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Infrared Spectrum of Formamide in the Solid Phase

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Abstract:

Infrared spectra of solid formamide are reported as a function of temperature.

Solid formamide samples were prepared at 30 K and then annealed to higher

temperatures (300 K) with infrared transmission spectra being recorded over the

entire temperature range. The NH_2 vibrations of the formamide molecule were found to

be particularly very sensitive to temperature change. The IR spectra revealed a phase

change occurring in solid formamide between 155 K to 165 K. Spectral changes

observed above and below the phase transition may be attributed to a rearrangement

between formamide dimers and the formation of polymers is proposed at higher

temperatures.

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1. Introduction

One of the characteristic features of molecular solids composed of chemical systems containing hydrogen bonds is the observation of substantial changes in their infrared spectra as a function of temperature. Studying the properties of molecular solids containing amide groups is particularly interesting due to the role such compounds may play in the formation of a number of synthetic and organic

compounds. Formamide, the simplest amide, contains the peptide linkage which is of crucial importance in protein chemistry and physics, since peptide links are known to be the basis for assembling proteins and polypeptides from amino acids. For example, purine, the base molecule from which adenine and guanine are derived, is known to be a by-product of formamide polymerisation [1] and poly (hydrogen cyanide), an important constituent of the prebiotic soup [2].

Therefore formamide has been the topic of interest for astrochemists and astrobiologists since its detection in the interstellar medium suggests that amide chemistry may be prevalent in astrochemically rich regions. Formamide was first detected (in 1971) in the gas phase in Sgr B2 and later in the long period comet C/1995 O1 Hale-Bopp (2000) and in the young stellar object W33A (1999), and recently (2004) there has been a tentative report of ice bound formamide in ISO-SWS spectra of the protostellar source NGC 7538 IRS9 [3-6].

Several experimental and theoretical studies have been carried out to understand the physical and chemical properties of formamide under astrochemical conditions. Laboratory experiments of astrophysical relevance carried out at very low temperatures have investigated (i) the formation of formamide during irradiation of ice mixtures containing H_2O , NH_3 , CO_2 , CO , HCN , CH_3OH and HNCO [7-12] and (ii) the products from solid formamide dissociation [13] under charged particle irradiation. The Raman and infrared spectral properties of formamide have been reported [14, 15] but to date there has been no extensive temperature dependent study of the IR spectra of solid formamide. Therefore we have performed a detailed temperature dependent study of solid formamide in the mid-infrared spectral region.

2. Experimental method

The experimental astrochemistry apparatus used to simulate the conditions of the interstellar medium operates under Ultra-High Vacuum (UHV) conditions (of the order of 10^{-10} Torr). The substrate was cooled to low temperatures (28 K) using a closed cycle helium refrigeration system, (Figure 1). A zinc selenide (ZnSe) window was used as an IR transmitting substrate on which formamide vapour was deposited at 30 K to form solid ice samples.

A Fourier Transform-Infrared Spectrometer (FTIR) operating in the mid infrared range $4000 - 400 \text{ cm}^{-1}$ and at 2 cm^{-1} resolution, was used to probe the morphology and chemical composition of the ice formed on the ZnSe substrate. The sample could be heated (at a rate of 0.5 K min^{-1}) to any desired temperature above the deposition temperature using the combination of a (Lakeshore) temperature monitor and an oxygen resistance UHV button heater. Infrared spectra of the sample were recorded after sample deposition at 30 K and at higher temperatures.

Formamide gas samples were derived from 99.5 % pure (purchased from Sigma Aldrich) liquid samples purchased from Sigma Aldrich. Before introducing the formamide vapour into the chamber to form the solid, the liquid sample was processed by three freeze-pump-thaw cycles to degas any impurities.

3. Results

3.1 Infrared spectra of formamide recorded at 30 K

An infrared spectrum of solid formamide was first recorded at 30 K (Figure 2). A broad band was observed from 3800 cm^{-1} to 2944 cm^{-1} with two peaks positioned

at 3372 cm^{-1} and 3179 cm^{-1} corresponding to the vibrational modes ν_1 and ν_2 ,

respectively. Five other fundamental bands were observed at 2895 cm^{-1} , 1698 cm^{-1} ,

1628 cm^{-1} , 1386 cm^{-1} , and 1334 cm^{-1} corresponding to the ν_3 , ν_4 , ν_5 , ν_6 and ν_7

modes, respectively (Table 1). All the bands are in good agreement with those observed previously [13,15] but four more bands were observed at 1172 cm^{-1} , 1117 cm^{-1} , 836 cm^{-1} and 710 cm^{-1} (Figure 2e) bands that were also observed by Torrie and Brown [15] albeit in a 20 K formamide ice.

In our spectra, three bands at 1022 cm^{-1} , 1056 cm^{-1} and 1226 cm^{-1} were observed for the first time at low temperatures (Figure 2e). The two bands observed in the region $1065 - 1040\text{ cm}^{-1}$ in solid formamide at 108 K, by Itoh [16], were assigned to the CH out of plane bend, therefore the bands observed at 1056 cm^{-1} and 1022 cm^{-1} in our spectra at 30 K were also assigned to the CH out of plane bend (Table 1). The 1226 cm^{-1} band was also reported to be present in the matrix isolation studies of formamide [17]. Comparing the spectra obtained at 30 K with the spectra recorded at 77 K by King [18] we found that at 30 K an amorphous solid film (Figure 3) was obtained by depositing formamide molecules on to the cold ZnSe substrate.

3.2 Infrared spectra of formamide recorded during warm-up (30 K – 210 K)

3.2.1 NH_2 asymmetric stretch

The broad band observed at 3372 cm^{-1} , is assigned to the NH_2 asymmetric stretch mode. Upon annealing the sample this band red shifted to 3360 cm^{-1} (at 70 K) and to 3351 cm^{-1} at 90 K. The band position then remains unchanged until 140 K when the band was observed to shift again to 3328 cm^{-1} . At 155 K, when a phase transition occurs (see below), this band was observed at 3329 cm^{-1} , with an additional peak appearing at 3377 cm^{-1} (Figure 2a). A further 10 K increase in the sample temperature showed another new peak centred at 3296 cm^{-1} . It must be noted that at 165 K all the three peaks are very clear resolved. Shifts in the band positions due to further heating up to 210 K are listed in Table 2. A new peak centred at 3242 cm^{-1} , was observed only at 180 K.

3.2.2 NH_2 symmetric stretch

The broad band observed in the 30 K sample at 3179 cm^{-1} is assigned to the NH_2 symmetric stretch. In contrast to the symmetric band there is no shift in the band position until the sample was heated to a temperature of 155 K at which temperature

the band was observed to shift to 3146 cm^{-1} (Figure 2a). The ν_2 band intensity also

grew when the sample is heated from 30 K – 140 K. Between 165 K and 175 K, only a small shift in the band was observed but at 210 K the band was observed to have shifted to 3156 cm^{-1} (Figure 2a).

3.2.3 CH stretch

The band observed at 2895 cm^{-1} in the 30 K sample, is ascribed to the CH stretching mode of the formamide molecule. There is no major change in the band position until the ice temperature reaches 165 K (Figure 2b) when the band was centred at 2890 cm^{-1} and a new band was observed at 2811 cm^{-1} . No major band shift was observed during warm up the sample from 165 K up to 210 K, where the band was observed at 2889 cm^{-1} (Figure 3). Table 2, presents the shift in CH stretch band position while the sample is annealed from 30 K to 210 K. The spectra recorded at 170 K revealed another new band at 2769 cm^{-1} (Figure 2b) which we assign to an overtone or combination band.

3.2.4 CO Stretch

The band observed at 1698 cm^{-1} in the 30 K sample, is ascribed to the CO stretching in the formamide molecule. There is no shift in the band position until the sample was heated to 165 K, where the band was observed at 1711 cm^{-1} together with a new shoulder at 1747 cm^{-1} . The 1711 cm^{-1} band shifted to 1719 cm^{-1} at 170 K, whereas the shoulder was observed at 1748 cm^{-1} (Figure 2c). Both the bands remain unchanged until approximately 200 K where the bands were observed at 1725 cm^{-1} and 1750 cm^{-1} , respectively.

3.2.5 NH₂ scissoring

The band observed at 1628 cm^{-1} in the 30K sample, the ν_5 fundamental is

ascribed to the in plane NH₂ scissoring mode. Annealing the sample from 30 K to higher temperatures and recording the infrared spectrum showed a red shift in the peak to 1621 cm^{-1} , at 165 K (Figure 2c). In addition a new band at 1677 cm^{-1} was

observed, similar to the NH_2 asymmetric stretching region where new bands appeared at the same temperature. At 170 K both the bands were observed to have shifted to 1594 cm^{-1} and 1645 cm^{-1} respectively and at 210 K they were observed at 1599 cm^{-1} and at 1641 cm^{-1} , (Figure 2c).

3.2.6 CH bending

The band observed at 1386 cm^{-1} in the 30 K sample is ascribed to the in plane CH bending mode. There is no significant change in the band position until the temperature reaches 165 K where the band was found to be centred at 1390 cm^{-1} (Figure 2d). No major band shift was observed by further heating the sample up to 210 K, (Figure 4). Table 2, shows the small shifts in the band positions due to in plane CH bending while the sample is annealed from 30 K to 210 K.

3.2.7 CN stretch

At 30 K the band observed at 1334 cm^{-1} , is ascribed to the CN stretch in the formamide molecule. The peak position of the CN stretch region remained unchanged until 165 K where the recorded spectrum showed the peak to have shifted to 1330 cm^{-1} (Figure 2d). Upon further heating to 210 K no significant shift in the band position was observed (Figure 4, Table 2).

3.2.8 Other NH_2 and CH vibrations

The bands observed at 710 cm^{-1} and 836 cm^{-1} in the 30K solid were assigned to the NH_2 twisting and wagging vibrations [15,16], respectively. The bands at 1117 cm^{-1} and 1172 cm^{-1} were assigned to the NH_2 rocking vibration [16]. The 710 cm^{-1} band disappeared in the spectra recorded at 165 K whereas the 836 cm^{-1} band was found to be at 830 cm^{-1} and at 827 cm^{-1} at 165 K and 210 K respectively (Figure 2e). Interestingly a new band, at 890 cm^{-1} , appeared in the spectra at 165 K which remained until 180 K. The 1117 cm^{-1} band was not observed in the spectra at 165 K whereas around 200 K a band appeared at 1128 cm^{-1} . Spectra recorded at 165 K also revealed a new band appearing at 2811 cm^{-1} which, on heating to 210 K shifted to 2805 cm^{-1} (Figure 2b). It is important to note that the band observed at 2811 cm^{-1} and shifted to 2805 cm^{-1} under the action of increasing temperature matches with

the ν_5 fundamental of N=NH₂ band observed in a formamide synthesis experiment at

12 K using varied concentrations of CO and NH₃ [12]. The observed band shift with respect to the increase in NH₃ concentration by Jones et al [12] was analogous to the shift observed in our experiment as a function of temperature.

Two more bands at 1022 cm⁻¹ and 1056 cm⁻¹ were also observed at 30 K, which correspond to the CH out of plane bend [16] in the formamide molecule. Upon annealing the sample to higher temperatures, the 1022 cm⁻¹ band remained unshifted until 165 K where it was observed to shift slightly to 1019 cm⁻¹ and the band disappeared in the spectra recorded at 190 K. However, the other band at 1056 cm⁻¹ was observed to shift to 1062 cm⁻¹ at 165 K and was observed at 1061 cm⁻¹ up until 210 K (Figure 2).

3.3 Infrared spectra after recooling (30 K)

It is interesting to compare the spectra acquired at 30 K, just after sample deposition, with the spectra of a sample that had been annealed to 210 K, and then cooled to 30 K. The spectra recorded at 30 K, after recooling the sample from 210 K, matches with the crystalline formamide spectra recorded at 77 K, by King [18], and the spectrum recorded at 20 K, by Khanna et al [19], after recooling the annealed sample.

While cooling down to 30 K from 210 K, the infrared spectra recorded revealed several new bands and shifts in those known band peak positions. The

region corresponding to the NH₂ asymmetric (ν_1) and symmetric stretch (ν_2) were

observed to have five bands at 3139 cm^{-1} , 3174 cm^{-1} , 3204 cm^{-1} , 3290 cm^{-1} and 3356

cm^{-1} . The ν_3 fundamental band was observed at 2891 cm^{-1} . The region $2820 - 2460$

cm^{-1} , was found to contain five peaks centred at 2813 cm^{-1} , 2771 cm^{-1} , 2742 cm^{-1} , 2705 cm^{-1} and 2472 cm^{-1} (Figure 5a).

The ν_4 fundamental region that corresponds to the CO stretch was observed

to contain two bands; one at 1719 cm^{-1} and the other at 1748 cm^{-1} . Likewise, two

peaks at 1600 cm^{-1} and 1655 cm^{-1} were observed in region that corresponds to the

in-plane NH_2 scissoring vibration. The ν_6 fundamental band, corresponding to in

plane CH bending, was observed at 1392 cm^{-1} , and the ν_7 fundamental,

corresponding to the CN stretch, was observed at 1332 cm^{-1} with an additional

shoulder band at 1315 cm^{-1} (Figure 5b). The other bands observed at 1134 cm^{-1} , 1069 cm^{-1} and at 840 cm^{-1} were found to be a good match to the 20 K data (Table 1) reported by Torrie and Brown [15]. In our spectra the band at 1069 cm^{-1} appeared as a doublet with a peak at 1065 cm^{-1} (Figure 5c).

4. Discussion

Analysis of IR spectra of formamide at higher temperatures (210 K) appear to show the integrated areas of the CH and CN stretching vibrations (Figure 6) increasing. As additional formamide molecules were not added to the sample while heating this suggests that the increase in the peak intensity whilst warming up the sample, this may be due to the formation of dimers or higher aggregates (polymer) formed from formamide association. However, the changes in infrared band intensities with respect to temperature cannot be neglected and the extent of such contributions can be estimated using theoretical calculations, which is beyond the scope of this experimental paper.

The crystal structure of solid formamide has been determined [20] to be a collection of centrosymmetric (C_{2h}) dimers. Matrix isolation studies coupled with quantum chemical calculations have shown the presence of four possible energetically stable formamide dimers; Dimer A, B, C, D, and also a less stable dimer, Dimer E (Figure 7; [21]). Matrix isolation studies have also revealed the formation of these dimers in various proportions depending on the matrix prepared (either Xenon or Argon), on the sample preparation and the sample temperature. The presence of such dimers was experimentally observed in the infrared spectra, using 0.5 cm^{-1} resolution, with the identification of the characteristic vibrations for formamide dimers occurring in the NH_2 and CO vibrational regions [21]. In the present work it was hard to distinguish these peaks in our spectra due to our limited 2 cm^{-1} resolution. However, even for a pure formamide sample, the existence of dimers (Dimer A, B and C/D) at different temperatures and the interchange to other dimer forms (Dimer B to A; [21]) suggest that strong dimer formation is likely to happen while annealing the sample.

While comparing the crystalline formamide spectra at 210 K and the spectrum recorded after recooling to 30 K we found the phase change was irreversible (Table 2; Figure 5). The shifts observed in the band positions after the phase change may be due to the interaction between (i) formamide monomers forming dimers and/or (ii) formamide dimers forming polymers. Experimental evidence [7, 12] suggests that the absence of formamide monomer signals in the mass spectrum at higher temperatures might be due to formamide aggregates being formed. Such rearrangement of dimers due to annealing may have contributed to the changes observed in the spectra. Indeed a significant change in the proportions of different formamide dimers would have taken place when solid formamide turns from amorphous to crystalline by annealing.

In fact spectral changes observed by annealing the solid formamide sample from 30 K up to 210 K, may be due to both (i) the molecular aggregation taking place within the ice by converting monomers to dimers or even to polymers [22] and (ii) the proportion of the dimers (Dimer A – D) that may vary as a function of temperature [22]. This claim is supported by the experimental identification of dimers in the crystalline [20] and amorphous [21] solid formamide and the absence of formamide monomer mass spectrometry signatures at higher temperatures [12]. Warming up the sample to 300 K we found that all formamide or the dimers / polymers had sublimed and left no residue on the substrate.

Further evidence for dimer formation arises from calculation of the ice density. The column density of formamide present in our sample at 30 K was calculated

using the A_{obs} value of 4.7×10^{-18} cm molecule⁻¹ [13] for the 2895 cm⁻¹ (ν_3 , CH

stretch), from which the column density was estimated at about 4.7×10^{17} molecules cm⁻². Using the A_{obs} values 6.8×10^{-18} cm molecule⁻¹ and 8.5×10^{-18} cm molecule⁻¹

[13], for the band at 1386 cm^{-1} (ν_6 , in plane CH bending) and 1334 cm^{-1} (ν_7 , CN

stretch), the column density was estimated to be about $7.4 \times 10^{17}\text{ molecules cm}^{-2}$ and $5.3 \times 10^{17}\text{ molecules cm}^{-2}$, respectively. Thus the estimated column density obtained therefore lay between $4.7 - 7.5 \times 10^{17}\text{ molecules cm}^{-2}$.

5. Conclusion

Solid formamide was prepared by depositing gaseous formamide on to a substrate cooled to 30 K. Infrared spectra were recorded after deposition and showed several peaks of an amorphous formamide ice. Annealing the sample to higher temperatures revealed several spectral changes and the emergence of several new bands. The shifts observed in the NH_2 asymmetric and symmetric stretching vibrations were much larger than shifts observed in the other vibrations. However, all the vibrational modes were observed to have shifted in the spectra recorded at 165 K which indicated a phase change in the sample between 155 K –

165 K. Changes in the spectral signature of NH_2 vibrations (ν_1 , ν_2 , ν_5) were observed

until 210 K. The spectra recorded by recooling the annealed sample to 30 K, showed the phase change to be irreversible.

The spectral changes that took place before and after the phase transition may be attributed to the association of formamide monomers to form dimers (and polymers) and also the rearrangement between formamide dimers under the action of temperature. Therefore both morphological changes as well as the rearrangement between formamide dimers have taken place in the solid formamide ice that was

deposited at 30 K and annealed to 210 K. Such morphological changes may also occur when formamide ice is processed in the interstellar medium and star forming regions either by shock or local heating, changes that may be identified by the new telescopes (e.g. ALMA).

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Figure captions

Figure 1: Schematic diagram of the experimental set-up used to measure temperature dependent infrared spectra of solid formamide.

Figure 2: Infrared spectra of a condensed molecular formamide ice recorded at 30 K, 90 K, 155 K, 165 K, 185 K, 200 K and 210 K, stacked from bottom to top, respectively. The plots from (a) to (e) shows the different regions of the mid infrared spectra.

Figure 3: Infrared spectra of condensed molecular formamide ice both recorded at 30 K (i) amorphous, after sample deposition, (ii) crystalline, re-cooled to 30 K after annealing to 210 K.

Figure 4: Shows the observed shifts in the band peak positions of CN (ν_7), CH (ν_3)

stretching and in plane CH bending (ν_6) vibrations of formamide as a function of

temperature.

Figure 5: Infrared spectra of the sample annealed to 210 K and then re-cooled to 30 K.

Figure 6: Shows the integrated band area of CN (ν_7), CH (ν_3) stretching and in plane

CH bending (ν_6) vibrations of formamide as a function of temperature.

Figure 7: Dimers of solid formamide (Adapted from Mardiyukov et al., 2007).

Table captions

Table 1: Observed vibrational frequencies of solid formamide.

Table 2: Observed peak positions in the infrared spectra of solid formamide at different temperatures.

Figure1

Figure2

Figure 5

Peak position, cm ⁻¹			Mode	Assignment	Reference
30 K	20 K ^[13]	20 K ^[15]			
710	-	685	?	NH ₂ twisting	16
836	-	841	?	NH ₂ wagging	15
1022	-	-	?	CH out of plane bend	16
1056	-	1068	?		
1117	-	1134	?	NH ₂ rocking	15
1172	-	1142	?		
1226	-	-	?	?	17
1334	1328	1333	ν_7	CN stretch	13
1386	1388	1388	ν_6	In plane CH bending	13*
1628	1631	1661	ν_5	In plane NH ₂ scissoring	13
1698	1708	1704	ν_4	CO stretch	13
2895	2881	2891	ν_3	CH stretch	13
3179	3181	3217	ν_2	sym NH ₂ stretch	13
3372	3368	-	ν_1	asym NH ₂ stretch	13

*In reference [13] this vibration is given as in plane CH scissoring.

Table2

30 K	70 K	90 K	105 K	119 K	130 K	140 K	155 K	165 K	170 K	175 K	180 K	190 K	201 K	210 K	210 K - 30 K
710	710	710	710	710	710	710	710								
836	836	836	836	836	836	836	836	830	830	830	830	830	827	827	840
								890	890	890	890				
1022	1022	1022	1022	1022	1022	1022	1022	1019	1018	1018	1018				
1056	1056	1056	1056	1056	1056	1056	1055	1062	1062	1062	1062	1062	1061	1061	1065/1069
1117	1117	1117	1117	1117	1117	1117	1117								
													1128	1127	1134
1172	1172	1172	1169	1169	1169	1168	1166	1165	1165	1165	1165				
1226	1226	1226	1226	1226	1226	1226	1213	1213	1213	1213	1213				
1334	1334	1334	1334	1334	1334	1334	1334	1330	1330	1330	1330	1330	1329	1329	1315/1332
1386	1386	1386	1386	1386	1386	1386	1386	1390	1389	1389	1389	1389	1392	1391	1392
1628	1628	1628	1628	1628	1628	1628	1628	1621	1594	1594	1594	1594	1596	1599	1600
								1677	1645	1645	1645	1645	1642	1641	1655
1698	1698	1698	1698	1698	1698	1698	1698	1711	1719	1719	1719	1719	1725	1722	1719
								1747	1748	1748	1748	1748	1750	1750	1748
									2468	2468	2467	2467	2467	2465	2472
															2705
															2742
									2769	2769	2769	2767	2767	2767	2771
								2811	2810	2810	2808	2809	2806	2805	2813
2895	2896	2896	2896	2896	2896	2896	2896	2890	2890	2890	2890	2890	2890	2889	2891
															3139
3179	3179	3179	3179	3179	3179	3179	3146	3149	3149	3145	3151	3154	3155	3156	3174
3372	3360	3351	3351	3351	3348	3328	3239	3236	3234	3210	3205	3204	3204	3204	3204
											3242	--	--	--	--
							3377	3296	3298	3295	3295	3299	3300	3301	3290
								3377	3374	3371	3363	3366	3367	3365	3356

- IR spectra recorded at multiple temperatures show conformers of formamide dimers.
- Formamide amorphous and crystalline ice spectra were found to be much different.
- The NH_2 vibrations in formamide molecule were very sensitive to temperature changes.
- Morphological changes as well as rearrangement between dimers in solid formamide.

ACCEPTED MANUSCRIPT