BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 50 (11), 2896—2898 (1977)

Violet Emission Spectra of CN($B^2\Sigma$) Produced in the Photodissociation of HCN and DCN

Setsuko TATEMATSU and Kozo KUCHITSU

Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

(Received June 17, 1977)

Emission spectra of the CN violet band system ($B^2\Sigma$-$X^2\Sigma$, $\Delta v=0$) produced in the photodissociation of HCN and DCN by Lyman-α radiation (121.6 nm) were observed with resolution of about 0.2 nm and with sample pressures of 0.01—1.5 Torr. The spectral features of the two were similar, but the main peaks ($v'=0$—4) from DCN appeared more sharply than the corresponding peaks from HCN. The relative vibrational populations and the effective rotational temperatures were estimated by a band-envelope analysis. No indication of vibrational population inversion was observed. The CN($B^2\Sigma$) radical produced from DCN is likely to have slightly higher vibrational (0.31 ± 0.08 eV measured from the zero-point energy) and rotational energies (0.15 ± 0.02 eV) than that from HCN (0.23 ± 0.08 and 0.11 ± 0.02 eV, respectively).

There has recently been a spate of theoretical and experimental investigations on the photofragmentation of simple polyatomic molecules. Many of them provide valuable information on the partitioning of internal and kinetic energies of fragments.[1,2] Diatomic radicals produced from linear molecules, particularly the CN($B^2\Sigma$) radicals from various cyanides, have been studied most extensively.[3] For instance, the CN($B^2\Sigma$) radicals from cyanogen halides were analyzed in detail by Mele and Okabe[4] and were recently reinvestigated by Ashfold and Simons[5,6] with much higher resolution.

One of the problems of current interest is the isotope effect on the production of CN($B^2\Sigma$) from HCN/DCN by vacuum ultraviolet radiation. In a number of recent theoretical studies,[7–10] model repulsive potentials for the C–H/C–D bond were estimated by fitting the vibrational distributions of CN($B^2\Sigma$) from HCN observed by Mele and Okabe,[4] and isotope effects on the photofragmentation probability and the vibtational distributions for the krypton and xenon resonance lines were predicted. The predictions made by Band and Freed[7] and by Atabek *et al.*[9,10] differed drastically from each other, but they equally emphasized the importance of an experimental measurement of this isotope effect for the elucidation of the mechanism and dynamics of photodissociation. It should be ideal for this purpose if the CN violet and red emission bands from HCN and DCN by radiations of several different wavelengths were to be measured with high resolution and high accuracy.

The present study is our effort in this direction but only to the limit of our current experimental facilities.[11] Relative vibrational distributions of the CN($B^2\Sigma$) produced from HCN and DCN with various sample pressures by Lyman-α radiation (121.6 nm) have been estimated by analyzing the violet emission spectra measured with medium resolution. The rotational distributions have been estimated by band-envelope simulation.

Experimental

The apparatus and experimental details have been reported previously.[11] The Lyman-α radiation was obtained by 2.45 GHz microwave discharge of a 1 : 3 mixture of hydrogen and helium. Fluorescence in the visible region from the sample cell was detected by a Nikon P-250 grating monochromator (1200 Gr/mm) blazed at 500 nm. The CN violet $\Delta v=0$ bands around 388 nm were observed with slit widths of 40—60 μm. The slit width of 50 μm corresponds to an energy resolution of about 0.2 nm. The signal from a photomultiplier (HTV R585) was measured by a photon counting system.

The sample of HCN was prepared by the reaction[12] of sodium cyanide with sulfuric acid at 60—80 °C. DCN was prepared in a similar way, D_2SO_4 and D_2O being used in place of H_2SO_4 and H_2O. The samples were purified by vacuum distillation. An infrared spectrum of HCN showed no trace of impurity. The isotopic purity of DCN was estimated from the Balmer emission intensities of H and D atoms produced by impact of 200 eV electrons.[13] The upper limit of hydrogen impurity was estimated from the observed intensity ratio to be about 10%.

Analysis

Spectral Features. The $\Delta v=0$ sequences of the CN violet band ($B^2\Sigma$-$X^2\Sigma$) produced from HCN and DCN were observed at pressures ranging from 0.01 to 1.5 Torr. The spectra observed around 388 nm were assigned according to the table prepared by Pearse and Gaydon.[14] The $\Delta v=-1$ sequence was also observed around 420 nm, but it was much weaker than the $\Delta v=$

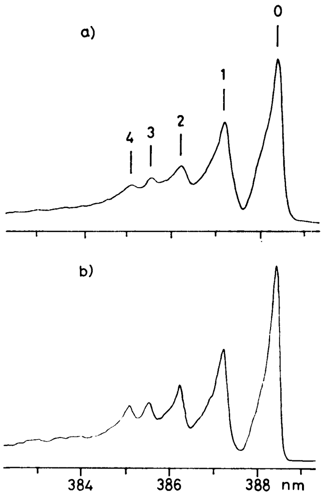

Fig. 1. Emission spectra of the CN violet ($B^2\Sigma$-$X^2\Sigma$) $\Delta v=0$ band from a) HCN, 0.04 Torr and b) DCN, 0.02 Torr with a slit width of 50 μm. The numbers indicate positions of the P-branch heads of the $v'=$ 0—4 bands.

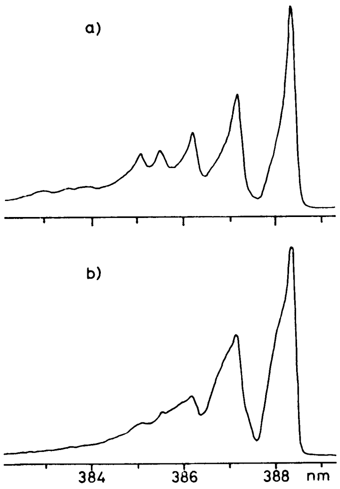

Fig. 2. Typical pressure dependence of the CN($B^2\Sigma$-$X^2\Sigma$) $\Delta v=0$ band from DCN at a) 0.01 Torr and b) 0.62 Torr. The effective rotational temperatures were estimated from best-fit analysis to be a) 1700±200 K and b) 1000±200 K.

0 sequence. Though the isotope effect on the emission yield was not measured quantitatively, there appeared to be no drastic isotope difference at this wavelength. Typical emission spectra measured under similar experimental conditions and at the lowest practicable sample pressures are shown in Fig. 1. The peak intensities of the bands decreased monotonically from $v'=0$ to 4, and no anomalous population distributions were observed. The bands from DCN had sharper peaks than those from HCN. The rotationally perturbed lines[5,6,15] were not observed significantly, but the spectral resolution was insufficient to prove or disprove their presence.

For both species the spectral features were essentially independent of the sample pressure below about 0.4 Torr, but they started to change when the pressure was further increased, as shown in Fig. 2: At a higher pressure the peaks were broadened and those with $v'=2$—4 became obscured. This trend has not been observed clearly for other cyanides studied concurrently[11,16] (BrCN, ICN, and $(CN)_2$).

Band-Envelope Analysis. The vibrational populations, $P_{v'}$, and the effective rotational temperatures, $T_r(v')$, of the CN($B^2\Sigma$) states immediately after production from HCN and DCN, *i.e.*, essentially free from subsequent collisional relaxations, were estimated by a band-envelope analysis.[11,17,19] Since the bands with $v'=5$—10 were buried within those of the lower vibrational levels, only crude estimates of $P_{v'}$ for $v'\geqq 5$ could be obtained. In addition, since the rotational lines were not resolved, the effective rotational temperatures for all the vibrational states were assumed to be equal. The parameters, $P_{v'}$ and T_r, were adjusted by trial and error to obtain the best fit of the calculated band envelope to the observed spectrum. A typical comparison of the observed and calculated band envelopes is shown in Fig. 3. The effective rotational temperatures were thus estimated to be 1300±200 and 1700±200 K for HCN and DCN, respectively. The relative vibrational populations, $P_{v'}/P_0$, in the low-pressure limit are listed in Table 1.

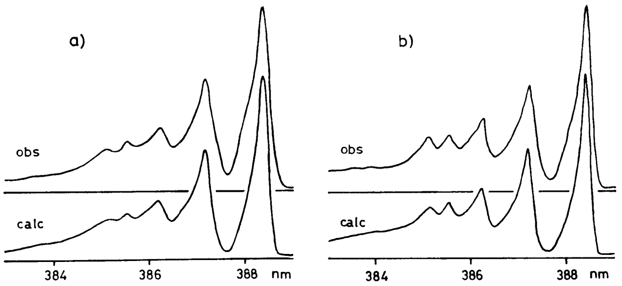

Fig. 3. Comparisons of the observed and best-fit calculated band envelopes of the CN($B^2\Sigma$-$X^2\Sigma$) $\Delta v=0$ from (a) HCN and (b) DCN.

TABLE 1. RELATIVE VIBRATIONAL POPULATIONS ($P_{v'}/P_0$) FOR CN($B^2\Sigma$) PRODUCED IN THE PHOTODISSOCIATION OF HCN AND DCN

v'	HCN[a)]	DCN[a)]	HCN[b)]
0	1.00	1.00	1.00
1	0.54(5)	0.56(5)	0.40
2	0.20(5)	0.28(5)	0.09
3	0.10(4)	0.17(4)	0.012
4	0.06(3)	0.09(3)	0.006
5	0.04	0.07	—
6	0.02	0.04	—
7	<0.01	0.01	—

a) The present study, by Lyman-α radiation (121.6 nm). Uncertainties represent estimated limits of error in the last significant digits. The relative populations for $v'\geqq 5$ are only crude estimates. b) Crude estimates made by Mele and Okabe (Ref. 4) for the CN($B^2\Sigma$) produced by krypton resonance lines (116.5 and 123.6 nm).

Discussion

Distributions of Internal Energy. By use of the relative populations estimated in Table 1 and the known vibrational energy levels,[20] the average vibrational energies (above the zero-point energy) of the CN($B^2\Sigma$) produced from HCN and DCN are calculated to be 0.23±0.08 and 0.31±0.08 eV, respectively. The average rotational energies, given by kT_r, are estimated to be 0.11±0.02 and 0.15±0.02 eV for HCN and DCN, respectively. The estimated uncertainties include those due to the overlapping of the observable bands, the approximations made in the analysis, and the various sources of experimental error.

The available excess energy in the production of CN($B^2\Sigma$) from HCN corresponds to the difference between the photon energy (10.2 eV) and the sum of the C–H bond dissociation energy (5.2[21] or 5.5[22] eV) and the electronic energy of CN($B^2\Sigma$) from the ground vibrational state of CN($X^2\Sigma$) (3.1 eV).[23] Thus, the fractions of the available energy used for vibrational and rotational excitations are about 15 and 8%, respectively. These estimates agree with those reported by Mele and Okabe[4] for the CN($B^2\Sigma$) produced from HCN by the Kr (and Xe) resonance lines, about 13 and 7%.

Notwithstanding the appreciable uncertainties estimated above, the present study indicates slight isotope effects on the vibrational and rotational excitations of CN($B^2\Sigma$) produced from HCN and DCN.[24] A further more accurate measurement is necessary for a critical comparison of experimental and theoretical distributions of vibrational and rotational energies. In this connection, it is noteworthy that significant isotope effects on the vibrational and rotational distributions of CN($B^2\Sigma$) produced from HCN and DCN have been found in our recent study of electron-impact dissociation (*ca.* 200 eV) with much higher resolution.[25]

Pressure Effect. The observed changes in the spectrum when the sample pressure is higher than 0.4 Torr— the decrease in the peak intensities corresponding to $v'=2$—4 and the apparent decrease in the effective rotational temperatures— may be ascribed to collisional relaxations. If one assumes that the rotational relaxation takes place effectively at about 0.5 Torr, where the mean time between the formation of the CN($B^2\Sigma$) radicals and their collisions with the parent molecules is comparable with their natural radiative lifetime (presumably about 60 ns[26—28]), then it is possible to estimate roughly the effective cross section for the rotational relaxation of CN($B^2\Sigma$). Since the mean velocity of CN($B^2\Sigma$) is estimated to be about 6×10^4 cm/s, the cross section for rotational relaxation is probably of the order of 150 Å^2.

The research has been supported by Science and Technology Grants of Toray Science Foundation.

References

1) S. A. Rice, "Dynamics of Primary Photochemical Processes" in "Excited States," Vol. 2, E. C. Lim, Ed., Academic Press, New York (1975), pp. 111—320.

2) J. P. Simons, "The Dynamics of Photodissociation," Chemical Society Specialist Periodical Reports, Gas Kinetics and Energy Transfer, Vol. 2, London (1977), p. 56.

3) S. Mukamel and J. Jortner, *J. Chem. Phys.*, **65**, 3735 (1976) and the references cited therein.

4) A. Mele and H. Okabe, *J. Chem. Phys.*, **51**, 4798 (1969).

5) M. N. R. Ashfold and J. P. Simons, *Chem. Phys. Lett.*, **47**, 65 (1977).

6) M. N. R. Ashfold and J. P. Simons, *J. Chem. Soc., Faraday Trans. 2*, **73**, 858 (1977).

7) Y. B. Band and K. F. Freed, *Chem. Phys. Lett.*, **28**, 328 (1974).

8) Y. B. Band and K. F. Freed, *J. Chem. Phys.*, **63**, 4479 (1975).

9) O. Atabek, J. A. Beswick, R. Lefebvre, S. Mukamel, and J. Jortner, *J. Chem. Phys.*, **65**, 4035 (1976).

10) O. Atabek, J. A. Beswick, R. Lefebvre, S. Mukamel, and J. Jortner, *Chem. Phys. Lett.*, **45**, 211 (1977).

11) S. Tatematsu, T. Nakagawa, T. Kondow, and K. Kuchitsu, *Bull. Chem. Soc. Jpn.*, **50**, 1056 (1977).

12) G. Bauer, "Handbook of Preparative Inorganic Chemistry," Vol. 1, Academic Press, New York (1963).

13) I. Nishiyama, private communication, 1976.

14) R. W. B. Pearse and A. G. Gaydon, "The Identification of Molecular Spectra," John Wiley & Sons, Inc., New York (1963).

15) H. E. Radford and H. P. Broida, *Phys. Rev.*, **128**, 231 (1962); *J. Chem. Phys.*, **38**, 644 (1963).

16) S. Tatematsu and K. Kuchitsu, unpublished data.

17) T. Urisu and K. Kuchitsu, *Chem. Phys. Lett.*, **18**, 337 (1973).

18) T. Urisu and K. Kuchitsu, *J. Photochem.*, **2**, 409 (1973).

19) I. Tokue, T. Urisu, and K. Kuchitsu, *J. Photochem.*, **3**, 273 (1975).

20) R. J. Fallon, J. T. Vanderslice, and R. D. Cloney, *J. Chem. Phys.*, **37**, 1097 (1962).

21) D. D. Davis and H. Okabe, *J. Chem. Phys.*, **49**, 5526 (1968).

22) B. deB Darwent, "Bond Dissociation Energies in Simple Molecules," NSRDS-NBS 31, U. S. Government Printing Office, Washington, D. C. (1970).

23) W. Jevons, *Proc. R. Soc. London, Ser. A*, **112**, 407 (1926).

24) The difference of 0.07 eV in the available energies, originating from the difference in the zero-point energies of HCN and DCN, is expected to have no appreciable influence on the isotope effect (unless the photon energy is very close to the threshold). This is because only a small fraction of the already small difference in the energies for the isotopic molecules is converted into the internal energy.

25) I. Nishiyama, I. Tokue, and K. Kuchitsu, to be published.

26) H. S. Liszt and J. E. Hesser, *Astrophys. J.*, **159**, 1101 (1970).

27) C. K. Luk and R. Bersohn, *J. Chem. Phys.*, **58**, 2153 (1973).

28) W. M. Jackson, *J. Chem. Phys.*, **61**, 4177 (1974).