

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 process 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.

Acknowledgements. This work was supported in part by the Korea Research Foundation through Non Directed Research Fund, 1993. The author thanks the Ohio State University for allowing to use the FT-spectrometer (Bruker IFS-120HR).

References

1. Griffiths, P. R. *Chemical Infrared Transform Spectroscopy*; John-Wiley & Sons: New York, New York, 1975.
2. Hollas, J. M. *Modern Spectroscopy*; John-Wiley & Sons: New York, New York, 1987.
3. Richard, E. C.; Donaldson, D. J.; Vaida, V. *Chem. Phys. Lett.* **1989**, 157, 295.
4. Lambert, D. L.; Brown, J. A.; Hinkle, K. H.; Johnson, H. R. *Astrophys. J.* **1984**, 284, 223.
5. Wootten, A.; Lichten, S. M.; Sahai, S.; Wannier, P. G. *Astrophys. J.* **1982**, 257, 151.
6. Johnson, J. R.; Fink, U.; Larson, H. R. *Astrophys. J.* **1983**, 270, 769.
7. Turner, B. E.; Gammon, R. H. *Astrophys. J.* **1975**, 198, 71.
8. Kratzer, A. *Ann. Phys.* **1923**, 71, 72.
9. Douglas, A. E.; Routly, P. M. *Atrophys. J. Suppl.* **1955**, 1, 295.
10. Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure, Vol. IV (Constants of Diatomic Molecules)*, Van-Nostrand-Reinhold: New York, New York, 1979.
11. Ito, H.; Kuchitsu, K.; Yamamoto, S.; Saito, S. *Chem. Phys. Lett.* **1991**, 186, 539.
12. Reh fuss, B. D.; Suh, M.-H.; Miller, T. A.; Bondybey, V. E. *J. Mol. Spectrosc.* **1992**, 151, 437.
13. Prasad, C. V. V.; Bernath, P. F.; Frum, C.; Engleman, Jr. R. *J. Mol. Spectrosc.* **1992**, 151, 459.
14. Prasad, C. V. V.; Bernath, P. F. *J. Mol. Spectrosc.* **1992**, 156, 327.
15. Engelking, P. C. *Rev. Sci. Instr.* **1986**, 57, 2274.
16. Lee, S. K.; Kim, U. S. *J. Korean Chem. Soc.* **1993**, 37, 371.
17. Lee, S. K. *Bull. Korean Chem. Soc.* **1993**, 14, 340.
18. Suh, M. H.; Lee, S. K.; Reh fuss, B. D.; Miller, T. A.; Bondybey, V. E. *J. Phys. Chem.* **1991**, 95, 2727.
19. Herzberg, G. *Molecular Spectra and Molecular Structure, Vol. 1 (Spectra of Diatomic Molecules)*, Van Nostrand Reinhold: New York, New York, 1950.
20. Jensen, P. *The Giessen Program Package*; Justus Liebig University: Giessen, Germany, 1990.
21. Mulliken, R. S. *Rev. Mod. Phys.* **1931**, 3, 89.
22. Cerny, D.; Bacis, R.; Guelachvili, G.; Roux, F. *J. Mol. Spectrosc.* **1978**, 73, 154.
23. Engleman, Jr. R. *J. Mol. Spectrosc.* **1974**, 49, 106.
24. Long, S. R.; Reilly, J. P. *J. Phys. Chem.* **1982**, 86, 56.

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

Sang Kuk Lee*, Iek Soon Choi, and Un Sik Kim

Department of Chemistry, College of Natural Sciences, Pusan National University, Pusan 609-735

Received November 19, 1993

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-

cules examined in the laboratory, CN radical has received much attention due to not only its abundance in a wide variety of extraterrestrial sources but also its strong fluorescence. The first analysis of the rotational structure of the $B^2\Sigma^+-X^2\Sigma^+$ band was carried out by Kratzer³ and by Jevons.⁴ Douglas and Routly⁵, and Huber and Herzberg⁶ have given a detailed review of the literature on this molecule.

In molecular spectroscopy, one of the most frequently used instruments is a Fourier transform (FT) spectrometer. Its advantages over the lasers are continuous tunability as well as accurate measurement of intensity of the transition peaks. Thus, most experiments on the transition intensity have been performed by using a FT-spectrometer under a precise condition of temperature and pressure.

Since 1970's, a FT spectrometer has been rapidly developed with advances in computation time and technique improving the signal to noise ratio of the spectra. Recently, it has become possible to obtain high resolution emission spectra of unstable molecules with a FT spectrometer in the UV/VIS region.⁷⁻⁹ From the analysis of intensity distribution of the FT emission spectra, the mechanism of the cooling process of the unstable molecules in a jet has been suggested. Similar works were also carried out on OH radical generated by a corona discharge.¹⁰ Very recently, Feher *et al.*¹¹ have used a diode laser kinetic spectroscopy to explain the mechanism of formation and decomposition of CN radical produced during a discharge pulse.

Thus, in this work, the FT emission spectroscopy coupled with a technique of supersonic expansion has been used to explain the mechanism of cooling process of CN radical in a jet. For this purpose, the effect of both carrier gases and concentration of the precursor, for the first time, has been measured from the spectra observed.

Experimental detail

The observation of CN emission spectra has been carried out using the experimental setup similar to those previously described.¹²⁻¹⁴ 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 made of stainless steel rod with a 2.0 mm diameter sharpened at the tip and inserted into the capillary through O-ring. The anode was connected a 3000 volts of dc power supply. The typical operating condition was 4-5 mA current. The discharge was stabilized using a 500 k Ω of current limiting ballast resistor. Since the tip was very sharp, small portion of the rod was through the orifice. Thus, CN radical was actually produced outside the nozzle. For the optimum discharge condition, the length of the tip outside the nozzle has been adjusted by a method of trial and error.

The precursor CH_3CN was expanded with an inert gas, He or Ar through a 0.2 mm diameter of quartz nozzle into the vacuum chamber which was made of a six-way cross Pyrex glass tube of 5.0 cm in diameter. In the case of nozzle with small pinhole, the discharge was quickly deteriorated with blocking the hole, while the rotational temperature was largely increased for large pinhole of nozzle. Of the several nozzles tested, 0.2 mm diameter of orifice with fairly round shape has worked well.

The concentration of CH_3CN in the gas mixture was con-

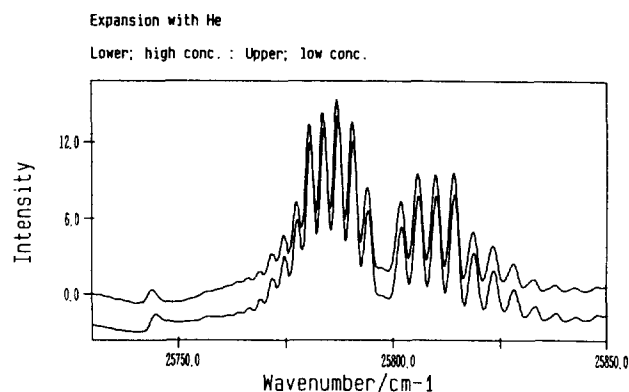


Figure 1. A portion of FT emission spectra of the 0-0 band of the $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ transition of CN radical generated in a supersonic expansion with He. The upper and lower parts were obtained at a limiting low and high concentration of CH_3CN , respectively. The numbers in the intensity are referenced to upper part. The lower part is shifted downward for easy comparison.

rolled by adjusting opening of the bypass valve connected to the sample chamber during the experiment. For the experiment of high concentration of sample, the vapor pressure of CH_3CN at room temperature was fed to the gas mixture. The amount of CH_3CN in the gas mixture is roughly estimated to be about 1.0 and 10.0% for a limiting low and high concentration in this experiment, respectively. The pressure of the gas mixture was about 2 atm inside the nozzle. The pressure in the vacuum chamber during operation was maintained to lower than 1.0 Torr by using a mechanical vacuum pump. With this difference in pressure, a rotational temperature of about 65 K has been easily achieved. However, using the boost pump (-40 CFM) could lower the rotational temperature of the sample to 50 K.¹⁵ The emission from CN radical in a jet was focussed onto the external port of a FT spectrometer using combination of 2 concave mirrors and 2 lenses. One ($f=5.0$ cm) of the quartz lenses has been placed 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 which was at 1000 volts dc potential. The output of PMT was 100 times amplified by a home-made ac preamplifier. For the improvement of signal to noise ratio of the spectrum, a B370 nm cutoff optical filter has been employed. The signal to noise ratio of the spectra was mainly limited by the source noise, *i.e.*, the fluctuations in the discharge intensity.

The spectral region from 25,000 to 28,000 cm^{-1} was scanned at the resolution of 2.0 cm^{-1} . Typically, 100 spectra have been averaged over 5 min to obtain the final spectra shown in Figures 1 and 2. The experiment has been repeated by varying the sample concentration as well as using different inert carrier gases.

Analysis and Discussion

The formation of CN radical from the precursor CH_3CN by an electric dc discharge can be proceed through two possible mechanisms.¹⁶ The first process is a formation of CN

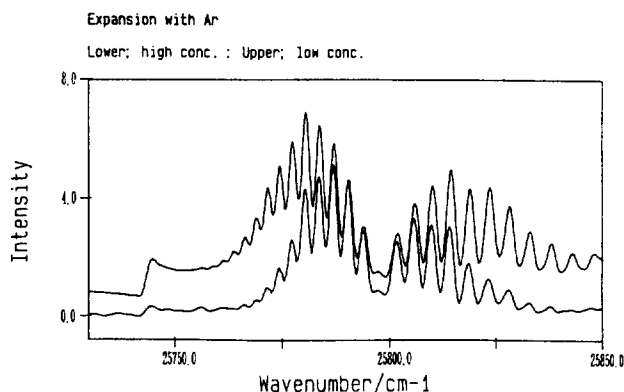
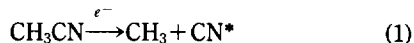
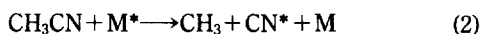


Figure 2. A portion of FT emission spectra of the 0-0 band of the $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ transition of CN radical generated in a supersonic expansion with Ar. The upper and lower parts were obtained at a limiting low and high concentration of CH_3CN , respectively. The numbers in the intensity are referenced to upper part. The upper part is shifted upward for easy comparison.

radical from direct decomposition of the precursor molecules by an electron bombardment such as.



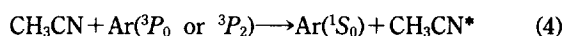
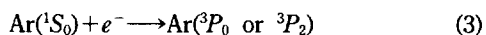
The second one is a decomposition of CH_3CN by a collision with a carrier gas as shown below.



where M^* denotes an inert carrier gas, He or Ar with excess energy.

The observation of intensity distribution in CN radical can be easily understood in terms of two different mechanisms of the formation at the electronically excited B state. From the measurement of the fluorescence intensity of CN radical, it has been found that the maximum intensity was obtained by adding small amount of CH_3CN in a large amount of carrier gas. It is believed, thus, that Eq. (2) is more favorable process rather than Eq. (1) in producing CN radical at the excited electronic state from CH_3CN . The similar results have been also reported by Engelking¹⁷ from the experiment using a corona discharge in a supersonic expansion.

The mechanism of the second process can be consisted of a series of reaction.¹⁸ First, electron from the anode collides with the carrier gas (Ar or He) promoting it to the metastable state which has enough energy to break down the chemical bond. Second, the metastable carrier gas loses the excess energy to the precursor molecule when it collides with. Finally the highly excited precursor molecule decomposes into the fragments. The whole processes can be written for a carrier gas, Ar as below



The energy levels of metastable $\text{Ar}(^3\text{P}_0)$ and $\text{Ar}(^3\text{P}_2)$ lie at

11.72 and 11.54 eV higher from the ground state, respectively.¹⁹ Producing $\text{CN}(B^2\Sigma^+)$ radical from CH_3CN requires an excitation energy $E \geq 8.22$ eV, hence these processes are energetically possible *via* dissociative excitation of CH_3CN . On the other hand, excitation to Penning ionization which subsequently leads to dissociation may not be expected to be significant because the energy level of CH_3CN^+ is 12 eV higher than the stable molecules.⁷ In the decomposition of CH_3CN^* , Eq. (5) generates the nascent CN radical which may be extremely hot with large amount of rotational energy as well as vibrational energy, while Eq. (6) produces relatively cold CN radical and hot CH_3 radical. From the examination of the intensity distribution over the vibrational states at the excited electronic state of the spectra, it has been found that the vibrational temperature of the $\text{CN}(B^2\Sigma^+)$ radical generated in this experiment was about 5500 ± 500 K after taking account of the Franck-Condon factors given by Sharp.²⁰ Thus, the most possible process for the generation of $\text{CN}(B^2\Sigma^+)$ radical from CH_3CN^* is given by Eq. (5) forming vibrationally hot CN radical. Also, there exists a small deviation from the single Boltzmann distribution in the least squares fitting to the spectra observed. However, this non-thermal factor may attribute to the nature of an electric dc discharge in a supersonic expansion. Similar results have been found from the previous experiment.¹⁷ Rotational cooling process in a supersonic expansion has been discussed in detail for OH radical by Droege and Engelking.¹⁰ As one possibility, the radical formed in the nozzle throat is initially cooled by expansion, then excited by a low momentum transfer mechanism such as electron impact to electronically excited, rotationally cold levels from which it radiates. Since this kinds of excitation spread the momentum into many parts, the molecular population at the excited electronic state is widely distributed over many rotational levels. Thus, this kind of process may produce a spectrum with many rotational peaks of comparable intensity. As another possibility, the discharge produces hot radicals in both ground and excited states, which subsequently relax during the expansion by collision. If rotational relaxation is much faster compared to the radiative lifetime of the radical, then rotationally cold spectrum could be observed. Since, however, vibrational relaxation is usually much slower than the rotational relaxation, the spectra must be consistent with a high vibrational temperature.

Figures 1 and 2 show the FT emission spectra of the 0-0 band of the $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ transition of CN radical generated in a jet with carrier gases He and Ar, respectively. The spectra were obtained with exactly same experimental conditions except for concentration of CH_3CN and carrier gas. The baseline of one of the spectra obtained has been shifted in the figures for clear comparison. Figure 1 shows the maximum intensity in the rotational quantum number $N=3$ located at 25786.9 and 25814.4 cm^{-1} for P- and R- branches, respectively. However, in Figure 2, the quantum number with maximum intensity increases with decreasing concentration of CH_3CN . The quantum number with maximum intensity is 3 for a limiting high concentration while it is 5 for a limiting low concentration. Also, it can be easily found that higher concentration of $\text{CN}(B^2\Sigma^+)$ radical is generated with He rather than with Ar from comparison of fluorescence

intensity.

On the other hand, it can be seen from Figure 1 that the intensity of fluorescence is independent of the concentration of CH_3CN in the gas mixture. With this observation, we can postulate that the amount of $\text{CN}(B^2\Sigma^+)$ radical generated in a jet is limited by the discharge current for this experiment, and, thus, the amount of unreacted CH_3CN in a jet rapidly increases with increasing concentration of the precursor. The formation of molecular cluster with CH_3CN is not feasible for case of this experimental condition due to the low backing pressure and an electric dc discharge.

It should be noted that the spectrum does not exhibit any sizable intensity of the bandhead located at 25743 cm^{-1} unless there is in a jet a Boltzmann distribution component with high rotational temperature ($>1000\text{ K}$). It is obvious, thus, that there are at least two kinds of rotational components, one at 55 and another one at $4500 \pm 500\text{ K}$ from the fitting of the spectra to the Boltzmann distribution. However, better agreement can be obtained between the experimental and calculated ones, if more than two Boltzmann distributions are included in the fit. Also, it is quite clear that the intensity of the bandhead reflects the contribution of the high temperature component to the whole spectrum, which can be more easily seen from the high resolution spectrum shown in Figure 1 of the preceding paper.¹⁵

For the effect of a carrier gas on rotational cooling, the spectra in Figure 1, obtained with He have been compared with those in Figure 2 taken with Ar. At a limiting high concentration, both spectra show almost same distribution of intensity over rotational quantum numbers, while at a limiting low concentration of CH_3CN , Figure 1 exhibits different distribution of intensity from Figure 2. The spectra in Figure 2 show increasing intensity of the bandhead with decreasing concentration of CH_3CN . From these observations, it is believed that He is more efficient than Ar in rotational cooling when excess CH_3CN does not exist in a jet. Thus, it can be suggested that the collision frequency play more important role than collision diameter in collisional relaxation process of CN. Similar result was also reported in the previous work.⁷ For concentration effect which has been observed for the first time, the spectra in each figure have been compared with each other. From Figure 1, any noticeable difference in intensity cannot be found with variation of CH_3CN concentration. However, large difference of the intensity distribution can be observed from Figure 2 with the CH_3CN concentration. For example, the degree of contribution of high temperature component to the whole spectrum decreases with increasing concentration. According to the well-known results,²¹ the effectiveness of quenching fluorescence increases with increasing number of internal modes of motion. For example, molecules with small spacings between the vibrational and rotational energy levels are more effective than those with larger spacings. Moreover, polar molecules are particularly effective. Consequently, CH_3CN should be much more effective than monatomic molecules Ar for quenching efficiency. Therefore, it can be reasonably suggested that overall rotational temperature of the CN emission spectrum be determined by the collision frequency for the case of He and by the effectiveness of collision with the excess CH_3CN for the case of Ar, respectively, even though

both spectra show the intensity distribution of same rotational temperature.

Conclusions

The present work has explained the rotationally cooling process of CN radical generated in a jet by observing the distribution of rotational intensity of the 0-0 band of the $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ transition with sample concentration and carrier gas for. From this experiment, it has been found that collision frequency is more important than collision diameter between He and Ar for rotational relaxation of $\text{CN}(B^2\Sigma^+)$ radical. Also, it can be suggested that excess CH_3CN in a jet play very important role in rotational cooling from the observation of concentration effect which has been applied for the first time.

Acknowledgements. This work was supported in part by the Korea Research Foundation through Non Directed Research Fund, 1993. Authors thank Professor Hosung Sun for his valuable discussions.

References

- Smalley, R. E.; Ramakrishna, B. L.; Levy, D. H.; Wharton, L. J. *Chem. Phys.* **1974**, *61*, 4363.
- Hollas, J. M. *Modern Spectroscopy*; John-Wiley & Sons: New York, New York, 1987.
- Kratzer, A. *Ann. Phys.* **1923**, *71*, 72.
- Jevons, W. *Proc. R. Soc. London* **1926**, *A112*, 407.
- Douglas, A. E.; Routley, P. M. *Astrophys. J. Suppl.* **1955**, *1*, 295.
- Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure Vol. IV, Constants of Diatomic Molecules*, Van Nostrand-Reinhold: New York, New York, 1979.
- Richard, E. C.; Donaldson, D. J.; Vaida, V. *Chem. Phys. Lett.* **1989**, *157*, 295.
- Rehfuss, B. D.; Suh, M.-H.; Miller, T. A.; Bondybey, V. E. *J. Mol. Spectrosc.* **1992**, *151*, 437.
- Prasad, C. V. V.; Bernath, P. F.; Frum, C.; Engleman, Jr. R. J. *J. Mol. Spectrosc.* **1992**, *151*, 459.
- Droege, A. T.; Engelking, P. C. *Chem. Phys. Lett.* **1983**, *96*, 316.
- Feher, M.; Rohrbacher, A.; Maier, J. P. *Chem. Phys.* **1993**, *173*, 187.
- Suh, M.-H.; Lee, S. K.; Rehfuss, B. D.; Miller, T. A.; Bondybey, V. E. *J. Phys. Chem.* **1991**, *95*, 2727.
- Lee, S. K.; Kim, U. S. *J. Korean Chem. Soc.* **1993**, *37*, 371.
- Lee, S. K. *Bull. Korean Chem. Soc.* **1993**, *14*, 340.
- Lee, S. K. *the preceding paper*.
- Suzuki, K.; Kuchitsu, K. *Bull. Chem. Soc. Japan* **1977**, *50*, 1449.
- Engelking, P. C. *Rev. Sci. Instru.* **1986**, *57*, 2274.
- Ozaki, Y.; Kondow, T.; Kuchitsu, K. *Chem. Phys.* **1983**, *77*, 223.
- Moore, C. E. *Atomic Energy Levels, Vol. 1*, NSRDS-NBS **35**, 1971.
- Sharp, C. M. *Astro. Astrophys. Suppl. Ser.* **1984**, *55*, 33.
- Castellan, G. W. *Physical Chemistry*, 3rd ed.; Addison-Wesley: Reading, Massachusetts, 1982.