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## Accepted Manuscript

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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<sub>2</sub> 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<sub>2</sub>O, NH<sub>3</sub>, CO<sub>2</sub>, CO, HCN, CH<sub>3</sub>OH 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<sup>-10</sup> 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  $2 \text{ cm}^{-1}$  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  $0.5 \text{ K min}^{-1}$ ) 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  $3800 \text{ cm}^{-1}$  to  $2944 \text{ cm}^{-1}$  with two peaks positioned at  $3372 \text{ cm}^{-1}$  and  $3179 \text{ cm}^{-1}$  corresponding to the vibrational modes  $\nu_1$  and  $\nu_2$ , respectively. Five other fundamental bands were observed at  $2895 \text{ cm}^{-1}$ ,  $1698 \text{ cm}^{-1}$ ,  $1628 \text{ cm}^{-1}$ ,  $1386 \text{ cm}^{-1}$ , and  $1334 \text{ cm}^{-1}$  corresponding to the  $\nu_3$ ,  $\nu_4$ ,  $\nu_5$ ,  $\nu_6$  and  $\nu_7$

modes, respectively (Table 1). All the bands are in good agreement with those observed previously [13,15] but four more bands were observed at  $1172 \text{ cm}^{-1}$ ,  $1117 \text{ cm}^{-1}$ ,  $836 \text{ cm}^{-1}$  and  $710 \text{ cm}^{-1}$  (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  $1022\text{ cm}^{-1}$ ,  $1056\text{ cm}^{-1}$  and  $1226\text{ cm}^{-1}$  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  $1056\text{ cm}^{-1}$  and  $1022\text{ cm}^{-1}$  in our spectra at 30 K were also assigned to the CH out of plane bend (Table 1). The  $1226\text{ cm}^{-1}$  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 $\text{NH}_2$ asymmetric stretch

The broad band observed at  $3372\text{ cm}^{-1}$ , is assigned to the  $\text{NH}_2$  asymmetric stretch mode. Upon annealing the sample this band red shifted to  $3360\text{ cm}^{-1}$  (at 70 K) and to  $3351\text{ cm}^{-1}$  at 90 K. The band position then remains unchanged until 140 K when the band was observed to shift again to  $3328\text{ cm}^{-1}$ . At 155 K, when a phase transition occurs (see below), this band was observed at  $3329\text{ cm}^{-1}$ , with an additional peak appearing at  $3377\text{ cm}^{-1}$  (Figure 2a). A further 10 K increase in the sample temperature showed another new peak centred at  $3296\text{ cm}^{-1}$ . 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  $3242\text{ cm}^{-1}$ , was observed only at 180 K.

#### 3.2.2 $\text{NH}_2$ symmetric stretch

The broad band observed in the 30 K sample at  $3179\text{ cm}^{-1}$  is assigned to the  $\text{NH}_2$  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  $3146\text{ cm}^{-1}$  (Figure 2a). The  $\nu_2$  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  $3156\text{ cm}^{-1}$  (Figure 2a).

### 3.2.3 CH stretch

The band observed at  $2895\text{ cm}^{-1}$  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  $2890\text{ cm}^{-1}$  and a new band was observed at  $2811\text{ cm}^{-1}$ . No major band shift was observed during warm up the sample from 165 K up to 210 K, where the band was observed at  $2889\text{ cm}^{-1}$  (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  $2769\text{ cm}^{-1}$  (Figure 2b) which we assign to an overtone or combination band.

### 3.2.4 CO Stretch

The band observed at  $1698\text{ cm}^{-1}$  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  $1711\text{ cm}^{-1}$  together with a new shoulder at  $1747\text{ cm}^{-1}$ . The  $1711\text{ cm}^{-1}$  band shifted to  $1719\text{ cm}^{-1}$  at 170 K, whereas the shoulder was observed at  $1748\text{ cm}^{-1}$  (Figure 2c). Both the bands remain unchanged until approximately 200 K where the bands were observed at  $1725\text{ cm}^{-1}$  and  $1750\text{ cm}^{-1}$ , respectively.

### 3.2.5 NH<sub>2</sub> scissoring

The band observed at  $1628\text{ cm}^{-1}$  in the 30K sample, the  $\nu_5$  fundamental is

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

observed, similar to the  $\text{NH}_2$  asymmetric stretching region where new bands appeared at the same temperature. At 170 K both the bands were observed to have shifted to  $1594\text{ cm}^{-1}$  and  $1645\text{ cm}^{-1}$  respectively and at 210 K they were observed at  $1599\text{ cm}^{-1}$  and at  $1641\text{ cm}^{-1}$ , (Figure 2c).

### 3.2.6 CH bending

The band observed at  $1386\text{ cm}^{-1}$  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  $1390\text{ cm}^{-1}$  (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  $1334\text{ cm}^{-1}$ , 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  $1330\text{ cm}^{-1}$  (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 $\text{NH}_2$ and CH vibrations

The bands observed at  $710\text{ cm}^{-1}$  and  $836\text{ cm}^{-1}$  in the 30K solid were assigned to the  $\text{NH}_2$  twisting and wagging vibrations [15,16], respectively. The bands at  $1117\text{ cm}^{-1}$  and  $1172\text{ cm}^{-1}$  were assigned to the  $\text{NH}_2$  rocking vibration [16]. The  $710\text{ cm}^{-1}$  band disappeared in the spectra recorded at 165 K whereas the  $836\text{ cm}^{-1}$  band was found to be at  $830\text{ cm}^{-1}$  and at  $827\text{ cm}^{-1}$  at 165 K and 210 K respectively (Figure 2e). Interestingly a new band, at  $890\text{ cm}^{-1}$ , appeared in the spectra at 165 K which remained until 180 K. The  $1117\text{ cm}^{-1}$  band was not observed in the spectra at 165 K whereas around 200 K a band appeared at  $1128\text{ cm}^{-1}$ . Spectra recorded at 165 K also revealed a new band appearing at  $2811\text{ cm}^{-1}$  which, on heating to 210 K shifted to  $2805\text{ cm}^{-1}$  (Figure 2b). It is important to note that the band observed at  $2811\text{ cm}^{-1}$  and shifted to  $2805\text{ cm}^{-1}$  under the action of increasing temperature matches with

the  $\nu_5$  fundamental of N=NH<sub>2</sub> band observed in a formamide synthesis experiment at

12 K using varied concentrations of CO and NH<sub>3</sub> [12]. The observed band shift with respect to the increase in NH<sub>3</sub> 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<sup>-1</sup> and 1056 cm<sup>-1</sup> 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<sup>-1</sup> band remained unshifted until 165 K where it was observed to shift slightly to 1019 cm<sup>-1</sup> and the band disappeared in the spectra recorded at 190 K. However, the other band at 1056 cm<sup>-1</sup> was observed to shift to 1062 cm<sup>-1</sup> at 165 K and was observed at 1061 cm<sup>-1</sup> 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 NH<sub>2</sub> asymmetric ( $\nu_1$ ) and symmetric stretch ( $\nu_2$ ) were

observed to have five bands at 3139  $\text{cm}^{-1}$ , 3174  $\text{cm}^{-1}$ , 3204  $\text{cm}^{-1}$ , 3290  $\text{cm}^{-1}$  and 3356  $\text{cm}^{-1}$ . The  $\nu_3$  fundamental band was observed at 2891  $\text{cm}^{-1}$ . The region 2820 – 2460  $\text{cm}^{-1}$ , was found to contain five peaks centred at 2813  $\text{cm}^{-1}$ , 2771  $\text{cm}^{-1}$ , 2742  $\text{cm}^{-1}$ , 2705  $\text{cm}^{-1}$  and 2472  $\text{cm}^{-1}$  (Figure 5a).

The  $\nu_4$  fundamental region that corresponds to the CO stretch was observed to contain two bands; one at 1719  $\text{cm}^{-1}$  and the other at 1748  $\nu_3$   $\text{cm}^{-1}$ . Likewise, two peaks at 1600  $\text{cm}^{-1}$  and 1655  $\text{cm}^{-1}$  were observed in region that corresponds to the in-plane  $\text{NH}_2$  scissoring vibration. The  $\nu_6$  fundamental band, corresponding to in-plane CH bending, was observed at 1392  $\text{cm}^{-1}$ , and the  $\nu_7$  fundamental, corresponding to the CN stretch, was observed at 1332  $\text{cm}^{-1}$  with an additional

shoulder band at  $1315\text{ cm}^{-1}$  (Figure 5b). The other bands observed at  $1134\text{ cm}^{-1}$ ,  $1069\text{ cm}^{-1}$  and at  $840\text{ cm}^{-1}$  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  $1069\text{ cm}^{-1}$  appeared as a doublet with a peak at  $1065\text{ cm}^{-1}$  (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  $0.5\text{ cm}^{-1}$  resolution, with the identification of the characteristic vibrations for formamide dimers occurring in the  $\text{NH}_2$  and CO vibrational regions [21]. In the present work it was hard to distinguish these peaks in our spectra due to our limited  $2\text{ cm}^{-1}$  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  $A_{\text{obs}}$  value of  $4.7 \times 10^{-18}$  cm molecule<sup>-1</sup> [13] for the 2895 cm<sup>-1</sup> ( $\nu_3$ , CH

stretch), from which the column density was estimated at about  $4.7 \times 10^{17}$  molecules cm<sup>-2</sup>. Using the  $A_{\text{obs}}$  values  $6.8 \times 10^{-18}$  cm molecule<sup>-1</sup> and  $8.5 \times 10^{-18}$  cm molecule<sup>-1</sup>

[13], for the band at  $1386\text{ cm}^{-1}$  ( $\nu_6$ , in plane CH bending) and  $1334\text{ cm}^{-1}$  ( $\nu_7$ , CN

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

## 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  $\text{NH}_2$  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  $\text{NH}_2$  vibrations ( $\nu_1$ ,  $\nu_2$ ,  $\nu_5$ ) 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 the 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) show 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 ( $\nu_7$ ), CH ( $\nu_3$ )

stretching and in plane CH bending ( $\nu_6$ ) 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 ( $\nu_7$ ), CH ( $\nu_3$ ) stretching and in plane

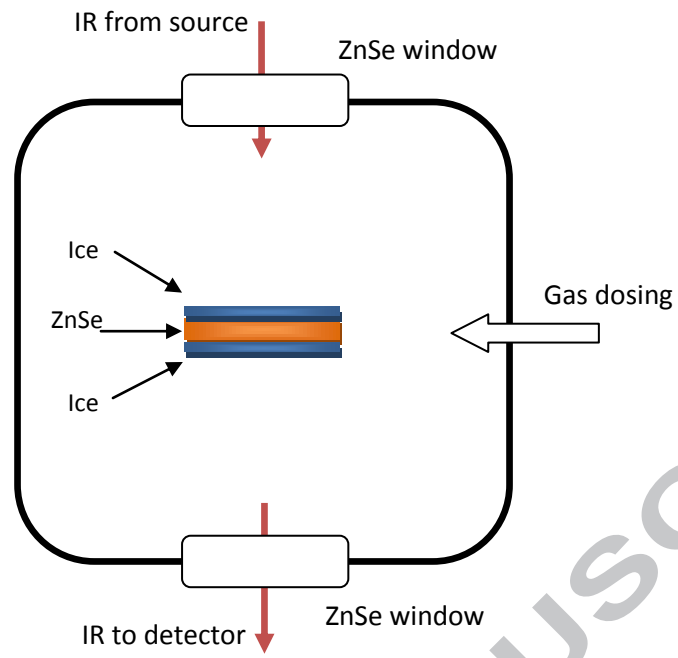
CH bending ( $\nu_6$ ) vibrations of formamide as a function of temperature.

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

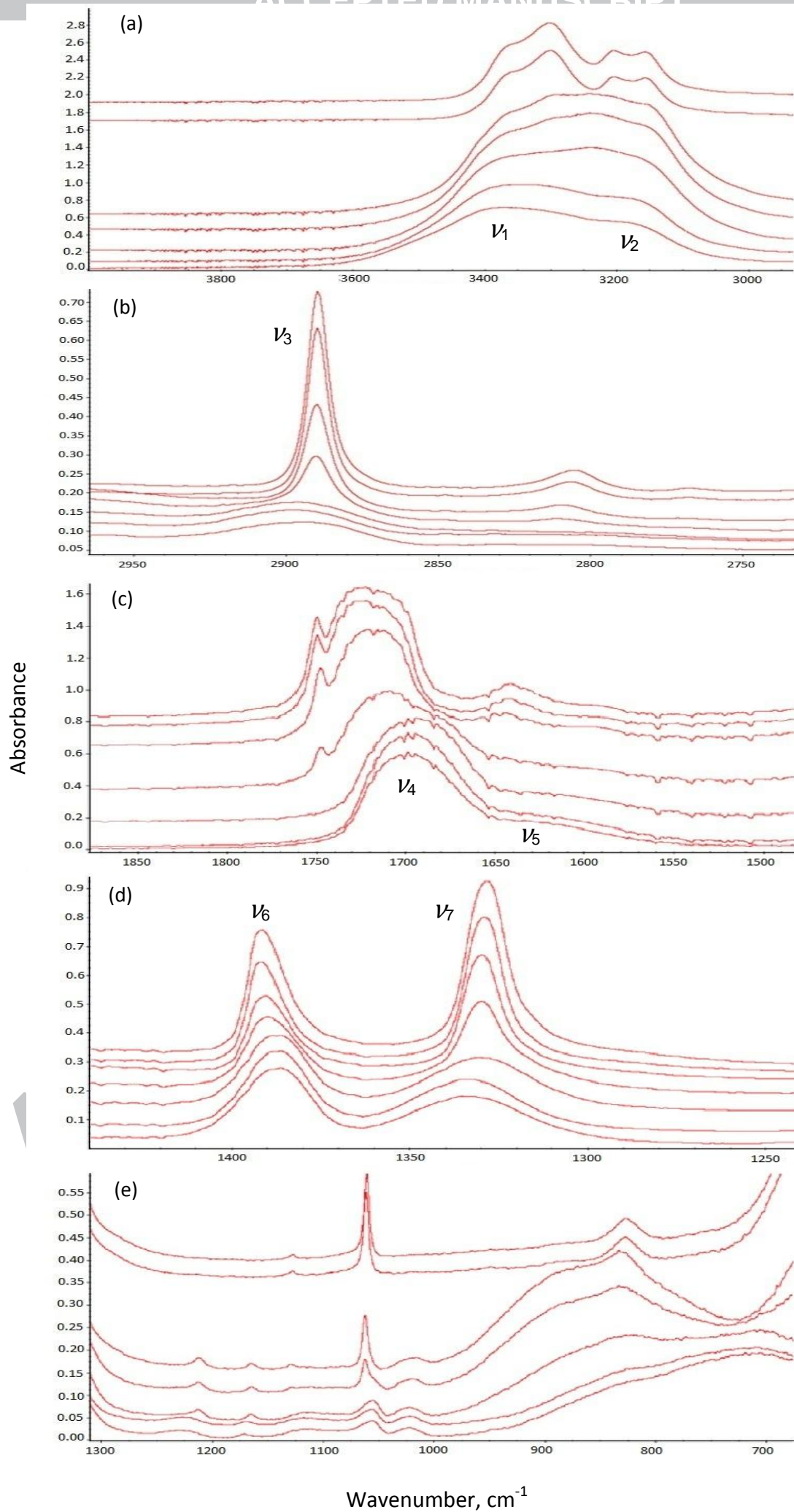
**Table captions**

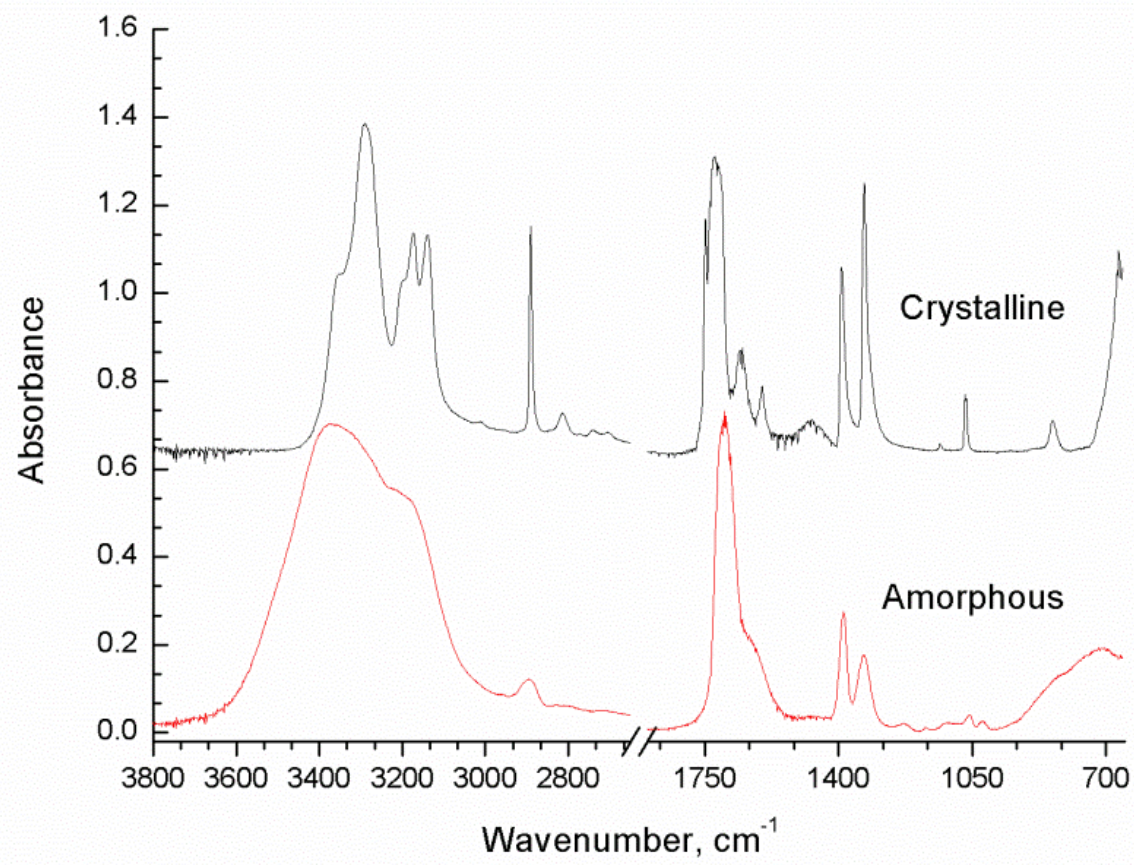
Table 1: Observed vibrational frequencies of solid formamide.

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

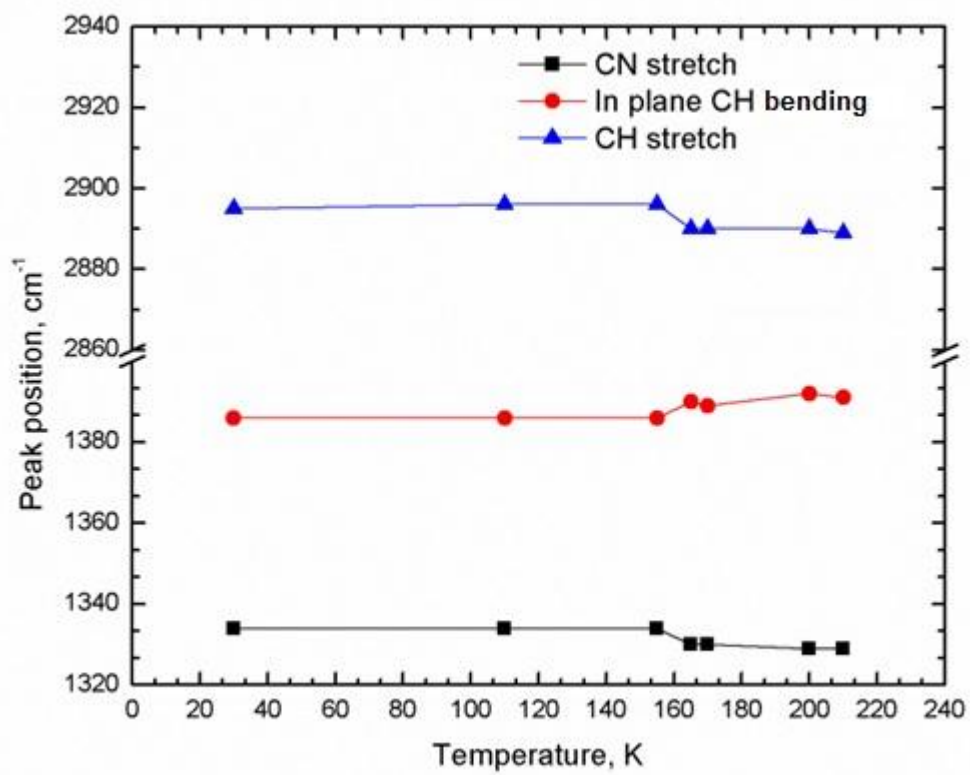


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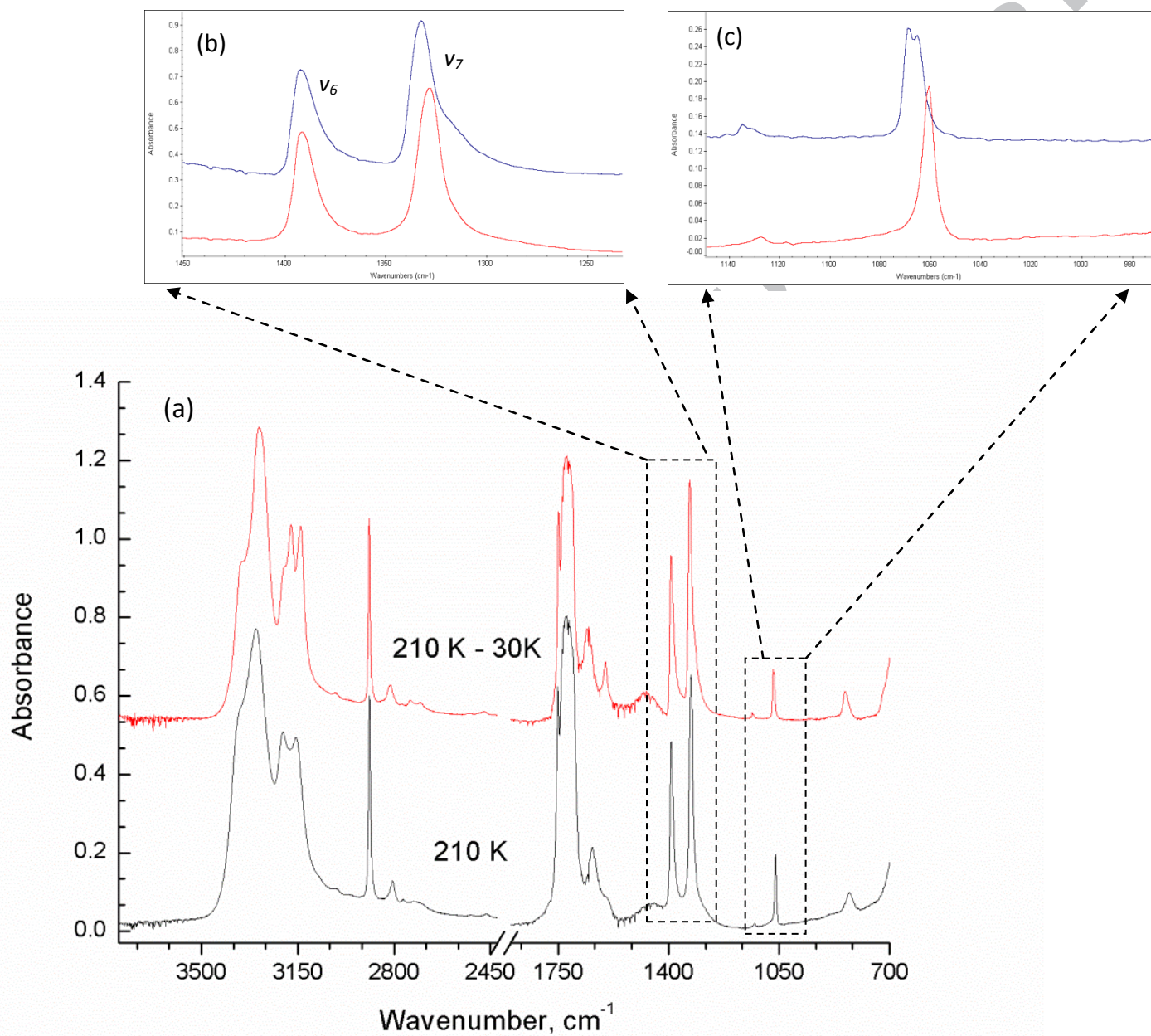
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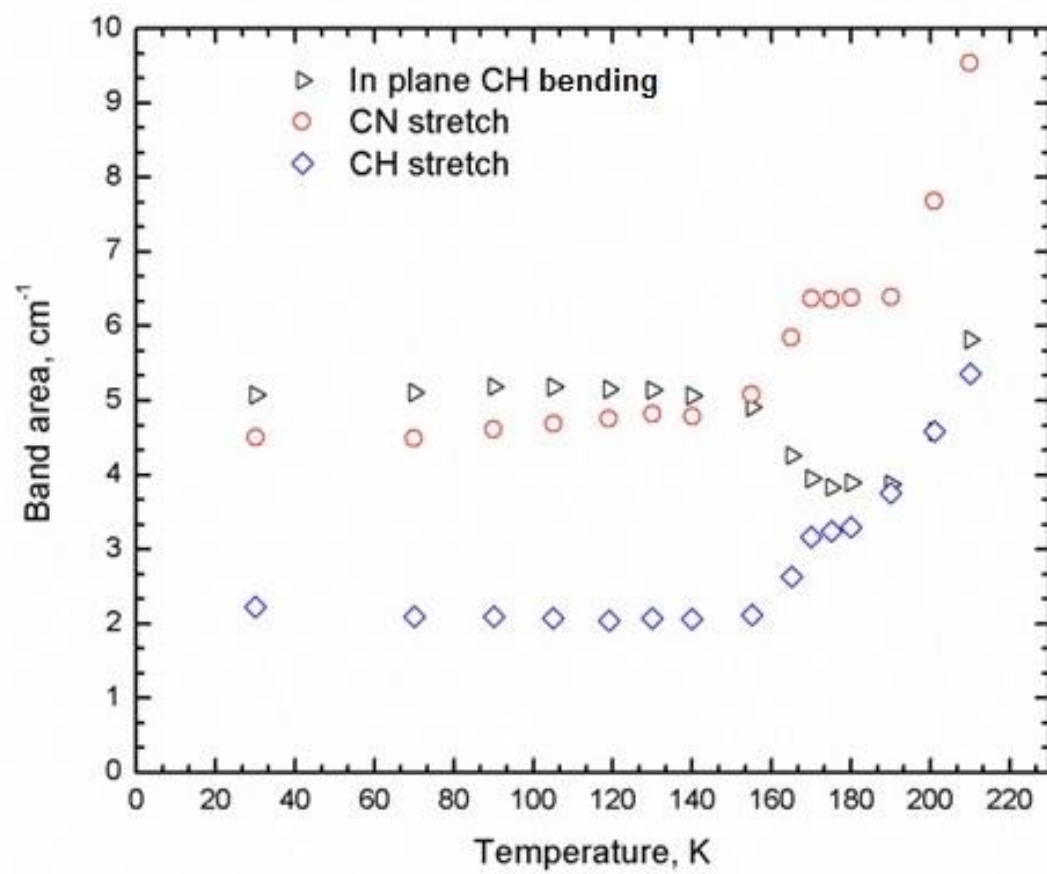


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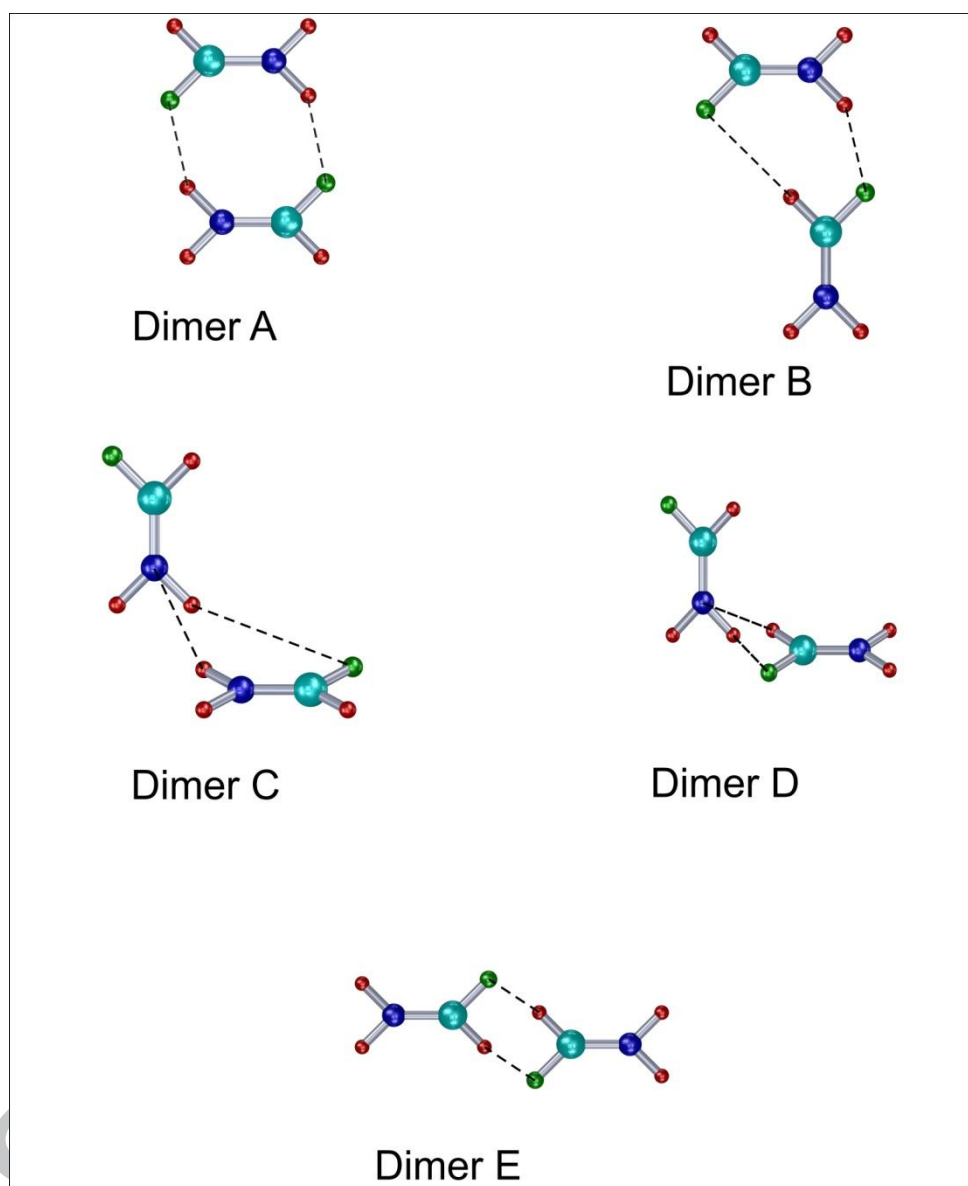
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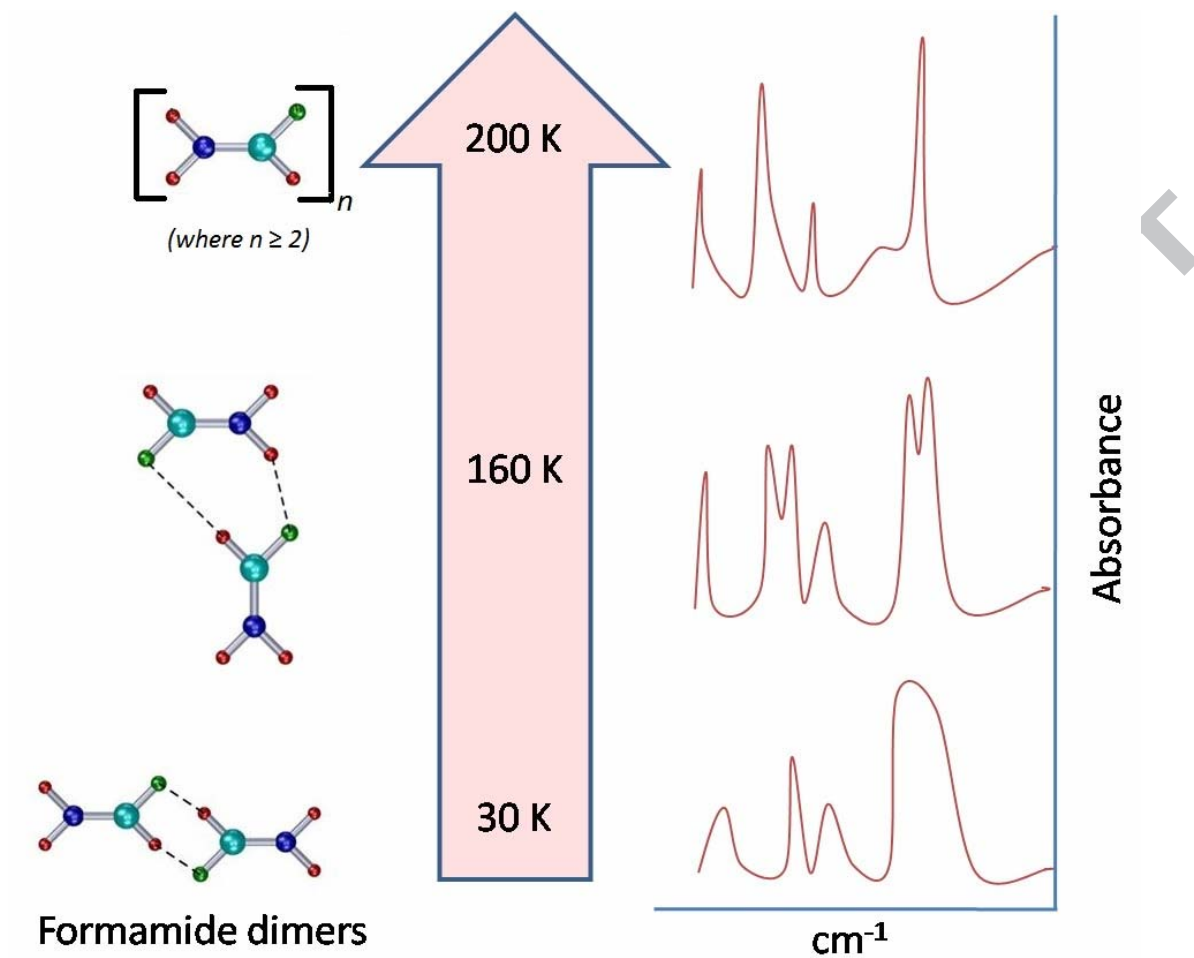
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| 30 K | Peak position, cm <sup>-1</sup> |                      | Mode    | Assignment                          | Reference |
|------|---------------------------------|----------------------|---------|-------------------------------------|-----------|
|      | 20 K <sup>[13]</sup>            | 20 K <sup>[15]</sup> |         |                                     |           |
| 710  | -                               | 685                  | ?       | NH <sub>2</sub> twisting            | 16        |
| 836  | -                               | 841                  | ?       | NH <sub>2</sub> wagging             | 15        |
| 1022 | -                               | -                    | ?       | CH out of plane bend                | 16        |
| 1056 | -                               | 1068                 | ?       |                                     |           |
| 1117 | -                               | 1134                 | ?       | NH <sub>2</sub> rocking             | 15        |
| 1172 | -                               | 1142                 | ?       |                                     |           |
| 1226 | -                               | -                    | ?       | ?                                   | 17        |
| 1334 | 1328                            | 1333                 | $\nu_7$ | CN stretch                          | 13        |
| 1386 | 1388                            | 1388                 | $\nu_6$ | In plane CH bending                 | 13*       |
| 1628 | 1631                            | 1661                 | $\nu_5$ | In plane NH <sub>2</sub> scissoring | 13        |
| 1698 | 1708                            | 1704                 | $\nu_4$ | CO stretch                          | 13        |
| 2895 | 2881                            | 2891                 | $\nu_3$ | CH stretch                          | 13        |
| 3179 | 3181                            | 3217                 | $\nu_2$ | sym NH <sub>2</sub> stretch         | 13        |
| 3372 | 3368                            | -                    | $\nu_1$ | asym NH <sub>2</sub> stretch        | 13        |

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

| 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  $\text{NH}_2$  vibrations in formamide molecule were very sensitive to temperature changes.
- Morphological changes as well as rearrangement between dimers in solid formamide.

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