

## Laser Excitation Spectra of the Vibrationally Excited CN Radical

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**Abstract** Laser excitation spectra were observed in the reaction system :  $\text{CH}_3\text{CN} + \text{CF}_4$  (MW discharged). The rotational analysis of the spectra indicated that the vibrationally excited CN radical was produced in this reaction system.

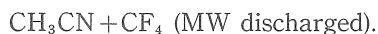
### INTRODUCTION

The spectrum of CN radical is observed in the atmosphere of stars, comets and sun, and appears in numerous chemical processes at high temperature.

So far, a number of works have been done on the most intense transitions,  $\text{B}^2\Sigma^+ - \text{X}^2\Sigma^+$  (violet system) and  $\text{A}^2\Pi - \text{X}^2\Sigma^+$  (red system).<sup>(1)</sup>

Basco et al.<sup>(2)</sup> produced the CN radical in vibrationally excited states by using the flash photolysis :  $\text{CNR} + h\nu \rightarrow \text{CN} (\text{B}^2\Sigma^+, v \geq 0) + \text{R}$ , where R is the halogen atom. They discussed the mechanism of such a vibrational excitation of the CN radical.

In the present experiment, the vibrationally excited CN radical was generated in the reaction system :



By analyzing the laser excitation spectra observed, it was confirmed that a vibrationally excited CN radical was generated in this reaction.

### RESULT and DISCUSSION

It has been known that an unstable polyatomic molecule is produced by reacting  $\text{CH}_3\text{CN}$  with microwave discharged  $\text{CF}_4$  under the condition of the partial pressure of 20~30 mTorr for  $\text{CH}_3\text{CN}$  and ~150 mTorr for  $\text{CF}_4$ , and that its excitation spectra are observed

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in the region of 16960 to 16990  $\text{cm}^{-1}$ . In the course of the measurements, the spectra from other species were observed at very low partial pressure ( $\sim 2$  mTorr) for  $\text{CH}_3\text{CN}$ . Fig. 1 shows the survey spectrum under the latter condition of the reaction. The intensity of the band in the wavenumber region of 16900 to 17050  $\text{cm}^{-1}$  was very sensitive to the partial pressure for  $\text{CH}_3\text{CN}$ . By recording the high resolution spectra, this band was found to be a part of the red system of the CN radical, and the other one was assigned to the  $\tilde{\text{A}}^1\text{A}''(000) \leftarrow \tilde{\text{X}}^1\text{A}'(000)$  transition of HCF. Fig. 2 gives a trace of the high resolution excitation spectrum of CN,  $\tilde{\text{A}}^2\Pi(v=7) \leftarrow \tilde{\text{X}}^2\Sigma^+(v=2)$ , which was observed in the experimental set-up described in detail previously<sup>(3)</sup>. Taking account of the intensity of the observed fluorescence and the vibrational frequency (2068  $\text{cm}^{-1}$ ) of the CN, the spectra obtained in the present observation are considered to be those of the CN radical in non-thermal equilibrium. Although Basco et al.<sup>(2)</sup> discussed three primary mechanisms for the vibrational excitation of the CN radical, the mechanism for the present case was not made clear. A presumable mechanism is that the CN radical may be produced in electronically excited states and the subsequent transitions to the ground electronic states could populate its excited vibrational levels. This way of the vibrational excitation was likely to be possible in the present reaction, because of the fact that red chemiluminescence was accompanied with the formation of the vibrationally excited CN radical.

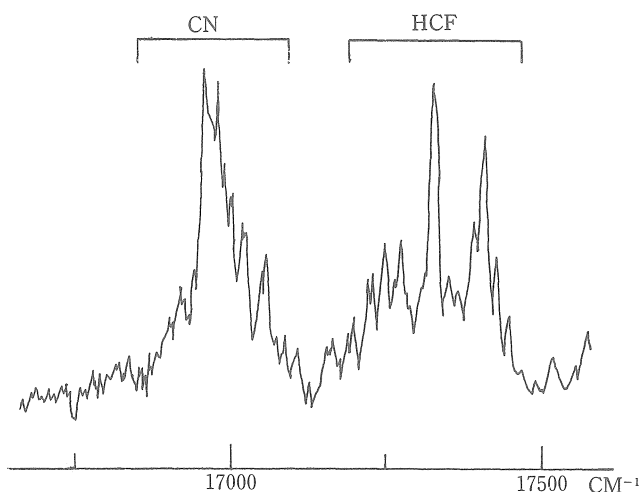


Fig. 1. Survey spectrum of  $\text{CH}_3\text{CN}$  (2 mTorr) +  $\text{CF}_4$  (MW dis. 150 mTorr).

The rotational assignment of observed spectral lines was made by calculating transition wavenumbers with the use of the molecular constants obtained by Kotlar et al.<sup>(4)</sup> 81 spectral lines, almost all of observed lines, could be assigned. For the assigned lines, the least squares fitting was made to re-determine the molecular constants using the Hamiltonian employed by Kotlar et al. The molecular constants thus determined were less precise than those obtained by Kotlar et al. because the number of observed lines in the present work was smaller than that in the latter. The assignments of the observed lines

are listed in Table 1.

Thus, the analysis of the high resolution excitation spectra indicated that the vibrationally excited CN radical was confirmatively produced by reacting  $\text{CH}_3\text{CN}$  ( $\sim 2$

Table 1. Assigned Lines in CN,  $\tilde{A}^2\Pi(v=7) \leftarrow \tilde{X}^2\Sigma^+(v=2)$

Obs <sup>a</sup> .	Trans <sup>b</sup> .	O-C <sup>c</sup>	Obs.	Trans.	O-C
16956.26	P <sub>1</sub> (10)	-0.07	17002.69	R <sub>1</sub> (16)	-0.01
16956.40	Q <sub>12</sub> (10)	0.02	17003.86	Q <sub>1</sub> (6)	0.06
16957.78	P <sub>12</sub> (7)	0.02	17003.86	R <sub>12</sub> (6)	0.03
16958.18	P <sub>2</sub> (13)	0.01	17006.01	Q <sub>1</sub> (5)	0.01
16962.81	P <sub>21</sub> (17)	0.05	17006.01	R <sub>12</sub> (5)	-0.02
16964.09	P <sub>1</sub> (9)	0.00	17006.19	P <sub>21</sub> (12)	-0.05
16964.15	Q <sub>12</sub> (9)	0.01	17006.30	Q <sub>2</sub> (12)	0.00
16966.80	P <sub>12</sub> (6)	0.03	17007.60	Q <sub>1</sub> (4)	0.01
16969.09	P <sub>2</sub> (12)	0.01	17007.60	R <sub>12</sub> (4)	-0.02
16969.60	Q <sub>21</sub> (23)	-0.04	17007.83	R <sub>1</sub> (15)	0.05
16971.23	P <sub>1</sub> (8)	-0.01	17007.90	P <sub>2</sub> (8)	0.01
16971.28	Q <sub>12</sub> (8)	0.00	17008.56	Q <sub>1</sub> (3)	0.00
16972.49	P <sub>21</sub> (16)	0.03	17008.56	R <sub>12</sub> (3)	-0.02
16972.72	Q <sub>2</sub> (16)	0.17	17008.63	Q <sub>1</sub> (1)	0.01
16977.77	Q <sub>12</sub> (7)	-0.05	17008.63	R <sub>12</sub> (1)	0.00
16977.81	R <sub>12</sub> (12)	-0.11	17008.91	Q <sub>1</sub> (2)	0.01
16977.81	P <sub>1</sub> (7)	-0.05	17008.91	R <sub>12</sub> (2)	-0.01
16979.50	P <sub>2</sub> (11)	0.00	17012.29	R <sub>1</sub> (0)	-0.05
16981.69	P <sub>21</sub> (15)	0.03	17012.29	R <sub>1</sub> (14)	0.03
16982.95	P <sub>12</sub> (4)	0.02	17012.35	Q <sub>21</sub> (18)	0.05
16983.70	Q <sub>1</sub> (11)	0.03	17012.38	R <sub>2</sub> (18)	-0.02
16983.77	R <sub>12</sub> (11)	0.02	17013.40	P <sub>21</sub> (11)	-0.05
16983.89	P <sub>1</sub> (6)	0.18	17013.49	Q <sub>2</sub> (11)	-0.01
16983.97	Q <sub>12</sub> (6)	0.23	17016.17	R <sub>1</sub> (13)	0.00
16988.98	P <sub>1</sub> (5)	-0.04	17016.34	R <sub>1</sub> (1)	0.01
16989.04	Q <sub>12</sub> (5)	0.00	17016.42	P <sub>2</sub> (7)	0.01
16989.44	P <sub>2</sub> (10)	0.00	17019.31	Q <sub>21</sub> (17)	-0.03
16990.09	P <sub>12</sub> (3)	0.02	17019.48	R <sub>1</sub> (12)	-0.01
16990.29	P <sub>21</sub> (14)	-0.06	17019.69	R <sub>1</sub> (2)	-0.01
16990.38	Q <sub>2</sub> (14)	-0.04	17020.12	P <sub>21</sub> (10)	-0.04
16993.54	Q <sub>1</sub> (9)	0.02	17020.20	Q <sub>2</sub> (10)	-0.01
16993.54	R <sub>12</sub> (9)	-0.03	17022.20	R <sub>1</sub> (11)	-0.03
16993.61	P <sub>1</sub> (4)	-0.09	17022.42	R <sub>1</sub> (3)	-0.02
16993.71	Q <sub>12</sub> (4)	-0.01	17024.35	R <sub>1</sub> (10)	-0.03
16997.16	R <sub>1</sub> (17)	0.11	17024.53	R <sub>1</sub> (4)	-0.02
16997.56	Q <sub>1</sub> (8)	0.01	17024.53	P <sub>2</sub> (6)	0.07
16997.56	R <sub>12</sub> (8)	-0.04	17025.90	R <sub>1</sub> (9)	-0.02
16997.80	P <sub>1</sub> (3)	0.04	17026.04	R <sub>1</sub> (5)	-0.01
16997.80	Q <sub>12</sub> (3)	0.02	17026.38	P <sub>21</sub> (9)	-0.02
16998.46	P <sub>21</sub> (13)	-0.08	17026.45	Q <sub>2</sub> (9)	0.00
16998.55	Q <sub>2</sub> (13)	-0.06	17026.82	R <sub>1</sub> (8)	-0.04
16998.90	P <sub>2</sub> (9)	-0.01	17026.90	R <sub>1</sub> (6)	-0.03
17000.95	Q <sub>1</sub> (7)	-0.04	17027.15	R <sub>1</sub> (7)	-0.05
17001.01	R <sub>12</sub> (7)	-0.01	17031.81	Q <sub>21</sub> (15)	-0.07
17001.22	P <sub>1</sub> (2)	0.22	17031.92	R <sub>2</sub> (15)	-0.04
17001.22	Q <sub>12</sub> (2)	0.01	17032.09	P <sub>2</sub> (5)	0.04

a Observed wavenumber in  $\text{cm}^{-1}$ .

b Transition. See Ref. (1).

c Observed wavenumber minus calculated one in  $\text{cm}^{-1}$ .

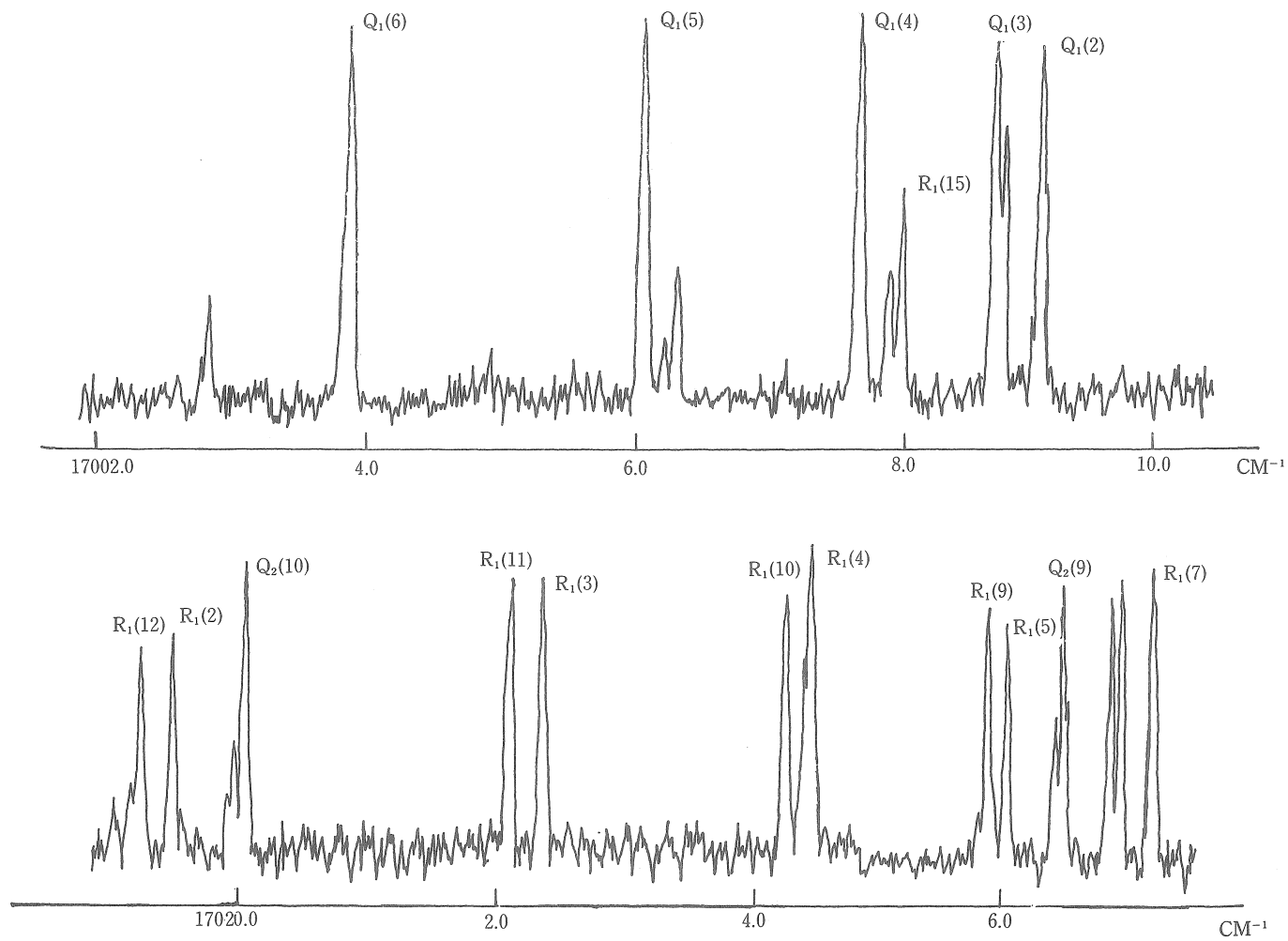


Fig. 2. A part of high resolution spectra of CN radical.

mTorr in pressure) with microwave discharged  $\text{CF}_4$  ( $\sim 150$  mTorr).

### References

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