



Perceptible isotopic effect in 3D-framework of α -glycine at low temperatures

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ABSTRACT

Glycine, the most fundamental amino acid, albeit studied for many decades, has kept researchers captivated with interesting structural variations relevant to important biological, astrophysical and technological applications. We report here a noticeable effect of deuteration on the three dimensional hydrogen bonding network of α -glycine using low temperature infrared absorption studies in a wide spectral range, corroborated with Raman scattering studies. These systematic studies in the range 300–4.2 K have demonstrated a relatively compact assembly of glycine molecules in the three dimensional bilayered structure of hydrogenated glycine (gly-*h*) at low temperatures. This is inferred from a remarkable temperature effect in the weak intra-bilayer hydrogen bond – along the *b*-axis, which strengthens upon cooling. A pronounced increase in the intensity of NH₃ torsional and NH stretching modes has been observed. This is accompanied with a large rate of stiffening and softening respectively of these modes upon cooling and a change in slope across 210 K and 80 K. In contrast, the D–O hydrogen bond lengths in fully deuterated isotope (gly-*d*), as estimated using empirical correlation, show that the weak intra-bilayer hydrogen bond is not strengthened upon cooling down to 180 K, whereas the stronger intra-layer hydrogen bonds in the *ac*-plane become further strong. The ND₃ torsional vibrations show no temperature effect. This implies a relatively stable two dimensional layered structure formed by strongly hydrogen bonded glycine sheets in the *ac*-plane. Below 180 K, similar qualitative trends have been obtained for the hydrogen bond lengths in the two isotopes. In addition, temperature induced variation of the characteristic “indicator” band of zwitterionic gly-*h* and gly-*d* has also been reported.

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1. Introduction

Glycine, the simplest amino acid and the building block of proteins, is among the most fundamental entities responsible for the evolution of life on earth [1–4]. The search and studies of glycine and H₂O/CO₂ ices [5–9], is therefore a prime research area to probe molecular assemblies and trace life in extra-terrestrial regions where thermodynamic conditions are drastically varied [5, 7, 10–15]. It is also the only achiral amino acid and in the solid state, crystallizes in three polymorphic forms [16–18]. With important applications in bio-materials and being the major constituent of macromolecular complexes in living organisms, glycine serves as an archetype system where weak interactions play a decisive role in structural stabilization. Further, glycine complexes have benchmarked the use of organic solids for ferroelectric and non-linear applications [19–21]. The substitution of deuterium for hydrogen has greatly helped in i) improving the properties of glycine

complexes (and in general organic or hydrogen bonded systems) in the applied fields of pyroelectric detectors [22–24], drug metabolism in pharmacology [25–28] etc. as well as ii) basic understanding of molecular structure and vibrational frequencies [29–35]. However, considering the varied consequences of deuteration, comparative studies on isotopic effect under varying conditions require attention. An understanding of the molecular structure and structural response under such conditions would be helpful in predicting the physico-chemical behavior of such compounds for various applications, for example crystal engineering, chemical synthesis, lyophilisation, pyroelectric/non-linear properties, etc.

Central to these properties and applications is the three dimensional hydrogen bonded network in glycine. Though it is capable of forming very strong hydrogen bonds in multi-component complexes [36, 37], in the native state its structural framework comprises of moderately strong hydrogen bonds which, as rightly phrased by researchers, “mimic the polypeptide chains” [38, 39]. The groups of these hydrogen bonds have been explained using various interpretations. For example, α -glycine, the most readily crystallizable polymorph, consists of

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strongly hydrogen bonded rings of glycine molecules in the *ac*-plane [16]. The glycine zwitterions form head to tail linked double layers lying perpendicular to the *b*-axis with a weak N–H–O intra- double layer and very weak C–H–O inter- double layer hydrogen bonds [16]. For external tuning of this network, high pressure provides an effective method for significant alterations of interatomic distances [15, 36, 40], whereas low temperature studies probe subtle details under homogeneous contraction (far less than the compression technique), by constraining thermal agitations, thus providing valuable information on structural stability and the possible reaction pathways. Though both techniques are expected to reduce the volume, the resulting molecular reorientations may sometimes lead to varying effects [20, 41].

Surprisingly, while glycine is being studied by various methods since nearly a century now, systematic variable temperature/pressure studies have started appearing only in the last two decades, thus renewing the interest in this fundamental compound. The crystal structure of glycine was first suggested in 1931 in the pioneering works of J. D. Bernal as monoclinic with lattice parameters $a = 5.04 \text{ \AA}$, $b = 12.1 \text{ \AA}$, $c = 5.41 \text{ \AA}$ and $\beta = 111^\circ 38'$ containing four molecules in a unit cell with $P2_1/n$ space group [42]. In the following decades, several studies have been carried out on glycine polymorphs using theory [43–47], infrared [46, 48–53], Raman [29, 30, 54, 55], ESR [56], NMR [44, 57–59], spectroscopy, inelastic neutron scattering [60, 61], powder/single crystal x-ray/neutron diffraction [16–18, 62, 63] etc. with improvements in computational and experimental techniques in order to provide finer details on the microscopic properties of its various ionic forms. In the condensed phase, it exists in zwitterionic form ($\text{NH}_3^+\text{CH}_2\text{COO}^-$) in contrast to the neutral ($\text{NH}_2\text{CH}_2\text{COOH}$) gas form [64]. Low temperature matrix isolation technique was used to study the neutral form of α -glycine to establish its vibrational mode assignments and it was speculated that the zwitterionic form would not show significant changes upon cooling [48]. In 1980 and 2000, electron density studies were reported on solid α -glycine (zwitterionic) at 120 K [65] and at 23 K [66] respectively, which provided the N–O distances of hydrogen bonds. The subsequent single crystal studies of all the polymorphs by Boldyreva et al. in 2003 at 300, 250, 200 and 150 K ascertained the absence of polymorphic transformations and provided evidences of N–O distance shortening implying strengthening of N–H–O hydrogen bonds [67]. The values of H–O distances are however at variance in various papers at ambient conditions, which were also provided at 120 K by Legros et al. [65]. Here, it is worth noting that, spectroscopy has emerged as a powerful tool to

understand the protonic motions in molecular solids and complement the structural studies at varying thermodynamic conditions [15, 36, 37, 68, 69]. Thanks to the efforts of various researchers that we now have standard scales or the correlation plots between covalent bond stretching frequencies and the corresponding hydrogen bonded lengths deduced from several compounds for various kinds of hydrogen bonds [70–75].

The presumptions of any phase transition in α -glycine close to room temperature due to anomalous behaviour of conductance between 323 K and 294 K [76], were not verified by the structural studies [67, 77]. However, temperature effect was noted in anisotropic distortion of unit cell and molecular layers, thus affecting the reorientation properties of dipoles upon the application of external electric field [77]. Subsequently, a series of papers by Boldyreva investigated the relative stability of glycine polymorphs using adiabatic and differential scanning calorimetry [78–81]. The low temperature spectra of glycine were measured by Fearheller et al. in 1971 at 113 K for verifying the mode assignments [82] and Andrews et al. (in the low frequency region below 350 cm^{-1}) at 85 K in 1983 to study the difference between inter- and intra-molecular forces [83]. Later, Ivanov et al. reported the mid-IR spectra ($400\text{--}3700 \text{ cm}^{-1}$) at 300 and 18 K in 1991 and revisited the mode assignments taking aid from the spectra of N-deuterated sample [84].

The first systematic variable temperature Raman study of α -glycine in the temperature range 83–360 K were reported in 2005 from our lab, which investigated the torsional ($470\text{--}540 \text{ cm}^{-1}$) and stretching regions ($3050\text{--}3200 \text{ cm}^{-1}$) revealing the splitting of NH_3 torsional and CO_2 rocking modes [85]. The corresponding IR measurements in the range $600\text{--}7800 \text{ cm}^{-1}$ were reported for α - as well as other glycine polymorphs in the temperature range 93–433 K by Chernobai et al. in 2007 highlighting distinct polymorphic behaviour [86]. The vibrational mode assignments in the low frequency region (below 200 cm^{-1}) have recently been refined by Aree et al. by estimating atomic displacement parameters deduced from synchrotron x-ray and neutron diffraction data at various temperatures [87]. This spectral range was also investigated using Raman spectroscopy to correlate the changes observed in a few selected modes of glycine polymorphs with the “dynamical transition” and conformational changes observed in biomolecules in the range 200–250 K by monitoring the deviations in anharmonicity [88]. The dynamical transition phenomenon has also been explored by Bordallo et al. using inelastic neutron scattering in the temperature range 5–300 K focussing on the NH_3 reorientational transitions upon

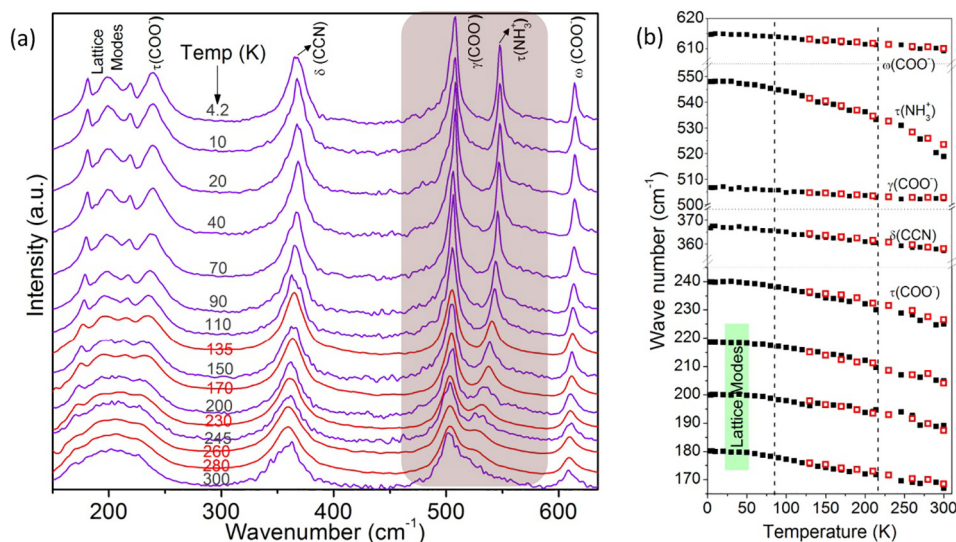


Fig. 1. (a) Low temperature IR spectra of α -glycine in the spectral range $150\text{--}650 \text{ cm}^{-1}$. Red color plots are at 4 cm^{-1} resolution using Liquid nitrogen (LN_2) and violet color plots are from the repeat measurements at 2 cm^{-1} resolution using Liquid Helium (LHe). (b) Frequency versus temperature plot in $150\text{--}650 \text{ cm}^{-1}$ spectral range. Red squares represent data at 4 cm^{-1} resolution and black squares represent repeat measurement data points at 2 cm^{-1} resolution. Symbols: τ -torsional, δ -bending, γ -rocking, ω -wagging. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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