Infrared dispersion analysis and Raman scattering spectra of taurine single crystals

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ABSTRACT

A comprehensive set of optical vibrational modes of monoclinic taurine crystals was determined by Raman scattering, and infrared reflectivity and transmission spectroscopies. By using appropriate scattering/reflection geometries, the vibrational modes were resolved by polarization and the most relevant modes of the crystal could be assigned. In particular, we were able to review the symmetry of the *gerade* modes and to resolve ambiguities in the literature. Owing to the non-orthogonal character of B_u modes in monoclinic crystals (lying on the optic axial plane), we carried out a generalized Lorentz dispersion analysis consisting of simultaneous adjust of infrared-reflectivity spectra at various light polarization angles. The A_u modes (parallel to the C_2-axis) were treated within the classical Lorentz model. The behavior of off-diagonal and diagonal terms of the complex dielectric tensors and the presence of anomalous dispersion were discussed as consequences of the low symmetry of the crystal.

1. Introduction

Taurine (2-aminoethyl sulfonic acid) is an amino acid derived from the methionine and cysteine metabolism. It is one of the few amino acids that are not incorporated into proteins, but it is the most abundant one in the muscle tissues and organs of most animal species [1–4]. This sulfonated amino acid has been identified as a major player in innumerous biological functions, which, in mammalian systems, include: bile salt formation [5], growth modulation [6], osmoregulation [7,8], membrane stabilization [9], vision [10], antioxidant action [11], calcium homeostasis [12], glycolysis and glycogenesis stimulation [4,13,14], neurotransmission [4], pro-inflammatory regulation [2], immune response [1,3–5], etc. It is considered a conditionally semi-essential amino acid in man, once humans have a limited ability to synthesize it [1,4,14]. The role of taurine supplementation in many therapeutic applications has been largely discussed in the literature [1,2,4,14,15].

In addition to the several pharmacological and nutritional actions mentioned above, taurine has also been considered for many biological or non-biological applications, among which we cite: electro-polymerized taurine thin films for biological [16–22] or chemical sensors [23]; incorporation into membranes and films for nanofiltration [24,25]; participation in chemoselective oxidation of sulfides [26] and in gold recovery from water [27]. Most of these recent studies are based upon modified taurine action by its interaction with nanoparticles [16,17,20,23,24]. In this respect, Raman and infrared spectroscopy emerge as very appropriate techniques to investigate the interaction of taurine with nanoparticles [28,29], owing to the many possibilities of these non-invasive and non-destructive analytical tools. Naturally, in order to take benefit of these techniques in all their possibilities a sound knowledge of the spectral features of the material is necessary. As an example, Raman and infrared spectra were used in the case of taurine to confirm the *zwitterion* configuration of its molecule (i.e., $NH_3^+-CH_2-CH_2-SO_3^-$), in solution and in crystal forms, as well as its *gauche* conformation in solids [29–31]. Several studies have also been performed by using Raman spectroscopy in taurine single crystals aiming to determine the behavior of its first-order Raman modes as functions of temperature [31–34] or hydrostatic pressure [35,36]. These studies, alongside lattice dynamic calculations, led to an assignment proposition of the main Raman-active vibrational modes of taurine crystals [30,32,35,37]. Although infrared spectroscopy has been employed to characterize taurine in many practical situations (mixtures, composites, and nanostructures) [25,28,38–42], a thorough investigation of the infrared-active vibrational modes in single crystals is still lacking. Indeed, the characterizations reported in the literature are based upon infrared absorbance (or, equivalently, transmission) spectra of taurine powders, which are rather poor in view of providing information about the dispersion parameters of the polar vibrations of the material – only the

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frequencies of the main absorption bands, without any possibility of symmetry attribution, are available so far [30,32,37].

In order to provide a comprehensive set of the optical vibrational modes of taurine single crystals, a careful Raman and infrared-reflectivity spectroscopic investigation of oriented samples, in appropriate scattering/reflection geometries, is presented in this work. We ought to mention that the main difficulty on attributing the vibrational modes of the crystal is due to its monoclinic structure. Indeed, taurine crystallizes within the $P2_1/c$ space group [43], and, therefore, its vibrational modes are decomposed into four orthogonal irreducible representations of the C_{2h} point group: the Raman-active A_g and B_g representations, and the infrared-active A_u and B_u ones. The infrared (*ungerade*) and Raman (*gerade*) modes are mutually exclusive, since the C_{2h} point group is centrosymmetric. Low-angle infrared reflectivity spectra were obtained in the crystallographic *ac*- and *bc*-planes, for several light polarization directions. By using an appropriate dispersion analysis technique, within a generalized Lorentz model [44–46], we were able to obtain a comprehensive set of dispersion parameters for the polar modes of the crystal. In addition, polarized Raman spectra in appropriate scattering geometries allowed us to revise the literature data, and to present a renewed attribution of the *gerade* modes of taurine. As a whole, the data obtained in this work are useful for the emerging applications of taurine, as well as for extending the relatively rare dispersion analysis studies of monoclinic crystals.

2. Experimental

Taurine single crystals were obtained by slow recrystallization of saturated water solution (pH = 5.6 and T = 25 °C) containing pharmacological grade L-Taurine solute supplied by Qianjiang Yongan (China). The as-received crystals were needle-shaped (up to 1 mm long and 200 μm at the transversal dimensions), with clear facets defining larger planes identified latter as the *ac*-plane (which is the optic axial plane of this biaxial crystal, i.e., the plane that contains the optical axes, or, equivalently, its lower and higher refractive indices). The growth direction is the crystallographic *a*-axis. The slow-crystallized crystals grew in form of elongated platelets (*ac*-plane), with circa 5 mm in the longest dimension (parallel to the *a*-axis), 2 mm width and 1 mm thickness (parallel to the *b*-axis). They also presented clear facets along the *a*-axis that helped us identifying the lattice directions. The crystal structure and the orientations of the crystallographic axes were checked by X-ray diffraction. The obtained lattice parameters matched perfectly those described in the literature ($a = 5.27$ Å, $b = 11.64$ Å, $c = 7.93$ Å, $\beta = 94.1°$ and Z = 4, within the $P2_1/c$ space group [43]). Previously to the spectroscopic measurements, *ab* and *ac*-planes of the slow recrystallized samples were cut and polished to an optical grade.

Polarized Micro-Raman spectra were collected in backscattering configuration with an Horiba LABRAM-HR spectrometer equipped with a helium neon laser as excitation source ($\lambda = 632.8$ nm, maximum power of 6 mW at the surface of the sample), a diffraction grating of 1800 grooves/mm, a Peltier-cooled CCD detector, and a confocal Olympus microscope (100× objective). The experimental resolution was typically 1 cm^{-1} and the spectra required 5 accumulations of 30 s. The collected spectra were corrected for the Bose-Einstein thermal factor [47]. Fourier-transform infrared (FTIR) transmission spectra of pelletized samples (crushed) into KBr matrices were collected in a Bruker Vertex 70 spectrometer (350–4000 cm^{-1}) with the following configuration: SiC source, Ge-coated KBr beamsplitter and DTGS detector. The spectra were obtained under nitrogen purge, by averaging 128 scans. The spectral resolution was 2 cm^{-1}. Polarized FTIR-reflectivity measurements onto the *ab* and *ac*-planes of taurine crystals were performed in a Nicolet Nexus 470 equipment with a Centaurus microscope (10× magnification, incident light beam with 500 μm diameter). The polarizer was placed at the entrance of the microscope, allowing us to freely choose the light polarization angle. The spectrometer configuration for the mid-infrared measurements (550–4000 cm^{-1}) was a SiC

source, a KBr:Ge beamsplitter, a wire grid polarized onto ZnSe substrate and a liquid-N$_2$ cooled HgCdTe (MCT) detector. For the far-infrared measurements, the Centaurus microscope was adapted according to procedures described previously [48]. For this spectral region (50–700 cm^{-1}), the same source was used, besides a solid-state (Si) beamsplitter, a holographic wiregrid on a polyethylene substrate polarizer and a liquid-He cooled *Si*-bolometer detector. In all cases, gold mirrors were used as reference and the spectra were obtained by averaging 128 scans, under nitrogen purge, using observation regions of 250 μm × 250 μm and spectral resolution of 2 cm^{-1}. The incidence angle was estimated to be less than 15°. The reflectivity spectra obtained in the mid- and far-infrared regions matched well in the superposition region (within 2%). The overall far-mid infrared spectra (50–4000 cm^{-1}) were analyzed within a generalized Lorentz model [44–46], as discussed in the next section.

3. Results

At room temperature, taurine crystals present a monoclinic structure, belonging to the $P2_1/c$ (#14, C_{2h}^5) space group, with four dipolar (*zwitterion*) NH$_3^+$-CH$_2$-CH$_2$-SO$_3^-$ molecules per unit cell (Z = 4), forming a three–dimensional network via N—H⋯O hydrogen bonds [43]. All ions occupy sites of general C_1 symmetry, so the 168 first-order vibrations at the Brillouin zone-center (Γ) can be decomposed into the irreducible representations of the C_{2h} point-group as follows [35]: 42 $A_g(xx,yy,zz,xz)$ ⊕ 42 $B_g(xy,yz)$ ⊕ 42 $A_u(y)$ ⊕ 42 $B_u(x,z)$. The base functions for each representation are indicated into parentheses. Therefore, we can see that pure B_g *gerade* modes must be excited for cross-polarized Raman spectra either onto *ab*- or *bc*-planes, when one of the polarizers is parallel to the unique polar *b*-axis. In such case, parallel-polarized light (*aa*, *bb* or *cc*) would give only the complimentary A_g *gerade* modes. These scattering configurations were used for identifying the symmetries of the first-order Raman modes of the taurine crystal, and double-checked with additional measured configurations, as presented in the next sub-section.

Concerning the infrared modes, the characteristics of the polar modes belonging to the A_u representation are directly obtained from infrared-reflectivity spectra by using polarized light along the unique *b*-axis. On the other hand, the vibrational features for the polar modes belonging to the B_u representation require the use of non-trivial procedures, since the transition moments of these vibrations are no longer parallel to one of the crystallographic axes (*a* or *c*). In fact, the direction of each dipolar vibration becomes one of the characteristics of the B_u modes, which must be determined alongside the other characteristic features. Different methods have been developed to perform dispersion analysis of monoclinic crystals with great success: a generalized Lorentz model applied to polarized reflectivity spectra obtained at near-normal incidence [44,45,49–56] or at oblique incident angles [57–61]; and, quite recently, a generalized spectroscopic ellipsometry extended to anisotropic crystals [62–64]. In each of these three models, at least three independent spectra must be obtained into the plane normal to the unique *b*-axis, in order to uniquely determine the vibrational dispersion parameters into the non-orthogonal *ac*-plane. In this work, low-angle reflectivity spectra were obtained and analyzed within the generalized Lorentz model. These results are presented in this section, after analyzing the experimental data from Raman scattering.

3.1. Polarized Raman Scattering Spectra and the "Gerade" Modes of Taurine Crystals

Polarized Raman spectra of taurine crystals (needles or platelets) were obtained for several scattering configurations. The needle-shaped crystals showed good *ac* optical planes, where the largest dimension was parallel to the *a*-axis. Therefore, parallel (*aa*) and crossed (*ac*) polarized spectra were obtained, both corresponding to the A_g symmetry. In addition, the *ab*-plane of a large polished sample (obtained by slow