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Low-wavenumber Raman spectra of L-tyrosine, L-tyrosine hydrochloride, and L-tyrosine hydrobromide crystals at high temperatures

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Abstract

Crystals of L-tyrosine and semiorganic L-tyrosine hydrochloride and L-tyrosine hydrobromide, known for their nonlinear optical properties, were studied by Raman spectroscopy in the temperature range from 298 to 453 K. Hydrogen bonding at room temperature and thermal decomposition are correlated with Raman bands in the low-wavenumber region at approximately 120 cm⁻¹. The detailed analysis of these bands and the temperature dependence of their wavenumbers show an interesting correlation between hydrogen bonds, vibrational properties, and thermal decomposition. In particular, we note a correlation between the lengths of the N–H•••X bonds and the wavenumber of a low-wavenumber band and that the introduction of Br and Cl in the L-tyrosine hydrochloride and L-tyrosine hydrobromide structures does not substantially modify the O–H•••O bonds when compared with the L-tyrosine crystal. Additionally, the hydrophobic character of the interactions apparently does not change during heating, and there is no evidence for the breakdown of the hydrophobic interactions.

Keywords: L-Tyrosine; Thermal decomposition; Raman spectroscopy

1. Introduction

The nonlinear optical (NLO) characteristics of materials can be applied in various areas of science and technology. However, to define suitable materials for these applications, one has to carefully analyze the physical properties of the material, such as thermal decomposition. With regard to amino acid crystals, correlation was found between thermal decomposition, lattices modes, and the intramolecular hydrogen bonds in the molecular structure [1, 2]. In amino acid crystals, several types of chemical bonds are possible, including hydrophobic interactions, and their chemical structures are a good example of a flexible system with equilibrium between molecular, ionic, and zwitterionic forms [3].

L-Tyrosine (LT) is a proteinogenic amino acid that crystallizes in an orthorhombic noncentrosymmetric structure ($P2_12_12_1$) [4]. Depending on the crystallization method, LT can form semiorganic compounds such as L-tyrosine hydrochloride (LTHCl) [5] and L-tyrosine hydrobromide (LTHBr) [6], both with a monoclinic crystal structure ($P2_1$) and exhibiting the special characteristic of NLO properties [7–11]. The LTHCl and LTHBr structures derive from the LT structure complexed with hydrochloric acid and hydrobromic acid, respectively. In these crystals the molecules are connected by N–H•••X (XT = O, Cl, or Br) and O–H•••O hydrogen bonds.

Hydrogen bonds are intermolecular interactions that occur in all amino acid crystal structures, being fundamental to the crystal stability of the molecules in the periodic network. On the basis of the unit cell parameters and symmetries, the salts of LT are isostructural [6]. The structure of LTHCl was determined by neutron diffraction, where the protons were determined with precision. In LTHCl, the oxygen atoms of the phenol ring O–H•••O (2.62 Å) form a hydrogen bond with the carboxyl group of the cation and not with the anion. Also, a very strong hydrogen bond is formed with the chloride anion O–H•••Cl (3.05 Å) [5]. In LTHBr, the same occurs with the oxygen atom of the phenol ring O–H•••O (2.65 Å), and a very strong hydrogen bond is formed with the bromide anion O–H•••Br (3.23 Å) [6].

According to data shown in Table 1, N–H•••X bonds are stronger in LT than in LTHCl and LTHBr. In the LT crystal, the molecules are connected by N–H•••O and O–H•••O hydrogen bonds, while in LTHCl and LTHBr, N–H•••Cl and N–H•••Br hydrogen

bonds are present. In LTHCl and LTHBr, the hydrogen bonds are much longer than in LT, and this can be explained in terms of the ionic radius of Cl^- (1.81 Å) and Br^- (1.96 Å).

Hydrogen bonds provide most of the directional interactions that support amino acid structures, being fundamental to define the main physical and chemical properties of this class of materials. For example, many amino acid crystals can exist in more than one polymorph, depending on the temperature and pressure. Additionally, there are several examples of phase transitions undergone by amino acid crystals when temperature or pressure changes, with consequent modification of the hydrogen-bond networks [12-14]. On one hand, a study performed with dilatometric techniques in Lalanine, L-threonine, and taurine crystals concluded that there is correlation between thermal expansion (a physical process) and the strength of local hydrogen bonding in these structures at room temperature [15]. On the other hand, thermal decomposition (a chemical phenomenon) is not always directly correlated with the strength of hydrogen bonds [15] because anharmonic effects (phonon dynamics) seem to also be important in this process. In fact, weakening of the intermolecular interactions occurs during heating of the materials. This explains why although L-alanine has strong hydrogen bonds compared with L-threonine and taurine it has a low decomposition temperature [2]. However, in other situations, thermal decomposition can be related to the geometry of the hydrogen bonds: the shorter the hydrogen bonds, the higher the decomposition temperature, making the material thermally stabler, which was observed in the present study with LT, LTHCl, and LTHBr.

A study on the temperature dependence of the lattice mode of β -alanine is also worth noting [1]. The behavior of the lattice modes as observed by Raman spectroscopy is consistent with intermolecular interactions favoring breaking of the hydrogen bonds in the decomposition process. Additionally, the calculated bulk expansion coefficient, obtained by X-ray powder diffraction and thermal analysis, is consistent with weakening of the intermolecular interactions [1]. The intermolecular N–H•••O angle of β -alanine was correlated with premature thermal decomposition compared with Lalanine, mainly because the N–H•••O angle in the former crystal is more acute, favoring breaking of the bonds.

Therefore, obtaining precise and accurate information on the effect of high temperature on hydrogen bonds is very important to understand the physical and chemical properties of these NLO materials. However, this is a hard experimental task.

Journal Pre-proot

Hydrogen atoms have only one electron, making them very difficult to detect accurately with X-rays because X-rays are scattered by the electron density. Therefore, a complete picture of the high-temperature effect in hydrogen bonds cannot be trivially obtained through only crystallographic experiments. The main strength of Raman spectroscopy is the ability to provide very rapidly easily analyzable qualitative information and a powerful diagnosis of this process. In other words, Raman spectroscopy can provide interesting insights into the effect of high temperature on hydrogen bonds, increasing our understanding of the effects of temperature on NLO materials.

In this article we report a temperature study of low-wavenumber Raman scattering from three compounds, LT, LTHCl, and LTHBr, with particular emphasis on the connection between the hydrogen bonds (representing intermolecular interaction), the phonon dynamics (physical phenomenon), and thermal decomposition (chemical phenomenon).

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2. Experimental

For the growth of the crystals, a very rigorous solution preparation method (agitation control, temperature control, and double filtration of the solution) was used to avoid impurities that could negatively affect the crystalline quality of the materials. Crystals of LTHCl and LTHBr were prepared by slow spontaneous evaporation of a solution of LT (97%; Sigma-Aldrich) in hydrochloric acid (37%; Sigma-Aldrich) and hydrobromic acid (48%; Sigma-Aldrich) in a molar ratio of 1:1 at 313 K, the solution being stirred for 3 h to achieve total solubilization. To confirm the structure, X-ray diffraction patterns of crushed powder samples were recorded with a Philips Analytical X-ray diffractometer (model PW1710) with Cu K α radiation. The samples were measured in steps of 0.02° for 2 s for each step, and in an angular 2 θ range from 10° to 50°. Rietveld refinement was performed with the program GSAS [16] and structures provided in [4–6]. Thermogravimetric and differential thermal analysis measurements were performed with a DTG-60 instrument (Shimadzu) at a heating rate of 5 °C min⁻¹ in a N₂ atmosphere.

Raman spectra were obtained for powdered samples of LT, LTHCl, and LTHBr. The scattered light was analyzed with a TriVista spectrometer system (Princeton Instruments) with three stages equipped with a PIXIS 256E CCD camera. The slits were

Journal Pre-proo

set for 2 cm⁻¹ spectral resolution. The excitation for the Raman experiments consisted of a He-Ne laser emitting at 632.8 nm with an output power of 75 mW. The high temperatures for experiments were obtained with a resistive furnace system; the temperature was monitored by a digital temperature control unit with accuracy of 1.0 K. The furnace consisted of a cylindrical closed glass capsule with a diameter of 5 mm into which the samples were placed in powder form. The capsule was surrounded by resistive furnace connected to a 0–30 V, 0–10 A power supply (Instrutherm FA-1030). Currents of about 3 A were sufficient to heat the samples to 453 K.

3. Results and discussion

Fig. 1 shows X-ray diffraction patterns for LT, LTHCl, and LTHBr crystals with Rietveld refinement data and Miller indices. The LT crystal structure at room temperature is orthorhombic and belongs to the space group $P2_12_12_1$, containing four molecules per unit cell. The unit cell parameters obtained from the refinement are a = 6.9235(9) Å, b = 21.146(3) Å, and c = 5.8395(3) Å. The LTHCl and LTHBr crystals crystallize in a monoclinic structure (space group P21), containing two molecules per unit cell. The LTHCl lattice parameters are a = 11.063(4) Å, b = 9.075(3) Å, c = 5.010(3) Å, and $\beta = 91.941(3)^\circ$, and the LTHBr cell parameters are a = 11.322(4) Å, b = 9.095(3) Å, c = 5.147(3) Å, and $\beta = 91.211(3)^\circ$. The unit cell parameters and space groups are in good agreement with data previously reported ($R_p = 13\%$, $R_{wp} = 10\%$, and S = 3) for the crystals.

Thermogravimetric and differential thermal analysis curves recorded for LT, LTHCl, and LTHBr crystal powders are shown in Figs. 2 and 3. Thermogravimetric analysis shows that LT is stabler than both LTHCl and LTHBr; this can be seen through the endothermic peak in the differential thermal analysis curves, characteristic of the decomposition process. Some endothermic peaks appear for all three materials, being recorded as follows: at 556 K for LT (melting point), at 505 K and 509 K for LTHCl (melting point), and at 513 K for LTHBr (melting point). In LTHCl, the first endothermic peak corresponds to decomposition of chlorine, and the second endothermic peak, at 509 K, is related to decomposition of tyrosine. The same does not occur for LTHBr, with there being only one peak, at 513 K, since bromine decomposes

together with tyrosine. Behavior similar to that reported for the LT compounds occurred in other studies, such as those with LTHCl [9] and LTHBr [8].

The different solid-phase decomposition temperatures can be interpreted in terms of differences in the strength of the hydrogen bonding at room temperature (Table 1). LT is the stablest crystal, with the highest decomposition temperature, also having the shortest hydrogen bonds at room temperature. This result is not general (i.e., the hydrogen bond is not the exclusive cause of the stability of the crystal structure); we recall that L-alanine even with strong hydrogen bonds has a low decomposition temperature because of anharmonic effects [2].

To investigate the connection between vibrational properties and thermal decomposition in more detail, Raman spectra of LT, LTHCl, and LTHBr were acquired in the low-wavenumber spectral region, since the low-energy region of the spectrum, which in most cases is associated with the lattice modes, is very sensitive to changes in intermolecular interactions. For amino acid crystals, the external modes can be interpreted as phonons corresponding to either translations or librations [17].

Fig. 4 presents the Raman spectra of LT, LTHCl, and LTHBr in the wavenumber region below 140 cm⁻¹ at two selected temperatures: 298 K and 423 K. Some particular bands, with similar wavenumbers, are highlighted by circles in Fig. 4, and are associated with similar vibrations in all structures. Detailed curve fitting to these Raman bands using Lorentzian profiles is shown in Fig. 5.

The temperature dependence of the modes with wavenumbers lower than 140 cm^{-1} is presented in Fig. 6. Bands highlighted by the circles in Fig. 4 are represented by circles in Fig. 6; the other bands are represented by squares. We fitted all wavenumber bands with linear functions. The linear equation $v = v_0 + \alpha T$ was used to fit the temperature dependence in Fig. 6, where v_0 is the extrapolated peak position at 0 K, and $\alpha = dv/dT$ is the first-order temperature coefficient. The best linear fitting is plotted in Fig. 6 as solid lines. Table 2 presents the dv/dT values for the bands in Fig. 4. Significant variations of the α values were observed for the bands corresponding to similar vibrations and denoted by a circle. One can observe from Table 2 that the α values are higher for LTHCl and LTHBr. For bands denoted by a square, between 20 cm⁻¹ and 80 cm⁻¹, in general, little variation of α values was observed.

Journal Pre-prooi

We now discuss a simple physical model correlating the vibrational modes observed in the Raman spectra and the hydrogen-bond behavior. The wavenumber region between 140 cm⁻¹ and 80 cm⁻¹ can be described as modes associated with the intermolecular N–H•••X bonds, where X = O, Cl, or Br. The temperature dependence of the band wavenumber denoted by a circle suggests high participation of the N–H•••X bonds. The α values for X = Cl and X = Br (longer hydrogen-bond distances, Table 1) vary more strongly than those for X = O (shorter hydrogen-bond distances, Table 1). Therefore, the "circle" values for these bands are correlated with the lengths of the N–H•••X bonds in the crystal structures (Table 2). At this point we note that the band at 23 cm⁻¹ has an α value similar to the values for the bands recorded between 140 cm⁻¹ and 80 cm⁻¹, suggesting it also has a contribution from N–H•••X hydrogen bonds.

On the other hand, O–H•••O bonds are the main contributors for the bands in the region between and 80 cm⁻¹ and 20 cm⁻¹; however, we observed that temperature changes have a small effect on the wavenumber of these bands. Figure 7 shows the Raman spectra in the external mode region of LT, LTHCl, and LTHBr in the temperature range between 298 K and 453 K. This suggests that complexation (i.e., the introduction of Br and Cl in the LTHCl and LTHBr structures) does not substantially modify the O-H•••O bonds when compared with the LT crystal. Additionally, it is worth mentioning that the wavenumber of a mode belonging to LT at approximately 25 cm⁻¹ exhibits a temperature evolution with a steplike form. Such behavior was previously observed for two bands of DL-alanine associated with torsion of CH₃ and rocking of COO⁻ [18]. The study on DL-alanine indicated that the steplike behavior should be interpreted as a change of molecular conformation due to changes related to hydrogen bonds along one specific direction. The investigation performed on the LT crystal suggests the discontinuous evolution of the wavenumber of some modes (steplike behavior) originating from hydrogen-bond motion is not only characteristic of the DL-alanine crystal but can also be a property of many amino acid structures. However, further studies will be necessary to unravel and to generalize such a finding.

Summarizing the previous paragraphs, the data acquired in this study are consistent with the hypothesis that there is a correlation between N–H•••X bonds at room temperature and specific Raman bands recorded between 140 cm⁻¹ and 80 cm⁻¹. The modes for the LT crystals were previously studied and, in particular, Raman bands located between 140 cm⁻¹ and 80 cm⁻¹ were associated with torsion of the LT molecule

Journal Pre-proo

[19–23]. The occurrence of torsional vibrations of the amino acid with low wavenumber confirms the interpretation that such a region can exhibit both external and internal modes [24]. This result is consistent with the fact that hydrogen-bonding interactions in molecular crystals can give rise to several types of phonon dynamics, such as relatively long-lived optical phonons [25, 26], vibrational solitons [27, 28], and anomalous thermal conductivities [29].

A previous study affirmed that torsional modes in LTHCl play an important role in the polymorphism at high pressure. In very recent work, assignment of the modes on the basis of density functional theory calculations was done for LTHCl, increasing our understanding of the changes observed in particular Raman-active modes [30]. Torsional bands of the LT crystal exhibiting inversion of the relative intensity and change of slope dv/dP between 1.0 GPa and 1.5 GPa were understood as corresponding to conformational changes of the molecules in the unit cell. The present work showed that the same modes carry fundamental information about the behavior of hydrogen bonds and the decomposition process occurring in LT and its salts.

Finally, we discuss two additional points. The first one concerns the so-called hydrophobic interaction. Features of aromatic amino acids serve as a probe to understand the environment of peptide chains, which plays important roles in biochemical processes related to some degenerative diseases [31]. Hernández et al. [31] showed the existence of a doublet, at 850/830 cm⁻¹, that is characteristic of the hydrophobic/hydrophilic balance of interactions involving the phenol ring. According to that study, different hydrophobic characters of tyrosine can be inferred from the ratio of the intensity of the doublet. Although the study of hydrophobic interaction was not the main objective of our study, we were able to perceive that the relationship between the two modes remains approximately constant as a function of temperature for the three powdered samples. This means that the hydrophobic character of interactions apparently does not change during heating and there is no evidence of breakdown of hydrophobic interactions in the Raman spectra in our experiments. However, from the ratio of the intensity of the doublet at 298 K, LTHCl and LTHBr exhibit strong inversion compared with LT. Thus, the hydrophobic/hydrophilic interaction probably changes with the insertion of chlorine and bromine in the crystal lattice. A molecular structure comparison between LT and LTHCl, performed by neutron diffraction, evidenced an

additional hydrogen bond (from LTHCl) associated with the phenol ring through the C– H bond [5].

The second point concerns the possibility to understand the donor/acceptor character of hydrogens bonds through the Raman spectroscopic data. When a hydrogen bond is formed, the O–H stretching vibration is redshifted (i.e., the frequency of the mode is observed at a lower value) [32–34]. Additionally, these previous studies showed that the redshifts induced in the donor molecules are larger than those in the acceptors because of the decreased bond strength of the donor O–H bonds. In the present study on the three LT compounds, it was not possible to obtain Raman spectra in the spectral region where O–H stretching occurs. Also, we were not able to correlate the donor/acceptor character of the hydrogen bond with the low-wavenumber bands, which should be attempted because of this interesting aspect of the bond. As a consequence, although a discussion of the thermal decomposition temperature of LT compounds and its connection with the length of N–H•••X bonds at room temperature was possible, no information regarding donor/acceptor character was clearly obtained.

4. Conclusions

The present study furnished some information to discover a connection between the decomposition process and the hydrogen bonds in the crystal structure of LT and its salts. The decomposition process in LT, LTHCl, and LTHBr seems to be dominated by the N–H•••X (X = O, Cl, or Br) bonds, while the O–H•••O bonds seem to have small participation in this process. The thermal decomposition temperatures of LT, LTHCl, and LTHBr are directly connected to the length of the N–H•••X bonds at room temperature. The behavior of the vibrational modes associated with torsion of the LT molecule is consistent with a weakening of these connections favoring breaking of the hydrogen bonds in the decomposition process.

Because the vibrational modes associated with librational motion are important in the analysis of the decomposition processes, a detailed study of the lattice dynamics of materials of this kind—doped and pure amino acids—can be very useful for the development of a model of the low-frequency dynamics and the thermal decomposition of certain NLO materials.

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Fig. 1. X-ray diffraction patterns with Rietveld refinement data for L-tyrosine (LT), L-tyrosine hydrochloride (LTHCl), and L-tyrosine hydrobromide (LTHBr) at room temperature.

Fig. 2. Thermogravimetric curves for L-tyrosine (LT), L-tyrosine hydrochloride (LTHCl), and L-tyrosine hydrobromide (LTHBr) powder from 293 K to 673 K.

Fig. 3. Differential thermal analysis (DTA) for L-tyrosine (LT), L-tyrosine hydrochloride (LTHCl), and L-tyrosine hydrobromide (LTHBr) powder from 350 K to 600 K.

Fig. 4. Raman spectra of polycrystalline L-tyrosine (LT), L-tyrosine hydrochloride (LTHCl), and L-tyrosine hydrobromide (LTHBr) at 298 K and 423 K in the region of the lattice modes.

Fig. 5. Raman bands associated with torsion of the L-tyrosine (LT) molecule (adjustment with Lorentz curve). LTHBr, L-tyrosine hydrobromide; LTHCl, L-tyrosine hydrochloride.

Fig. 6. Temperature dependence of the lattice mode wavenumber (linear fitting) for (a) L-tyrosine, (b) L-tyrosine hydrochloride, and (c) L-tyrosine hydrobromide.

Fig. 7. Raman spectra of polycrystalline L-tyrosine (LT), L-tyrosine hydrochloride (LTHCl), and L-tyrosine hydrobromide (LTHBr) for all temperatures in the region of the lattice modes.

Table 1. Distances and angles in the hydrogens bonds in L-tyrosine, L-tyrosinehydrochloride, and L-tyrosine hydrobromide.

А–Н···В−С	$\mathbf{A}\cdots\mathbf{B}(\mathbf{A})$	HB (Å)	< A–H … B (°)					
L-Tyrosine								
$N-H_2\cdots O_1-C_4$	2.88	2.120	129.8					
$N-H_4\cdots O_3-C_9$	2.83	1.789	169.8					
$N-H_3\cdots O_3-C_9$	2.88	1.853	172.7					
$O_1 - H_1 \cdots O_2 - C_9$	2.67	1.689	173.8					
L-Tyrosine hydrochloride								
$N – H_1 \cdots Cl$	3.25	2.378	144.5					
$N-H_5\cdots Cl$	3.45	2.471	161.8					
N-H ₉ …Cl	3.33	2.505	137.4					
$O_3-H_2\cdots Cl$	3.05	2.078	165.6					
$O_2 - H_6 \cdots O_3 - C_8$	2.62	1.609	170.7					
$N-H_5\cdots O_1-C_1$	2.90	2.420	108.0					
L-Tyrosine hydrobromide								
$N\!\!-\!\!H_1\!\cdots\!Br$	3.46	2.436	144.2					
$N-H_5\cdots Br$	3.50	2.493	161.4					
N–H ₉ …Br	3.46	2.531	136.9					
$O_3-H_2\cdots Br$	3.23	2.120	165.6					
$O_2 - H_6 \cdots O_3 - C_8$	2.65	1.628	170.6					
$N-H_5\cdots O_1-C_1$	2.94	2.464	108.1					

Table 2. Variation of the wavenumber as a function of temperature, dv/dT, for L-tyrosine (LT), L-tyrosine hydrochloride (LTHCl), and L-tyrosine hydrobromide (LTHBr).

Mode	LT		LTHCl		LTHBr	
	v (298	dv/dT (cm ⁻¹ K ⁻	v (298	dv/dT (cm ⁻¹ K ⁻¹)	v (298	dv/dT (cm ⁻¹ K ⁻
	K)	1)	K)		K)	1)
	23	-0.015	23	-0.03	23	-0.04
	27	-0.002	30	-0.01	29	-0.02
	35	-0.012	40	-0.01	34	-0.01
	55	-0.002		<u>,</u> ,	52	-0.02
	76	-0.02	61	-0.01	58	-0.02
•	96	-0.02	105	-0.03	107	-0.03
•	112	-0.03	117	-0.06	113	-0.05
•	128	-0.03	120	-0.07	125	-0.04
•		0,21	125	-0.02		



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Highlights

- A high-temperature Raman scattering study was performed on L-tyrosine, L-tyrosine hydrochloride, and L-tyrosine hydrobromide crystals.
- There is correlation between hydrogen bonds, the phonon dynamics, and thermal decomposition.
- Hydrogen bonding and thermal decomposition are correlated with Raman bands in the low-wavenumber range.
- The behavior of the phonons is important in the analysis of decomposition processes.

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