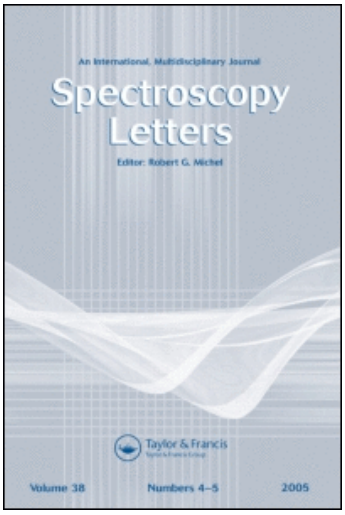

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Fourier-Transform Infrared and Raman Spectra of Glutarimide

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FOURIER-TRANSFORM INFRARED AND RAMAN SPECTRA OF GLUTARIMIDE

Keywords: Polycrystalline Glutarimide, FT IR and Raman spectra, hydrogen bond, temperature effect

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ABSTRACT

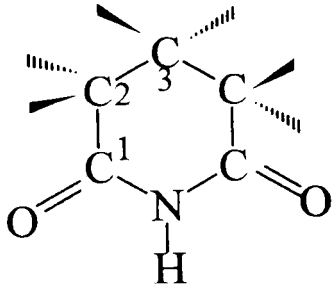
The FT-IR (from 50 to -180°C) and the FT-Raman spectra at 25°C of glutarimide in in the solid state are investigated. The data are compared with recent results of Bienko et al.(J.Phys.Chem.*A* 101,7834 (1997) on glutarimide isolated in a low-temperature argon matrix. The vibrational changes induced by hydrogen bond formation in the crystalline state are discussed. The ν(NH...O) vibration is observed at 3189 cm^{-1} at 25°C and at 3163 cm^{-1} at -180°C. These values correspond to a contraction of the N...O distance of 0.022 Å.

INTRODUCTION

As discussed in a recent paper[1], glutarimide derivatives possess interesting biochemical activity such as significant anticancer activity and are also components of

recently synthesized antibiotics. It has been suggested that the biological activity of glutarimide

drugs is determined by the specific hydrogen bonding of the CO-NH-CO imide group and other molecules in biological systems. The significant flattening of the glutarimide ring also enables some glutarimide drugs to intercalate between nucleic base pairs in the DNA helix. The infrared spectra of glutarimide (GLU)



isolated in low-temperature argon and nitrogen matrixes have been recently reported and the vibrational frequencies have been obtained at the D95V** level[1]. The main scope of this work is to discuss the vibrational spectra of glutarimide in the polycrystalline state where the molecules are linked by NH...O hydrogen bonds[2]. It must be pointed that the infrared spectrum and the self-association of glutarimide in solution have been discussed [3-4] but the assignment of some vibrations seems somewhat ambiguous.

EXPERIMENTAL

The FT-IR spectra have been recorded on the Bruker 66 spectrometer (resolution = 2 cm^{-1}, 32 scans, KBr beam-splitter, DTGS detector). The Raman spectra have been taken on the same instrument equipped with a FRA-106 Raman module (resolution = 2 cm^{-1}, 64 scans, CaF_2 beam-splitter, cooled Ge detector, YAG laser with a power of 200 mW). The infrared spectra at low temperature have been recorded with a

commercial Specac cryostat. The IR spectra of polycrystalline GLU have been taken in KBr suspension.

Glutarimide from Aldrich has been used without further purification.

RESULTS AND DISCUSSION

In the crystalline state, the conformation of GLU may be described as a half-chair, with C3 0.58Å out of the essentially coplanar system. The NH...O hydrogen bonds of length 2.90Å link the molecules in zig-zag chains[2]. The dimers are not formed by NH...O bonds around centers of symmetry like in substituted glutarimides[5] and the vibrational modes are IR and Raman active.

The experimental frequencies of glutarimide isolated in an argon matrix and the assignment of the vibrational modes from MP2 calculations[1] are indicated in Table 1. It must be pointed here that PED calculation indicates a strong mixing of the vibrations and only the predominant contributions or those relevant for the discussion are reported in this Table. Table 1 also lists the IR frequencies observed in solid glutarimide at 25 and -180°C and the Raman frequencies at room temperature. Some IR data observed in CCl_4 at low concentrations (0.008 mol dm^{-3}) where the concentration of self-associated species is low are also included in this Table. The IR and Raman spectra are reproduced in FIG. 1 and 2.

The ν(NH) and ν(C=O) frequencies of the monomer of GLU are slightly higher in argon than in CCl_4 solution. It must be pointed here that in solid argon, five absorptions assigned to Fermi resonance with other modes are observed in the C=O stretching region. The same behavior has been observed in uracil and several uracil derivatives[6-8]. In CCl_4, only one ν(C=O)band is observed which can be split into two components at 1734 and 1720 cm^{-1} after a deconvolution procedure.

Comparison of the vibrational spectra of solid and matrix-isolated GLU reveals substantial changes due to the formation of hydrogen bonding in the crystal lattice. The main component of the ν(NH...O) vibration is observed at 3189 cm^{-1} (25°C) and 3163 cm^{-1} (-180°C). Two other absorptions assigned to Fermi resonance (Table 1) at 3109

TABLE 1.

Infrared and Raman data for glutarimide

IR(25°C)	IR(-180°C)	Raman (25°C)	Ar matrix[a]	CCl_4 solution	Assignment[a]
			3406 s	3383 s	$\nu(NH)^{free}$
3189 m	3164 m	3185 w		3214 w	ν(NH...O)
3109 m	3117 s				ν^{as}(C=O) + δ(NH)
3091 m	3093 m	3089 w		3089 w	ν^{s}(C=O) + w(CH2)
2969 w	2668 m	2976 s	2973(R)	2964 m	ν(CH2)
			2925	2940	ν(CH2)
2907 w	2908 m	2903 vs	2902(R)	2903	ν(CH2)
2839 w	2864 m				
	2841 m	2839 w			
1810 w	1819 w		1792	1792 w	$2\nu^{as}$(C-C)
		1759 vw			
1722 s,br	1722 s,br	1719 m	1748	1734 m	ν^{s}(C=O)
1703 s,br	1703 s,br	1689 vs	1739	1720 s	ν^{as}(C=O)
1667 s	1667 s				ν^{as}(C=O)
			1652	1651 w	916 + 720
1470 m	1476 m	1472 w	1465	1462 w	δ(CH2)
1441 m	1441 w	1465		1432	δ(CH2)
1423 m	1423 m	1424 m	1423(R)	1427 w	δ(CH2)
1408 m	1409 m	1408 w	1392	1391 w	δ(NH)(48%) + ν^{as}(C-N)
1368 s	1371 s		1374	S	
		1368 vw	1362	S	combination
1352 s	1353 s		1348	1347 s	ν(C-C) + ν^{s}(C-N)
1336 s	1339 s	1337 w	1334	S	w(CH2) + t(CH2)
1326 m	1326 s		1318	S	w(CH2) + ν^{s}(C-N)

TABLE 1. Continued

1272 s	1275 s	1255 m	1246	1245 m	w(CH2) +
	1263 s				δ(NH)(20%)
1178 s	1180 s	1179 m	1181	1175 s	t(CH2) + ν^{as}(C-N)
1155 s	1157 s	1151 vw	1144	1139 s	t(CH2)
			1061	S	r(CH2)
1051 m	1053 m	1059 m	1051	1050 w	ν^{as}(C-C)
		972 w	968	S	δ(ring) + r(CH2)
919 w	921 m	920 w	916	913 vw	ν^{s}(C-C)
	864 w		858(R)	S	r(CH2) + γ(C=O)
759 m	761 m	761 s	754	S	r(CH2) + γ(C=O) +
					γ(NH)(18%)
836 m,br	847 s,br		720	S	γ(NH)(71%)
665 w	674 m	674 s	652	S	δ(ring) + γ(C=O)
613 m	614 m	614 vw	611	626 m	γ(C=O)
550 m	554 m	561 m	541	539 w	δ(C=O)
444 m	448 m	467 m	451	S	δ(ring)
	442 m	442 m	435	S	δ(ring)
		392 w	376		δ(C=O)
		264 w	263(R)		τ(ring)
		119	(118)b		τ(ring)
		92	(94)b		τ(ring)

[a]: ref 1. [b]: computed frequencies.

ν = stretching, δ = in-plane deformation, γ = out-of-plane deformation, w = wagging, t = twisting, r = rocking, τ = torsion, (R)= observed in Raman, S= solvent absorption

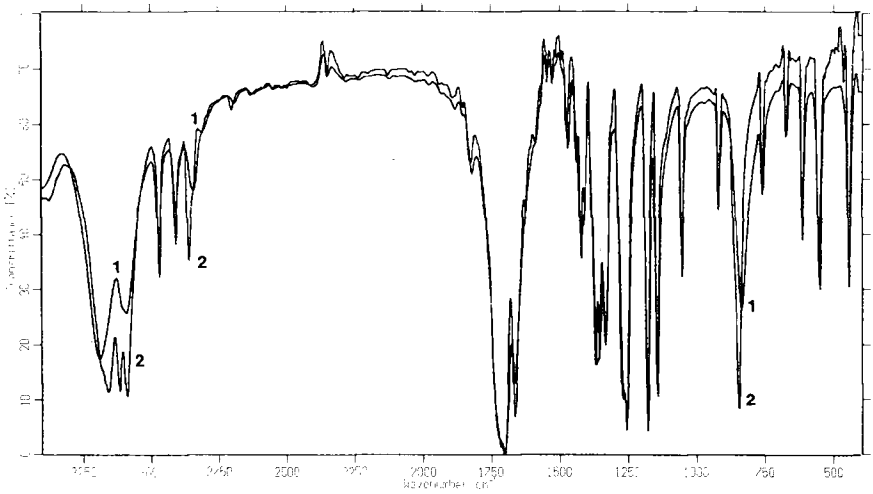


FIG. 1. FT-IR spectrum of polycrystalline GLU

1. T = 25°C. 2. T = -180°C

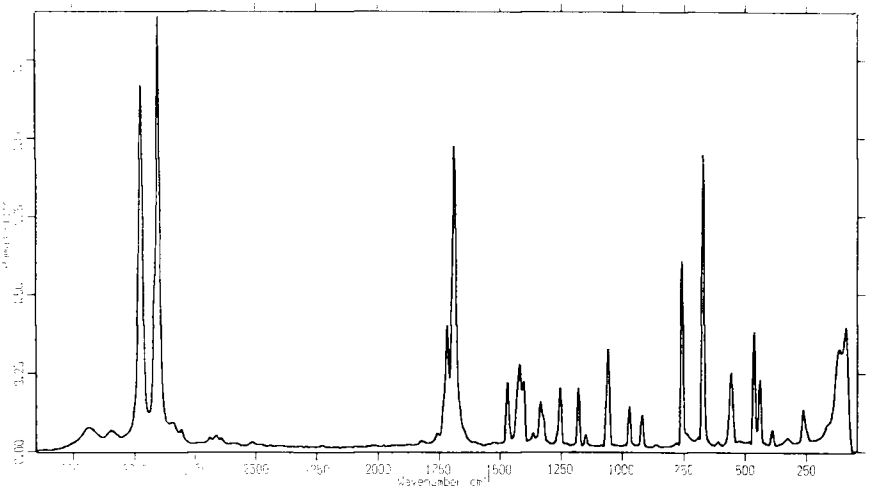


FIG. 2. FT-Raman spectrum of polycrystalline GLU at 25°C.

and 3091 cm^{-1} (25°C), and 3117 and 3093 cm^{-1} (-180°C) are also observed in the NH stretching range. The influence of the temperature on the ν(NH...O) vibration will be later discussed. The modes observed at 1392 and 1246 cm^{-1} in isolated GLU involve a δ(NH) motion and are shifted to 1408 and 1272 cm^{-1} (IR) in the solid state. Both modes are slightly sensitive to the temperature. As expected, the ν(NH) and δ(NH) vibrations are much weaker in the Raman spectrum. The γ(NH) vibration, generally very sensitive to intermolecular interactions is observed at 720 cm^{-1} in the monomer and at 836 cm^{-1} in the solid state ($\Delta\nu = +116$ cm^{-1}); its frequency is also higher (847 cm^{-1}) at -180°C. The modes involving a deformation of the C=O group are less sensitive to hydrogen bond formation. The absorption at 652 cm^{-1} which is a strongly coupled mode involving some γ(C=O) contribution (17%) is shifted to 665 cm^{-1} in solid GLU; the mode at 541 cm^{-1} which is assigned to the main δ(C=O) contribution (76%) is shifted upward by 9 cm^{-1}.

The vibrations involving the CH2 group are usually less sensitive to hydrogen bond formation. Two bands at 2973 and 2902 cm^{-1} were observed in the Raman spectrum of solid GLU[1]. We observed also a weak band at 2839 cm^{-1}. The IR absorption at 2839 cm^{-1} is split at low temperature into two components at 2864 and 2841 cm^{-1} and a strong intensity enhancement of these absorptions is observed. These features can be explained by different orientation of the CH2 groups at low temperature. A similar behavior has been observed in succinimide[9]. An alternative explanation is a Fermi resonance between the CH stretching levels and the overtones of the scissoring modes, the fundamentals being observed at 1426 and 1441 cm^{-1}.

It is also interesting to note that the ring torsional modes predicted at 118 and 94 cm^{-1} are observed at 119 and 92 cm^{-1} in the Raman spectrum.

The effect of intermolecular interactions on the IR spectrum of 1-methyluracil has been investigated and the IR spectra of argon-isolated and the crystalline phase compared[10]. In this case also, the most sensitive vibrations are those involving the NH group. Further the 3500-2500 cm^{-1} region shows a complicated pattern with a strong intensity increase of the ν(CH) modes.

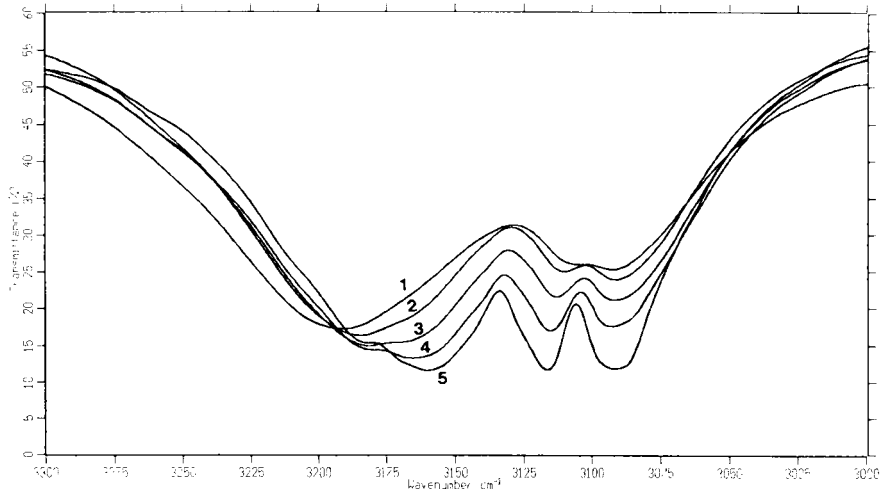


FIG.3. FT-IR spectrum (3300-3000 cm^{-1}) at different temperatures.

1. T = 50°C 2. T = 0°C 3. T = -75°C

4. T = -125°C 5. T = -175°C

FIG.3 reproduces the IR spectrum of GLU at different temperatures. This figure shows that the main component of the ν(NH...O) vibration shifts to lower frequencies and becomes more intense with decreasing temperature. The intensities of the satellite bands at 3109 and 3091 cm-^{1} also increase. A shoulder at 3180 cm^{-1} is also observed and the frequencies of the ν(NH...O) have been corrected taking into account the absorbances of the two bands. The observations are summarized in Table 2.

These data show that the ν(NH...O) frequencies are linearly related to the temperature:

$$\nu(NH...O)(cm^{-1}) = 3187 + 0.122T(°C) \quad (r = 0.9919)$$

The decrease of the temperature results in a strenghtening of the hydrogen bond or with other words in a decrease of the R(N...O) distance. Several correlations between the frequencies or frequency shifts of the stretching vibration and the distances have

TABLE 2

IR data (3300-3000 cm^{-1}) of solid GLU at different temperatures

T(°C)	ν(NH...O) (cm^{-1})	Subcomponents (cm^{-1})	
50	3192	3109	3091
25	3189	3109	3091
0	3187	3109	3091
-25	3185	3110	3092
-50	3183	3111	3092
-75	3176	3113	3092
-100	3174	3115	3092
-125	3172	3116	3092
-150	3169	3116	3093
-175	3166	3117	3093
-180	3163	3117	3093

been established. We have used in the present work the correlation of Bellamy and Owen[11] which supposes a (6-12) Lennard-Jones potential and allows to predict with a very good accuracy the experimental X-ray distances :

$$\Delta\nu\ (cm^{-1}) = A\ [\ (d/R)^{12} - (d/R)^{6}\ ]$$

where $\Delta\nu$ is the frequency shift from the monomer, A = 50 cm^{-1} and d = 3.4 A Å for NH...O hydrogen bonds. The R(N....O) distance determined by X-ray at room temperature is 2.940 Å. In order to obtain this distance, the A coefficient of the correlation must be replaced by the value of 65 cm^{-1}. The computed distance at -180°C is 2.918 Å. The contraction of the N...O distance from 25 to -180°C is thus 0.022Å.

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