are the same for $\gamma=1.2$, $\kappa_x=6$ and $\gamma=0.8$, $\kappa_x=4$, shown in Figure 3 b) and c), respectively. The susceptibility curves are qualitively very similar to the results published by Ohya-Nishiguchi. This is, however, the first result that anisotropic susceptibilities in the paramagnetic region are obtained with the simple mean field theory.

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Analysis of Fourier Transform Jet Emission Spectra of CN ($B^2\Sigma^+\rightarrow X^2\Sigma^+$)

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The CN radical was generated in a jet with an inert buffer gas, helium from high voltage dc discharge of the precursor CH_3CN. The Fourier transform emission spectra of the 0-0 band of the $B^2\Sigma^+\rightarrow X^2\Sigma^-$ transition of CN have been obtained with a Bruker IFS-120HR spectrometer. The spectra show an anomalous distribution of rotational intensity which cannot be explained by a simple Boltzmann distribution. The analysis of the transition frequencies provides molecular constants with high accuracy for both the ground and the excited electronic states of the CN radical.

Introduction

Fourier transform(FT) spectroscopy is one of the most convenient methods in obtaining a high resolution spectra of molecules. With development of techniques improving the signal to noise ratio and the resolution of the FT spectra, it has become possible to obtain the rotationally resolved emission spectra of unstable molecules with a FT spectrometer.[1,2] Recently, FT-UV/VIS spectroscopy has been applied to the study of vibronic transition of unstable molecules which emit relatively strong fluorescence.[3]

Among many unstable molecules studied in the laboratory, CN radical is one of the most intensively studied diatomic free radicals because of its strong fluorescence and abundance in flames. Astronomically, CN has been observed from several extraterrestrial sources including stellar atomospheres,[4,5] comets,[6] and dark interstellar molecular clouds[7] by a variety kinds of spectroscopic techniques.

The first analysis of the rotational structure of the $B^2\Sigma^+$ $-X^2\Sigma^+$ band was accomplished by Kratzer[8] in the violet system. Douglas and Routly[9], and Huber and Herzberg[10] summarized a detailed review of the literature on this molecule. Recently, the microwave and millimeter wave works by Ito *et al.*[11] have given very accurate molecular parameters in the ground state. From the analysis of the millimeter wave spectrum, they have determined the spin-rotation interaction constants γ over several vibrational states in the ground electronic state. Very recently, a few papers[12-14] have reported the molecular parameters from the analysis of the rotationa-

lly resolved electronic spectra with a high resolution FT-UV/VIS spectrometer since the pioneering works of Richard *et al.*[3] For this study, they employed a very simple corona-excited supersonic expansion system developed by Engelking[15] which produces continuous, high density of rotationally cooled radicals for spectroscopic studies of unstable molecules. Although they used very similar techniques and experimental setup, the molecular constants obtained did not exactly agree well.

Thus, in this work which is an extension of the previous work,[16-18] the CN radical was generated in a jet with an inert He gas by an electric dc discharge of CH_3CN. The emission spectra of the 0-0 band of the $B\rightarrow X$ transition have been obtained using a FT-UV/VIS spectrometer. The analysis of these spectra provides more accurate molecular parameters for the ground and the excited electronic states.

Experimental Detail

The observation of CN emission spectra has been carried out using the experimental setup similar to those previously described.[17] The precursor CH_3CN was expanded with an inert gas He through a 0.2 mm quartz nozzle into the vacuum chamber which was made of a six-way cross Pyrex glass tube of 5.0 cm in diameter. Since CN radical emits strong fluorescence around 26,000 cm^{-1}, the concentration of CH_3CN in the gas mixture was kept as low as possible by adjusting the opening of the bypass valve connected to the sample chamber during the measurement. The concentration
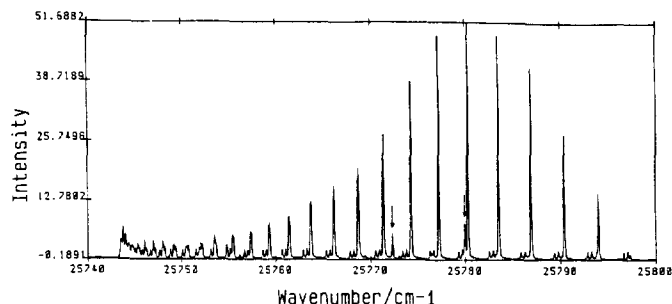
Figure 1. A portion of FT emission spectrum of the 0-0 band of the $B^2\Sigma^+ \to X^2\Sigma^+$ transition recorded at 0.05 cm^{-1} resolution. Arrows at 25772.3 and 25780.0 cm^{-1} indicate the extra lines resulting from the perturbation of A-state rotational levels.

of CH_3CN in a gas mixture is believed to be less than 1.0%. The pressure of the gas mixture was about 2 atm inside the nozzle. The pressure in the expansion chamber during operation was maintained to lower than 1.0 Torr by using the mechanical vacuum pump. Under these conditions, the rotational temperature of about 65 K has been achieved for CN radical. However, using the boost pump (~40CFM) has lowered the rotational temperature of the sample to 50 K.

The CN radical was generated by an electric dc discharge between the anode fixed inside the nozzle and the pump which acts as the cathode. The anode was connected to a 3000 volts of dc power supply *via* a 500 kΩ current limiting ballast resistor. Under typical operating conditions, the discharge current was 4-5 mA.

The emission from CN radical in a jet was focussed onto the external port of a Bruker IFS-120HR Fourier transform spectrometer using combination of 2 concave mirrors and 2 lenses. One (f=5.0 cm) of the quartz lenses has been inserted inside the chamber to enhance the solid angle of emission. Typically, an area of the jet below the nozzle orifice of 2 mm in diameter was viewed by the PMT (Hamamatsu model 1P28) detector. For the improvement of signal to noise ratio of the spectrum, 390 nm narrow band interference optical filter has been used to get rid of strong emission of He. The spectral region from 22,000 to 28,000 cm^{-1} was scanned at the resolution of 0.05 cm^{-1}. Typically, 100 spectra have been averaged over 30 min to obtain the final spectrum shown in Figure 1. The frequency of the spectrum was calibrated with I_2 transition, and believed to be better than 0.003 cm^{-1} in this frequency region.

Analysis and Discussion

The $B^2\Sigma^+ \to X^2\Sigma^+$ band of the CN radical is a transition between electronic states which belong to Hund's case (b). In the case of the $^2\Sigma$ states, the rotational term values at the ground vibrational state are given as[19]

$$F_1(N) = B_0\ N(N+1) - D_0\ N^2(N+1)^2 + \gamma_0\ N/2$$

$$F_2(N) = B_0\ N(N+1) - D_0\ N^2(N+1)^2 + \gamma_0(N+1)/2 \qquad (1)$$

where $F_1(N)$ refers to the components with $J = N + 1/2$ and $F_2(N)$ refers to those with $J = N - 1/2$, respectively. The selection rule $\Delta N = \pm 1$ holds, $\Delta N = 0$ being forbidden. From the above energy level expression, it is easily expected that the

separation between two components increases with $\gamma_0(N+1/2)$. Usually, the splitting constant γ_0 is much smaller compared to the rotational constant B_0. With high resolution, each line of the P and R branches, according to the rule $\Delta J = 0$, ± 1, is split into three components. However, since the intensity of the transition with $\Delta J = 0$ falls off very rapidly with increasing N, only two components of about equal inte-

Table 1. [a] Transition Frequencies of the 0-0 Band of the $B^2\Sigma^+ \to X^2\Sigma^+$ of CN

Transitions[b,c]	OBS. FREQ.	Difference[d]	Accuracy[e]
P2(33)	25745.0457	−.0085	.005
P2(23)	25745.3012	.0148	Omit
P1(33)	25745.3012	−.0290	Omit
P1(23)	25745.4754	.0014	.005
P2(34)	25745.7845	−.0055	.005
P2(22)	25746.0650	−.0013	.005
P2(34)	25746.0650	−.0079	.005
P1(22)	25746.2457	.0005	.005
P2(35)	25746.6548	−.0068	.005
P2(21)	25746.9622	−.0214	Omit
P1(35)	25746.9622	.0091	.005
P1(21)	25747.1567	.0029	.005
P2(36)	25747.6656	−.0053	.005
P2(20)	25748.0000	−.0383	Omit
P1(36)	25748.0000	.0290	Omit
P1(20)	25748.2071	.0072	.005
P2(37)	25748.8033	−.0144	.005
P2(19)	25749.1650	−.0655	Omit
P1(37)	25749.1650	.0385	Omit
P1(19)	25749.3862	.0028	.005
P2(38)	25750.0967	−.0053	.005
P2(18)	25750.5446	−.0153	Omit
P1(38)	25750.5446	.1251	Omit
P1(18)	25750.7184	.0142	.005
P2(39)	25751.5224	−.0014	.005
P1(39)	25751.8574	.0074	.005
P2(17)	25752.0117	−.0150	.005
P1(17)	25752.1915	.0292	Omit
P2(40)	25753.0827	−.0005	.005
P2(16)	25753.4577	−.1729	Omit
P1(40)	25753.4577	.0397	Omit
P1(16)	25753.6184	−.1392	Omit
P2(41)	25754.7760	−.0039	.005
P1(41)	25755.1310	.0076	.005
P2(15)	25755.3724	.0007	.005
P1(15)	25755.4662	−.0238	Omit
P2(42)	25756.6176	.0036	.005
P1(42)	25756.9721	.0060	.005
P2(14)	25757.2547	.0048	.005
P1(14)	25757.3546	−.0049	.005
P2(43)	25758.5866	.0012	.005
P1(43)	25758.9418	−.0044	.005
P2(13)	25759.2622	−.0028	.005
P1(13)	25759.3567	−.0093	.005
P2(44)	25760.7022	.0081	.005
P1(44)	25761.0575	−.0060	.005
P2(12)	25761.4193	.0022	.005
P1(12)	25761.5120	.0026	.005

P2(45)	25762.9394	−.0005	.005	P2(8)	25837.9418	.0052	.005
P1(45)	25763.3341	.0161	.005	P1(8)	25838.0422	.0161	Omit
P2(11)	25763.7027	−.0032	.005	P2(9)	25843.0605	.0010	.005
P1(11)	25763.7969	.0073	.005	P1(9)	25843.1682	.0105	.005
P2(46)	25765.3289	.0061	.005	P2(10)	25848.3071	−.0089	.005
P1(46)	25765.7319	.0223	Omit	P1(10)	25848.4335	.0106	.005
P2(10)	25766.1327	.0013	.005	P2(11)	25853.7110	.0052	.005
P1(10)	25766.2000	−.0065	.005	P1(11)	25853.8240	.0027	.005
P2(47)	25767.8673	.0245	Omit	P2(12)	25859.2280	−.0007	.005
P1(47)	25768.2353	−.0029	.005	P1(12)	25859.3550	.0021	.005
P2(9)	25768.6974	.0038	.005	P2(13)	25864.8460	−.0384	Omit
P1(9)	25768.7580	−.0019	.005	P1(13)	25864.9930	−.0243	Omit
P2(48)	25770.5115	.0118	.005	P2(14)	25870.5510	−.1218	Omit
P1(48)	25770.9273	.0235	Omit	P1(14)	25870.6652	−.1491	Omit
P1(8)	25771.3496	−.1003	Omit	P2(15)	25876.5848	−.0088	.005
P2(8)	25771.3496	−.0426	Omit	P1(15)	25876.7767	.0329	Omit
P2(49)	25773.2910	−.0024	.005	P2(16)	25882.6388	−.0078	.005
P1(49)	25773.6990	−.0072	.005	P2(17)	25888.8115	−.0200	Omit
P2(7)	25774.2480	−.0283	Omit	P1(17)	25889.0263	.0273	Omit
P2(7)	25774.2480	.0207	Omit	P1(18)	25895.3233	−.0009	Omit
P2(50)	25776.2367	.0127	.005	P2(19)	25901.5876	−.0086	.005
P1(50)	25776.6450	−.0004	.005	P1(19)	25901.8084	.0275	Omit
P2(6)	25777.2213	−.0177	Omit	P2(20)	25908.1633	−.0121	.005
P2(6)	25777.2213	.0227	Omit	P1(20)	25908.3775	.0087	.005
P2(51)	25779.2900	−.0012	.005	P2(21)	25914.8790	−.0066	.005
P1(51)	25779.6990	−.0222	Omit	P1(21)	25915.1000	.0123	.005
P1(5)	25780.3487	.0109	Omit	P2(22)	25921.7160	−.0104	.005
P2(5)	25780.3487	.0426	Omit	P1(22)	25921.9300	−.0072	.005
P2(52)	25782.5050	.0101	.005	P2(23)	25928.6732	−.0244	Omit
P1(52)	25782.9200	−.0136	.005	P1(23)	25928.8000	−.1171	Omit
P2(4)	25783.5620	.0124	Omit	P2(24)	25935.7915	−.0075	.005
P1(4)	25783.5620	−.0106	Omit	P1(24)	25936.0395	.0124	.005
P2(53)	25785.8465	.0114	.005	P2(25)	25943.0337	.0035	.005
P1(53)	25786.2743	−.0082	.005	P1(25)	25943.2744	.0073	.005
P2(3)	25786.9372	.0083	Omit	P2(26)	25950.3821	−.0088	.005
P1(3)	25786.9372	−.0061	Omit	P1(26)	25950.6960	.0597	Omit
P2(54)	25789.3283	.0167	Omit	P2(27)	25957.8908	.0099	.005
P1(54)	25789.7500	.0177	.005	P2(28)	25965.4887	−.0112	.005
P2(2)	25790.4537	.0096	Omit	P1(28)	25965.7692	.0066	.005
P1(2)	25790.4537	.0039	Omit	P1(29)	25973.5100	−.0089	.005
P2(55)	25792.9300	.0056	.005	P2(30)	25981.1230	−.0005	.005
P1(55)	25793.3850	−.0041	.005	P1(30)	25981.4055	.0019	.005
P1(1)	25794.1025	.0106	Omit	P2(31)	25989.1256	−.0020	.005
P2(1)	25794.1025	.0077	.005	P1(31)	25989.4333	.0170	.005
P2(0)	25801.7960	.0137	Omit	P2(32)	25997.2543	−.0050	.005
P1(0)	25801.7960	−.0066	.005	P1(32)	25997.5820	.0253	Omit
P2(1)	25805.8545	.0242	Omit	P2(34)	26013.9085	.0037	.005
P1(1)	25805.8545	−.0048	.005	P1(34)	26014.2178	−.0017	.005
P2(2)	25810.0498	.0364	Omit	P2(37)	26039.8303	.0075	.005
P1(2)	25810.0498	−.0011	.005	P1(37)	26040.1547	−.0088	.005
P2(3)	25814.3781	.0469	Omit				
P1(3)	25814.3781	.0077	.005				
P2(4)	25818.8170	.0333	Omit				
P1(4)	25818.8170	−.0216	Omit				
P2(5)	25823.3977	.0270	Omit				
P1(5)	25823.3977	−.0365	Omit				
P2(6)	25828.0589	−.0330	Omit				
P1(6)	25828.0589	−.1052	Omit				
P2(7)	25832.9531	.0058	.005				
P1(7)	25833.0608	.0326	Omit				

[a]In units of wavenumber (cm^{-1}). [b]The number in parentheses is N quantum number in the $X^2\Sigma^+$ state. [c]The numbers 1 and 2 correspond to the transitions belonging to the F_1 and F_2 components, respectively. [d]Difference in observed minus calculated frequency. [e]An "Omit" means that the transitions frequency was omitted from the least squares fits due to overlap with nearby peaks or strong perturbation.

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Table 2. Molecular parameters of the CN radical[a,b]

Parameters	X-state	B-state
T_0		25797.8774(9)
B_0	1.890955(28)	1.958612(29)
$D_0(10^5)$	0.6351(13)	0.6564(14)
$\gamma_0(10^3)$	7.25505[c]	15.915(32)

[a]Number in parentheses is one standard error in units of last digit of the parameter. [b]In units of wavenumber (cm^{-1}). [c]Constrained to the value given in Ref. (11).

nsity and of a separation increasing with N is expected to be observable. Thus, the rotational structure of a band consists of four main branches, R_1, R_2, P_1, and P_2.

Figure 1 shows the FT emission spectrum of the 0-0 band of the $B \rightarrow X$ transition of CN radical generated by an electric dc discharge from the gas mixture of CH_3CN and He. For observation of high J transitions, the rotational temperature has been purposely increased by reducing the pumping speed of the expansion chamber. The spectrum clearly shows well-resolved rotational fine structure with a bandhead located at 25743 cm^{-1} and splitting due to the spin-rotation interaction. The signal to noise ratio of the strongest line is about 100. The frequency of each peak was measured using the GIESSEN program developed by Per Jensen.[20] In this measurement, the accuracy of the frequency is believed to be better than 0.001 cm^{-1} in favorable cases. From the spectrum observed, the frequency of 158 transitions has been measured, 79 transitions belonging to F_1 components and another 79 transitions belonging to F_2 components.

For the least squares fitting to the Hamiltonian given in Eq. (1), the transition peaks which are well-resolved are included with accuracy of 0.005 cm^{-1} which is believed to be the accuracy of this experiment. Of 158 transitions observed, 99 transitions have been included in the least squares fits. The frequency of the peaks blended with others was not included in the least squares fitting. The frequencies of the transitions observed in this work are listed in Table 1 together with the difference from the calculated frequencies using the parameters given in Table 2.

For the assignment of low N transitions which were strongly overlapped, the calculated intensity according to Mulliken[21]

has been used. In this calculation, F_1 components have a larger intensity than F_2. The difference in intensity is slight for high N values but quite appreciable for low N values.

Since very good ground splitting constant γ_0 was available from the millimeter wave work, we have constrained this value in the least squares fitting to that reported by Ito *et al.*[11] The molecular parameters obtained for a fit in which all of the parameters except γ_0 for the ground state were allowed to vary. The molecular parameters obtained from the least squares fit are given in Table 2.

The molecular parameters determined in this work are compared in Table 3 with the previous works.[12,13] Good agreement in band origin, rotational constants, and centrifugal distortion constants are found among the data.[3,22,23] Slight difference in splitting constant γ_0 in the excited state among the data mainly attributes to the maximum rotational quantum number involved in the fitting. Since the splitting between two components increases with increasing J number, it is believed that the inclusion of high J transitions is more important in the fitting. From the comparison of experimental frequencies with the calculated ones, the standard deviation of the fit is about 0.007 cm^{-1} which is slightly larger than that of the experimental accuracy because of the inclusion of weakly perturbed transitions.

Since the spectrum observed in this experiment shows high N transition up to 55, it may be necessary to include the sextic centrifugal distortion constants H_0 for the best fit. The value of H_0 was reported[12] to be an order of 10^{-12} compared to 10^{-5} for D_0. From the least squares fit, it was found that including H_0 did not improve the standard deviation of the overall fits significantly. Thus it can be suggested that the higher order centrifugal distortion constant do not play an important role in this case.

It is well known that one spin component of each of the $N=4$, 7, and 15 rotational levels of the B state is strongly perturbed by a rotational level of the same J in $v=10$ of the $A^2\Pi_i$ state.[24] As shown in Figure 1, there appear extra lines at 25772.3 and 25780.0 cm^{-1} resulting from $N=4$, 7 transitions originating in the perturbed A state level. The extra line resulting from $N=15$ is not clearly resolved well.

The intensity distribution of the transition peaks of the spectrum shown in Figure 1 indicates at least two quite different rotational temperatures being involved in the ex-

Table 3. Comparison of the Molecular Parameters[a]

Parameters	This work	Ref. (3)[b]	Ref. (12)[c]	Ref. (13)
X-state				
B_0	1.890955(28)	1.89108		1.89109115(45)
$D_0(10^5)$	0.6351(13)	0.64078		0.6432(19)
$\gamma_0(10^3)$	7.25505	7.258		7.25539(88)
B-state				
T_0	25797.8774(9)		25797.8665(1)	25797.8694(17)
B_0	1.958612(29)	1.95874±0.005	1.958816(26)	1.958713(18)
$D_0(10^5)$	0.6564(14)	0.6626±0.03	0.694(12)	0.6598(37)
$\gamma_0(10^3)$	15.915(32)	15.53±0.07	16.617(81)	17.14(14)

[a]In units of wavenumber (cm^{-1}). [b]The values in the ground state were given in Ref. (22). [c]The ground state was fixed to those given in Ref. (11)

Rotational Cooling of CN(B²Σ⁺) Radical

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pansion with He. From the experiment with Ar carrier under the exactly same conditions, it has been found that Ar is less efficient in rotational cooling precess which confirms the previous result.[3] The mechanism of the rotational cooling with different carrier gases will be discussed in the subsequent paper.

Conclusions

The present work has demonstrated that using a FT-spectrometer coupled with a technique of supersonic expansion is a very useful method for obtaining a high resolution spectra of unstable molecules. The emission spectrum of CN radical obtained by this method exhibits good resolution as well as very accurate frequencies up to the transitions of high *J*. Also, the least squares fitting of the observed frequencies has provided accurate molecular parameters which are in good agreement with the previous ones.

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Observation of Rotational Cooling of CN($B^2\Sigma^+$) Radical Generated in a Supersonic Expansion

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The CN($B^2\Sigma^+$) radical was produced in a jet using an electric dc discharge of the precursor CH_3CN with inert carrier gases. The rotationally resolved Fourier transform emission spectra of the 0-0 band of the $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ transition of CN have exhibited different distribution of the intensity for the carrier gases He and Ar, respectively. From the analysis of intensity distribution in the spectra, the mechanism for rotational cooling process of CN radical in a supersonic expansion has been suggested.

Introduction

The supersonic free jet expansion has become an important technique in spectroscopy since the first introduction

by Smalley *et al.*[1] It has made possible with free jet not only to obtain rotationally resolved spectra of large molecules at low temperature but also to study molecular clusters formed from the stable molecules.[2] Among many unstable mole-