consumed in the internal degrees of freedom of the methyl radical.

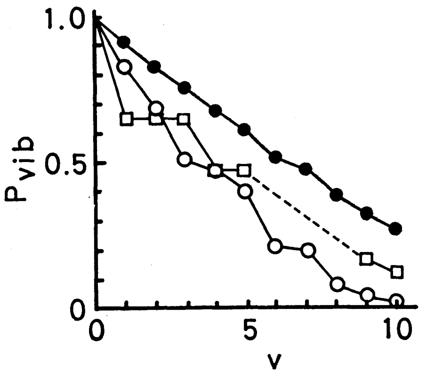

Fig. 4. Relative vibrational populations of the CN ($B^2\Sigma^+$) formed by impact of argon metastable atoms from CH$_3$CN (○, this work), HCN (●, Ref. 2), and HCN (□, Ref. 5).

Relative vibrational populations for the CN($B^2\Sigma^+$) from CH$_3$CN are compared with those from HCN[2,3,5] in Fig. 4. In spite of a slight discrepancy existing in the published populations for HCN, a clear difference is observed in the CH$_3$CN and HCN cases; populations in higher vibrational states are lower in the former case. The rotational excitation in the CN($B^2\Sigma^+$) from CH$_3$CN is higher than that from HCN (Table 1) in the $v'=0$—3 states.

TABLE 1. RELATIVE VIBRATIONAL POPULATIONS, P_{vib}, AND EFFECTIVE ROTATIONAL TEMPERATURES, T_{rot}, OF CN($B^2\Sigma^+$) FORMED IN Ar(^{3}P$_{2,0}$) REACTIONS

v	from CH$_3$CN[a]		from HCN[b]	
	P_{vib}	T_{rot}/K	P_{vib}	T_{rot}/K
0	0.23	5000	0.137	2400
1	0.19	5000	0.126	
2	0.15	5000	0.114	
3	0.12	4000	0.105	1900
4	0.11	3000	0.094	
5	0.09	2000	0.084	
6	0.05	2000	0.073	
7	0.04	2000	0.066	
8	0.02	2000	0.054	
9	0.01	2000	0.045	
10	$\lesssim$0.01	2000	0.038	

a) Errors in P_{vib} are about 0.02 for $v < 5$ and about 0.01 for $v \gtrsim 5$. Errors in T_{rot} are estimated to be about 1000 K for $v < 4$ and about 1500 K for $v \gtrsim 4$. b) Ref. 2.

Average energies distributed to vibration and rotation are 0.79±0.10 and 0.35±0.09 eV, respectively, for the $CN(B^2\Sigma^+)$ from CH_3CN, to be contrasted with those for HCN,[2] 1.2 and 0.2 eV, respectively. Accordingly, the $CN(B^2\Sigma^+)$ produced from CH_3CN is vibrationally less populated than that produced from HCN. This trend may be explained as that the methyl radical acts as an energy absorber,[3] *i.e.*, the residual energy may be used to excite the internal motions of the methyl radical. A similar trend was observed in the reaction of active nitrogen with organic compounds.[23]

Rotational Perturbation

The CN $A^2\Pi$ and $B^2\Sigma^+$ states are coupled through rotational perturbation,[24] and extra lines and anomalies in emission intensities have been observed. In order to estimate the ratio of the formation rates to the $A^2\Pi$ and $B^2\Sigma^+$ states, relative intensities for rotationally perturbed lines were analyzed. The analysis followed the scheme used in the analyses of the CN radicals formed in the reaction of active nitrogen with organic compounds,[25] in the electron impact on XCN (X=H, Br, and CN),[11] in the metastable-Ar impact on HCN and BrCN,[5] and in the photodissociation of ICN.[12]

Enhancement of intensities of the transitions from $N'=4$, 7, 11, and 15 in the $v'=0$ state were observed in a low resolution spectrum (Fig. 2). These states are known to be rotationally perturbed by the corresponding rotational levels in the $v=10$ level of the $A^2\Pi$ state. The R(14) transition was used for the analysis as the most suitable case.

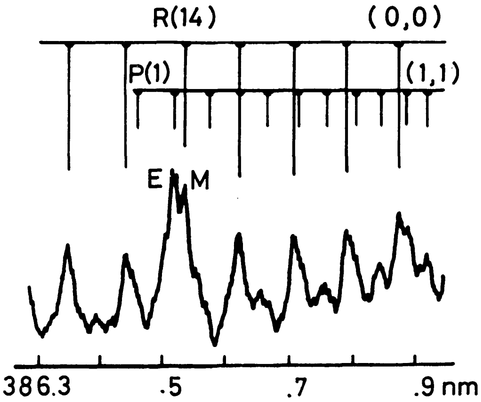

Fig. 5. A portion of the CN violet 0-0 band showing the rotationally perturbed R(14) lines (indicated as E and M).

A typical observed spectrum showing a rotationally perturbed line is given in Fig. 5. The spectrum was taken with a slit width of 10 μm. An extra line and a main line, which is overlapped by an unperturbed line, were observed. The relative intensities of the extra and main lines were essentially independent of the argon pressure between 0.3 and 0.8 Torr. Therefore, the effect of collisional relaxation is ignored in the following analysis.

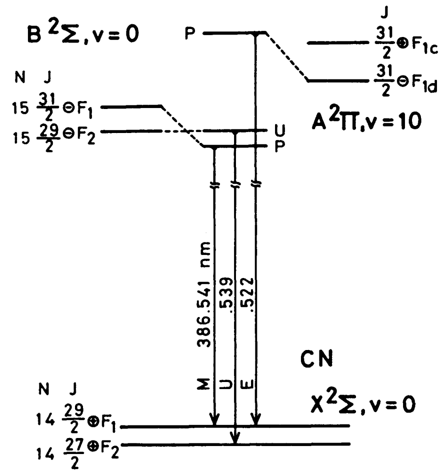

Fig. 6. Energy level diagram (schematic) for the rotational perturbation at the $B^2\Sigma^+$, $v=0$, $N=15$ level, drawn after Refs. 11, 24, and 26.

The energy-level relations relevant to the rotational perturbation at the $B^2\Sigma^+$, $v=0$, $N=15$ level are shown in Fig. 6. The rate equations for the states shown in Fig. 6 lead to

$$\frac{I_E}{I_M+I_U} = \frac{1+\beta\rho^2/(1-\rho^2)}{1+\beta(1-\rho^2)/\rho^2} \times \frac{1-\rho^2+\alpha\rho^2}{\rho^2+\alpha\{2-\rho^2+\beta\rho^2/(1-\rho^2)\}}, \tag{2}$$

where α is the ratio of formation rates to the $B^2\Sigma^+$ and $A^2\Pi$ states, F_B/F_A, β is the ratio of the radiative lifetimes of the states, τ_B/τ_A, and ρ^2 is a parameter representing the degree of mixing of the states. The values for β and ρ^2 are characteristic of the states and reported to be 0.14 and 0.22 respectively. Thus, the relative formation rate, α, is a function of the observable value, $I_E/(I_M+I_U)$. In deriving Eq. 2 the following assumptions are made: 1) Collisional transitions to and from the states shown in Fig. 6 are negligible. This implies that Eq. 2 is an exact expression for the low pressure limit. 2) The rates of formation of the different spin sublevels are equal. 3) A steady state is established. 4) The transition moment for the $A^2\Pi$ to $X^2\Sigma^+$ states is negligible in comparison with that for the $B^2\Sigma^+$-$X^2\Sigma^+$ transition. In addition, the difference in the transition frequencies between the extra and main lines is disregarded.

Since the rotational temperatures of the $CN(B^2\Sigma^+)$ levels obtained by a band envelope analysis are several thousand kelvins, the R(14) line is overlapped by the P-branches of $v'=0$ and 1. The intensities, I_E and I_M+I_U, are estimated by subtracting the overlapping band intensities estimated from the rotational temperatures.

The α value is then estimated from I_E and I_M+I_U to range between 0.14 and 0.23. In other words, the $A^2\Pi$ state is formed 4—7 times faster than the $B^2\Sigma^+$ state. This value is consistent with those produced from BrCN ($\alpha \simeq 0.08$ obtained by extrapolating the values in Ref. 5 to zero pressure) and from HCN ($\alpha < 0.18$).[5] Accordingly, a typical value of α in metastable argon reactions seems to be of the order of 0.1. This is in striking contrast with the corresponding values in electron-impact dissociative excitations of HCN, BrCN, and C_2N_2 ($0.5 \lesssim \alpha \lesssim 1.3$)[11] and in photodissociation of HCN and BrCN ($\alpha \gg 1$)[7] by rare-gas (Xe, Kr), Hg (184.9 nm), and Br (145—170 nm) lamps. (Note, however, that a recent photodissociation experiment with the hydrogen Lyman-α line (10.2 eV) on ICN gave α=0.3—0.5.[12]) The difference in α by different methods of excitation indicates a difference in the excited states of the parent molecules from which CN $A^2\Pi$ and $B^2\Sigma^+$ are produced.

Note added in proof. According to a recent report by Ashfold and Simons (*Chem. Phys. Lett.*, **47**, 65 (1977)), CN($A^2\Pi$) as well as CN($B^2\Sigma^+$) was formed in the vacuum UV photodissociation of BrCN. See also Luk and Bersohn, *J. Chem. Phys.*, **58**, 2153 (1973).

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