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Infrared spectra of $(HCN)_n$ clusters in low-temperature argon matrices[1]

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Abstract

The infrared spectra of the HCN monomer, linear $(HCN)_2$ and cyclic $(HCN)_3$ were measured using a low-temperature matrix isolation technique. Linear $(HCN)_2$ and cyclic $(HCN)_3$ were produced by the photolysis of s-tetrazine and s-triazine respectively. Vibrational analyses of the infrared bands for the C–H stretching, the C–N stretching and H–C–N bending modes were performed with the aid of ab initio calculations; geometrical optimization was carried out using the density functional theory (DFT) method with a 6-31++G** basis set. © 1997 Elsevier Science B.V.

Keywords: HCN clusters; Infrared spectra; Matrix isolation

1. Introduction

Matrix isolation infrared spectroscopy is one of the preferred techniques for the investigation of clusters. In the low-temperature environment composed of inert rare gas atoms, clusters are stabilized by relaxation of the excess energy and monitored by infrared spectroscopy. Vibrational analyses of the infrared spectra of clusters provide important information on their geometrical structures. For example, methanol clusters have been studied by this technique with the conclusion that the geometrical structure of $(CH_3OH)_3$ clusters is cyclic [1].

The infrared spectra of the HCN monomer and clusters in solid argon have been reported by some research groups. King and Nixon [2] observed the infrared spectra of HCN and DCN in Ar matrices at temperatures from 4.5 to 20.5 K. They concluded that the dimer had a linear or nearly linear structure. The infrared spectra of linear $(HCN)_3$ and $(HCN)_4$ were measured by Walsh et al. [3]. Recently, Beichert et al. [4] have studied the cluster formation of HCN in molecular beams and argon matrices. They observed the C–H stretching infrared bands of some cyclic clusters.

An interesting and intriguing approach for the production of $(HCN)_2$ and $(HCN)_3$ was reported by Pacansky [5] and Schrems et al. [6]. They isolated s-tetrazine or s-triazine in solid argon and irradiated the matrix samples with visible or UV light in order to produce $(HCN)_2$ or $(HCN)_3$. However, no infrared band for the C–N stretching or H–C–N bending mode for cyclic $(HCN)_3$ has been reported. In the present study, the infrared spectra of the HCN monomer, linear $(HCN)_2$ and cyclic $(HCN)_3$ were measured, and vibrational analyses were performed of the C–H stretching, C–N stretching

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[1] Dedicated to Professor Kozo Kuchitsu on the occasion of his 70th birthday.

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and H–C–N bending regions with the aid of ab initio calculations.

2. Experimental details

Hydrogen cyanide (HCN) was prepared by dropwise addition of concentrated H_2SO_4 to a small amount of KCN and used after vacuum distillation. s-Tetrazine was synthesized from formamidine acetate and hydrazine hydrate according to the method given by Marcelis and van der Plas [7]. A commercial sample of s-triazine was purchased from Tokyo Kasei Kogyo Co. Ltd. (better than 95% purity). Samples for matrix isolation were prepared by mixing hydrogen cyanide, s-tetrazine or s-triazine vapour at room temperature with argon gas (Takachiho Co., 99.9999% purity). The mixing ratio of the sample to argon was about 1 : 1000.

A diagram of the experimental system used is shown in Fig. 1. The sample chamber was connected to a turbomolecular pump (Mitsubishi Co. Ltd., model PT-150) and a rotary pump (Alcatel model 2010). Pressures in the sample chamber were typically less than 1×10^{-7} Torr after baking out at 360 K for 10 h. Traces of residual gas, such as water vapour, were monitored by a gas analyser with a mass filter (Anelva, model QIG-066). The cryostat used was a closed cycle helium refrigeration unit (CTI Cryogenics Co. Ltd., model M-22). Infrared spectra were measured by an FTIR spectrophotometer (JEOL, model JIR-7000), in which the infrared beam was introduced from the spectrophotometer to the sample chamber using concave and flat mirrors. The liquid nitrogen-cooled MCT detector was also placed outside the spectrophotometer. Spectra were taken at a resolution of 0.5 cm^{-1} and accumulated 64 times. A superhigh-pressure mercury lamp (Ushio Electronics Co. Ltd., model UI-501C) was used for the photolysis of s-tetrazine or s-triazine in an argon matrix. A water filter was placed between the mercury lamp and the sample chamber to remove any thermal reaction of the matrix sample. A cut-off filter (Toshiba, Y-49) was used in the photolysis of s-tetrazine.

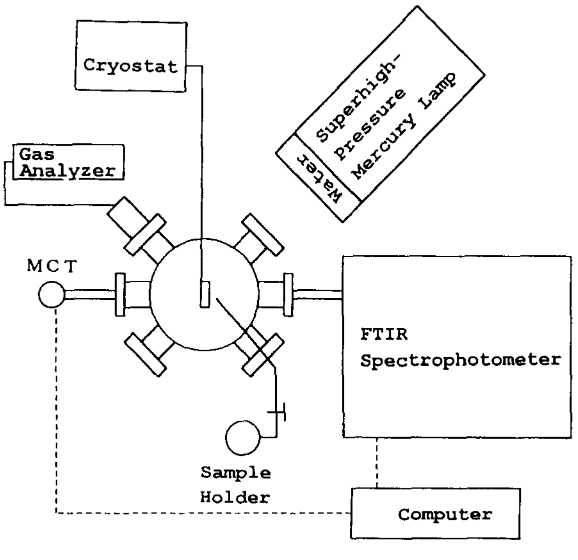


Fig. 1. Diagram of the experimental set-up.

3. Results and discussion

3.1. HCN monomer

The infrared spectrum of the matrix sample of HCN/Ar is shown in Fig. 2(a); bands due to the C–H stretching, C–N stretching and H–C–N bending modes of the HCN monomer are observed at 3306, 2098 and 721 cm^{-1}. They correspond to the results (3306, 2098 and 720 cm^{-1} respectively) reported by Abbate and Moore [8] within a few cm^{-1}. As suggested by previous workers [2,3,8], the weak band appearing at 3202 cm^{-1} is assigned to the hydrogen-bonded C–H stretching mode of linear $(HCN)_2$. Bands due to the other vibrational modes of linear $(HCN)_2$ are also observed at 2114, 2093, 796 and 733 cm^{-1}, as described later. Other weak bands may be due to larger clusters.

3.2. Linear $(HCN)_2$

The matrix sample of s-tetrazine/Ar was irradiated with UV light from a superhigh-pressure mercury lamp through water and cut-off filters. It is well known that N_2 and two HCN molecules are produced by the photolysis of s-tetrazine in the gas phase [9] and in matrix-isolated states [5] (Scheme 1).

An infrared difference spectrum of the observations before and after irradiation is shown in Fig. 2(b). Two C–H stretching bands are observed at 3304 and

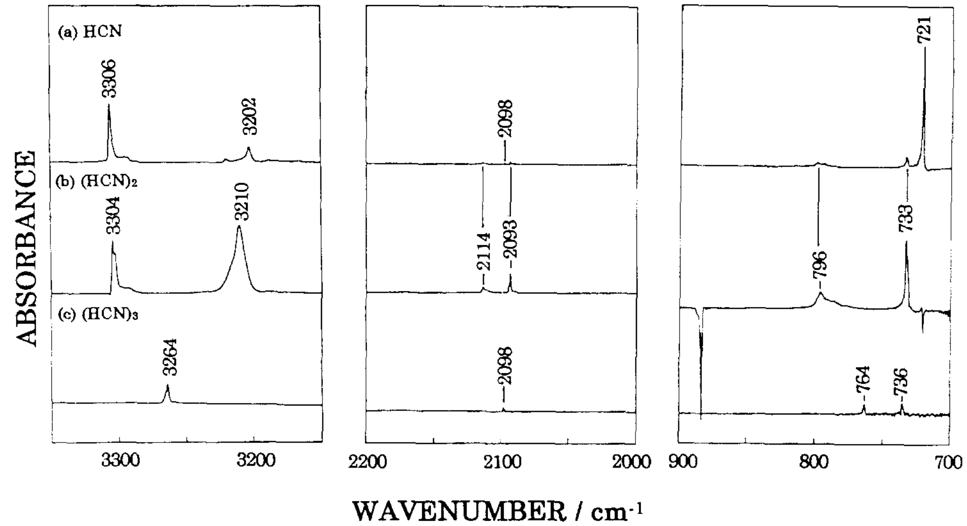


Fig. 2. Infrared spectra of $(HCN)_n$ clusters in low-temperature argon matrices: (a) HCN/Ar = 1/1000; (b) linear $(HCN)_2$ produced by photolysis of s-tetrazine; (c) cyclic $(HCN)_3$ produced by photolysis of s-triazine.

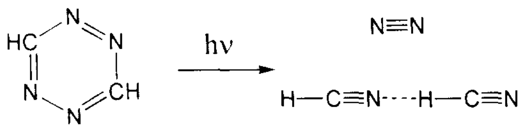
3210 cm^{-1}. The higher frequency band is easily assigned to the free C–H stretching mode, because its frequency is almost identical with that of the monomer. The lower frequency band, which shows about a 100 cm^{-1} shift from the HCN monomer band, is assigned to the hydrogen-bonded C–H stretching mode. The width of this band seems to be larger, probably because of the influence of the co-photoproduct N_2. When the matrix sample is annealed at 30 K after irradiation, the intensity of the 3210 cm^{-1} band decreases and a new band appears at 3202 cm^{-1}. This new band corresponds to that of linear $(HCN)_2$ in the HCN/Ar matrix sample shown in Fig. 2(a). This implies that the HCN dimer produced by the photolysis of s-tetrazine is slightly different from the stable linear $(HCN)_2$.

In the C–N stretching region, two bands are observed at 2114 and 2093 cm^{-1}, which are assigned to the bound and free C–N stretching modes of linear $(HCN)_2$ respectively. Two bands are also observed at 796 and 733 cm^{-1}, which are assigned to the hydrogen-bonded and free H–C–N bending modes respectively, as concluded by Pacansky [5]. These four bands do not shift on annealing.

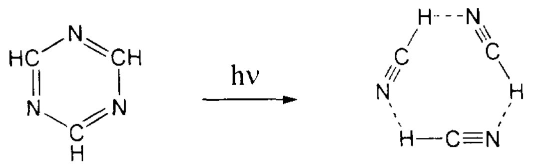
3.3. Cyclic $(HCN)_3$

The matrix sample of s-triazine/Ar was irradiated with UV light from a superhigh-pressure mercury lamp through a water filter. It is well known that three HCN molecules are produced by the photolysis of s-triazine in the gas phase [10] and matrix-isolated states [6] (Scheme 2).

An infrared difference spectrum of the observations before and after irradiation is shown in Fig. 2(c). Only one band is observed at 3264 cm^{-1} in the C–H stretching region. This means that the three HCN molecules are located in an equivalent environment, i.e. in cyclic $(HCN)_3$. This is consistent with the result of Schrems et al. [6]. A small amount of cyclic $(HCN)_3$ exists in the gas phase. Jucks and Miller [11] analysed the rotationally resolved infrared band of the C–H



Scheme 1.



Scheme 2.

Table 1
Calculated and observed vibrational frequencies of $(HCN)_n$ clusters (cm^{-1})

	C–H stretch		C–N stretch		H–C–N bend		Comment
	Obs.	Calc.[a]	Obs.	Calc.[a]	Obs.	Calc.[a]	
HCN	3306	3306	2098	2098	721	721[b]	
Linear $(HCN)_2$	3304	3303	2114	2111	733	728[b]	HCN···
	3210	3219	2093	2088	796	850[b]	···HCN
Cyclic $(HCN)_3$	3264	3274[b]	i.a.[c]	2097	764	774	i.p.[d]
	i.a.	3269	2098	2096[b]	i.a.	768[b]	i.p.
					i.a.	740	o.p.[e]
					736	736[b]	o.p.

[a] Scaling factors are assumed to be 0.955, 0.952 and 0.960 for C–H stretching, C–N stretching and H–C–N bending respectively (see text).
[b] Degenerate mode.
[c] Infrared-inactive mode.
[d] In-plane mode.
[e] Out-of-plane mode.

stretching mode, where cyclic $(HCN)_3$ was assumed to be an oblate planar symmetric top. They determined its central frequency to be 3274 cm^{-1}, which is shifted by about 10 cm^{-1} from our result.

In the C–N stretching region, only one band appears at 2098 cm^{-1}. When the matrix sample is annealed after irradiation, no spectral change is observed. It is concluded that cyclic $(HCN)_3$ is stable in argon matrices.

Cyclic $(HCN)_3$ has in-plane and out-of-plane H–C–N bending modes, observed at 764 and 736 cm^{-1} respectively. To our knowledge, this is the first report on the infrared bands for the C–N stretching and H–C–N bending modes of cyclic $(HCN)_3$. The observed vibrational frequencies for the HCN monomer, linear $(HCN)_2$ and cyclic $(HCN)_3$ are summarized in Table 1.

3.4. Ab initio calculations

Ab initio calculations with the GAUSSIAN 94 computer program package [12] were performed at the 6-31++G** basis set level. The hybrid density functional [13], in combination with the Lee, Yang and Parr correlation functional (B3-LYP) [14], was used to optimize the geometrical structures of the HCN monomer, linear $(HCN)_2$ and cyclic $(HCN)_3$. In the case of cyclic $(HCN)_3$, it was found that the dihedral angle composed of two HCN molecules was less than 0.2°. Therefore we re-optimized the geometry on the assumption that cyclic $(HCN)_3$ is planar with C_{3h} symmetry. The optimized structures of the HCN monomer, linear $(HCN)_2$ and cyclic $(HCN)_3$ are shown in Fig. 3.

The calculated vibrational frequencies of the C–H stretching, C–N stretching and H–C–N bending modes for the HCN monomer are 3461.8, 2202.9 and 751.1 cm^{-1} respectively. A comparison of these

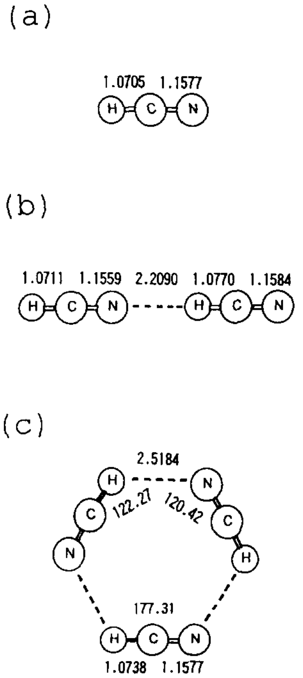


Fig. 3. B3-LYP/6-31++G** optimized structures: (a) HCN monomer; (b) linear $(HCN)_2$; (c) cyclic $(HCN)_3$. Bond lengths (in angstroms) and bond angles (in degrees) are given.

values with the observed frequencies produced scaling factors of 0.955, 0.952 and 0.960 for the C–H stretching, C–N stretching and H–C–N bending modes respectively. These scaling factors were then used to scale the vibrational frequencies for the HCN clusters. The scaled vibrational frequencies are listed in Table 1 with the corresponding observed values. They are consistent (within 10 cm^{-1}) with each other, except for the hydrogen-bonded H–C–N bending mode of linear $(HCN)_2$.

Pai et al. [15] have utilized ab initio calculations to investigate the reaction mechanisms for the formation and decomposition of s-triazine. They also used the MP2/cc-pVTZ method to calculate the vibrational frequencies for cyclic $(HCN)_3$. They predicted the doubly degenerate C–H asymmetric stretching mode to be 3274 cm^{-1}, which is comparable with our result. The doubly degenerate C–N asymmetric stretching mode was 2033 cm^{-1}, which seems to be rather low. On the other hand, the out-of-plane and in-plane H–C–N bending modes were 769 and 729 cm^{-1} respectively. These non-scaled frequencies correspond to our experimental values.

4. Conclusions

The infrared spectra of the HCN monomer, linear $(HCN)_2$ and cyclic $(HCN)_3$ in low-temperature argon matrices were measured using an FTIR spectrophotometer. The infrared bands of the C–H stretching mode for linear $(HCN)_2$, produced by the photolysis of s-tetrazine, showed an 8 cm^{-1} shift from those for the matrix sample of HCN/Ar. The infrared bands of the C–H stretching, C–N stretching and H–C–N bending modes for cyclic $(HCN)_3$, produced by the photolysis of s-triazine, were also observed. Their frequencies were consistent with those of ab initio calculations.

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References

[1] S. Coussan, N. Bakkas, A. Loutellier, J.P. Perchard, S. Racine, Chem. Phys. Lett. 217 (1994) 123.
[2] C.M. King, E.R. Nixon, J. Chem. Phys. 48 (1968) 1685.
[3] B. Walsh, A.J. Barnes, S. Suzuki, W.J. Orville-Thomas, J. Mol. Spectrosc. 72 (1978) 44.
[4] P. Beichert, D. Pfeiler, E. Knözinger, Ber. Bunsenges. Phys. Chem. 99 (1995) 1469.
[5] J. Pacansky, J. Phys. Chem. 81 (1977) 2240.
[6] O. Schrems, M. Huth, H. Kollhoff, R. Wittenbech, E. Knözinger, Ber. Bunsenges. Phys. Chem. 91 (1987) 1261.
[7] A.T.M. Marcelis, H.C. van der Plas, J. Heterocycl. Chem. 24 (1987) 545.
[8] A.D. Abbate, C.B. Moore, J. Chem. Phys. 82 (1985) 1255.
[9] L. Nahon, P. Morin, M. Larzilliere, I. Nenner, J. Chem. Phys. 96 (1992) 3635, and references cited therein.
[10] T. Gejo, J.A. Harrison, J.R. Huber, J. Phys. Chem. 100 (1996) 13941, and references cited therein.
[11] K.W. Jucks, R.E. Miller, J. Chem. Phys. 88 (1988) 2196.
[12] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T.A. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, J. Cioslowski, B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzalez, J.A. Pople, GAUSSIAN 94, Gaussian Inc., Pittsburgh, PA, 1995.
[13] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.
[14] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785.
[15] S.V. Pai, C.F. Chabalowsky, B.M. Rice, J. Phys. Chem. 100 (1996) 5681.