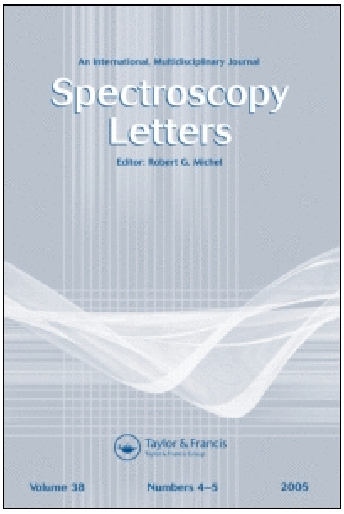

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Near-infrared characterization of N-tertiobutoxycarbonyl-L amino acids.

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To cite this Article De Wael, K. , Bruyneel, C. and Zeegers-Huyskens, Th.(1998) 'Near-infrared characterization of N-tertiobutoxycarbonyl-L amino acids.', Spectroscopy Letters, 31: 2, 283 — 298
To link to this Article: DOI: 10.1080/00387019808003253
URL: http://dx.doi.org/10.1080/00387019808003253

SPECTROSCOPY LETTERS, 31(2), 283–298 (1998)

Near-infrared characterization of N-tertiobutoxycarbonyl-L amino acids.

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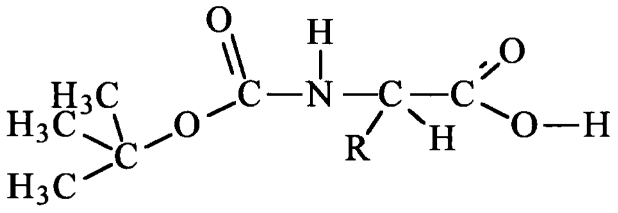
Keywords: FT-near-infrared spectra (7000-4000 cm^{-1}), N-tertiobutoxycarbonyl amino acids, anharmonicity of the vibrations

INTRODUCTION

The near-infrared absorption spectra of open-chain secondary amides and small-ring lactams have revealed the sensitivity of certain NH combination bands to conformation of the amide grouping[1,3] more specifically to the *cis* and *trans* conformations of the secondary amide grouping[2]. Some near-infrared characteristics of the peptide groups have been reported a long time ago[4,5] but despite their biological interest, no data are available for N-tertiobutoxycarbonyl amino acids. In this work, the near infrared spectra of the following molecules



R = H, (BGLY), R = CH_3 (BALA) R = CH_2-CH_2-SCH_3 (BMET) and
R = CH_2-C_6H_5 (BPALA)

have been investigated in the solid state and in carbon tetrachloride solution.

It is useful to remember here that if ν_{01} and ν_{02} are the frequencies of the fundamental transition and of the overtone, the anharmonicity of the vibration can be computed from the relation

$$X = \nu_{01} - \nu_{02}/2$$

Further the coupling coefficient between two different vibrations 1 and 2 can be computed from the expression [6]:

$$X_{12} = (\nu^1_{01} + \nu^2_{01}) - \nu_{02}$$

EXPERIMENTAL

The near-infrared spectra have been recorded on the Bruker 66 spectrometer at a resolution of 2 cm^{-1}. The spectrometer was equipped with a cooled InSb detector, a KBr beamsplitter and a Tungsten source. For the spectra in solution, cells equipped with quartz-infrasil windows and a pathlength of 5 or 10 cm have been used. The spectra in the solid state have been taken in KBr pellets containing 10% of the product. The experimental errors on the frequencies are ± 1 cm^{-1} for the sharp bands and ± 5 cm^{-1} for the broad bands.

The N-tertiobutoxycarbonyl amino acids from Sigma have been used without further purification.

RESULTS AND DISCUSSION

Bands observed in the near-infrared are primarily attributable to overtones and combinations of fundamental and as a consequence, the assignment of the vibrational modes in the fundamental region must precede interpretation of the near-infrared spectra.

1. Fundamental vibrations of BGLY, BALA, BMET and BPALA.

The mid-infrared spectra of BGLY, BALA and BMET have been investigated in carbon tetrachloride solution in the ν_{OH} and ν_{NH} stretching range (3600-2500 cm^{-}

^{1})[7]. The mid-infrared spectra of BGLY and BALA in the solid state have been recently studied [8]. In the present work, the mid-infrared and Raman spectra of BMET and BGLY have been investigated .The assignment of the vibrations which are important for the discussion of the near-infrared spectra are summarized in Table 1.

It is important to stress here that BGLY, BALA and BPALA have not the same structure in the solid state. In BGLY, the shorter hydrogen bonds are formed between the OH and urethane carbonyl groups and two longer hydrogen bonds characterized by distances of 3.02 and 3.12 Å are formed between the NH and acid carbonyl groups [9]. This bonding scheme results in two different ν_{NH} stretching frequencies at 3407 and 3344 cm^{-1} and two different $\nu_{C=O}$ frequencies for the carboxylic and urethane groups. In BALA, the molecules are held together by intermolecular OH...O hydrogen bonds between the carboxyl groups which are in a cyclic arrangement and weak hydrogen bonds are formed between the NH and carbonyl urethane. In this molecule, only one ν_{NH} vibration is observed at 3383 cm^{-1}. In both BGLY and BALA, the HN-C=O group has the *trans* conformation. BPALA has a different structure; the molecules form cyclic dimers between the carboxyl and urethane groups. Two different NH...O hydrogen bonds of 2.85 and 2.99 Å are observed [10,11] and two ν_{NH} vibrations are observed at 3314 and 3265 cm^{-1}. The HN-C=O group has the *cis* conformation. The X-ray structure of BMET is not known. The infrared and Raman spectra of BALA and BMET are very similar and this suggests that the two molecules have the same structure. More specifically, the non-coincidence of the $\nu_{C=O}$ infrared and Raman frequencies suggests a centrosymmetric structure for the carboxylic group of BMET.

The N-tertiobutoxycarbonyl -L- amino acids are strongly associated in carbon tetrachloride solution and at the studied concentrations (0.03 to 0.1 mol dm^{-3}), about 55% of the NH groups and about 95% of the OH groups are hydrogen bonded, forming homodimers or heterodimers[7] . Absorptions at about 3525 and 3445 cm^{-1} corresponding to the ν_{OH} and ν_{NH} vibrations of the monomers are

TABLE 1: Fundamental assignments for BGLY, BALA, BMET and BPALA in the solid state and in carbon tetrachloride solution.(data in cm^{-1}) [a]

BGLY		BALA		BMET		BPALA		Assignment
solid	CCl_4	solid	CCl_4	solid	CCl_4	solid	CCl_4	
	3528		3528		3524		3526	$\overset{f}{V_O}$
	3453		3446		3439		3444	$\overset{f}{V_{NH}}$
3407								$\overset{wb}{V_{NH}}$
3343	3273	3383	3264	3365	3256	3265	3257	$\overset{b}{V_{NH}}$
3100	3050	3105	3100	3100	3050	≈3100	3102	$\overset{b}{V_{OH}}$
	(2675) (2590)			(2600)		(2580)	(2575)	combination
	1768		1764		1762		1760	$\overset{Af}{V_{c=o}}$
1749	1737	1739(IR)	1718	1728(IR)	1718	1712	1717	$\overset{Ab}{V_{c=o}}$
1741		1693(R)		1692(R)				
			1714		1718		1717	$\overset{Uf}{V_{c=o}}$
1683 1669	1671	1691	1666	1693	1665	1648	1667	$\overset{Ub}{V_{c=o}}$
1535	1503	1518	1497	1520	1498	1496	1497	amide II
1423	1428	1454	1410	1444	1445	1455	1399^{b}	$\overset{b}{\delta_{OH}}$
1410							1394^{a}	$\overset{f}{\delta_{OH}}$
1281	1233	1254	1244 b	1250	1253	1278	1280^{b}	amide III^{b}
1257			1231^{c}		1231	1250	1246^{c}	amide III^{f}, amideIII^{w} b

[a] ν = stretching, δ = deformation, ^{A} and ^{U} refers to the carbonyl of the carboxylic and urethane groups, ^{f} = free, ^{b} = bonded, ^{wb} = weakly bonded, ^{b} dimer absorption, ^{c} monomer absorption

observed. In some case, a small concentration effect on the δ_{OH} and amide III vibrations is observed.

It is also worth mentionining that in the solid state and in solution, the ν_{OH} vibration of the hydrogen-bonded species culminate between 3100 and 3000 cm^{-1}. Absorptions of weaker intensity are observed between 2700 and 2000 cm^{-1}. The band shaping mechanism is likely the same as in the acetic acid dimer where the maximum of the $\nu_{OH...O}$ absorption is observed near 3030 cm^{-1} . The secondary absorptions observed between 2900 and 2100 cm^{-1} have been assigned to combinations involving internal modes of the acid [12].

2. *Near-infrared spectra of BGLY, BALA, BMET and BPALA.*

The near-infrared spectra of amides are well-documented in the literature [1-3] but there are very few data on the near-infrared spectra of carboxylic acids. The first overtone of the ν_{CH3} vibration and the second overtone of the $\nu_{C=O}$ have been observed in acetic acid [13] and the first overtone of the ν_{OH} vibration in the dimers of carboxylic acids has been localized between 5880 and 5455 cm^{-1} [14]. In view of a better assignment of the overtone spectra of the amino acids, the spectrum of acetic acid has been studied between 7250 and 4000 cm^{-1}. The near infrared spectra taken at different concentrations of acetic acid are reproduced in FIG.1 The first overtones of the ν_{CH3} vibrations are observed at 5949 and 5809 cm^{-1} and the absorptions oberved at 4338 and 4223 cm^{-1} are assigned to combinations of the ν_{CH3} and δ_{CH3} vibrations. The intensity of the absorptions at 5653, 5400, 5017 cm^{-1} and the doublet at 4691-4654 cm^{-1} increases with increasing concentration of acetic acid and are therefore assigned to the dimer. A tentative assignment of these absorptions which are characterized by weak intensities is presented in Table 2. Some of these combinations (δ_{OH}(IR) + δ_{OH}(R), δ_{OH}(IR) + ν_{C-O}(R)) are also observed in the mid-infrared region [12]. The overtone spectrum of methanol in carbon tetrachloride is also characterized by very weak side bands assigned to combinations involving the ν_{OH} and the δ_{OH}, ν_{C-O} or δ_{CH3} vibrations [15-16].

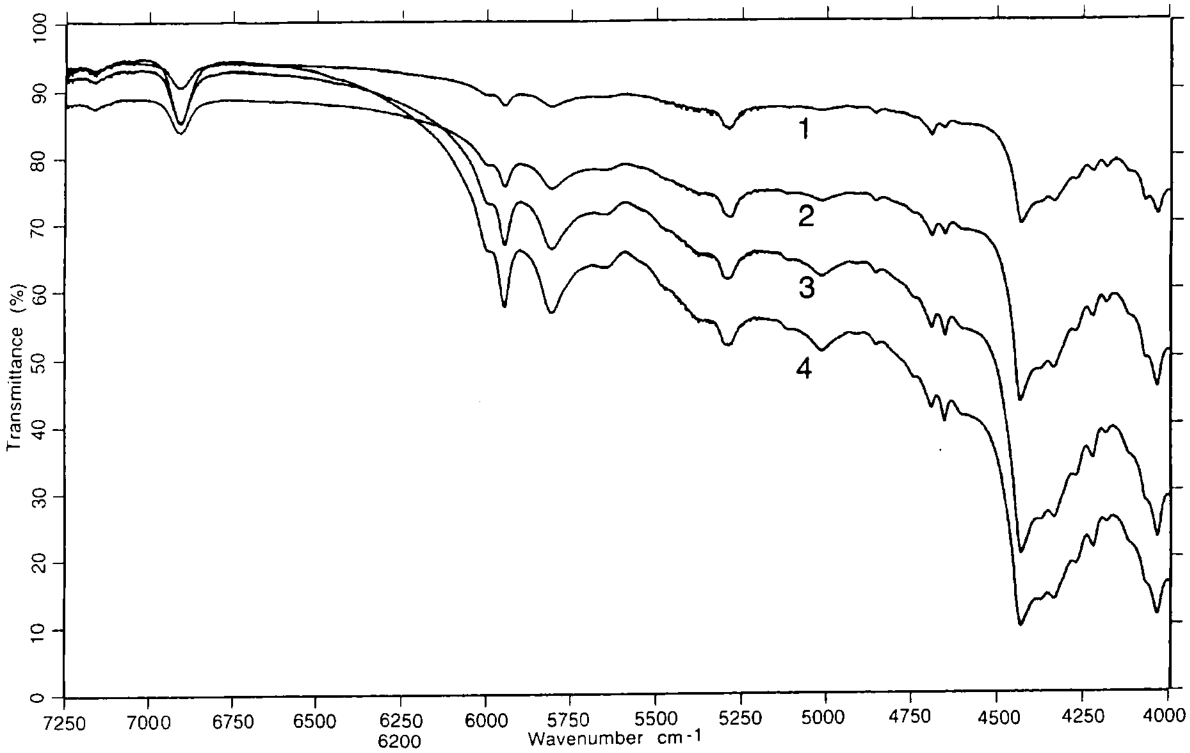


FIG. 1 Near-infrared spectrum of acetic acid in carbon tetrachloride. Concentration of acetic acid 1: 0.02 mol dm^{-3} 2: 0.05 mol dm^{-3} 3: 0.1 mol dm^{-3} 4: 0.15 mol dm^{-3}

TABLE 2 : Near-IR absorptions of acetic acid in carbon tetrachloride, tentative assignment and anharmonicities or coupling constants(data in cm^{-1}) [a]

$\nu_{obs}(cm^{-1})^a$	Assignment[b]	$\nu_{calc}(cm^{-1})$	$X(cm^{-1})$
6907w	$2\ \nu^{f}_{OH}$	2x3533=7066	79
5653vw	$2\ \delta^{b}_{OH}(IR){+}2\ \delta^{b}_{OH}(R)$	2x1436+2x1415=5702	49
	$2\ \delta_{CH_3}(IR){+}2\ \delta^{b}_{OH}(R)^c$		
5400w,br	$2\ \delta^{b}_{OH}(IR){+}2\ \delta^{b}_{C-O}(R)$	2x1436+2x1283=5438	38
5290w	$3\ \nu^{f}_{C=O}$	3x1775=5325	12
5017w,br	$3\ \nu^{b}_{C=O}$	3x1675=5025	-3
4691w	$\nu^{b}_{OH}+\nu^{b}_{C=O}(IR)$	3030+1712=4742	51
4654w	$\nu^{b}_{OH}+\nu^{b}_{C=O}(R)$	3030+1675=4705	51
4433	$\nu^{b}_{OH}+\delta^{b}_{OH}{}^{c}$ $\nu^{b}_{OH}+\delta_{CH_3}$	3030+1436=4466	33

[a] w = weak, br = broad, [b] f and b are the vibration in free and hydrogen-bonded acetic acid, [c] the δ_{OH} and δ_{CH3} vibration are coupled[12]

The near-infrared spectra of BGLY and BALA in the solid state and in carbon tetrachloride solution are reproduced in FIG.2 and FIG.3. The observed frequencies, the assigment of the absorptions and the anharmonicities or coupling coefficients are indicated in Tables 3-6.

The first overtone of the ν_{CH3} vibrations of the tertiobutyl group are observed at 5955-5965 cm^{-1} and the combinations between the ν_{CH3} and δ_{CH3} at 4410 and 4235 cm^{-1}. In alanine, these combinations are observed at 4455 and 4385 cm^{-1}.[17] and will no more be discussed in this work.

For the four amino acids in solution, the 2 ν_{OH} vibration of the free OH group is observed between 6900 and 6910 cm^{-1} and the corresponding anharmonicity

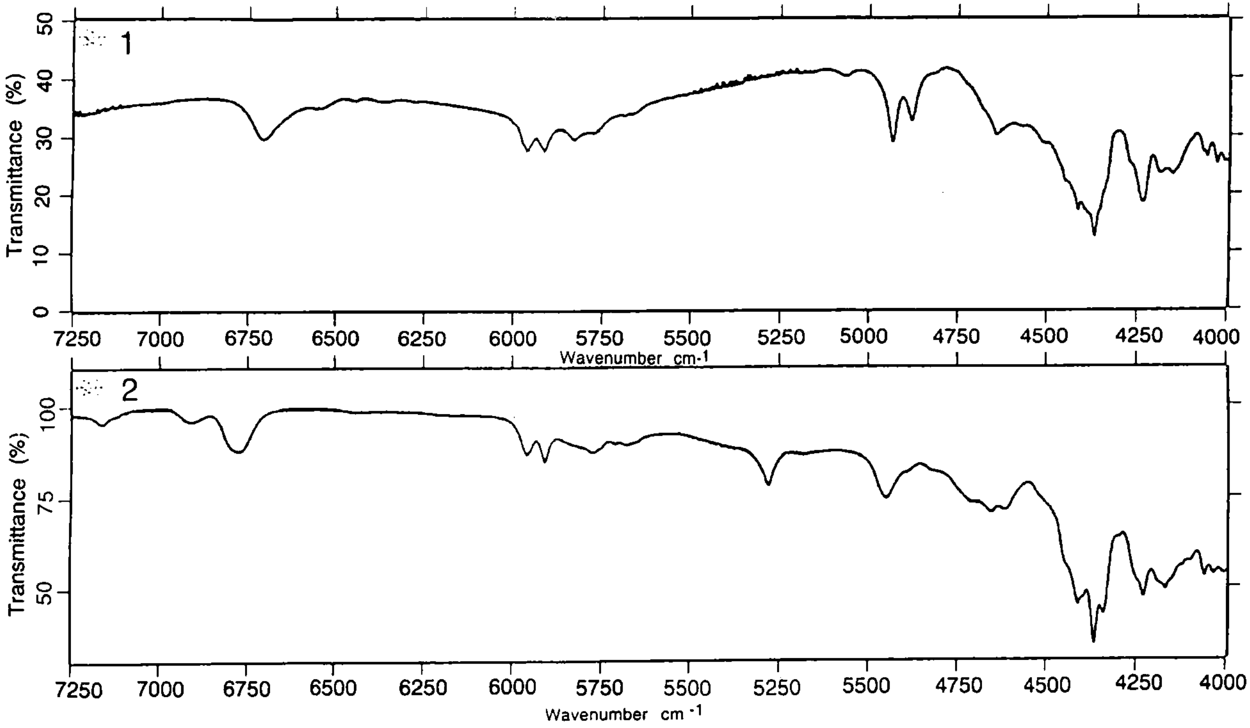


FIG. 2 **Near-infrared spectrum of BGLY**

1. in the solid state (KBr suspension)

2. in CCl_4 solution (c = 0.013 mol dm^{-3}). Pathlength = 10 cm

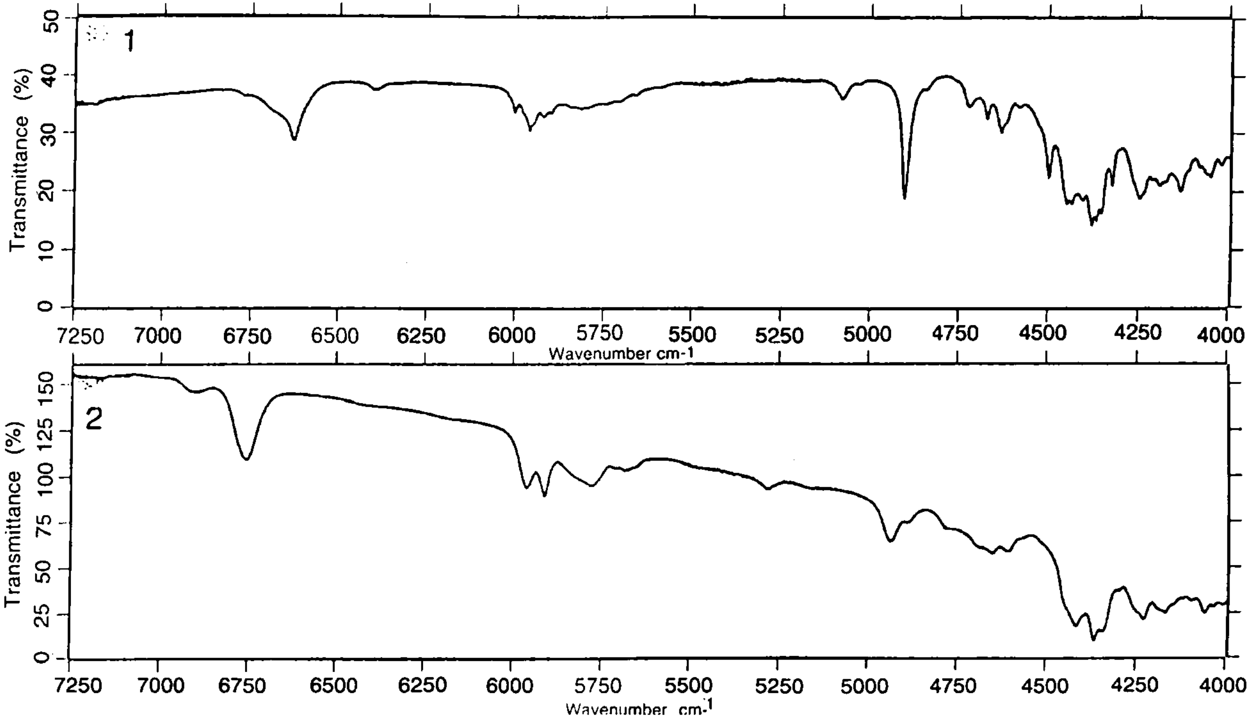


FIG. 3 Near-infrared spectrum of BALA

1. in the solid state (KBr suspension)

2. in CCl_4 solution (c = 0.05 mol dm^{-3}). Pathlength = 5 cm

TABLE 3: Near IR absorptions of BGLY in the solid state and in carbon tetrachloride. Tentative assignment and anharmonicities or coupling constants.(data in cm^{-1}) [a]

solid			CCl$_4$	solution	
$\overline{\nu}_{obs}$	assignment	X	$\overline{\nu}_{obs}$	Assignment	X
			6910	$2\ \overset{f}{\nu}_{OH}$	73
6710m	$2\cdot\ \overset{wb}{\nu}_{NH}$	52	6777	$2\cdot\ \overset{f}{\nu}_{NH}$	64
6550w	$2\cdot\ \overset{b}{\nu}_{NH}$	69	6380vw	$2\cdot\ \overset{b}{\nu}_{NH}$	83
6442w	$\overset{b}{\nu}_{NH}$ + 2 amide II	-28			
6366w	$\overset{b}{\nu}_{NH} + \nu_{CH}$	-32			
6281w	$\overset{b}{\nu}_{NH} + \nu_{CH}$	21			
5782m	$2\ \overset{b}{\nu}_{OH}$	209	5778w,br	$2\ \overset{b}{\nu}_{OH}$	161
≈5700vw	$\overset{b}{\nu}_{OH} + 2\ \overset{b}{\delta}_{OH}$	220	5679w,br	$\overset{b}{\nu}_{OH} + 2\ \overset{b}{\delta}_{OH}$	227
5069w	$\overset{wb}{\nu}_{NH} + \overset{U}{\nu}_{C=O}$	21			
4938m	$\overset{wb}{\nu}_{NH}$ + amide II	4	4954m	$\overset{f}{\nu}_{NH}$ + amide II	1
4885m	$\overset{b}{\nu}_{NH}$ + amide II	-6	4710m	$\overset{b}{\nu}_{NH}$ + amide II	66
4646m	$\overset{wb}{\nu}_{NH}$ + amide III	18	4658m	$\overset{f}{\nu}_{NH}$ + amide III	+28
4585vw	$\overset{b}{\nu}_{NH}$ + amide III	15	4623w	$2\ \overset{U}{\nu}_{C=O}$ + amide III	-48
	$2\ \overset{U}{\nu}_{C=O}$ + amide III	8			

[a] same remarks as below TABLE 1

ranges between 72 and 77 cm^{-1}. In the solid state and in solution, a broad and weak band is observed between 5770 and 5820 cm^{-1}. This broad absorption is assigned to the 2 ν_{OH} vibration of the hydrogen-bonded OH groups. In the fundamental region, this absorption is observed between 3000 and 3100 cm^{-1}. The anharmonicities of these vibrations range between 160 and 210 cm^{-1} and this clearly show that the formation of these strong hydrogen bonds results in an increase of the anharmonicity which is more than twice higher than in the free ν_{OH} vibration. Anharmonicities higher than 200 cm^{-1} have also been found for the ν_{OH}

TABLE 4 : **Near-IR absorptions of BALA in the solid state and in carbon tetrachloride. Tentative assignment and anharmonicities or coupling constants.(data in cm^{-1}) ^{a}**

solid			CCl4	solution	
$\overline{\nu}_{obs}$	assignment	X	$\overline{\nu}_{obs}$	assignment	X
			6902w	$2\ \nu_{OH}^{f}$	77
6628m	$2.\ \nu_{NH}^{b}$	59	6755s	$2.\ \nu_{NH}^{f}$	68
			6365vw	$2.\ \nu_{NH}^{b}$	82
6400w	ν_{NH}^{b} + amide II	10			
5820w,br	$2\ \nu_{OH}^{b}$	190	5779m,br	$2\ \nu_{OH}^{b}$	161
≈5740vw	$\nu_{OH}^{b}+2\ \delta_{OH}^{b}$	132	5683w	$\nu_{OH}^{b}+2\ \delta_{OH}^{b}$	94
5082m	$\nu_{NH}^{b}+\nu_{C=O}^{U}$	-3			
4907s	ν_{NH}^{b} + amide II	-3	4938m	ν_{NH}^{f} + amide II	3
4726vw			4755w	ν_{NH}^{b} + amide II	6
4676w	$2\ \nu_{C=O}^{Ub}$ + amide III	-40	4653m	ν_{NH}^{f} + amide III	9
4637m	ν_{NH}^{b} + amide III	-10	4608vw	$2\ \nu_{C=O}^{U}$ + amide III	-32
4503m	$\nu_{OH}^{b}+\delta_{OH}^{b}$	56			

^{a} same remarks as below TABLE 1

vibration in strong hydrogen bonds involving aliphatic alcohols and trimethylamine[18].

The $2\nu_{NH}$ vibration of the free NH group is observed 6750 and 6777 cm^{-1} and the corresponding anharmonicities take values between 64 and 68 cm^{-1}. For weakly hydrogen-bonded NH groups such as BGLY and BALA in the solid state, the anharmonicities are weaker (52 and 59 cm^{-1} respectively) than for the free ν_{NH} vibrations. When the NH group is involved in a stronger hydrogen bond such as in the heterodimers in solution, the anharmonicities increase and take values between 83 and 86 cm^{-1}. The variation of the anharmonicities as a function of the experimental ν_{NH} frequencies are illustated in FIG.4 which clearly shows that the

TABLE 5 : Near-IR absorptions of BMET in the solid state and in carbon tetrachloride. Tentative assignment and anharmonicities or coupling constants (data in cm^{-1}) [a]

solid			CCl_4	solution	
$\bar{\nu}_{obs}$	assignment	X	$\bar{\nu}_{obs}$	assignment	X
			6904w	$2\ \nu^{f}_{OH}$	72
			6750m	$2.\ \nu^{f}_{NH}$	64
6600m	$2\ \nu^{b}_{NH}$	65	≈6340	$2.\ \nu^{b}_{NH}$	86
6380vw	ν^{b}_{NH} + 2 amide II	25			
5776m,br	$2\ \nu^{b}_{OH}$	212	5775m	$2\ \nu^{b}_{OH}$	162
			5718w	$\nu^{b}_{OH} + 2\ \delta^{b}_{OH}$	228
5070w	$3\ \nu^{Ab}_{C=O}$	-1			
	$\nu^{b}_{NH} + \nu^{U}_{C=O}$	-12			
4888s	ν^{b}_{NH} + amide II	-3	4932m	ν^{f}_{NH} + amide II	5
				$\nu^{b}_{NH} + \nu^{Ub}_{C=O}$	-11
4713w	$\nu^{Ub}_{C=O}$ + 2 amide II	20			
4650w	$2\ \nu^{Ub}_{C=O}$ + amide III	-14	4651m	ν^{f}_{NH} + amide III	19
4628m	ν^{b}_{NH} + amide III	-13	4606vw	$2\ \nu^{Ub}_{C=O}$ + amide III	-23
4560w					
4515w	$\nu^{b}_{OH} + \delta^{b}_{OH}$	29			

[a] same remarks as below TABLE 1

anharmonicity of the ν_{NH} vibration in the bonded NH group is lower than that of the free NH group and that the anharmonicity regularily increases with the strength of the hydrogen bond. Owing to the experimental errors on the frequencies which are equal to ± 5 cm^{-1}, this increase is significant. No data on the variation of the anharmonicities in the same family of complexes can be found in the literature. In free diethylamine, the anharmonicity of the ν_{NH} vibration is 93 cm^{-1} and decreases to 45 cm^{-1} in the self-associated amine where the NH...N hydrogen bond is weak [19]. In self-associated imidazole, where the NH...N hydrogen bond is strong (the

TABLE 6 : Near-IR absorptions of BPALA in the solid state and in carbon tetrachloride. Tentative assignment and anharmonicities or coupling constants (data in cm^{-1}) [a, b]

solid			CCl_4	solution	
$\bar{\nu}_{obs}$	assignment	X	$\bar{\nu}_{obs}$	assignment	X
			6902vw	$2\,\nu^{f}_{OH}$	73
			6751m	$2.\,\nu^{f}_{NH}$	68
5776w	$2\,\nu^{b}_{OH}$	212	5771w,br	$2.\,\nu^{b}_{OH}$	216
			5680vw	$\nu^{b}_{OH} + 2\,\delta^{b}_{OH}$	220
			≈5157vw		
5009w,br	$3\,\nu^{Ab}_{C=O}$	42			
			4937m	ν^{f}_{NH} + amide II	4
4764m	ν^{b}_{NH} + amide II	-3			
4668m			4670m	ν^{f}_{NH} + amide III	20
4618m	$2\,\nu^{Ub}_{C=O}$ + amide III	-4	4617m	$2\,\nu^{Ub}_{C=O}$ + amide III	-3
4579w	$\nu^{Ab}_{C=O} + \delta^{b}_{OH}$	-24	4579w	ν^{b}_{NH} + amide III	-42
	ν^{b}_{NH} + amide III	-36			

[a] same remarks as below TABLE 1 , [b] no absorption corresponding to the overtones of the ν_{NH} vibrations at 3314 and 3265 cm^{-1} (solid state) could be detected

$\nu_{NH...N}$ vibration is observed at 2800 cm^{-1}), the anharmonicity increases from 40 to 175 cm^{-1} on going from the monomer to the associated species [20]. These results are in qualitative agreement with the present data.

In the 5100-4585 cm^{-1} region typical absorptions of the peptide group are observed [5,17]. More specifically, in fibrous proteins, absorptions at 4950 cm^{-1}(ν_{NH} + $\nu_{C=O}$),4860cm^{-1}($2\nu_{C=O}$ + amide II), 4840cm^{-1} (ν_{NH} + amide II) and 4750 cm^{-1} ($\nu_{C=O}$ + 2amide II) have been identified[5]. Similar combinations such as ν_{NH} + amide II, ν_{NH} + amide III, $2\nu_{C=O}$ + amide III are observed in secondary amides [1-3] and in these molecules, the coupling constants range between 40 and -10 cm^{-1}. The band observed between 4618 and 4646 cm^{-1}, assigned in this work to the ν_{NH} + amide

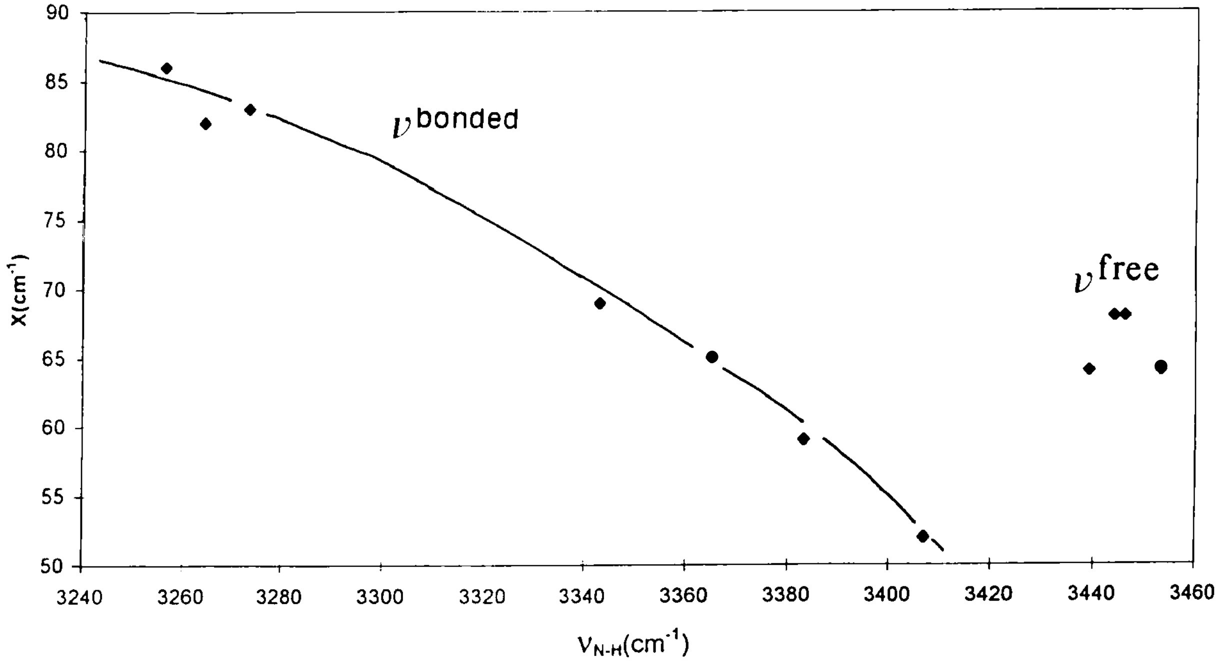


FIG. 4 Anharmonicities of the ν_{NH} vibration as a function of the frequencies of the ν_{NH} vibration for the fundamental transition

III combination is observed with an high intensity in lactams [1] so that the assignment of the absorptions in this region to the carboxylic group of the amino acid seems unlikely owing to the weak intensities of the bands observed in this region in acetic acid. The absorption observed in the solid state between 4580 and 4500 cm^{-1} probably arises from the $\nu_{OH} + \delta_{OH}$ combination.

As mentioned before, the urethane group has in the solid state the *trans* conformation in BGLY and BALA and the cis conformation in BPALA. A $\nu_{NH} + \nu_{C=O}$ combination is observed near 5100 cm^{-1} in the *cis*-lactams but not in the *trans* open-chain secondary amides [1]. This combination is observed near 5070 cm^{-1} in BGLY, BALA and BPALA and does not allow to characterize the conformation of the urethane group in the amino acids.

ACKNOWLEDGEMENTS

The authors thank the FWO (Fund of Scientific Research-Vlaanderen) for financial support.

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Date Received: August 1, 1997
Date Accepted: September 11,1997