ELSEVIER

Spectrochimica Acta Part A 58 (2002) 73–78

SPECTROCHIMICA
ACTA
PART A

www.elsevier.com/locate/saa

Infrared spectrum of solid isocyanic acid (HNCO): vibrational assignments and integrated band intensities

M.S. Lowenthal [a,*], R.K. Khanna [a], Marla H. Moore [b]

[a] *Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742, USA*
[b] *Code 691, Goddard Space Flight Center, Greenbelt, MD 20771, USA*

Received 19 March 2001; accepted 21 April 2001

Abstract

Infrared spectra of thin films of solid HNCO condensed from the gas phase are characterized in terms of their vibrational frequencies, mode assignments, and integrated band intensities at low temperatures (~20–145 K). Isocyanic acid is shown to react with water (H_2O) and ammonia (NH_3) even at low temperatures; consequently, it may be an important species in the chemistry of interstellar ices and comets. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Isocyanic acid; Infrared spectroscopy; Solid-state; Absolute intensities; Interstellar ices

1. Introduction

Isocyanic acid is the simplest molecule containing all four of the elements (H, C, N, O) of the biosphere. It is among more than 100 molecules presently identified in the gas phase in the interstellar medium [1]. As such, it is possible that HNCO is a relevant molecule in the chemistry of comets as well. Even though the solid phase of HNCO has not yet been detected in interstellar grains, several other molecular species (e.g. CH_4, CO_2, NH_3, H_2O) are characterized by astronomers as ices on interstellar grains. In several recent reports [2–7] identifications of absorption peaks at 6.85 μm (1470 cm^{-1}) and 4.6 μm (2170 cm^{-1}) have been suggested to be due to NH_4^+ and OCN^- ions, respectively. Production of these ionic species in interstellar icy grains may be due to cosmic processing by cosmic rays and/or UV photons. A complete understanding of the infrared spectrum of solid HNCO is desirable in order to evaluate its role in the production of other C, H, N and O containing species in the interstellar medium. In this report we present a complete characterization of the infrared bands of solid HNCO at low temperatures (20–145 K) in terms of the peak frequencies and their integrated band intensities. Preliminary results of possible reactions of HNCO with H_2O and NH_3 leading to a complex species are also reported here, but the major thrust is to give the complete vibrational assignments of solid HNCO.

---

* Corresponding author. Tel.: +1-301-405-7022; fax: +1-301-314-9121.

PII: S1386-1425(02)00524-8

Isocyanic acid, the most stable isomer of cyanic acid, has been investigated by infrared spectroscopy as a gas and as a matrix-isolated species [8–12]. The data on the gas phase vibrational frequencies of HNCO is complete, but the IR spectrum of the solid phase (which is fundamental to the characterization of the interstellar species) is not known except for a recent communication [10] which identifies three of the six vibrational modes of solid HNCO. In this report, we present the infrared spectrum of a condensed thin film of HNCO from 4000 to 400 cm^{-1} at low temperature (20–145 K). For absolute intensity determination, the real part of the refractive index and the thickness of the film are determined from the interference fringes overlaying the absorption bands.

2. Experimental

A number of methods reported in the published literature were attempted to synthesize HNCO. Reaction of sodium cyanate (NaOCN) with an acid (concentrated as well as dilute) produced relatively large amounts of CO_2 in addition to the desired product, HNCO. The vapor pressures of CO_2 and HNCO are similar, and therefore purification of the compound by vacuum distillation was unsuccessful. Production of HNCO by thermal decomposition of isocyanuric acid (a trimer of HNCO) also produced decomposition of the sample and low product yield. The best yield of the pure compound was obtained by reaction of NaOCN with HCl gas. NaOCN (Aldrich Chemical Co., 96%) was contained in a flask connected to a vacuum manifold that was then evacuated. Hydrogen chloride gas (Aldrich Chemical Co., 99%) was added to the manifold at a measured pressure and was then frozen onto the NaOCN solid by immersing the NaOCN-containing flask into a liquid nitrogen bath. On repeated warming and freezing of the sample, a reaction resulted yielding almost pure HNCO with less than 0.1% CO_2. The sample was then transferred to a collection tube and kept at liquid nitrogen temperature until it was deposited on a cold substrate for spectroscopic evaluation.

IR spectra were recorded on a Perkin-Elmer GX FTIR instrument with a resolution of 2.0 cm^{-1}. Low temperature spectra were recorded by depositing the sample on a KRS-5 substrate attached to the cold finger of a helium closed cycle cryo-cooler (Air Products Displex model 202). Several depositions of 1 ml gas sample at 10 torr resulted in clear films indicated by the production of interference fringes. Details of the experimental set-up are given in several previous publications from our laboratory. Three films of different thickness were employed in our investigations. Spectra of a 1.6 μm thick film of solid HNCO, deposited from the gas phase onto a substrate at 20 K, along with an overlay for the same sample warmed to 145 K, are reproduced in Fig. 1.

3. Discussion

3.1. Band assignments

Ab initio quantum mechanical calculations at the MP2/6-31G** level for HNCO [8] predict a planar structure where the HNC and NCO bond angles are 124.7 and 187.4°, respectively. The six vibrational modes of the molecule correspond to three in plane stretches, two in plane bends and one out of plane bend. Reported infrared frequencies for the gas phase and matrix isolated species [8] are given in Table 1. Along with the gas phase frequencies, the vibrational frequency data we measured for the thin film of solid HNCO, and the results of ab initio calculations of the harmonic frequencies of the molecule are reported. A recent report on the infrared spectrum of interstellar ices containing cyanic acid isomers [10] identifies three of the six modes for solid HNCO. In terms of comparison with the theoretical calculations, it is to be stated that the calculated frequencies correspond to harmonic force field derived from the ab initio evaluated potential function. In matrix isolated species, there may be solvent-like induced frequency shifts, and in the solid phase (our studies) there is an additional effect due to hydrogen bonding which is not included in the theoretical calculations. Thus, the theoretically derived vibrational frequency data is useful primarily in establishing a pattern for the band identifications.

The spectral features due to the OCN^- group of HNCO show resemblance to those of CO_2 with which it is isoelectronic. In the case of CO_2, there is Fermi resonance of the ν_1 fundamental mode with the overtone of the doubly degenerate ν_2 fundamental leading to two Raman active peaks (also weakly observed in the IR spectrum at 1285 and 1385 cm^{-1}). In the spectrum of HNCO solid (Fig. 1), there are weak bands at 1325 and 1244 cm^{-1} which may be assigned to the Fermi resonance split components involving ν_3 and $2\nu_5$, $2\nu_6$ and $\nu_5+\nu_6$. Keane [10] assigns a weak band at 3553 cm^{-1} in the spectrum of solid HNCO to the NH stretch, the strong bands around 3200 cm^{-1}

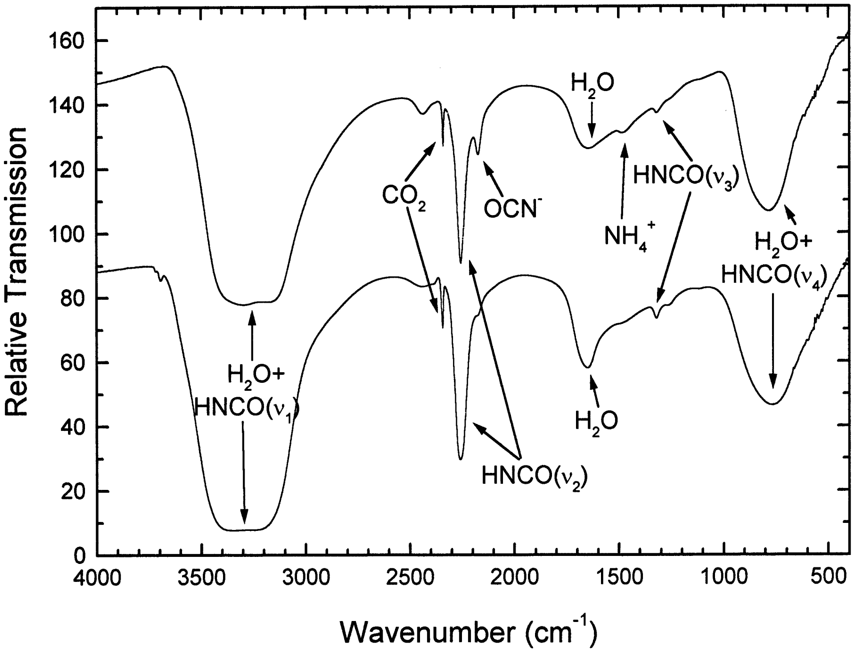

Fig. 1. Pure, solid HNCO deposited from the gas phase onto a 20 K KRS-5 substrate. Overlay of the initial deposit at 20 K and a warm-up of the same deposit to 145 K (annealing temperature).

Table 1
Fundamental band frequencies of HNCO

Mode	Frequency			
	Solid 145 K (this work)	Solid 20 K [10]	Ab initio [8]	Gas [8,11,12]
ν_1	3203	3555.4	3796	3538.24469
ν_2	2254	2252.1	2377	2268.8921
[a]ν_3	1325, 1320, 1245, 1194	–	1316	1327
[b]ν_4	937, 873, 793	863.6	792	776.623
ν_5	612	–	564	577.347
ν_6	649	–	617	656.29

–, not reported.

[a] Fermi resonance of $2\nu_5$, $2\nu_6$, and $\nu_5+\nu_6$ causes splitting of this mode.

[b] At least three components are observed for this mode. Part of the reason for such splitting is hydrogen bonding.

Table 2
Integrated band strengths of HNCO

Mode	Assignment	Symmetry	Band strength (cm molecule^{-1} × 10^{16} at 145 K)
ν_1	NH stretch	A′	2.3
ν_2	C=N, C=O asymmetric stretch	A′	1.6
ν_3	C=N, C=O symmetric stretch	A′	0.0079
ν_4	HNC bend	A′	0.70
ν_5	NCO in plane bend	A′	0.034
ν_6	NCO out of plane bend	A″	–

are ignored as due to a water impurity. In our study of the spectrum of pure HNCO, only one band around 3203 cm^{-1} is observed and is assigned to the NH stretch. The weak shoulder at 3557 cm^{-1} is a possible combination band ($\nu_2+\nu_3$). The shift in the frequencies of the NH stretch (ν_1) and HNC bend (ν_4), from those in the gas phase, is due to hydrogen bonding in the solid phase — which results in lowering the frequencies of the stretching modes and raising those of the bending modes. Thus, the assignment of the fundamental vibrational modes of HNCO (Table 2) is complete.

3.2. Extinction coefficients

Evaluation of the extinction coefficients requires determination of the film thickness and the real part of the refractive index of the sample material. Both of these parameters can be obtained from infrared spectra of films of suitable thickness. If deposited on a clear and highly polished substrate, the spectrum of the sample displays absorption peaks underlying an interference fringe pattern. The fringe pattern arises due to interference of the multiply reflected radiation beam at the film–substrate and film–vacuum interface. The spacing between the two adjacent maxima, $\Delta\nu$, is related to the film thickness, d, as:

$$d \text{ (film thickness)} = 1/(2n_f\Delta\nu) \qquad (1)$$

In Eq. (1), n_f is the refractive index of the film material. In order to calculate the thickness, independent information on n_f is required which is evaluated as follows: The transmission of radiation through a transparent film (refractive index, n_f) deposited on a substrate (refractive index, n_s) and surrounded by vacuum (refractive index = 1) is given below [13,14]:

$$T = (8\ n_s n_f^2)/[(n_s^2+n_f^2)\ (n_f^2+1) + 4n_s n_f^2 + (n_s^2-n_f^2)\ (n_f^2-1)\cos 2\Theta] \qquad (2)$$

where $\Theta = 2\pi\nu n_f d$.

The cosine function is responsible for the fringes in the transparent regions of the spectrum. The ratio of the maximum and minimum intensity (T_{max}/T_{min}) in the region of no characteristic absorption is evaluated to be:

$$R = T_{max}/T_{min} = [n_f^2(n_s+1)^2]/[(n_s+n_f^2)^2] \qquad (3)$$

This gives a quadratic equation in n_f for a given ratio, R. The best procedure is to calculate R for several values of n_f until agreement with the observed ratio is achieved. In our studies, we employed KRS-5 as the substrate ($n_s = 2.21$) [15]. The observed $R = 1.16$ results in the value of $n_f = 1.41$. An estimated accuracy for such a measurement is better than 10% [16] since n_f is very sensitive to the ratio R.

The integrated band strengths, α (cm^{-2}) = $(2.303/d)\int \log (I_o/I)\ d\nu$, of the strong fundamental modes of HNCO are given in Table 2. Published integrated band intensities give the values in cm molecule^{-1} units. This conversion is:

$$(\text{cm molecule}^{-1}) = (\text{cm}^{-2})\ (1/\rho = \text{cm}^3\ \text{g}^{-1})\ (43\ \text{g mol}^{-1})\ (\text{mol}/(6.02\times10^{23}\ \text{molecules})) \qquad (4)$$

This equation requires information on the density of solid HNCO that is not available in the literature. In Table 2, the integrated band strengths in cm molecule^{-1} assume a value of 1 g cm^{-3} for the density of solid HNCO.

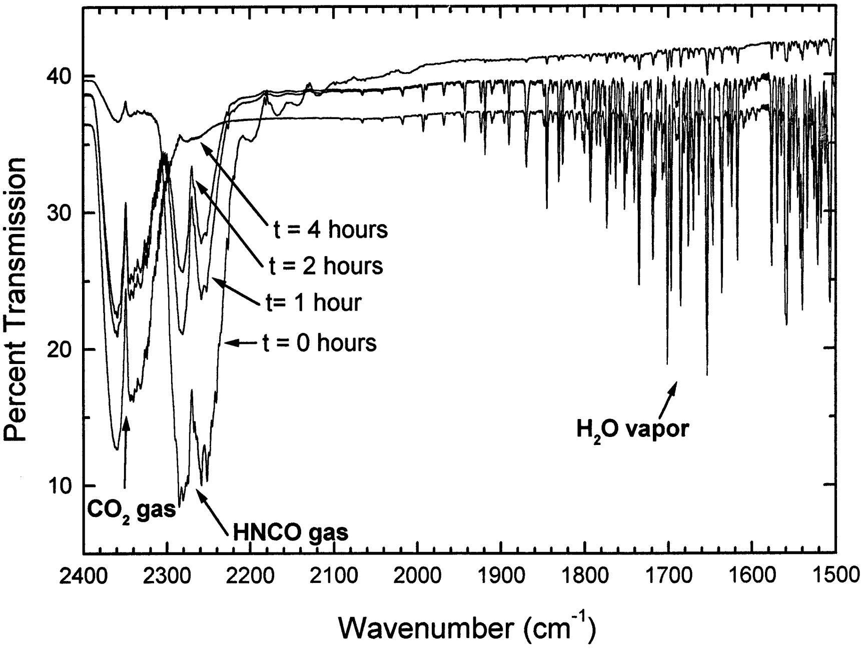

Fig. 2. Decomposition of HNCO: illustration of the time dependence of the infrared spectrum of HNCO in a gas cell. Increase of the CO_2 band around 2350 cm^{-1} and the H_2O band centered at 1650 cm^{-1} relative to the decrease of the HNCO $\nu 2$ band at 2260 cm^{-1}.

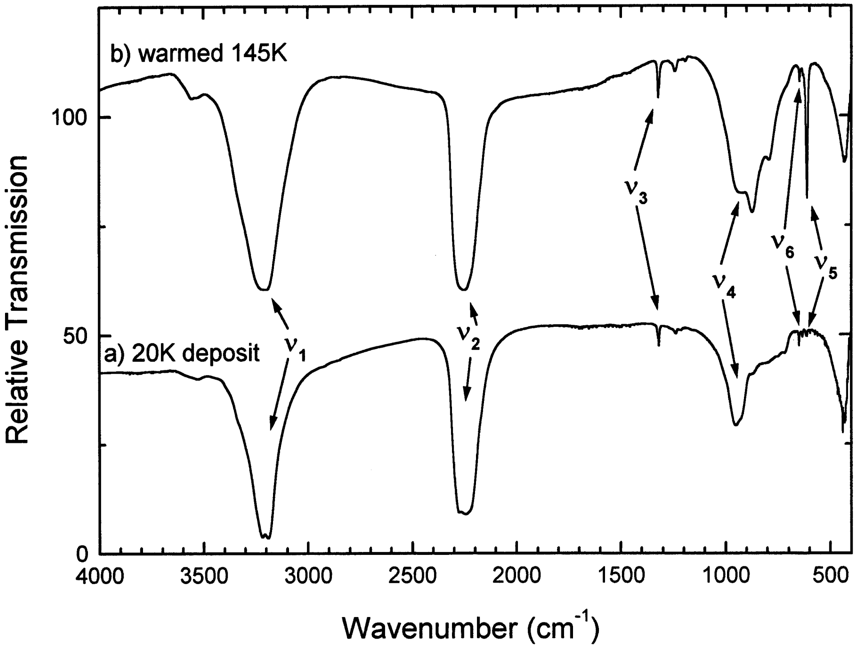

Fig. 3. Figure shows the spectrum of (a) a dual deposit of H_2O and HNCO at 25 K and (b) the spectrum of the warm-up of the same sample to 150 K. Additional bands at 2170 and 1470 cm^{-1} are due to OCN^- and $NH4^+$, respectively. Formation of the additional bands first becomes evident near 100 K.

3.3. Reactions of HNCO with H_2O and NH_3

During the course of analysis of the spectrum of HNCO, it was discovered that a gas sample decomposes slowly into H_2O and CO_2 (when catalyzed by the walls and/or tungsten wires of a gas cell) as seen by an increase in the intensities of the H_2O and CO_2 bands (Fig. 2). HNCO on interstellar icy grains can be understood to undergo a similar decomposition due to the analogous catalyzing properties of interstellar grains. This may provide an explanation for the lack of identification of solid HNCO on interstellar ices. Comparatively, dual deposits of pure HNCO and H_2O ice films at 15 K do not produce any such reaction. Instead, warming the mixed HNCO and H_2O ices to 150 K resulted in additional peaks around 1470 and 2170 cm^{-1}, which can be assigned to NH_4^+ and OCN^- species, respectively (Fig. 3). Keane [10] reports reaction of HNCO with NH_3 at low temperatures resulting in NH_4^+ and OCN^- species that are confirmed by our studies. Preliminary studies of proton irradiationof HNCO solid films reveal several additional peaks suggesting the importance of cosmic radiation of interstellar grains containing HNCO and other important ice components like H_2O and NH_3. Detailed results of such studies will be reported in a separate publication.

Acknowledgements

Funding from NASA's Planetary Atmospheres Program, which made this work possible, is gratefully acknowledged.

References

[1] G. Winnewisser, C. Kramer, Space Sci. Rev. 90 (1999) 181.
[2] R.J.A. Grim, J.M. Greenberg, Astrophys. J. 321 (1987) L91.
[3] J.H. Lacy, F. Baas, L.J. Allamandola, Astrophys. J. 276 (1984) 533.
[4] G. Strazzulla, M.E. Palumbo, Planet. Space Sci. 46 (1998) 1339.
[5] M.P. Bernstein, S.A. Sandford, L.J. Allamandola, Astrophys. J. 476 (1997) 932.
[6] J.A. Nuth, M.H. Moore, Astrophys. J. 373 (1988) L113.
[7] R.L. Hudson, M.H. Moore, P.A. Gerakines, Astrophys. J. 550 (2001) 1140–1150.
[8] J.H. Teles, G. Maier, B.A. Hess Jr, L.J. Schaad, M. Winnewisser, B.P. Winnewisser, Chem. Ber. 122 (1989) 753.
[9] M.E. Jaycox, D.E. Milligan, J. Chem. Phys. 40 (1964) 2457.
[10] J.V. Keane, M.S. Thesis, Leiden University, 1997.
[11] L. Fusina, M. Carlotti, B. Carli, Can. J. Phys. 62 (1984) 1452.
[12] D.A. Steiner, K.A. Wishah, S.R. Polo, T.K. McCubbin, J. Mol. Spectrosc. 76 (1979) 341.
[13] M. Born, E. Wolf, Principles of Optics, Pergamon, Oxford, 1964.
[14] K.L. Chopra, Thin Film Phenomena, McGraw-Hill, New York, 1969.
[15] W.S. Rodney, I.H. Malitson, J. Opt. Soc. Am. 46 (1956) 956.
[16] C. Masterson, R.K. Khanna, Icarus 83 (1990) 83.