Dissociative Excitation of CH_4 *via* Triplet Superexcited State by Collisions with the Metastable $Ne(^3P_{0,2})$ Atoms in a Neon Flowing Afterglow

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The CH(A-X,B-X,C-X) emission systems have been observed in the energy transfer reaction of the metastable $Ne(^3P_{0,2})$ atoms with CH_4 in a neon flowing afterglow. The nascent rovibrational distributions of CH(A,B) were determined by a spectral simulation: N_0:N_1:N_2=100(T_0=3500±300 K):58±3(T_1=2800±200 K):9±1(T_2=2400±300 K) for CH(A) and N_0=100 (T_0=3000±300 K) for CH(B).

There has been a continuous interest in dissociative excitation of methane by collisions with rare gas metastable atoms. Since the energies of the metastable $He(2^3S$:19.82 eV) and $Ne(^3P_2$:16.62 eV and $^3P_0$:16.72 eV) atoms are higher than the ionization potential of methane 12.61 eV, optical studies on the $He(2^3S)/CH_4$ and $Ne(^3P_{0,2})/CH_4$ reactions provide useful information on the decay processes of superexcited CH_4** states. Although dissociative excitation of methane by collisions with the metastable $He(2^3S)$ atoms has been studied by observing UV and visible emission spectra from the excited products,[1-3] no study has been made for the reaction with the metastable $Ne(^3P_{0,2})$ atoms. In this letter, the first spectroscopic study on the $Ne(^3P_{0,2})/CH_4$ reaction is reported. The nascent rovibrational distributions of CH(A,B) were determined from a spectral simulation. The energy disposal to CH(A,B) is estimated from their rovibrational distributions.

The flowing afterglow (FA) apparatus used in this study was similar to that reported previously.[2,4] Active species of neon were generated by a microwave discharge of Ne gas operated at 0.06-0.15 Torr. The effects of Ne^+ and Ne_2^+ ions were examined by using a pair of ion-collector grids placed between the discharge section and the reaction zone. Although there are two spin-orbit components, $^3P_0$ and $^3P_2$, the latter component was found to be dominant by observing the $CO^+(A^2\Pi_i$-$X^2\Sigma^+)$ emission due to the $Ne(^3P_{0,2})$/CO Penning ionization.[4] The sample gas pressure ranged from 5 to 20 mTorr. The emission spectrum in the 200-840 nm region was dispersed with a Spex 1250M monochromator.

By the addition of a small amount of CH_4 into the Ne afterglow, the $A^2\Delta$-$X^2\Pi_r$, $B^2\Sigma^-$-$X^2\Pi_r$, and $C^2\Sigma^+$-$X^2\Pi_r$ transitions of CH radicals are identified in the 300-450 nm region. When ionic active species were trapped by using ion-collector grids or a small amount of an electron scavenger, SF_6, was added into the reaction zone, no appreciable change in the CH(A-X,B-X,C-X) emissions was found. These findings indicated that ionic species and electron-ion recombination processes do not participate in the formation of CH(A,B,C). It was thus concluded that the CH(A,B,C) states are exclusively produced by the primary reaction of $Ne(^3P_{0,2})$ with CH_4 under the operating conditions:

$$Ne(^3P_2) + CH_4 \rightarrow CH(A^2\Delta) + H_2(X) + H(n=1) + Ne + 4.53\ eV, \quad (1a)$$

$$\rightarrow CH(A^2\Delta) + 3H(n=1) + Ne + 0.01\ eV, \quad (1b)$$

$$\rightarrow CH(B^2\Sigma^-) + H_2(X) + H(n=1) + Ne + 4.17\ eV, \quad (2)$$

$$\rightarrow CH(C^2\Sigma^+) + H_2(X) + H(n=1) + Ne + 3.46\ eV. \quad (3)$$

On the basis of our recent optical spectroscopic studies on the dissociative excitation of SiH_4 and GeH_4 by the metastable $Ar(^3P_{0,2})$ and $He(2^3S)$ atoms,[5,6] the spin-conservation rule generally holds during the reaction. It is therefore reasonable to assume that this rule also holds for the $Ne(^3P_{0,2})/CH_4$ reaction. According to the spin-conservation rule, CH_4 molecules should be initially excited into triplet states at ~16.6 eV in the processes (1)-(3). The formation of $CH(A^2\Delta, B^2\Sigma^-, C^2\Sigma^+)$ through triplet CH_4** states is allowed, because $H_2(X^1\Sigma_g^+)$, $He(1^1S)$, and CH_4 (X^1A_1) are singlet, while H is doublet. The formation of CH(A,B) has been studied by photoexcitation[7] in which only singlet CH_4** states can be precursor states based upon the spin-conservation rule. The emission cross sections of CH(A,B) at ~16.6 eV are nearly zero, indicating that the formation of CH(A,B) through singlet CH_4** states is closed in this range. This result also suggests that the contribution of singlet CH_4** states is unimportant in the $Ne(^3P_{0,2})/CH_4$ reaction.

The CH(A,B,C) production by the $Ne(^3P_{0,2})/CH_4$ reaction at thermal energy implies that the appearance potentials of these excited species through triplet CH_4** states are ≤ 16.62 eV. There are two possible pathways (1a) and (1b) for the CH(A) production, while only single pathways (2) and (3) are open for the CH(B,C) production. The appearance potential of CH(A) from CH_4 has been measured by electron-impact, in which CH(A) can be produced through both singlet and triplet CH_4** states.[8-10] The upper limit of the appearance potential for CH(A) obtained in this study (≤ 16.62 eV) is higher than the first appearance potential at 13.4-14.6 eV, which is correlated with the CH(A) + H_2 + H(n=1) dissociation limit. However, it is lower than the second one at ~21 eV, which is believed to be correlated with the CH(A) + 3H(n=1) dissociation limit. It was therefore concluded that CH(A) is exclusively formed via the lowest energy process (1a). Since the first appearance potential of CH(A) lies above the first adiabatic ionization potential of CH_4(12.61 eV) and well below any dissociation limit containing an ionic fragment. Therefore, CH(A) must be formed via dissociative superexcited states at ~16.6 eV. The superexcited states of CH_4 below 80 eV have been studied by comparing absorption and ionization cross sections under the electron-impact excitation.[11] Neutral superexcited states below 17 eV have been attributed to high vibrationally-excited Rydberg states converging to the vibrationally-excited ground state of CH_4^+,$(1t_2)^{-1}$.[11,12] In the present $Ne(^3P_{0,2})/CH_4$ reaction, it was found that some part of these superexcited states is dissociated into CH(A) + H_2 + H.

The relative emission intensities of CH(A-X):CH(B-X):CH(C-X) were determined to be 0.85:0.14:0.004, respectively. These ratios are slightly different from those for the $He(2^3S)/CH_4$ system: 0.79:0.21:0.002.[2] The rovibrational distributions of CH(A,B) were determined by a computer simulation of the CH(A-X,B-X) transitions. The simulation method used was the

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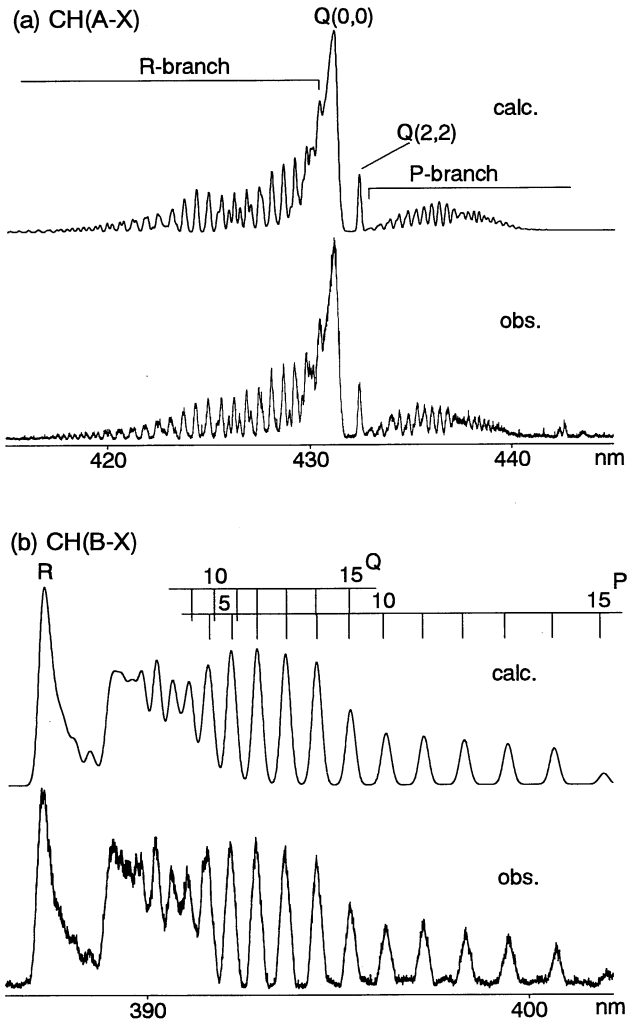

Figure 1. Observed and calculated emission spectra of the (a) $A^2\Delta$-$X^2\Pi_r$ and (b) $B^2\Sigma^-$-$X^2\Pi_r$ transitions of CH obtained from the $Ne(^3P_{0,2})/CH_4$ reaction in a Ne flowing afterglow.

same as that reported previously.[2] In Figs. 1(a) and 1(b) are shown the observed and best fit spectra of the $\Delta v=0$ sequence of CH(A-X) and the (0,0) band of CH(B-X) obtained by assuming single Boltzmann rotational distributions for each v' level. The rovibrational distributions thus obtained are given in Table 1 along with our previous results for the $He(2^3S)/CH_4$ system.[2] The rovibrational distributions of CH(A,B) were independent of the Ne pressure range of 0.06-0.15 Torr, indicating that the vibrational and rotational relaxation of CH(A) and CH(B) by collisions with the buffer Ne gas is insignificant in the FA experiment during radiative lifetimes of ~0.53 and ~0.35 μs, respectively.[13] CH(A) in the $Ne(^3P_{0,2})$ reaction is more rovibrationally excited than that in the $He(2^3S)$ reaction, while CH(B) in the former reaction is less rotationally excited. The observed rovibrational distributions were much less excited than the statistical prior ones.[14] This indicated that the CH(A,B) formation does not proceed through a near-resonant long-lived complex, where the excess energy is statistically randomized.

The average vibrational and rotational energies of CH(A,B), $\langle E_v \rangle$ and $\langle E_r \rangle$, respectively, were evaluated from the nascent rovibrational distributions:

Table 1. Observed vibrational populations and rotational temperatures of CH(A,B) produced from the $Ne(^3P_{0,2})/CH_4$ and $He(2^3S)/CH_4$ reactions at thermal energy

		$Ne(^3P_{0,2})$ This work		$He(2^3S)$ Ref. 2	
		$N_{v'}$	T_r (K)	$N_{v'}$	T_r (K)
CH(A)	v'=0	100	3500±300	100	3200±200
	v'=1	58±3	2800±200	37±3	2600±300
	v'=2	9±1	2400±300	7±3	2200±500
CH(B)	v'=0	100	3000±300	100	3300±200

$\langle E_v \rangle = 0.15$ eV, $\langle E_r \rangle = 0.28$ eV for CH(A), (4a)
$\langle E_v \rangle = 0$ eV, $\langle E_r \rangle = 0.26$ eV for CH(B). (4b)

The average fractions of available energies deposited into vibrational and rotational energies of CH(A,B), $\langle f_v \rangle$ and $\langle f_r \rangle$ are estimated for the processes (1a) and (2):

$\langle f_v \rangle = 0.033$, $\langle f_r \rangle = 0.062$ for CH(A), (5a)
$\langle f_v \rangle = 0$, $\langle f_r \rangle = 0.062$ for CH(B). (5b)

Only $\leq$ 10% of the total available energies is deposited into the vibrational and rotational energies of CH(A,B) in the $Ne(^3P_{0,2})/CH_4$ reaction, where the CH* + H_2 + H pathways are product channels. These values are comparable for the $He(2^3S)/CH_4$ reaction, $\leq$ 11%, where the CH* + 3H pathways are dominant product channels.[3] It is unlikely that most of the excess energies are deposited into vibrational and rotational energies of the elimination H_2 product in the processes (1a) and (2). Thus, most of the excess energies is expected to be deposited into relative translational energies of products.

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