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Emission Spectra of $CH(A^2\Delta)$ Produced from CH_3CN in the Argon Flowing-Afterglow Reaction

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Emission spectra from $CH(A^2\Delta)$ formed in the reaction of positive ionic species of argon with CH_3CN were studied by the flowing-afterglow method. The rotational distributions for the $v'=0$, 1, and 2 of $CH(A^2\Delta)$ are characterized by effective rotational temperatures of *ca.* 5000, 2000, and 1500 K, respectively, whereas the distributions in lower levels ($N'\lesssim 11$), especially for $v'=0$, are characterized by that of *ca.* 700 K. The average vibrational and rotational energies distributed in the CH radicals produced initially are estimated to be 0.32 ± 0.04 and 0.34 ± 0.06 eV, respectively.

When a rare gas is subjected to microwave discharge, metastable atoms and ions are generated. The active species can react with molecules and produce fragments in electronically excited states. Photoemissions of such fragments formed in reactions of metastable argon atoms have been studied in detail.[1,2] On the other hand, emissions followed by dissociative reactions with active ionic species of thermal kinetic energy have scarcely been reported.

When the flowing afterglow method was applied to the reaction of metastable argon atoms with CH_3CN, it was suggested that the formation of $CH(A^2\Delta)$ was caused by a different mechanism from that of $CN(B^2\Sigma^+)$, because the dependence of CH $A^2\Delta$-$X^2\Pi$ and CN $B^2\Sigma^+$-$X^2\Sigma^+$ emission intensities on the argon pressure was different.[3,4] The present article reports that the active species of argon mainly contributing to the production of $CH(A^2\Delta)$ radicals in the reaction with CH_3CN are ionic. The vibrational and rotational structures of the visible emission spectrum from $CH(A^2\Delta)$ have been analyzed to obtain information about the energy distributed to the vibrational and rotational motions of the $CH(A^2\Delta)$ radical.

Experimental

The experimental apparatus is essentially the same as that described in previous reports.[3-5] The flow tube was evacuated by a 500 l/s mechanical booster pump. The argon gas of 99.99% nominal purity was purified by passage through a trap at 77 K before it was introduced into the discharge section. Positive ions and metastable atoms, $Ar(^3P_{2,0})$, were produced by a 2450 MHz microwave discharge. An output power of about 450 W from a magnetron was fed into the discharge section. The reactant gas was introduced into the flow through a nozzle (0.4 mm in diameter) placed 15 cm downstream from the discharge section. The acetonitrile sample was of extra pure grade.

The gas pressure was measured in the reaction zone by a Pirani gauge calibrated against a McLeod gauge. The argon pressure was varied from 0.3 to 1.7 Torr. The pressure of CH_3CN was about 0.01 Torr.

Emission spectra were observed through a quartz window by using a 1-m Spex 1704 scanning monochromator with a 1200 grooves/mm grating blazed at 500 nm, an HTV R585 photomultiplier, and a photon counting system.

The $CH(A^2\Delta$-$X^2\Pi$, 0-0, 1-1, and 2-2) emission was observed in the 420—440 nm region at an argon pressure above about 0.3 Torr. The spectrum shown in Fig. 1 was obtained at an argon pressure of about 0.7 Torr with a spectral resolution of about 0.05 nm FWHM. The R-branch lines of the 0-0 band were resolved from those of the 1-1 band for $N'\gtrsim 6$ (except for $N'=12$). The CH $B^2\Sigma^-$-$X^2\Pi$ band was also observed in the 385—405 nm region, where the R-branch was overlapped by the CN violet band.

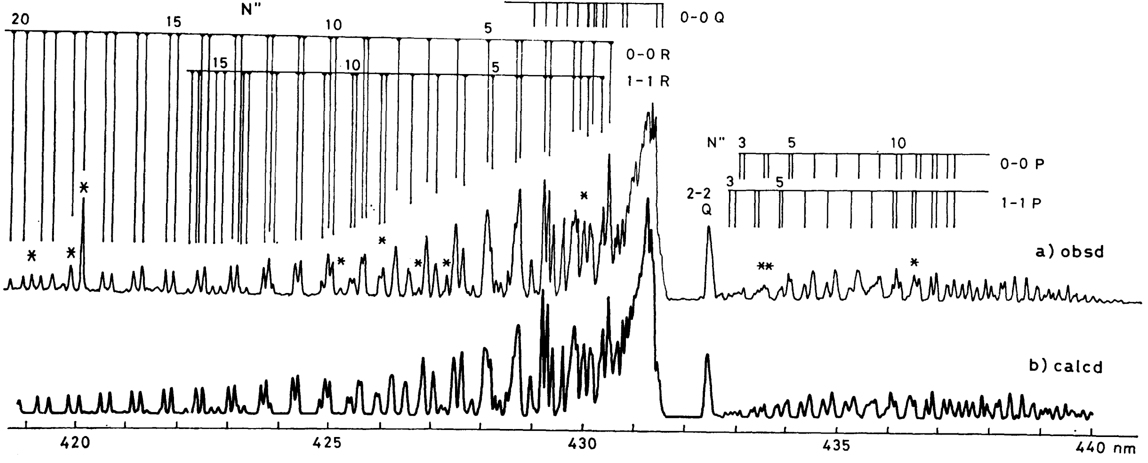

Fig. 1. Observed (a) and simulated (b) spectra of CH $A^2\Delta$-$X^2\Pi$. Lines marked * are overlapped by stray argon lines.

Estimation of Active Ionic Species

In order to remove the ionic species reaching the reaction zone, grids (stainless steel mesh, transparency *ca.* 0.74) were placed between the discharge section and the reaction zone, and an electrostatic potential was applied. The collected ion currents and the emission intensities of CH $A^2\Delta$-$X^2\Pi$ and CN $B^2\Sigma^+$-$X^2\Sigma^+$ are plotted against the potential applied to the grid in Fig. 2. The CH $A^2\Delta$-$X^2\Pi$ emission intensity was monitored at 431 and 424 nm, which correspond to the 0-0 head and the R(12) line of the 0-0 band, respectively, with a band pass of about 1.6 Å. These emission intensities had essentially the same dependence on the potential applied to the grid. Therefore, the trend for CH $A^2\Delta$-$X^2\Pi$ shown in Fig. 2 is regarded as representing that of the total emission from CH($A^2\Delta$), *i.e.*, the dependence of the density of CH($A^2\Delta$) produced in the reaction on the potential. The CN $B^2\Sigma^+$-$X^2\Sigma^+$ emission monitored at 385 and 386 nm had only slight dependence on the potential. It is therefore evident that ionic species are mainly responsible for the CH($A^2\Delta$) formation, whereas CN($B^2\Sigma^+$) is mainly produced by neutral atoms.

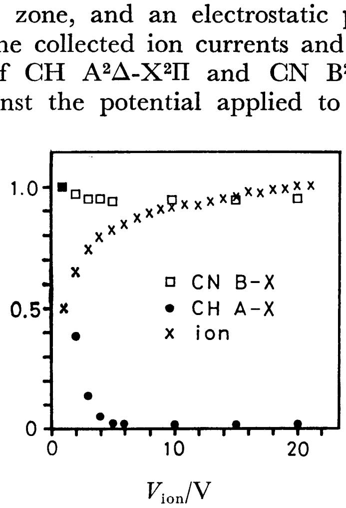

Fig. 2. The relative emission intensities of CN $B^2\Sigma^+$-$X^2\Sigma^+$ (□) and CH $A^2\Delta$-$X^2\Pi$ (●) formed from CH_3CN in the flowing afterglow reaction of argon, and the relative ion currents (×) collected with an ion-collector grid are plotted against a potential applied to the ion-collector grid, V_{ion}, at an argon pressure of 0.4 Torr. The relative currents due to the ions reaching the reaction zone is proportional to the difference from the saturated ion current at $V_{ion} > 20$ V.

Attempts have been made to identify the ionic species. If a single collision of active species produces CH($A^2\Delta$), there are energetically possible channels in which singly charged argon ions in the metastable states, $Ar^{+M}(^4D_{7/2}, {}^4F_{9/2,7/2}, {}^2F_{2/7}, {}^2G_{9/2,7/2})$,[6] and multiply charged ions, especially doubly charged ions, are involved. In the present experiment, Ar^{+M} seems to have a lifetime long enough to reach the reaction zone and take part in the dissociative excitation. The radiative lifetime of Ar^{+M} has not been measured, but it is estimated to be longer than 1 s[7] if multiple-quantum transitions do not contribute significantly. The lifetime for collisional relaxation is also estimated to be longer than the time of flight under the present experimental conditions. Hence, Ar^{+M} seems to be a plausible candidate. On the other hand, argon ions in the ground electronic state, $Ar^+(^2P_{3/2,1/2})$, or argon molecular ions, Ar_2^+, can be excluded by energetic considerations: Their available energies are 15.76[6] and 14.4 eV,[8] respectively, whereas the minimum energy to produce CH($A^2\Delta$) by charge exchange and dissociation is 25.3 eV.[9]

However, the possibility that CH($A^2\Delta$) is produced by successive collisions of ionic and neutral species (Ar^+, Ar_2^+, $Ar(^3P_{2,0})$, *etc.*) cannot be excluded. In order to specify the reaction channels involved in the CH($A^2\Delta$) formation, it is necessary to identify and monitor the positive ions present in the flow at the reaction zone.

Analysis of Rotational and Vibrational Distributions

The relative intensities of the emission spectrum was analyzed to estimate the vibrational and rotational populations of CH($A^2\Delta$) formed in the reaction with active species discussed above. In the following procedure, production of the CH($A^2\Delta$) state by cascading from higher states is ignored for the following reasons: a) The CH $B^2\Sigma^-$-$A^2\Delta$ and CH $C^2\Sigma^+$-$A^2\Delta$ transitions are forbidden. b) The allowed CH $D^2\Pi$-$A^2\Delta$ emission (near 280 nm) was not observed in the present experiment. c) No cascading effect from higher states (D, E, F, *etc.*) has been reported in the lifetime measurement of CH($A^2\Delta$)[10,11] produced by electron impact on CH_4 and C_2H_2.

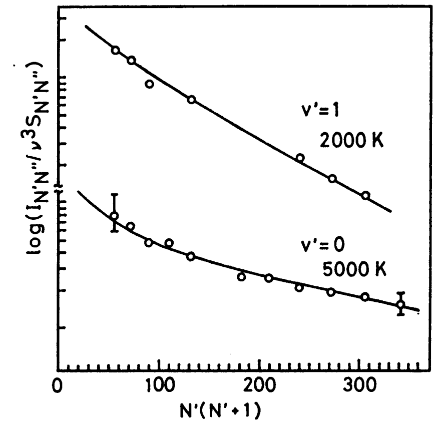

Fig. 3. Estimation of effective rotational temperatures from the slopes of $\log(I_{N'N''}/\nu^3 S_{N'N''})$ *vs.* $N'(N'+1)$. Solid lines represent a two-temperature distribution estimated by Eq. 2, with $n_L/n_H = 0.27$, $T_L = 700$ K, and $T_H = 5000$ K for the $v' = 0$ state and $T_H = 2000$ K for the $v' = 1$ state. Typical uncertainties are indicated by error bars.

Relative rotational populations are estimated by using the intensities of the R-branch. In Fig. 3, $I_{N'N''}/\nu^3 S_{N'N''}$ is plotted against $N'(N'+1)$, where $I_{N'N''}$ is the relative transition intensity, ν is the transition frequency, and $S_{N'N''}$ is the rotational line-strength calculated by the Hönl-London formula.[12]

An approximately linear relationship, *i.e.*, approximately a Boltzmann distribution, is obtained for the $v' = 1$ state. From the slope, $-hcB_{v'}/kT_{rot}$, where $B_{v'}$ is the rotational constant,[13] the effective rotational temperature, T_{rot}, is estimated to be 2000 ± 500 K. For the $v'=0$ state, however, the populations at lower ($N'\lesssim11$) levels appear to deviate from the linear relationship, their effective rotational temperature being an order of magnitude lower. A similar remark was made by Brennen and Carrington,[14] who observed a two-temperature distribution in the $CH(A^2\Delta)$ spectrum produced in the $O+C_2H_2$ reaction. Though they seem to have disregarded the overlapping of the R-branch by the Q-branch near 430 nm, as remarked by Beenakker *et al.*,[15] their observations indicate that the distribution characterized by a lower effective rotational temperature was produced by rotational relaxation to the equilibrium distribution corresponding to the ambient temperature. They also observed that the distribution corresponding to the higher temperature was unaffected by the rotational relaxation.

The observed rotational distribution is analyzed on the assumption that the distribution is represented by a superposition of two Boltzmann distributions. It is called a two-level model;[14,16] *i.e.*, CH radicals initially produced in a distribution with a higher rotational temperature, T_{H}, are relaxed by collisions to another distribution with a lower temperature, T_{L} (see Appendix). In this model the ratio of the number of CH radicals in the "relaxed" low-temperature distribution, n_{L}, to that in the "initial" high-temperature distribution, n_{H}, is given by

$$n_{\mathrm{L}}/n_{\mathrm{H}} = \tau k_{\mathrm{e}}[\mathrm{Ar}], \tag{1}$$

where τ is the radiative lifetime of the $CH(A^2\Delta)$ state, k_{e} is the effective rate constant for the rotational relaxation of $CH(A^2\Delta,\ v'=0)$, and [Ar] is the number density of the argon atoms. The observed values of τ and k_{e} are 460 ns[17] and 2.6×10^{-11} cm^3 molecule^{-1} s^{-1}, respectively. (The k_{e} value reported in Ref. 14 has been modified slightly in accordance with the τ taken from Ref. 17.) The ratio, $n_{\mathrm{L}}/n_{\mathrm{H}}$, is thus estimated to be 0.27 when the argon pressure is 0.7 Torr. The relative intensity, $I_{N'N''}/\nu^3S_{N'N''}$, is expressed as

$$I_{N'N''}/\nu^3S_{N'N''} \propto (n_{\mathrm{H}}/T_{\mathrm{H}})\exp[-hcB_{v'}N'(N'+1)/kT_{\mathrm{H}}] + (n_{\mathrm{L}}/T_{\mathrm{L}})\exp[-hcB_{v'}N'(N'+1)/kT_{\mathrm{L}}]. \tag{2}$$

By adjustment of the T_{H} and T_{L} in Eq. 2 to reproduce the observed relative intensity, as shown in Fig. 3, the temperatures are estimated to be $T_{\mathrm{H}}=5000\pm1000$ K and $T_{\mathrm{L}}=700\pm200$ K. These T_{H} and T_{L} values are essentially independent of the argon pressure between 0.4 and 0.7 Torr.

It is shown in Fig. 3 that the observed relative intensities are well represented by Boltzmann distributions with two different effective rotational temperatures, T_{H} and T_{L}. This implies that the two-level model adopted in our analysis holds good for accounting for the observed relative intensities phenomenologically.

The distribution for the $v'=1$ state is also consistent with a two-temperature distribution with $T_{\mathrm{H}}=2000\pm500$ K and $T_{\mathrm{L}}=700\pm200$ K, although the contribution from the low-temperature component is less conspicuous, as shown in Fig. 3.

Relative vibrational populations for $v'=0$, 1, and 2 and the effective rotational temperature for $v'=2$ are estimated by simulation of the spectrum. A computer program was written following Baas and Beenakker[18] for the MELCOM 7700 computer at the Educational Computer Center of the University of Tokyo. Transition frequencies, line intensities, and the band envelope were calculated using the molecular constants reported in the literature.[12,13,19,20]

The ratio of the vibrational populations, $P_{\mathrm{vib}}(1)/P_{\mathrm{vib}}(0)=0.5\pm0.1$, is obtained by simulation of the R-branch 0-0 and 1-1 transitions for $N'\gtrsim11$. For the $v'=2$ level, the effective rotational temperature, $T_{\mathrm{rot}}=1500\pm500$ K, and the vibrational population, $P_{\mathrm{vib}}(2)/P_{\mathrm{vib}}(0)=0.07\pm0.02$, are obtained by simulation of the Q-branch of the 2-2 transition. The calculated spectrum based on the estimated values reproduces the overall feature of the observed spectrum, as shown in Fig. 1.

Distributions of mean internal energies listed in Table 1 are estimated in the following way.[5] The mean rotational energy possessed by the $CH(A^2\Delta)$ radicals produced "initially" is approximated by

$$\langle E_{\mathrm{rot}}\rangle = [\sum_{N'=2} hcB_{v'}\{N'(N'+1)-4\}R_{N'}]/(\sum_{N'=2} R_{N'}), \tag{3}$$

where $R_{N'}$ is the rotational distribution,

$$R_{N'} = (2N'+1)\exp[-hcB_{v'}N'(N'+1)/kT_{\mathrm{H}}]. \tag{4}$$

The mean vibrational energy is calculated from the vibrational energies, $E_{\mathrm{vib}}(v)$, and the relative vibrational population, $P_{\mathrm{vib}}(v)$, by

$$\langle E_{\mathrm{vib}}\rangle = \sum_{v} E_{\mathrm{vib}}(v)P_{\mathrm{vib}}(v). \tag{5}$$

As shown in Table 1, approximately equal energies, *ca.* 0.3 eV, are distributed to the vibrational and rotational motions of the CH radicals formed in the reaction of CH_3CN with active ionic species of argon.

TABLE 1. RELATIVE VIBRATIONAL POPULATIONS, EFFECTIVE ROTATIONAL TEMPERATURES, AND AVERAGE VIBRATIONAL AND ROTATIONAL ENERGIES FOR $CH(A^2\Delta)$ PRODUCED IN THE ARGON AFTERGLOW REACTION WITH CH_3CN

v	P_{vib}	$E_{\mathrm{vib}}/\mathrm{eV}^{\mathrm{a)}}$	$T_{\mathrm{rot}}/\mathrm{K}$
0	0.63 ± 0.05	0.179	$5000\pm1000^{\mathrm{b)}}$
1	0.32 ± 0.10	0.518	$2000\pm500^{\mathrm{b)}}$
2	0.05 ± 0.02	0.834	1500 ± 500
		$\langle E_{\mathrm{vib}}\rangle/\mathrm{eV}$	$\langle E_{\mathrm{rot}}\rangle/\mathrm{eV}$
		0.32 ± 0.04	0.34 ± 0.06

a) Calculated from the ω_{e} and $\omega_{\mathrm{e}}x_{\mathrm{e}}$ values given in Ref. 13. b) Effective rotational temperatures derived from higher rotational levels, $N'\gtrsim11$.

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Appendix. Two-level Model.

The two-level model for rotational relaxation is a phenomenological treatment, in which microscopic level-to-level transitions among the rotational levels are overlooked. Its main idea[14,16] is to represent the whole rotational distribution by two distributions characterized by different parameters. In the present case an effective Boltzmann temperature was chosen as one of the parameters. A sophisticated treatment was

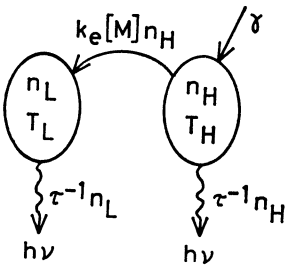

Fig. 4. Schematic diagram of the two-level model for rotational relaxation by collisions.

carried out by Sokabe[16] for the OH($A^2\Sigma^+$) rotational distributions formed from H_2O in the reaction with metastable argon atoms, but in the present study a simpler model shown in Fig. 4 was used. Photoemitting species are formed in the distribution characterized by an effective rotational temperature, T_H, at a rate, γ. These species, then, suffer collisional relaxation with surrounding particles to the other distribution characterized by a lower temperature, T_L, at an effective rate constant, k_e. The populations in these "levels" are denoted by n_H and n_L. Photoemissions are observed from these levels with a radiative lifetime, τ.

Rate equations for the two states are written as

$$dn_H/dt = \gamma - k_e[M]n_H - n_H/\tau, \tag{6}$$

$$dn_L/dt = k_e[M]n_H - n_L/\tau. \tag{7}$$

When the steady-state condition, *i.e.*, $dn_H/dt = dn_L/dt = 0$, is assumed, the following relation is obtained from Eq. 7:

$$n_L/n_H = \tau k_e[M]. \tag{8}$$

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