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Vibrational spectra in the carbonyl stretching region of isotopomers of formamide in the gaseous and liquid states

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Abstract

IR spectra in the carbonyl stretching region of six isotopomers of formamide ($HCONH_2$, $HCOND_2$, $DCONH_2$, $DCOND_2$, $H^{13}CONH_2$, and $HCO^{15}NH_2$) in the gaseous state at a temperature of 120 °C are presented. From the frequency shifts observed it is concluded that the carbonyl stretching band is largely a stretching of the carbonyl group with only minor contributions from the CN stretching and CH bending vibrations. Calculations with a known force field confirm these results. However, some discrepancies between the observed and calculated frequencies are observed. This is most likely due to a Fermi resonance in some of the isotopomers. Changing the gas phase values of the CO and CN stretching diagonal force constants only gives satisfactory agreement between the calculated frequencies and the observed frequencies in the liquid state. Upon heating, the Raman carbonyl bands of neat liquid $HCONH_2$, neat liquid $HCOND_2$, and an equimolar mixture of the two shift to different extents. This is most likely due to differences in the carbonyl stretching normal coordinate.

Keywords: Carbonyl; Formamide; Gas; Isotopomer; Liquid

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1. Introduction

Recently, we have undertaken a study of intermolecular interactions in formamide and its various isotopomers in the liquid state and in solution [1,2], focusing our attention on the carbonyl stretching band. This revealed a distribution between aggregates with hydrogen-bonded and "free" carbonyl groups. As expected, the frequency of the carbonyl stretching band corresponding to "free" carbonyl groups was found at a higher frequency than the band corresponding to hydrogen-bonded carbonyl groups. In a further understanding of these complex systems, the frequencies of the carbonyl band of the various isotopomers in the gaseous state could be helpful because the gas phase is a state of very weak interactions, and thus represents the frequency for real free carbonyl groups. The gas phase spectrum of formamide ($HCONH_2$) itself has been studied extensively in the past [3–6]. However, as regards the various isotopomers of formamide, only the gas phase spectrum of $DCONH_2$ has been reported previously [3]. IR-matrix isolation studies of $HCONH_2$, $HCOND_2$, $DCONH_2$ and $DCOND_2$ have been performed as well [7]. In order to compare with our studies in the liquid state, we need carbonyl

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stretching frequencies of all the isotopomers studied, and we present here the IR gas phase spectra of six isotopomers of formamide ($HCONH_2$, $HCOND_2$, $DCONH_2$, $DCOND_2$, $H^{13}CONH_2$ and $HCO^{15}NH_2$) in the carbonyl stretching region. Although the spectra of $HCONH_2$ and $DCONH_2$ have been published before [3-6], they are shown here for comparison. Matrix isolation data of all isotopomers could have been of great importance. However, these studies are excluded due to experimental limitations. The vapour phase IR spectra were studied in the frequency region 500-4000 cm^{-1}, and most of the in-plane fundamentals were observed. However, difficulties due to the presence of water vapour and decomposition products made it impossible to perform a complete assignment of all vibrations. The observed frequencies are compared to frequencies calculated using the ab initio harmonic force of Fogarasi and Balázs [8]. The calculations are extended to include liquid state by changing some of the force constants. Finally, the Raman spectra as a function of temperature of $HCONH_2$, $HCOND_2$ and an equimolar mixture of the two will be presented.

2. Experimental

$HCONH_2$ (puriss. p.a.) was obtained from Fluka, $HCO^{15}NH_2$ (99% ^{15}N) from Stohler Isotope Chemicals, $DCONH_2$ (99.1% D) from Campro Scientific B.V. and $H^{13}CONH_2$ (99% ^{13}C) from IC Chemikalien GmbH.

$HCOND_2$ and $DCOND_2$ were obtained by letting an excess of D_2O react overnight with $HCONH_2$ and $DCONH_2$, respectively, and subsequently distilling off the water *in vacuo*. The process was repeated twice.

The IR spectra were obtained with a Bruker IFS 120 HR FTIR spectrometer equipped with an MCT detector cooled by liquid nitrogen. The gas phase spectra were obtained at a resolution of 1.0 cm^{-1}. The samples were held in a Perkin-Elmer 10 cm heatable cell with KBr windows at a temperature of 120 °C. IR spectra of the liquids were recorded at a resolution of 4.0 cm^{-1} as thin films between two CaF_2 plates. Since only IR spectra of thin films could be obtained, it was not possible to record IR spectra as a function of temperature. This has been done by Raman spectroscopy instead.

The Raman spectra were obtained with a Dilor Z24 spectrometer using the 488.0 nm excitation line of a Spectra Physics argon-ion laser providing an output of 400 mW. Both the polarized and depolarized scattering were measured and the isotropic spectra were constructed in the usual way ($I_{iso} = I_{vv} - 4/3 I_{vh}$).

2.1. Calculations

The moments of inertia have been calculated for all isotopomers using the computer program IMOM [9]. The planar configuration found by Hirota et al. [10] was adopted. The gas phase frequencies were calculated by use of the computer program VIBROT [9] using the experimentally found geometry [10] and the harmonic force field of Fogarasi and Balázs [8] found by ab initio calculations. This force field was preferred over others [11,12] as it has been scaled in order to reproduce the experimentally determined frequencies [8]. Previously, only calculations of the frequencies of the various deuterated isotopomers have been performed [8]. Our calculations are in agreement with these, and we extend them to include the frequencies of $H^{13}CONH_2$ and $HCO^{15}NH_2$.

The frequencies of "liquid" formamide were calculated by changing the diagonal force constants only, i.e. no interaction force constants were changed. The program VIBROT calculates both the frequencies and the potential energy distribution (PED), the input parameters being the geometry and the force field. The same definition of the internal and symmetry coordinates was used [8] in the calculations. The in-plane symmetry coordinates relevant for this work (i.e. contributing to the CO stretching mode) are: S_1, CH stretching; S_2, CO stretching; S_3, CN stretching; S_6, OCN bending; S_7, CH bending; S_8, NH_2 bending; S_9, NH_2 rocking. The NH stretching coordinates S_4 and S_5 do not contribute to the CO stretching mode.

3. Results and discussion

3.1. Gas phase spectra

In Fig. 1, IR spectra of the six isotopomers of formamide are shown. All the carbonyl bands have several Q-branches. This could be due to different rotational constants in the vibrational ground and first excited state, or could be caused by hot bands due to low-lying levels (expecially the very anharmonic NH_2 wagging mode at 289 cm^{-1} [13]; the Boltzmann factor at the temperature used here is 0.35 for this level and 0.09 for the second excited state at 657.7 cm^{-1} [13]). The Q-branches observed in the carbonyl band of $HCOND_2$ are more intense than the ones observed in $HCONH_2$, since the ND_2 wagging mode is found at 208.7 cm^{-1}, giving a Boltzmann factor of 0.47 and 0.18 for the second excited state at 466.4 cm^{-1} [14].

The observed frequencies of the carbonyl bands of the various isotopomers are given in Table 1, together with the frequencies calculated from the harmonic force field [8]. Due to the multitude of Q-branches, the peak frequencies were calculated as the mean of the maxima of the P- and R-branches. In most cases the frequency determined in this way agreed well with the frequency of the most intense Q-branch.

The PEDs in percent for the carbonyl band of all the isotopomers are given in Table 2. From this it can be seen that the carbonyl band mainly involves stretching of the CO bond (S_2). Calculations using an unscaled force field show that the CO stretching mode consists of CO stretching NH_2 bending and CH bending [15]. This is not in accordance with the present calculations (Table 2).

As can be seen from Table 1, there is a frequency shift of only 4–5 cm^{-1} between the N-deuterated ($HCOND_2$ and $DCOND_2$) and the corresponding N-hydrogenated ($HCONH_2$ and $DCONH_2$) isotopomers. The difference in frequency between $HCONH_2$ and $HCOND_2$ and between $DCONH_2$ and $DCOND_2$ can be attributed to the higher

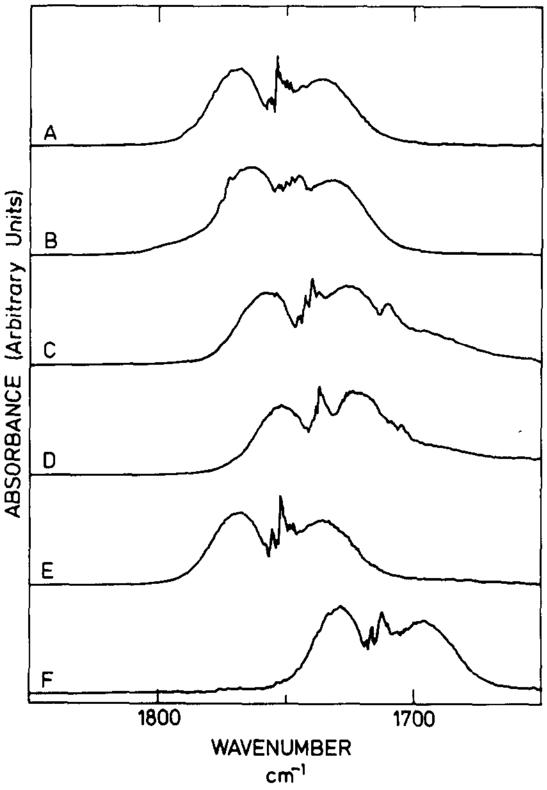

Fig. 1. IR spectra of the carbonyl bands of the six isotopomers in the gas phase. (A) $HCONH_2$; (B) $HCOND_2$; (C) $DCONH_2$; (D) $DCOND_2$; (E) $HCO^{15}NH_2$; (F) $H^{13}CONH_2$.

Table 1
Frequency of the carbonyl bands of the six isotopomers of formamide in the gaseous state, calculated as a mean of the maxima of the *P*- and *R*-branches, and frequencies calculated with the harmonic force field of Fogarasi and Balázs [8]

Compound	Observed frequencies (cm^{-1})	Calculated frequencies (cm^{-1})	$\nu_{calc} - \nu_{obs}$ (cm^{-1})	Obs. isotope shifts	Calc. isotope shifts
$HCONH_2$	1753.2 ± 1.0	1760.2	7.2	0	0
$HCOND_2$	1747.9 ± 1.0	1751.5	3.6	−5.3	−8.7
$DCONH_2$	1740.9 ± 1.0	1732.3	−8.6	−12.3	−27.9
$DCOND_2$	1737.0 ± 1.0	1725.7	−11.3	−16.2	−34.5
$HCO^{15}NH_2$	1752.0 ± 1.0	1759.1	7.1	−1.2	−1.1
$H^{13}CONH_2$	1712.2 ± 1.0	1717.5	5.3	−41.0	−42.7

mass attached to nitrogen in the case of the isotopomers with deuterium on nitrogen, and might also be caused by different contributions from the NH_2 rocking motion to the CO stretching mode (Table 2).

Deuteration on carbon causes a significant isotopic shift of 11–12 cm^{-1} regardless of whether nitrogen is deuterated or not. This shift is not only caused by the heavier mass attached to carbon but might also be due to a small change of the normal coordinate (Table 2), i.e. differences in the contribution from the CH/CD stretching (S_1) and bending (S_7) motions to the CO stretching mode.

The carbonyl band of $HCO^{15}NH_2$ is shifted only very little ($\sim 1\ cm^{-1}$) relative to the carbonyl band of $HCONH_2$ (Table 1). Only a small shift is expected, since the CN stretching motion (S_3) only contributes around 10% to the CO stretching mode (Table 2). As expected, the ^{13}C compound shows a large isotopic shift of the carbonyl band. This shift is very close to that expected for a diatomic CO molecule, confirming that the carbonyl band arises largely from stretching of the C=O bond.

The principal axes of inertia for formamide are shown in Fig. 2. The *c*-axis is perpendicular to the molecular plane. The pricipal axes of inertia change very little upon isotopic substitution and, therefore, the type of bands (A-, B- or C-type) are the same for all isotopomers for a given mode when the normal coordinate is not altered too much by isotopic substitution as revealed by the PEDs.

Having established that the carbonyl band is mainly due to stretching of the C=O bond (i.e. the transition dipole moment is primarily along the C=O bond), it is possible to predict the type of band. As Fig. 2 shows, the ν(C=O) mode is an A,B-type hybrid with the largest contribution along the *a*-axis. Comparing the carbonyl band with the predicted band contour [16] shows that it resembles an A-type band (the parameters x and y of Ref. [16] are 1.73 and 0, respectively, for formamide). The separation in frequency between the *R*- and *P*-branches is some 30 cm^{-1}, which is exactly what is predicted for an A-type band with this ratio of rotational constants [16].

Table 2
Potential energy distribution for the carbonyl band of the various isotopomers of formamide in the gaseous state; for definition of the symmetry coordinates, see text

	$HCONH_2$	$HCOND_2$	$DCONH_2$	$DCOND_2$	$HCO^{15}NH_2$	$H^{13}CONH_2$
S_1	0	0	3	3	0	0
S_2	75	77	74	76	76	75
S_3	10	9	13	12	9	9
S_6	1	1	0	0	1	1
S_7	11	10	6	6	11	11
S_9	3	1	2	1	3	3

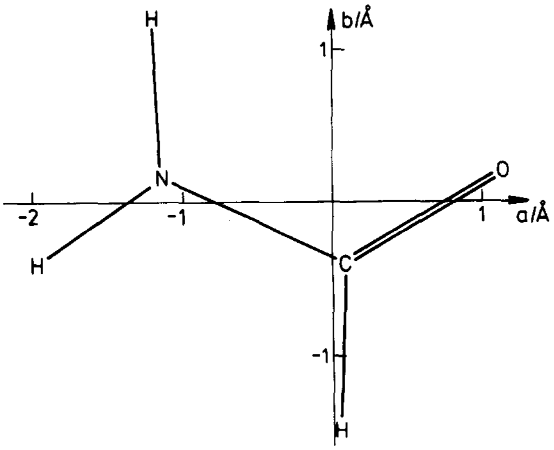

Fig. 2. Principal axes of inertia for formamide. The c-axis is perpendicular to the plane of the molecule.

In general, the scaled force field of Fogarasi and Balázs [8] reproduces the observed frequencies quite well; the deviations from the observed frequencies are less than 2%. In the case of the carbonyl band, the deviation is less then 1% (Table 1). However, the frequency shifts between the isotopomers are less well reproduced. The calculated frequencies of the carbonyl band of the isotopomers with deuterium on carbon are a little too small, whereas in the case of isotopomers with ^1H on carbon, the calculated frequencies are a little too high (Table 1). A comparison of the calculated and observed isotope shifts reveals that the calculated isotope shift of the carbonyl bands of $DCONH_2$ and $DCOND_2$ is more than twice as large as the actual shift, whereas the calculated and observed shifts of the other isotopomers are in closer agreement (Table 1).

Comparing the carbonyl bands of the C-deuterated (Fig. 1C, D) and the C-hydrogenated (Fig. 1A, B, E, F) isotopomers shows that in the former compounds, the P-branch is more intense than the R-branch, whereas the reverse is true of the C-hydrogenated isotopomers. This apparent reverse of intensity is caused by an overlapping band whose R-branch coincides with the P-branch of the carbonyl band of the C-deuterated isotopomers and whose Q-branch is seen around 1700 cm^{-1}. The Q-branch of this band is quite broad due to hot bands, which also caused the multitude of Q-branches observed in the carbonyl bands. The P-branch of the band around 1700 cm^{-1} is the cause of the tail on the low-frequency side of the carbonyl band. This band is also observed in the IR (see below) and Raman spectra [17] of the neat liquids. That the band is found at approximately the same frequency in both $DCONH_2$ (1710 cm^{-1}) and $DCOND_2$ (1705 cm^{-1}) suggests that it involves mainly a vibration of the DC group and no contribution from the NH_2 group. No fundamental is observed at approximately half the frequency of this band and a combination band thus seems to provide the best explanation. However, the calculations show that the CD out-of-plane bending mode, is expected to be found around 868 cm^{-1}. The CD out-of-plane mode belongs to the A'' species of the point group C_s. The overtone, however, belongs to the totally symmetric symmetry species and Fermi resonance with the CO stretching mode is thus possible. The overtone is observed on the low-frequency side of the carbonyl band, and Fermi resonance also leads to a "repulsion" of the two levels involved, i.e. the frequency of the CO stretching mode is increased. This could be why the calculated frequencies are too low for the isotopomers with deuterium and carbon as compared to the experimentally observed frequencies (Table 1).

3.2. *Liquid phase spectra*

The IR spectra of the six isotopomers in the liquid state are shown in Fig. 3, and the frequencies of the carbonyl bands are given in Table 3. First of all, it is observed that

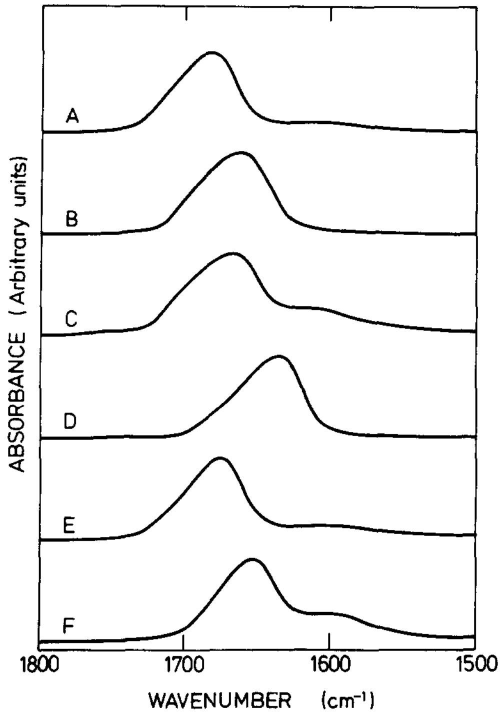

Fig. 3. IR spectra of the carbonyl bands of the six isotopomers in the liquid state. (A) $HCONH_2$; (B) $HCOND_2$; (C) $DCONH_2$; (D) $DCOND_2$; (E) $HCO^{15}NH_2$; (F) $H^{13}CONH_2$.

there is a red shift of the carbonyl bands in the liquid state as compared to the gaseous state (Table 3). The overtone of the CD out-of-plane bending is seen at 1750 cm^{-1} (Fig. 3C, D) but is now at higher frequency than the CO stretching band due to the red shift of the latter. The red shift is caused by a weakening of the C=O double bond caused by hydrogen bonding. The CN stretching band around 1256 cm^{-1} (in $HCONH_2$) shifts to 1307 cm^{-1} in the liquid state. That is, the double bond character of the CO bond decreases, whereas it increases for the CN bond.

Changing the CO stretching diagonal force constant from 12.223 mdyn Å^{-1} (gas phase value) in the original work [8] to 10.5 mdyn Å^{-1} and the CN stretching diagonal force constant to 8 mdyn Å^{-1} from 6.684 mdyn Å^{-1} gave reasonable agreement between observed and calculated carbonyl stretching frequencies (Table 3), and the calculated CN stretching frequencies were within 3 cm^{-1} of the observed values. Besides the NH stretching bands (which do not mix with other modes) and the CO and CN stretching

Table 3

Frequencies of the carbonyl bands of the six isotopomers of formamide in the liquid state, gas–liquid shifts and frequencies calculated changing the harmonic force field of Fogarasi and Balázs [18]

Compound	Observed frequencies (cm^{-1})	Observed $\nu_{gas} - \nu_{liq}$ (cm^{-1})	Calculated ($k_{CO} = 10.5$, $k_{CN} = 8$) (cm^{-1})
$HCONH_2$	1682	−71	1685
$HCOND_2$	1661	−87	1668
$DCONH_2$	1666	−75	1667
$DCOND_2$	1635	−102	1650
$HCO^{15}NH_2$	1675	−77	1681
$H^{13}CONH_2$	1653	−59	1648

In the calculations (fourth column) the CO and CN stretching diagonal force constants have been changed from their original values of 12.223 and 6.684 mdyn Å^{-1} [8], respectively.

Table 4
Potential energy distribution for the carbonyl band of the various isotopomers of formamide in the liquid state, calculated with k_{CO} = 10.5 mdyn Å^{-1} and k_{CN} = 8 mdyn Å^{-1}

	$HCONH_2$	$HCOND_2$	$DCONH_2$	$DCOND_2$	$HCO^{15}NH_2$	$H^{13}CONH_2$
S_1	0	0	0	0	0	0
S_2	52	60	51	63	55	44
S_3	23	21	28	25	22	24
S_6	0	0	0	0	0	0
S_7	15	16	7	8	16	14
S_8	7	1	11	1	5	16
S_9	2	1	2	1	2	2

For definition of the symmetry coordinates, see text.

bands, the other bands do not shift appreciably on going from the gaseous to the liquid state, and it was hence not necessary to change any other force constants.

Changing the force constants changed the normal coordinates as compared to the gas phase values (Tables 2 and 4). Now, the PEDs are markedly different from the values in the gas phase, and they are different for the various isotopomers as compared to the gas phase PEDs, which only showed minor differences between the isotopomers (Table 2). As discussed recently by us, changing the CO stretching diagonal force constant only leads to minor differences in the PEDs on going from the gaseous to the liquid state [17].

The different PEDs are in accordance with the experimental data, as shown below. In the case of $H^{13}CONH_2$ (Fig. 3F), the CO stretching band is relatively less intense than the NH_2 band as compared to the other isotopomers with NH_2 groups (Fig. 3A, C, E). Comparing the PEDs shows that the CO stretching vibration only contributes 44% to the carbonyl stretching mode in the case of $H^{13}CONH_2$, but 52% in the case of $HCONH_2$. The CO stretching vibration contributes 21% to the NH_2 bending mode in the case of $H^{13}CONH_2$ and 11% in the case of $HCONH_2$. Stretching of the CO bond usually gives rise to a large change in dipole moment and hence high IR intensity. The relative intensity changes are thus easily explained due to different normal modes of vibration in the various isotopomers, i.e. the NH_2 bending mode of $H^{13}CONH_2$ contains more CO stretching and the CO stretching mode contains less CO stretching then they do in the other isotopomers.

3.3. *Variation of temperature*

Figures 4 and 5 show the isotropic and anisotropic, respectively, Raman spectra of $HCONH_2$, $HCOND_2$ and an equimolar of the two at temperatures ranging from −10 to 160 °C. Formamide melts at 2.5 °C but it was possible to supercool it below −10 °C. At high temperatures (the boiling point is 210 °C) formamide decomposes, leading to fluorescense. This is observed in the spectra at 140 and 160 °C (Figs. 4 and 5), thus making it pointless to increase the temperature further.

Only one carbonyl stretching band is observed in the isotropic Raman spectra of the equimolar mixture of $HCONH_2$ and $HCOND_2$, even though the carbonyl bands of $HCONH_2$ and $HCOND_2$ are separated by 30 cm^{-1} [1]. The apparent coalescence of the carbonyl bands was shown not to be due either to exchange of hydrogen with deuterium or to the presence of *cis*- and *trans*-HCONHD. The phenomenon is believed to be due to intermolecular coupling, which causes oscillators with different intrinsic frequencies to oscillate with the same frequency [17]. The isotropic and anisotropic carbonyl bands have different peak frequencies. This is called the non-coincidence effect [1] and is caused by intermolecular interactions in liquids.

Upon heating, both the isotropic and anisotropic carbonyl bands shift upwards. The isotropic carbonyl band of $HCOND_2$ shifts by around 13 cm^{-1} on going from −10 to 120 °C, whereas the carbonyl band of $HCONH_2$ only shifts by 3 cm^{-1}. The carbonyl band of the equimolar mixture shifts by approximately the same amount as the carbonyl band of $HCOND_2$. The anistropic carbonyl bands of $HCONH_2$, $HCOND_2$ and the equimolar mixture seem to shift a little less than the corresponding isotropic bands. This is in accordance with theory [18], which predicts a smaller non-coincidence splitting (i.e. $\nu_{aniso} - \nu_{iso}$) when the temperature is raised and the density decreases [18].

Consider a dipolar interaction potential, i.e. $V \propto \mu \cdot \mu$. A Taylor expansion of this potential in the normal coordinates leads to an expression for the shifts of the isotropic and anisotropic bands on going from the gaseous to the liquid state [19]. The shifts are proportional to $(\partial\mu/\partial Q)_0^2/T$, where $(\partial\mu/\partial Q)_0$ is the transition dipole moment and T is the temperature. Now, since the normal coordinates of the carbonyl stretching vibration of $HCONH_2$ and $HCOND_2$ are different (Table 4), they are expected to show different shifts on going from the gaseous to the liquid state. This has been verified by experiment (Tables 1 and 3). Furthermore, the shift as a function of temperature should also be different, which is also in accordance with experiment (Figs. 4 and 5). Since the shift of the carbonyl band of $HCOND_2$ is larger upon heating than it is in case of $HCONH_2$, the transition dipole moment of the former compound should be larger than that of the latter compound. It has not been possible to verify this experimentally, since the extinction coefficient of the carbonyl band is very high [1]. However, the PED shows (Table 4) that the carbonyl stretching band of $HCOND_2$ contains more CO stretching vibration than the corresponding band of $HCONH_2$ does, and the carbonyl stretching band of the former compound is hence believed to be more intense.

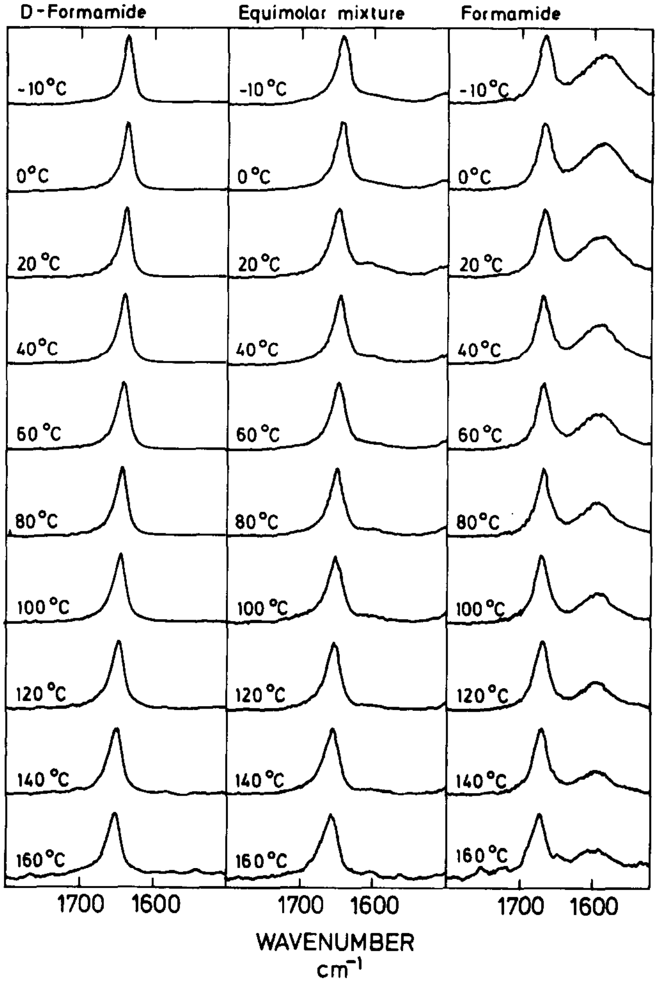

Fig. 4. Isotropic Raman carbonyl bands of $HCONH_2$, $HCOND_2$ and an equimolar mixture of the two as a function of temperature.

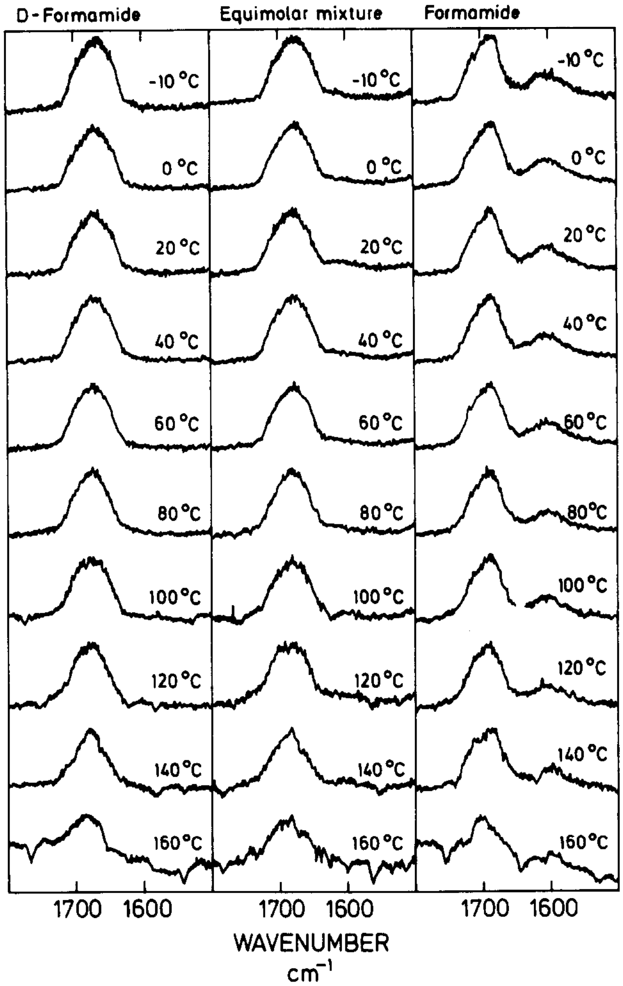

Fig. 5. Anisotropic Raman carbonyl bands of $HCONH_2$, $HCOND_2$ and an equimolar mixture of the two as a function of temperature.

Both isotropic and anisotropic carbonyl bands are asymmetric (Figs. 4 and 5). The carbonyl bands could be decomposed into two bands, the high-frequency band being assigned to "free" (i.e. non-hydrogen bonded) formamide molecules and the low-frequency band to hydrogen-bonded formamide [1,2]. There seems to be an increase in the intensity of the high-frequency component upon heating (Figs. 4 and 5). The increase, however, is small, probably because the temperature is still well below the boiling point.

4. Conclusions

The carbonyl band of formamide in the gaseous state mainly consists of CO stretching motion with some small contributions from the CH bending and CN stretching motions. The carbonyl bands of the six isotopomers are largely type A bands. The CO stretching frequencies calculated using a harmonic force field reproduce the observed frequencies quite well, but in the case of $DCONH_2$ and $DCOND_2$, the agreement is less good. This could be due to a Fermi resonance with the overtone of the CD out-of-plane bending mode.

In the liquid state, the carbonyl band is still mainly stretching of the CO bond, but with large admixtures of other vibrations. As compared to the gas phase, the carbonyl stretching normal coordinate is now markedly different for the various isotopomers.

Upon heating, the Raman carbonyl band of $HCOND_2$ shifts more than the carbonyl band of $HCONH_2$. The different shifts are probably due to different normal coordinates. Besides shifting, the relative intensity of "free" species increases upon heating due to changes in the proportion of "free" and hydrogen-bonded formamide.

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