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The infrared spectrum of matrix isolated aminoacetonitrile, a precursor to the amino acid glycine

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Abstract

We present infrared (IR) spectral data from matrix isolation experiments and density functional theory calculations on the pre-biologically interesting molecule aminoacetonitrile, a precursor to glycine. We find that this nitrile has an unusually weak nitrile (C≡N) stretch in the infrared, in contrast to expectations based on measurements and models of other nitriles under astrophysical conditions. The absence of an observable nitrile absorption feature in the infrared will make the search for this molecule by IR considerably more difficult, if not impossible. This is also of relevance to assessing the formation routes of the amino acid glycine, since aminoacetonitrile is the putative precursor to glycine via the Strecker synthesis, the mechanism postulated to have produced the amino acid glycine in meteorites.
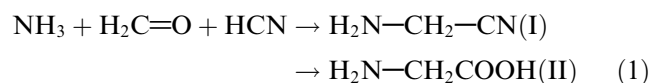© 2003 COSPAR. Published by Elsevier Ltd. All rights reserved.

Keywords: Amino acid; Glycine; Meteorite; IR spectroscopy; Nitrile

1. Introduction

Recent experimental (Bernstein et al., 2002; Muñoz-Caro et al., 2002) and theoretical (Woon, 2002) studies of ice photochemistry suggest that glycine and other simple amino acids could form at low temperature in ices, of the type seen in the interstellar medium, cometary bodies, and on satellites and other objects in the outer solar system. Meteoritic amino acids such as glycine, as well as related hydroxy acids such as glyceric acid, may have formed by way of the Strecker synthesis (Peltzer et al., 1984). The mechanism is the one in which ammonia (NH_3), an aldehyde, and hydrogen cyanide (HCN) form an amino nitrile, which is then hydrolyzed to form an amino acid. If, as seen in Eq. (1), one starts with the simplest aldehyde (formaldehyde, $H_2C=O$)

then the intermediate nitrile formed is aminoacetonitrile (I) and the product amino acid is glycine (II)

$$NH_3 + H_2C=O + HCN \rightarrow H_2N-CH_2-CN(I)$$
$$\rightarrow H_2N-CH_2COOH(II) \quad (1)$$

Glycine is both the simplest and most abundant amino acid in meteorites (Cronin and Pizzarello, 1983), and a glycine detection was recently claimed in molecular hot cores (Kuan et al., 2003; Kuan et al., this issue). If the glycine and glyceric acid in meteorites form by a Strecker-like synthesis then one would expect amino-acetonitrile – the nitrile intermediate corresponding to glycine – to be present in parent bodies from which these meteorites come. Similarly, depending on the mechanism of interstellar glycine formation, one might expect aminoacetonitrile to be present in interstellar space as well. We determined the IR spectrum of aminoaceto-nitrile at low temperature to facilitate the use of IR observations to put upper limits on its abundance in cold space environments. However, the absence of an absorbtion in the IR spectrum corresponding to the C≡N stretch indicates that IR will not be an effective

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method for detecting aminoacetonitrile. Instead, rotational spectra, which have been used so effectively in the past to detect other gas phase nitriles, will be required.

2. Method

2.1. Experimental

The techniques and equipment employed for this paper were typical of those used in matrix isolation studies in the chemical literature. Aminoacetonitrile samples were prepared on a 14 K CsI substrate in a ($\sim 10^{-8}$ mbar) vacuum chamber that has been described in detail elsewhere (Allamandola et al., 1988). The mid-IR spectrum of aminoacetonitrile isolated in solid Argon was measured with a Nicolet 740 spectrometer at 1 wavenumber resolution. The nitrile, purchased as the free base (98% Sigma A5802), was vacuum transferred away from a non volatile yellow oil, and its vapor mixed in a glass bulb with Argon in a ratio of 1:300. At this concentration one expects the vast majority of the nitrile molecules to be isolated from one another by the argon matrix, so there should not be any major peaks that stem from nitrile dimers. The background pressure in the glass line used for mixing the samples was typically 10^{-5} mbar, so we estimate the contamination level in the matrix from the sample preparation is less than one part in 10^6 relative to argon. However, water and carbon dioxide were observed in the matrix at a higher level because of background atmospheric gas in the vacuum chamber and,

more significantly, an unidentified peak from contamination in the purchased aminoacetonitrile, which was only 98% pure. Specifically, in addition to H_2O, and CO_2 features a peak appears in the spectrum at 975 cm^{-1} that we could not attribute to aminoacetonitrile and was tentatively ascribed (by Dr. Andrew Mattioda) to a contaminant bearing a sulphur–oxygen bond. According to Sigma their synthesis involves a sulfate intermediate, so that is presumably the source of this feature.

2.2. Computational

The geometry of aminoacetonitrile was optimized and the harmonic frequencies computed using B3LYP/6-31+G(d) (Frisch et al., 1984; Becke, 1993; Stephens et al., 1994). Calibration calculations (Scott and Radom, 1996) which have been carried out for selected systems, show that a single scale factor of 0.9614 brings the frequencies computed using this basis set into best agreement with experimental fundamental frequencies. All calculations were performed using the Gaussian 98 computer code (Frisch et al., 2001). The vibrational modes and displacement vectors are viewed using the interactive molecular graphics tool MOLEKEL (Flukiger et al., 2000; Portmann and Luthi, 2000).

3. Results and discussion

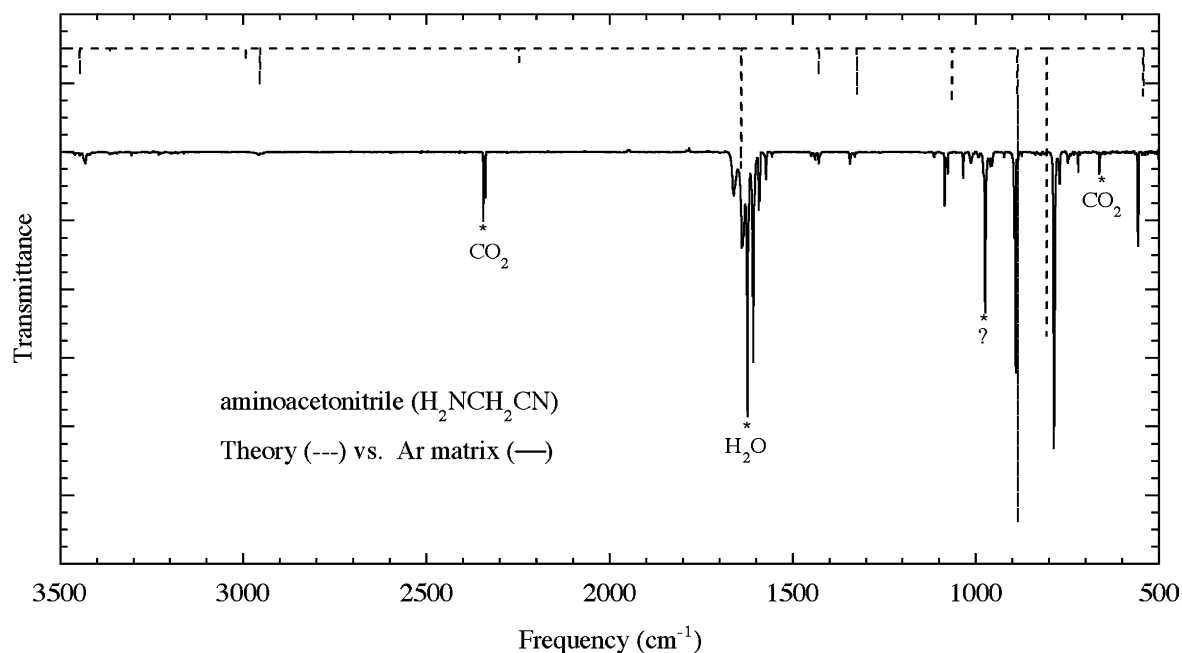The mid-IR spectrum of aminoacetonitrile is presented in Fig. 1, in comparison to its calculated

Fig. 1. The 3500–500 cm^{-1} (2.86–20 mm) IR spectrum of a solid intimate mixture of Argon:aminoacetonitrile (H_2N–CH_2–CN) = 300:1 compared to a synthetic spectrum calculated by density functional theory. Peaks attributed to contaminants are indicated by an asterix (see text). Positions and intensities of both experimental and calculated peaks are listed in Table 1.

Table 1
Matrix isolated aminoacetonitrile peak position (cm^{-1}) and intensity vs. theory

Matrix experiment		Theory B31YP/6-31+G(d)			Comments[a]	Gas phase[b] Bak et al. (1975)
Position (cm^{-1})	Normalized area	Position (cm^{-1})	Peak intensity			
			km/mol	Normalized		
3461	0.013					
3447	0.012	3447	7.7	0.056	N–H asym stretch	
3436	Doublet					
3432	0.115					3431 (m/w)
3365	0.032	3364	1.7	0.012	N–H sym stretch	3367 (m/w)
3346	0.00718					
3306	0.01437					
		2994	3.8	0.028	C–H asym stretch	2975 (m)
2958	0.042575	2955	10.6	0.077	C–H sym stretch	2950 (m)
		2247	3.8	0.028	ON stretch	
1638[c]	C	1641	34.6	0.251	N–H wag	1642 (m)
1450	0.00838					
1439	0.02215					
1429	0.03772	1429	7.65	0.055	H–C–H clap	1444 (m)
1344	0.03113					
1331	0.01197	1325	13.0	0.094	H–C–H swim	1331 (m)
1114	0.01736					
1085	0.08383					
1077	0.04910	1065	15.8	0.114	NH, CH and C–C	1077 (m)
1035	0.04431					
1013	0.05389					
993	0.01736					
975[d]	0.50240					
961	Doublet					
956	0.050					
923	0.0072					
891	0.47904	886.1	138	1.00	NH, CH and C–C	901 (s)
787	1.0000	807.2	83.5	0.605	NH wag and N–C–C	790 (vs)
772	0.06107					
749	0.02574					
721	0.01796					
557	0.10719	543.4	13.7	0.099	N–C–C bend	558 (m)
		377.2	15.8	0.114	NH$_2$–CH$_2$ torsion	370 (w)
		259.6	56.1	0.407	NH$_2$ torsion	247 (m/s)
		204.9	12.4	0.090	C–C≡N bend	235 (m)

[a] Atomic motions derive from theory, so they are included only for calculated transitions.
[b] Only those features corresponding to our observations or calculations are included.
[c] Estimate only. The area is unclear because of obscuring features caused by matrix isolated H$_2$O.
[d] Presumed sulfate contaminant derived from the synthesis of aminoacetonitrile, see Section 2.

spectrum. The data are also summarized in Table 1. It is well known that most nitriles have a strong cyano (C≡N) stretch in the 2325–2125 cm^{-1} (4.30–4.71 μm) region (Bernstein et al., 1997). We have calculated that aminoacetonitrile should display an anomalously small IR active C≡N stretching feature at 2247 cm^{-1}. The comparisons of calculations with the 4-31G basis set predicted this peak should be ∼44 times less than that of 9-cyanoanthracene, the spectrum of which we presented in a previous paper (Bernstein et al., 1997). This feature is either absent or so weak that we were not able to observe it in our measured spectrum. This feature was also not detected in the measured IR spectrum of gas phase aminoacetonitrile, although a very strong peak at

2236 cm^{-1} was reported in the Raman spectrum of liquid aminoacetonitrile (Bak et al., 1975).

In general, there is good agreement between the theoretical calculations and the observed spectrum. For example, the average absolute discrepancy between our measured and calculated band positions is ∼7 cm^{-1}, comparable to the shift between matrix and gas phase. The largest difference between a calculated and observed peak position was 20 cm^{-1} for the combination NH wag and N–C–C bend. This feature was calculated to appear at 807 cm^{-1} but appeared at 787 cm^{-1} in our spectrum of matrix isolated nitrile, and was reported at 790 cm^{-1} in the gas-phase spectrum by Bak et al. (1975).

The theory provided some features that cannot be directly compared with our measurement. First, the peaks predicted to be at 213, 270, and 392 cm^{-1} that are outside of our measured wavelength range, but we compare them in Table 1 to the previously measured room temperature gas-phase spectrum (Bak et al., 1975). Second, the N–H wag predicted to be near 1640 cm^{-1} was observed in the room temperature gas-phase spectrum (Bak et al., 1975) but is not obvious in our spectrum because of obscuring features near 1600 cm^{-1} caused by contaminant H_2O in our argon matrix. We assume that the broad multi-peaked absorption centered near 1637 cm^{-1} contains this N–H wag, perhaps in the component peaking at 1638 cm^{-1}.

Finally, there are also some peaks present in our spectrum that are not predicted by theory, i.e., those between 1035 and 895 cm^{-1} and between 772 and 721 cm^{-1}. The one at 1035 cm^{-1} seems to correspond with the 1030 cm^{-1} feature in the Raman spectrum of liquid aminoacetonitrile, suggesting that it may be IR forbidden but enhanced by intermolecular interactions in the solid state, something our modeling does not take into account. In addition, our theoretical modeling does not calculate overtones and combination modes, so these peaks may be from overtones and combinations of lower frequency modes.

4. Conclusions and implications

Our measured IR spectrum of aminoacetonitrile isolated in an argon matrix, and corresponding calculations, both confirm that the C≡N stretch fundamental, usually used to identify and quantify cyanide compounds is extremely weak in this pre-biologically important compound. This will make any IR observations designed to identify and/or put upper limits on this amino acid precursor extremely difficult.

Our theoretical modeling has done a very good job of predicting the IR spectrum of an unusual nitrile that is predicted to be a precursor to the amino acid glycine. Such theoretical modeling can provide good predictions for the IR spectra of such molecules in Argon matrices or in similar non-interacting solids, such as nitrogen ices of the type observed to be on Pluto and Triton.

Acknowledgements

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