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# A Flowing Afterglow Study of the Reaction $C_2 + NO \rightarrow$ $CN (B^2\Sigma^+, A^2\Pi) + CO$

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The  $C_2 + NO$  reaction has been studied by observing the  $CN(B-X)$  and  $CN(A-X)$  chemiluminescence. Experiments have been performed by using either a conventional flowing afterglow or a low-pressure apparatus. The  $C_2$  radicals have been generated by Ar afterglow reaction of  $C_2H_2$ ,  $CH_4$ , or  $CO$  molecule. In the flowing afterglow experiment, very intense perturbed rotational lines of  $CN(A, v' = 10)$  appear in the  $CN(B-X)$  emission spectrum when  $C_2H_2$  is used, while the perturbed rotational lines are relatively weak when  $CH_4$  or  $CO$  is employed. Possible excitation sources for creating the  $CN(B, A)$  states are  $C_2(a)$  and  $C_2(X)$ . On addition of  $C_6H_6$  as a scavenger of  $C_2(X)$ , both the spectral features of the  $CN(B-X, A-X)$  emissions and the product branching ratio  $k_{CN(A)}/k_{CN(B)}$  have not changed in the former spectra, whereas they changed considerably in the latter spectra. These results can be explained by the facts that the  $CN(B, A)$  states are excited from the  $C_2(a) + NO$  reaction when  $C_2H_2$  is used, while they are produced from both the  $C_2(a) + NO$  and  $C_2(X) + NO$  reaction when  $CH_4$  and  $CO$  are employed. The rovibrational distribution of  $CN(B)$  and the vibrational distribution of  $CN(A)$  resulting from the  $C_2(a) + NO$  reaction have been determined. These distributions are in agreement with statistical prior ones, suggesting that the  $CN(B, A)$  states are formed through long lived complexes.

## Introduction

Reactions of  $C_2$  molecule are known to play important roles in many combustion systems because of its high reactivity. The reaction of  $C_2$  with  $NO$  has been studied by several groups<sup>1-3)</sup>. Krause<sup>1)</sup> detected the  $CN(B^2\Sigma^+ - X^2\Sigma^+)$  chemiluminescence in a crossed molecular beam study. Possible electronic states of  $C_2$  are the ground  $X^1\Sigma_g^+$  state and the first excited  $a^3\Pi_u$  state located only  $610\text{cm}^{-1}$  above the ground state. On the basis of an adiabatic correlation diagram, it was concluded that the  $C_2(a)$  state was responsible for the  $CN(B-X)$  chemiluminescence. Reisler et al. (hereafter referred to as RMW)<sup>2)</sup> and Lurle and El-

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Sayed (referred to as LE)<sup>3)</sup> studied the  $C_2 + NO$  reaction by using multiple photon dissociations of polyatomic molecules. RMW<sup>2)</sup> observed the  $CN(B-X)$  and  $CN(A-X)$  chemiluminescences and determined their decay rates by using a time-resolved method. The total quenching rate of  $C_2(a)$  with NO was in good agreement with the above decay rates of CN luminescences. The removal rate constant of  $C_2(X)$  by NO was measured to be  $(21 \pm 3.3) \times 10^{-11} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ , which is faster than that of  $C_2(a)$  by NO  $((7.5 \pm 0.3) \times 10^{-11} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1})$ .<sup>4)</sup> Based on these kinetic data, it has been concluded that the products  $CN(B)$  and  $CN(A)$  correlate to the reactant  $C_2(a)$ , not to  $C_2(X)$ . These results are consistent with the adiabatic correlation diagram for the reaction of  $C_2 + NO \rightarrow CN + CO$ .

The vibrational distributions of  $CN(B)$  were presented by the above three groups. However, these distributions significantly disagree with each other and the differences in the  $CN(B)$  vibrational distributions have not been ascertained. We have generated the  $C_2$  radicals from the Ar afterglow reactions of  $C_2H_2$ ,  $CH_4$ , and CO molecules. Although both the  $CN(B-X)$  and  $CN(A-X)$  chemiluminescence is observed from the reactions of the three  $C_2$  sources with NO, these chemiluminescences provide different spectral features.

On the basis of changes of the spectral features of the  $CN(B-X)$  and  $CN(A-X)$  emissions and the product branching ratio  $k_{CN(A)}/k_{CN(B)}$  on addition of  $C_6H_6$  as a scavenger for  $C_2(X)$ , it has been suggested that  $CN(B)$  and  $CN(A)$  can be produced from both the  $C_2(X) + NO$  and  $C_2(a) + NO$  reactions. The formation of  $CN(B, A)$  from the  $C_2(X) + NO$  reaction has been also supported from experiments in the low-pressure apparatus. This proposition is inconsistent with the conclusion of the selective formation of  $CN(B)$  and  $CN(A)$  from the  $C_2(a) + NO$  reaction, which was proposed previously by Krause, RMW, and LE.

We have determined the rovibrational distributions of  $CN(B, A)$  produced from the  $C_2(a) + NO$  reaction and compared them with the statistical prior ones.

## Experimental

Experiments were performed by using a conventional flowing afterglow apparatus and a low-pressure apparatus. The flowing afterglow apparatus was described in detail in a previous paper.<sup>5)</sup> The flow reactor was continuously evacuated by a 10000L/min mechanical booster pump. The  $C_2$  radicals were obtained from the Ar afterglow reaction of  $C_2H_2$ ,  $CH_4$ , or CO molecule by a 2450-MHz microwave discharge. The  $C_2H_2$ ,  $CH_4$ , or CO gas was introduced through a gas inlet placed near the exit of quartz discharge tube. The formation of  $C_2(a)$  radical was confirmed by observing the  $C_2(d^3\Pi_g - a^3\Pi_u)$  laser-induced fluorescence (LIF) spectrum. The flowing afterglow apparatus coupled with a LIF detection system has been reported previously.<sup>6)</sup> The NO gas was introduced through a gas inlet placed 15cm downstream from the gas inlet of  $C_2$  source gas. The Ar pressure ranged from 0.12 to 0.25Torr, while the  $C_2H_2$ ,  $CH_4$ , CO, and NO pressures were varied from 1 to 10mTorr. The low

-pressure apparatus used in this work is essentially the same as that described previously.<sup>7)</sup> Briefly, it consists of flowing afterglow source mentioned above for the generation of  $C_2$  radicals and an interaction chamber evacuated by a 10-inch diffusion pump. The  $C_2$  radicals generated in the flow tube are expanded into the interaction chamber through a nozzle orifice centered on the flow tube axis. The Ar,  $C_2H_2$ ,  $CH_4$ , and NO pressures in the interaction chamber were varied from 1 to 25mTorr. Emissions were observed through a quartz window by using either a Spex 1.26-m monochromator or a Nippon Jarrell Ash 1-m monochromator equipped with a cooled photomultiplier (HTV R376).

### Results and discussion

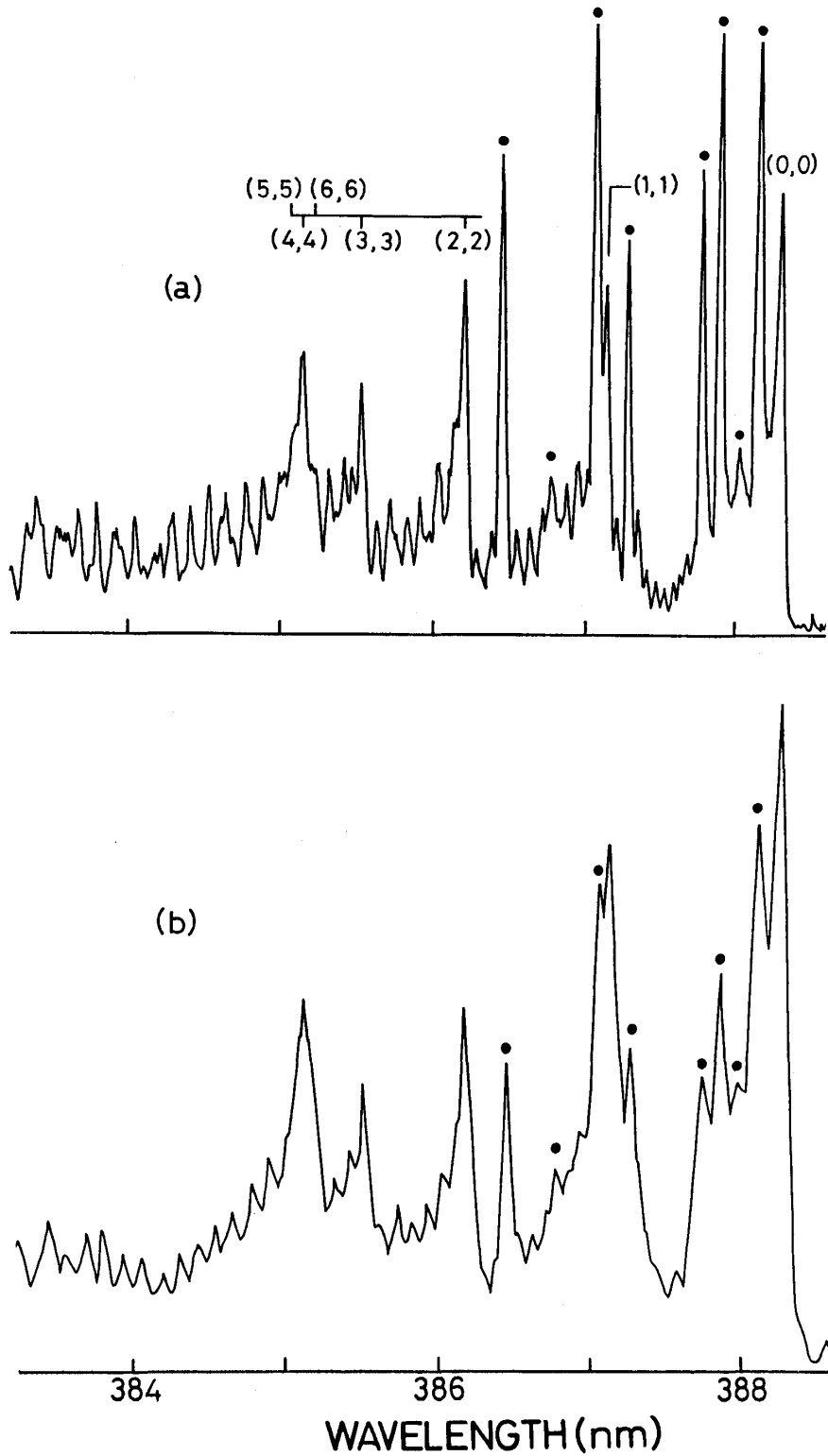
A.  $CN(B-X, A-X)$  chemiluminescent spectra obtained by employing the Ar afterglow reactions of  $C_2H_2$ ,  $CH_4$ , and CO

By using the Ar afterglow reactions of the  $C_2H_2$ ,  $CH_4$ , and CO molecules as  $C_2$  sources,  $CN(B-X)$  and  $CN(A-X)$  chemiluminescence was observed when the NO gas was introduced. The  $CN(B-X)$  emission spectrum in using  $C_2H_2$  is shown in Fig.1a. The lines corresponding to rotational levels  $K = 4, 7, 11,$  and  $15$  of  $CN(B, \Delta v = 0)$  are much more intense than the other rotational lines. These intense lines are due to the perturbed rotational levels of  $CN(A, v' = 10)$ .<sup>8)</sup> On the other hand, the perturbed rotational lines in the observed  $CN(B-X)$  emission are relatively weak when  $CH_4$  is employed, as shown in Fig.1b. The  $CN(B-X)$  emission spectrum observed with the use of CO was similar to that in the case of  $CH_4$ . These results show that  $CN(A, v' = 10)$  is much more populated in the former case than the latter two cases. In Fig.2 are shown the  $CN(A-X)$  emission spectra obtained by employing  $C_2H_2$  and  $CH_4$  for generating reactant  $C_2$  radicals, respectively. In the two cases, the  $CN(A-X)$  emissions from  $v' = 2-16$  are observed. The spectral features of the observed  $CN(B-X, A-X)$  emissions were independent of the pressures of Ar and reactant gases used in this work.

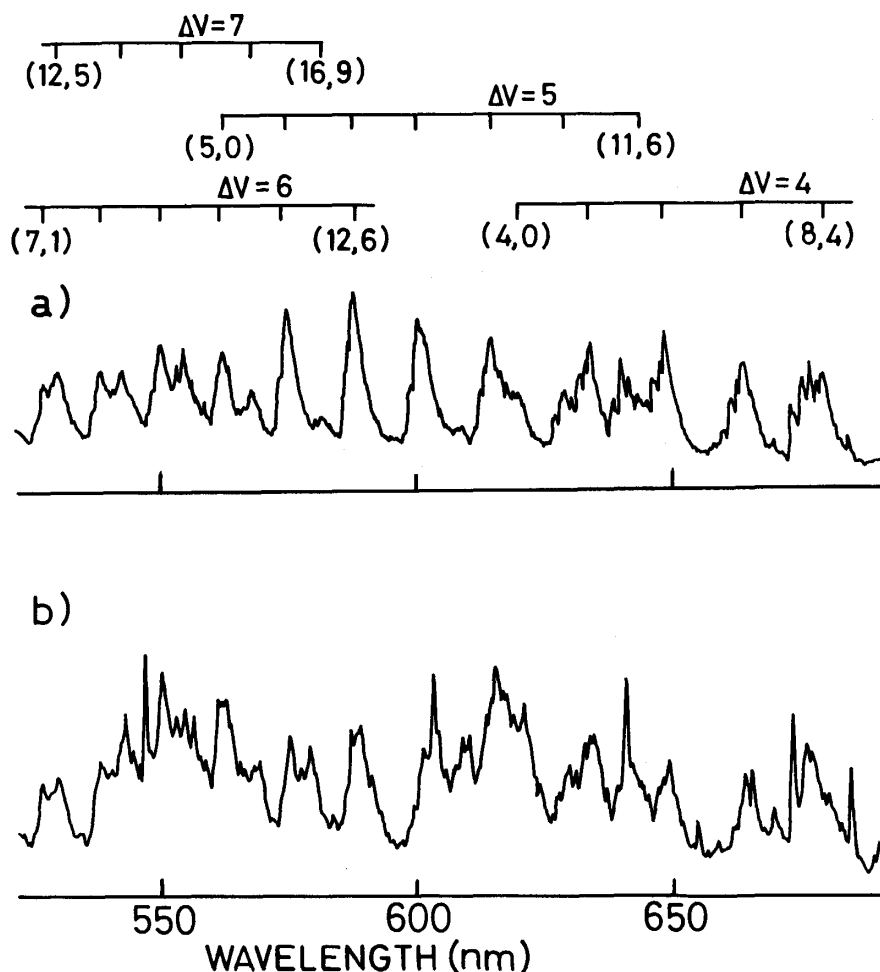
It was confirmed through measuring the  $C_2(d-a)$  LIF spectra that the  $C_2(a)$  radicals were produced from the Ar afterglow reactions of  $C_2H_2$ ,  $CH_4$ , and CO molecules. The CH radical as well as the  $C_2$  radical is expected to be produced from the Ar afterglow reactions of  $C_2H_2$  and  $CH_4$ . The  $CN(B)$  formation is endoergic in the reaction of CH with NO. Since the  $CN(A-X)$  chemiluminescence was absent in the optical spectroscopic study of the CH + NO reaction<sup>9)</sup>, CH can be removed from the possible excitation source of the  $CN(A-X)$  chemiluminescence.

The  $CN(B-X, A-X)$  chemiluminescent spectra obtained from the Ar afterglow reactions of CO closely resemble to those observed from the Ar afterglow reactions of  $CH_4$ . Possible excitation sources of the  $CN(B-X, A-X)$  emissions are the atomic carbon and/or the  $C_2$  radicals, which can be produced in the Ar afterglow reactions of  $CH_4$  and CO. The

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**Fig.1:** (a)  $CN(B-X)$  chemiluminescent spectrum arising from the reaction of  $C_2$  with  $NO$ . The  $C_2$  radical was prepared from the Ar afterglow reaction of  $C_2H_2$ . Experimental conditions were as follows: Ar, 0.21Torr;  $C_2H_2$ , 3mTorr;  $NO$ , 4mTorr. (b)  $CN(B-X)$  chemiluminescent spectrum observed by utilizing the Ar afterglow reaction of  $CH_4$  for the source of  $C_2$ . Experimental conditions were as follows: Ar, 0.16Torr;  $CH_4$ , 2mTorr;  $NO$ , 5mTorr. The perturbed rotational levels of  $CN(A, v' = 10)$  are indicated by closed circles.



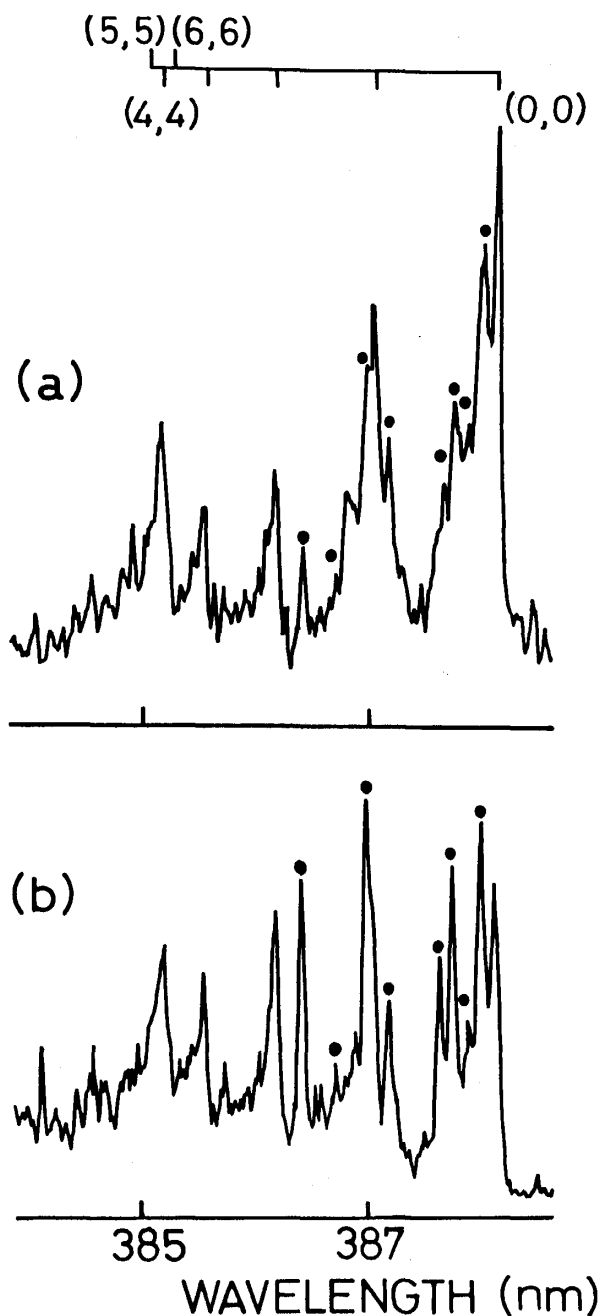
**Fig.2:** (a) CN(A-X) emission spectrum resulting from the reaction of  $C_2$  with NO when  $C_2H_2$  was employed for the source of  $C_2$ . The pressures of Ar,  $C_2H_2$ , and NO used were: Ar, 0.21Torr;  $C_2H_2$ , 5mTorr; NO, 10mTorr. (b) CN(A-X) emission spectrum when  $CH_4$  was employed for the source of  $C_2$ . Experimental conditions were as follows: Ar, 0.15Torr;  $CH_4$ , 1mTorr; NO, 4mTorr.

formation of CN(B) from the reaction of the ground state atomic carbon  $C(^3P)$  with NO is 1.81eV endoergic and the CN(A) formation, which is 0.28eV exoergic, has not been observed.<sup>6)</sup> As is the case for  $C(^3P)$ , the formation of CN(A) is energetically possible in the reaction of the metastable-state atomic carbons  $C(^1S, ^1D)$  with NO. The CN(B) production is exoergic up to  $v' = 3$  in the  $C(^1S) + NO$  reaction, while the formation of CN(B) from the  $C(^1D) + NO$  reaction is 0.53eV endoergic. According to the LIF study of Sekiya et al.<sup>6)</sup>, the observed vibrational distribution of CN(X) in the presence of  $C(^1S, ^1D)$  as well as  $C(^3P)$  was essentially the same as that from the  $C(^3P) + NO$  reaction. This suggests that the formation of CN(B, A) is insignificant in the  $C(^1S, ^1D) + NO$  reaction. From the above considerations, significant changes in the spectral features observed from the different source gases can be explained by the difference in reactivities of the two electronic states of  $C_2$ ,  $C_2(a)$  and  $C_2(X)$ .

B. Changes of CN(B-X) and CN(A-X) spectral features in the presence of  $C_6H_6$  as the

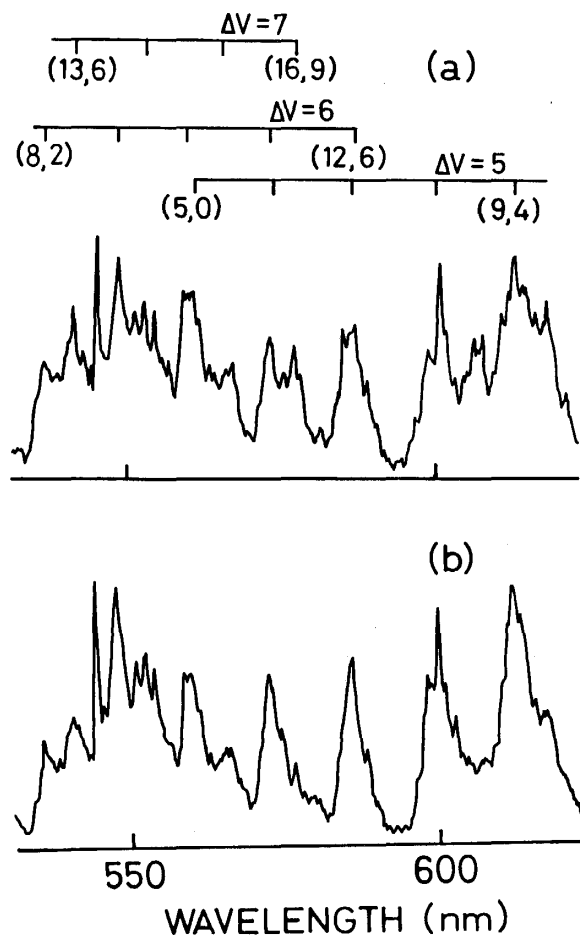
scavenger for  $C_2(X)$

In order to verify the previous assumption, the  $C_6H_6$  gas was introduced into the flow tube. The reaction rate constant of  $C_2(X)$  with  $C_6H_6$  has been reported to be  $(5.2 \pm 0.4) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , which is larger than that of  $C_2(a)$  with  $C_6H_6$  ( $(7.6 \pm 0.4) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ). As shown in Fig.3, the spectral feature of the  $CN(B-X)$  emission obtained by using  $CH_4$  changes on addition of  $C_6H_6$ : The relative intensities of the perturbed rotational



**Fig.3:**  $CN(B-X)$  chemiluminescent spectrum observed in the presence of (a) Ar, 0.18Torr;  $CH_4$ , 1mTorr; NO, 10mTorr, (b) Ar, 0.18Torr;  $CH_4$ , 1mTorr; NO, 10mTorr;  $C_6H_6$ , 10mTorr. The perturbed levels of  $CN(A, v' = 10)$  are indicated by closed circles.

lines increased with the  $C_6H_6$  pressure. At a  $C_6H_6$  pressure of 10mTorr, the  $CN(B-X)$  emission spectrum obtained from  $CH_4$  is identical with that from  $C_2H_2$ , as shown in Fig. 3b. It should be noted that relative intensity of each P branch head for the  $\Delta v = 0$  sequence changes by introducing  $C_6H_6$  gas. On the other hand, the  $CN(B-X)$  emission spectrum obtained using  $C_2H_2$  was essentially the same as that measured without the  $C_6H_6$  gas.



**Fig.4:** (a)  $CN(A-X)$  chemiluminescent spectrum when  $CH_4$  was employed for the source of  $C_2$ . The pressures of Ar,  $CH_4$ , and NO used were : Ar, 0.15Torr ;  $CH_4$ , 1mTorr ; NO, 4mTorr. (b)  $CN(A-X)$  chemiluminescent spectrum in the presence of 17mTorr  $C_6H_6$ .

As shown in Fig.4, the spectral feature of the  $CN(A-X)$  emission changes on addition of  $C_6H_6$  as is the case for the  $CN(B-X)$  emission spectrum obtained using  $CH_4$ . It has been found that the relative intensities of the emissions from the higher vibrational levels ( $v' > 13$ ) to lower ones become smaller by introducing  $C_6H_6$ .

One reasonable explanation for the changes of the spectral features on addition of  $C_6H_6$  is that  $CN(B)$  and  $CN(A)$  are produced from both the  $C_2(a) + NO$  and the  $C_2(X) + NO$  reactions. This proposition was also supported from the measurements of the product branching ratio  $k_{CN(A)}/k_{CN(B)}$ . The branching ratio  $k_{CN(A)}/k_{CN(B)}$  was measured by comparing



the bandarea of the  $CN(A-X)$  emission spectrum with that of the  $CN(B-X)$  emission spectrum. The ratio  $k_{CN(A)}/k_{CN(B)}$  in utilizing  $CH_4$  was estimated to be  $3.9 \pm 0.5$ , which is smaller than that measured in the case of  $C_2H_2$  ( $k_{CN(A)}/k_{CN(B)} = 10.5 \pm 1.3$ ). On addition of the  $C_6H_6$  gas of 10mTorr,  $k_{CN(A)}/k_{CN(B)}$  increased to  $7.2 \pm 0.6$ , which shows an approach to the value measured in the case of  $C_2H_2$ .

As described above, no change in the spectral features of the  $CN(B-X)$  emission obtained from  $C_2H_2$  has been found on addition of the  $C_6H_6$  gas, in contrast with the case of employing  $CH_4$ . If our proposition is true, the above observation implies that  $C_2(a)$  is predominantly produced from the Ar afterglow reaction of  $C_2H_2$ . A preferential formation of  $C_2(a)$  from the Ar afterglow reactions of  $C_2H_2$  was suggested from the measurements of  $C_2(d-a)$  LIF spectrum. The intensity of the LIF spectrum obtained from the Ar afterglow reaction of  $C_2H_2$  was 20 times larger than that obtained from CO at pressures of 0.2Torr Ar, 5mTorr  $C_2H_2$ , and 5mTorr CO.

C.  $CN(B-X, A-X)$  emission spectra in the low-pressure apparatus

A  $CN(B-X)$  emission spectrum obtained by utilizing  $C_2H_2$  is shown in Fig.5. In

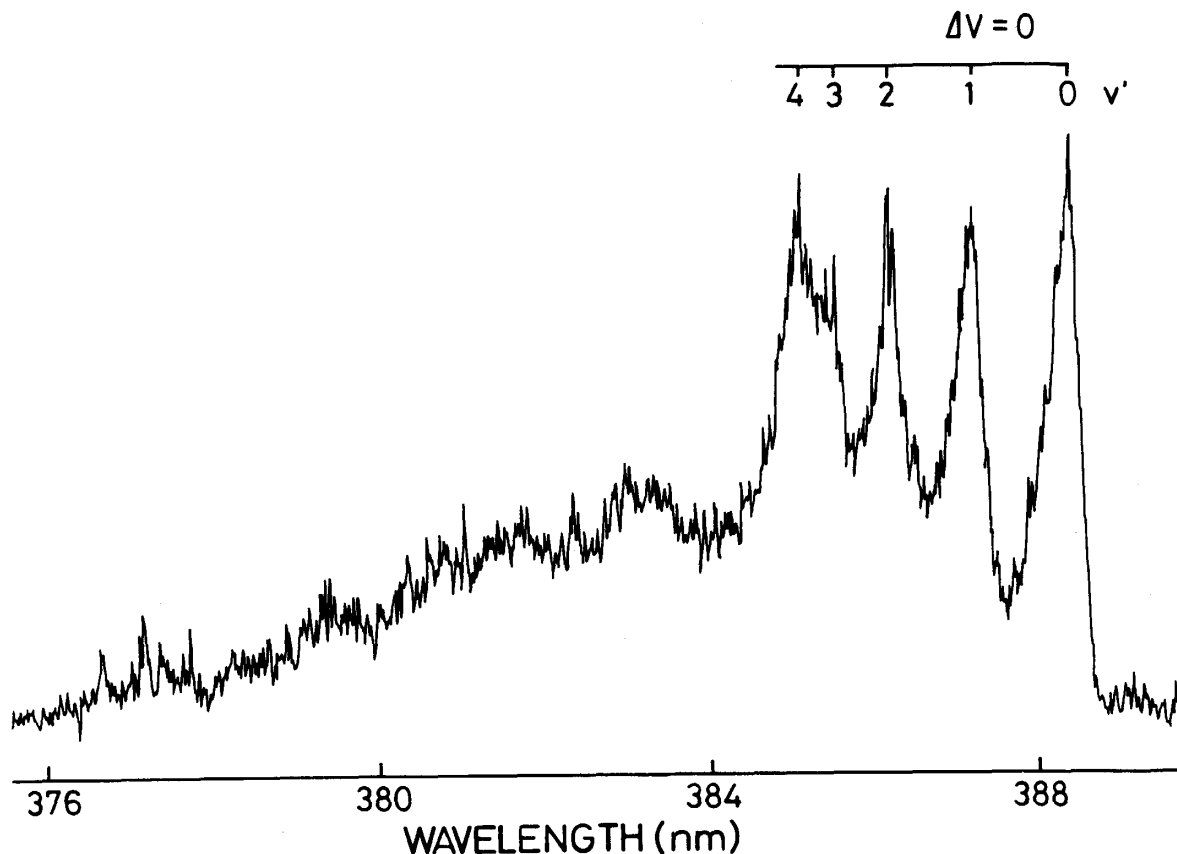


Fig.5:  $CN(B-X)$  chemiluminescent spectrum detected in the low pressure apparatus when  $C_2H_2$  was employed for the source of  $C_2$ . The pressures of Ar,  $C_2H_2$ , and NO were : 8mTorr ;  $C_2H_2$ , 5mTorr ; NO, 25mTorr.

contrast with the  $CN(B-X)$  emission spectrum shown in Fig.1a, no perturbed rotational line is observed under the low-pressure conditions. In employing  $CH_4$ , the perturbed rotational

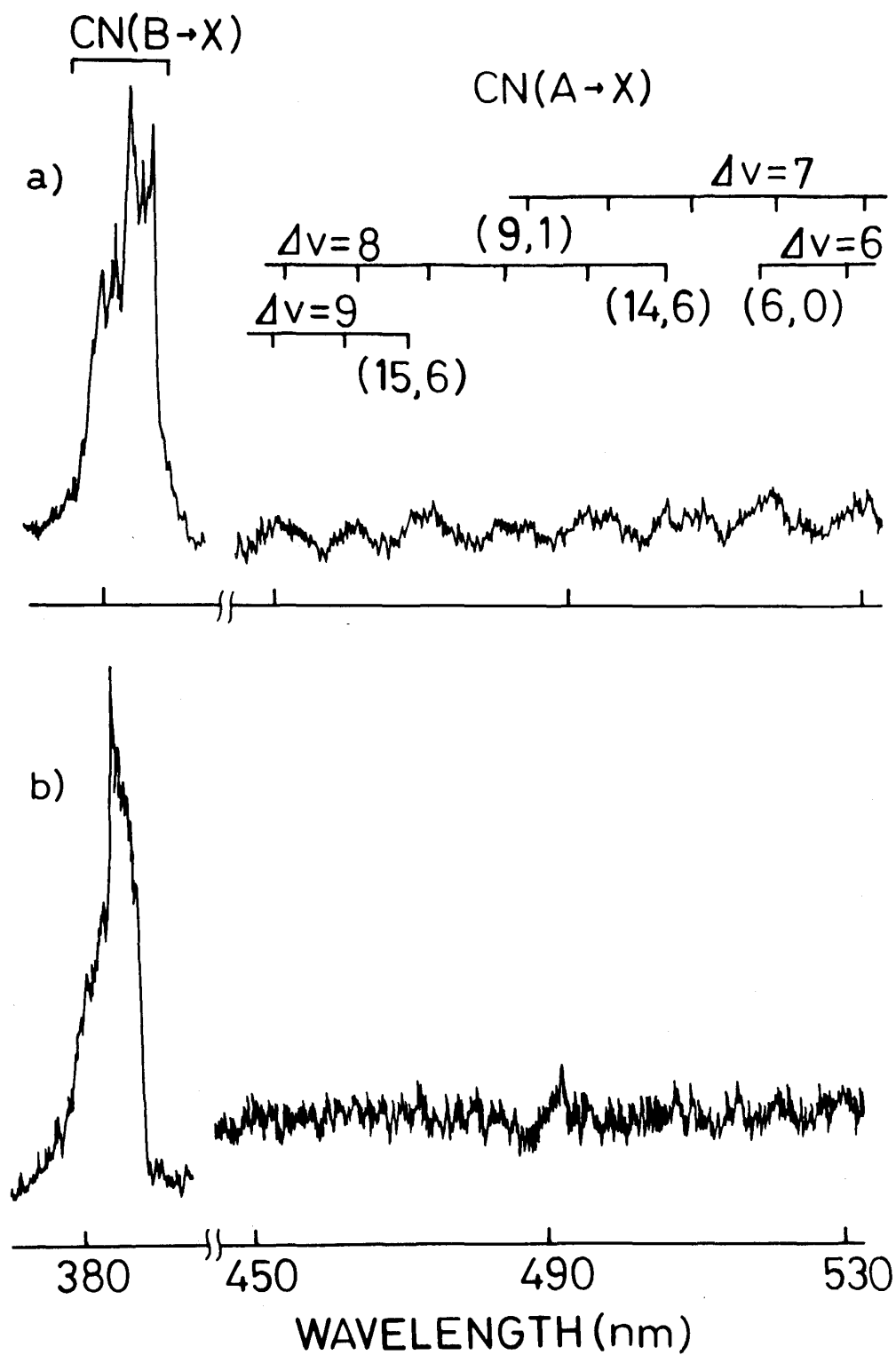


Fig.6 : CN( $B-X$ ,  $A-X$ ) chemiluminescent spectra obtained from  $C_2H_2$  (a) and  $CH_4$  (b) as precursors of  $C_2$  by using the low pressure apparatus. Experimental conditions are as follows: (a) Ar, 8mTorr;  $C_2H_2$ , 5mTorr; NO, 25mTorr (b) Ar, 10mTorr;  $CH_4$ , 10mTorr; NO, 22mTorr.

lines in the  $CN(B-X)$  emission spectrum did not appear as is the case for  $C_2H_2$ . These results suggest that the effect of collisions by surrounding gases to the  $CN(B-X)$  emission spectra is insignificant under the used low-pressure conditions. The  $CN(B-X, A-X)$  emission spectra observed by using  $C_2H_2$  and  $CH_4$  are shown in Fig.6. For comparison, these spectra have been measured with the same spectral resolution. The emission intensity ratio  $I_{CN(A)}/I_{CN(B)}$  is considerably small in Fig.6b. comparing with that in Fig.6a. This result is consistent with the high pressure experiments (0.15–0.25Torr Ar), where  $I_{CN(A)}/I_{CN(B)}$  obtained from  $CH_4$  is smaller than that obtained from  $C_2H_2$ . This suggests that  $CN(B)$  is produced directly from the  $C_2(X) + NO$  reaction, which contradicts the previous conclusion by RMW<sup>4)</sup> that  $CN(B)$  is produced indirectly from the  $C_2(X) + NO$  reaction. RMW<sup>4)</sup> observed a slower component in the rise portion of the time resolved  $CN(B-X)$  emission in addition to a fast component in the presence of a large excess Ar ( $> 0.5$ Torr) with a mixture of vinyl cyanide and NO. The result was interpreted as due to the formation of  $CN(X)$  from the  $C_2(X) + NO$  reaction following the radiationless energy transfer from the  $X$  state to the  $B$  state of CN. A comparison of  $I_{CN(A)}/I_{CN(B)}$  measured under the low and high pressure conditions supports that such a collisional energy transfer is insignificant in our experiments. If  $CN(B)$  is produced directly only from the  $C_2(a) + NO$  reaction,  $I_{CN(A)}/I_{CN(B)}$  measured with  $CH_4$  will approach the value measured with  $C_2H_2$  at low pressures.

In order to discuss the collisional energy transfer between the  $CN(X)$  and  $CN(B)$  states, it is necessary to take into account of the radiative lifetime of  $CN(B)$ , which is very short (50ns). For this reason, it will be able to detect enhanced rotational lines in the  $CN(B-X)$  emission spectrum as is the case for the perturbed rotational lines of  $CN(A, v' = 10)$ , if the collisional energy transfer occurred between the  $X$  state and  $B$  state of CN. However, no remarkable enhancement of the rotational lines has been detected in the  $CN(B-X)$  emission spectra measured at high Ar pressures ( $\sim 0.25$ Torr), except for the perturbed rotational lines of  $CN(A, v' = 10)$ .

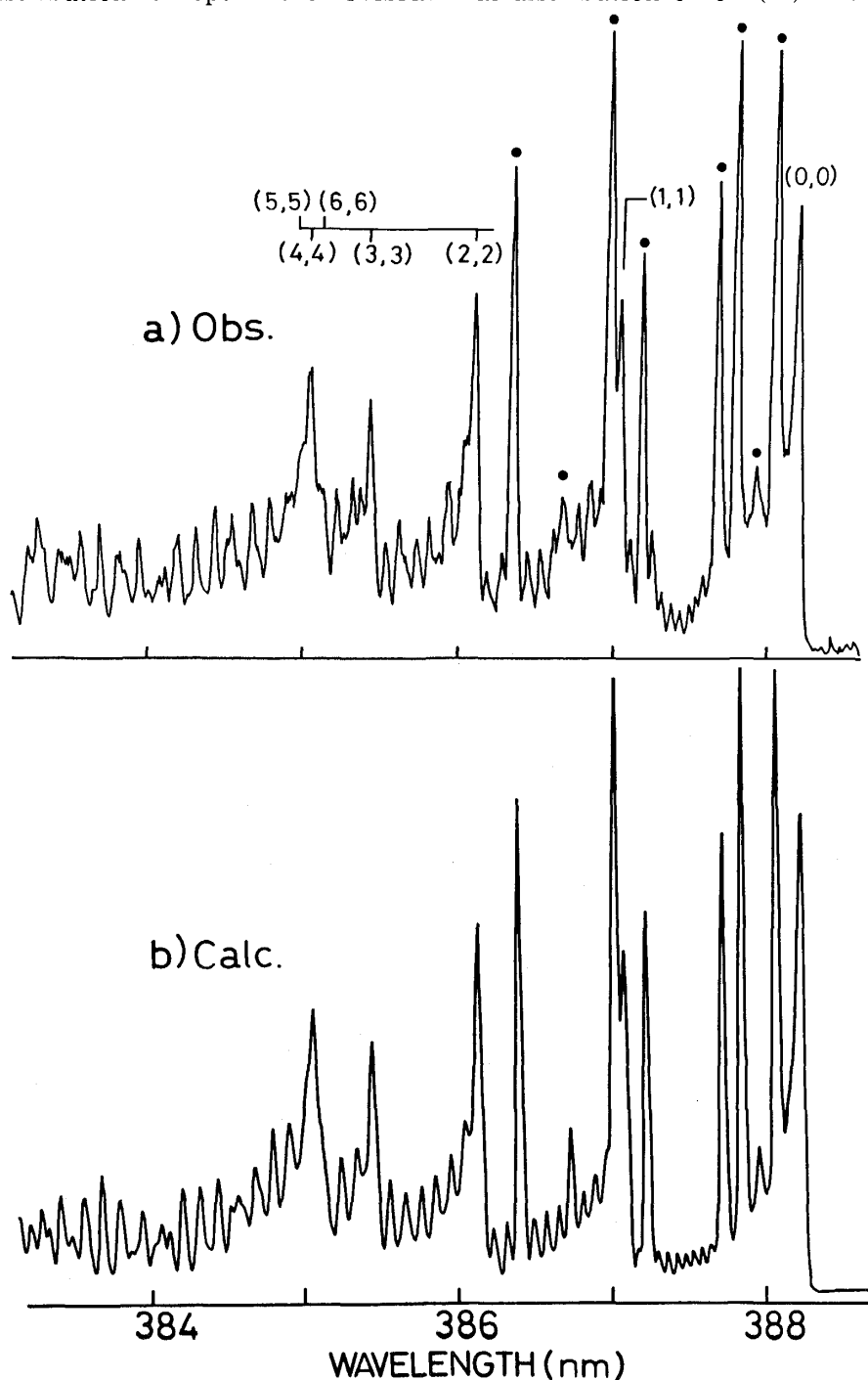
From the above consideration, the observation of the slower component by RMW is deduced to be due to the energy transfer from the perturbed rotational levels of  $CN(A)$  rather than the collisional energy transfer from the  $X$  state to the  $B$  state. They have not reported the resolved  $CN(B-X)$  chemiluminescent spectrum at high Ar pressures ( $> 0.5$ Torr). It will be possible to observe the perturbed rotational lines as the slower component, since they observed the  $CN(B-X)$  emission by using a filter centered at 390nm (5nm bandwidth). Thus, we have confirmed that  $CN(B)$  is produced directly from the  $C_2(X) + NO$  reaction as well as from the  $C_2(a) + NO$  reaction.

D. Rovibrational distribution of  $CN(B)$  and vibrational distribution of  $CN(A)$  resulting from the  $C_2(a) + NO$  reaction

As described above, it was suggested that  $C_2(a)$  is predominantly produced in the Ar

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 afterglow reaction of  $C_2H_2$ . Therefore, we determined the vibrational and rotational distributions of  $CN(B)$  and the vibrational distribution of  $CN(A)$  produced from the  $C_2(a) + NO$  reaction and compared those with the results presented in previous studies.

In order to examine the rovibrational relaxation of  $CN(B)$ , the Ar pressure was varied between 0.01 and 0.25 Torr by using the conventional flowing afterglow apparatus and the low-pressure apparatus. No appreciable change in the spectral feature was found, indicating that the initial distribution is kept in the rovibrational distribution of  $CN(B)$  shown in Fig.7a.



**Fig.7:** Observed (a) and simulated (b) spectra of the  $CN(B-X)$  transition when  $C_2H_2$  was employed for the source of  $C_2$ . Experimental spectrum (a) was observed under the same condition as that in Fig. 1(a).

Since the rotational lines are overlapped heavily in Fig.7a, the rovibrational distribution of  $CN(B)$  have been obtained by comparing the observed spectrum with the spectrum simulated by a computer. In the spectrum simulation, a single Boltzmann temperature was assumed for each vibrational level of  $CN(B, v' = 0-6)$ . The Franck-Condon factors and the electronic transition moments of the  $CN(B-X)$  emission system were taken from Refs. 10 and 11, respectively. The frequencies and the line strengths of the band system were calculated by using reported molecular constants<sup>12)</sup> and formulas,<sup>13)</sup> respectively. In Fig.7b. is shown the best fit with the experimental spectrum (Fig.7a). The observed perturbed rotational lines of the 0-0 transition were reproduced in the calculated spectrum by using the line strengths corresponding to the perturbed rotational lines as variable parameters.

According to the procedure reported by Krause,<sup>1)</sup> we calculated the prior vibrational distribution of  $CN(B)$  resulting from the  $C_2(a) + NO$  reaction. The experimental and prior distributions are summarized in Table 1. It is found that the experimental vibrational

**Table 1.** Comparison of Experimental and "Prior" Vibrational and Rotational Distributions for  $CN(B^2\Sigma^+)$  produced from the  $C_2(a) + NO$  reaction

v	exptl.		prior
	P(v)	T <sub>R</sub>	Po(v)
0	0.267 ± 2.05	7,000 ± 2,000	0.285
1	0.179 ± 2.05	6,000 ± 2,000	0.215
2	0.176 ± 0.05	5,000 ± 2,000	0.159
3	0.102 ± 0.05	5,000 ± 2,000	0.115
4	0.107 ± 0.03	3,000 ± 2,000	0.081
5	0.088 ± 0.03	2,500 ± 2,000	0.056
6	0.080 ± 0.03	2,500 ± 2,000	0.037

distribution of  $CN(B)$  is relatively close to the prior statistical one. This suggests that the  $CN(B)$  formation in the  $C_2(a) + NO$  reaction probably proceeds via forming a long lived complex rather than through a direct mode. For the  $CN(B)$  formation from the  $C_2(a) + NO$  reaction, we estimated the fractions of available energy deposited in vibration,  $\langle f_v \rangle$ , and in rotation,  $\langle f_R \rangle$ , to be 0.17 and 0.13, respectively.

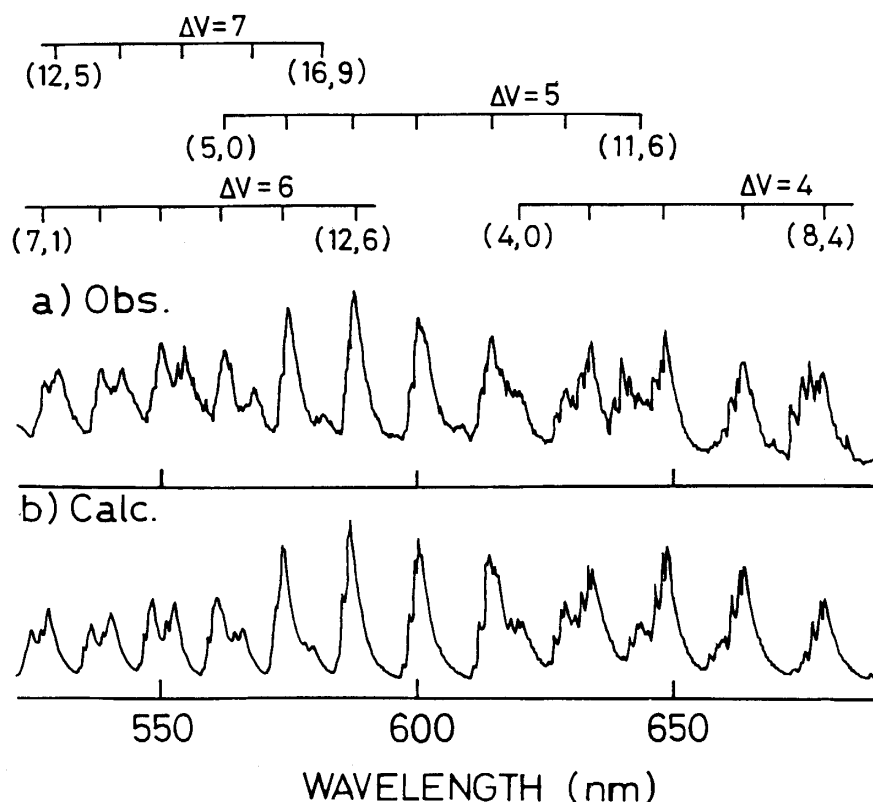
The vibrational distributions and vibrational temperatures of  $CN(B)$  measured in the previous studies are shown in Table 2 together with those determined in this work. It should be noted that the vibrational temperature strongly depends on the author. The highest temperature of 15400 K has been obtained in this work, while the temperatures in the other works are lower than our value. If our proposition for the formation processes of  $CN(B)$  is true, the highest temperature obtained in this work might reflect that the contribution of the  $C_2(X) + NO$  reaction for the formation of  $CN(B)$  is very small when  $C_2$  is prepared from the Ar afterglow reaction of  $C_2H_2$ .

To determine the vibrational distribution of  $CN(A)$  generating from the  $C_2(a) + NO$

**Table 2.** Comparison of relative vibrational populations and vibrational temperatures for CN(B,  $\Delta v = 0$ ) with the other works.

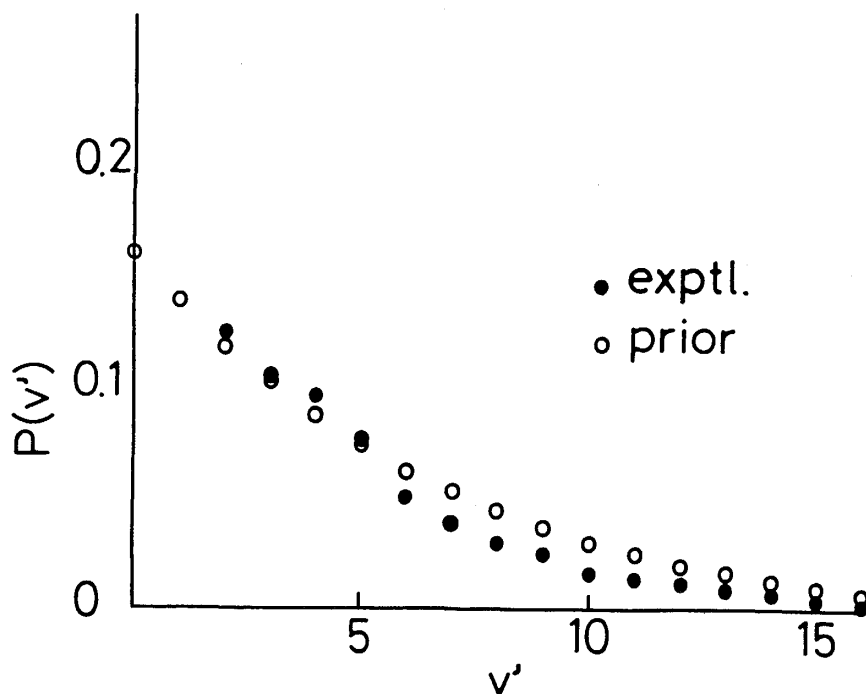
$v$	Krause	RMW	LE	This work
0	0.40	0.30	0.49	0.27
1	0.25	0.21	0.24	0.18
2	0.17	0.17	0.14	0.18
3	0.14	0.11	0.07	0.10
4	0.04	0.09	0.05	0.11
5		0.07	0.01	0.09
6		0.05		0.08
$T_v(K)$	$6,900 \pm 700$	$10,500 \pm 1,500$	$4,700 \pm 650$	$15,400 \pm 2,000$

reaction, the simulation method was also applied to the reproduction of the observed CN(A-X) spectrum indicated in Fig.8a. The radiative lifetime ( $7\mu s$ ) of CN(A)<sup>14)</sup> is much longer than that of CN(B) (50ns).<sup>15)</sup> Accordingly, the CN(A) state undergoes a number of collisions with Ar atoms before radiation under operating conditions. Therefore, the rotational distribution of CN(A) in Fig.8 will probably be relaxed. On the other hand, the vibrational relaxation of CN(A) in collisions with Ar atoms is inefficient. Coxon et al.<sup>16)</sup> measured the vibrational distributions of CN(A) resulting from the reactions of Ar\* with BrCN and ICN. It has been reported that the vibrational relaxation of CN(A,  $v' < 20$ ) in collisions with Ar is insignificant at Ar pressures below 0.8Torr. This suggests that the vibrational relaxation

**Fig.8:** Observed (a) and simulated (b) spectra of CN(A-X) transition when C<sub>2</sub>H<sub>2</sub> was employed for the source of C<sub>2</sub>. Experimental spectrum was observed under the same condition as that in Fig.2(a).

of  $CN(A)$  is negligible in Fig.8a, which has been measured at a Ar pressure of 0.21 Torr. In the spectrum simulation, the Franck-Condon factors and the molecular constants were taken from Refs. 10 and 17, respectively. Since there is a considerable controversy regarding the variation of the electronic transition moment,<sup>14,16,18</sup>  $Re^2(\bar{r})$ , with the  $r$  centroid,  $\bar{r}$ , we assumed that the electronic transition moment was constant. The best fit calculated spectrum is shown in Fig.8b together with the observed  $CN(A-X)$  spectrum. The observed vibrational distribution was approximated by a Boltzmann temperature of  $9500 \pm 1500K$ . The relative vibrational populations of  $v' = 0$  and  $v' = 1$  were determined by extrapolating with the straight line corresponding to  $T = 9500 \pm 1500K$  in logarithmic scale, since emissions from the  $v' = 0$  and 1 levels could not be detected in our detection system. The rotational temperatures were estimated to be  $700 \pm 200K$  for  $v' = 2-5$ , and  $500 \pm 200K$  for  $v' = 6-16$ , respectively. The resulting vibrational distribution of  $CN(A)$  was compared with the prior one calculated by the same procedure as is the case for  $CN(B)$  and is shown in Fig.9. It is found that the experimental vibrational distribution of  $CN(A)$  is relatively close to the prior statistical one. This suggests that the  $CN(A)$  formation in the  $C_2(a) + NO$  reaction probably proceeds via forming a long-lived complex rather than through a direct mode.

The vibrational temperature of  $CN(A)$  resulting from the  $C_2(a) + NO$  reaction has been estimated to be  $9500 \pm 1500K$ , which is lower than a value ( $13000 \pm 3000K$ ) measured by RMW.<sup>2)</sup> It has been suggested in the present study that the concentration of  $C_2(a)$  predomi-



**Fig.9:**  $CN(A)$  vibrational populations produced from the  $C_2(a) + NO$  reaction. Experimental values are compared with the prior ones.

nates over that of  $C_2(X)$  when  $C_2$  is created from the Ar afterglow reaction of  $C_2H_2$ , while the concentration of  $C_2(X)$  was higher than that of  $C_2(a)$  in the experiment of RMW ( $C_2(X)/C_2(a) = 2.7 \pm 1.2$ ).<sup>4)</sup> According to our proposition that  $CN(A)$  is produced from the  $C_2(X) + NO$  reaction, the difference in the vibrational temperatures implies that the vibrational distribution of  $CN(A)$  arising from the  $C_2(X) + NO$  reaction is more excited than that produced from the  $C_2(a) + NO$  reaction. This is able to account for the change in the spectral features of the  $CN(A-X)$  emission on addition of  $C_6H_6$  shown in Fig.4.

### Conclusions

The  $C_2 + NO \rightarrow CN(B, A) + CO$  reaction was studied by using Ar afterglow reaction of  $C_2H_2$ ,  $CH_4$ , or  $CO$  molecule for the source of  $C_2$ . Experiments were performed by using the conventional flowing afterglow apparatus and the low-pressure apparatus. On the basis of the changes in the spectral features of the  $CN(B-X)$  and  $CN(A-X)$  chemiluminescence and the product branching ratio  $k_{CN(A)}/k_{CN(B)}$  in introducing a scavenger for  $C_2(X)$ , it was suggested that both  $CN(B)$  and  $CN(A)$  are produced from the  $C_2(X) + NO$  reaction as well as the  $C_2(a) + NO$  reaction. Our proposition is inconsistent with the conclusion that  $CN(B)$  and  $CN(A)$  are selectively produced from the  $C_2(a) + NO$  reaction, which was previously proposed by several groups. The rovibrational distribution of  $CN(B)$  and vibrational distribution of  $CN(A)$  resulting from the  $C_2(a) + NO$  reaction have been obtained by spectrum simulation for the  $CN(B-X, A-X)$  emissions observed by employing  $C_2H_2$ .

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