Infrared Spectroscopy of Molecular Solids under Extreme Conditions

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Abstract. The first infrared beamline at the Indian synchrotron radiation source, Indus-1 has been designed, fabricated and installed based on extensive beam extraction and propagation simulations and a comprehensive facility for spectroscopy has been developed. The development of beamline, lab based facilities and research on technologically and bio-geologically important molecular solids were taken up in parallel. The proton dynamics of strong hydrogen bonds across the potential barrier under extreme thermodynamic conditions of high pressure (upto 30 GPa) and low temperature (upto 4.2 K) were examined in the family of oxalic acid, the simplest dicarboxylic acid and glycine, the simplest amino acid, which are abundant in planetary gasses and ices. Upon reaching the symmetrization limits, the subtle, drastic and as well as rare high pressure behaviours depicted by these systems, of great relevance to basic physics, crystal engineering and biology, indicate that they can be the model systems to study proton dynamics in complex bio-geological processes.

Keywords: Hydrogen bond, dynamics, infrared beamline, spectroscopy, synchrotron, glycine, oxalate, high pressure.

Introduction
Hydrogenous materials such as water, organic acids and minerals (the fundamental constituents of life) under extreme thermodynamic conditions are of immense importance to the understanding of bio-geological processes in earth’s interior as well as other celestial bodies. Hydrogen bonds play a decisive role in their structural stabilization. For example, at high pressures, the structure of non-molecular phase of ice (~100 GPa) is predicted to be stabilized by a symmetric hydrogen bond formed through translational proton tunneling. However, because of the high barrier in the potential energy, in general, localized proton at the hydrogen bond centre and proton transfer are rare events or dynamical bottlenecks. These fundamental problems have direct relevance with various bioprocesses and applications. Glycine, the building block of proteins, provides vast opportunities to understand proton dynamics in the complex bio-geological processes in nature where inter-molecular interactions are governed by diverse chemical environments. Among various carboxylic acids, only oxalic acid yields crystallized salts with glycine in different stoichiometries from either slow evaporation or other techniques. The hydrogen bonded networks in these complexes are also ideal to look for novel structures like ferroelectric/ non-linear optic materials or dynamic polymers through hydrogen bond assisted supramolecular assembly, a path adopted in nature for bio-material synthesis. Glycine and oxalic acid complexes form a special class as these compounds contain very strong hydrogen bonds which are in the limit of symmetrization even at ambient conditions. Infact, oxalates are capable of forming strong hydrogen bonds in various complexes including in its ambient structure as dihydrate. Oxalic acid dihydrate (OAD), although a benchmark hydrogen bonding and crystallographic system, remains one of the most debated compounds in molecular solids for nearly a century with regard to proton dynamics. The present work reviews the proton dynamics studies under high pressure in glycine and oxalic
acid family of crystals [1-5], we claim to have solved the long standing debate on proton dynamics in oxalic acid dihydrate (OAD) by demonstrating a complete mechanism of proton transfer and effects on the cooperative molecular structure. In addition, a novel mechanism of the ‘rare’ pressure induced hydrogen bond symmetrization has been proposed in glycinium oxalate (GO) using experiments as well as theory. Possible phase transitions to the technologically important structures in ferroelectricity and supramolecular engineering has also been discussed in Bis(glycinium)oxalate (BGO) and GO respectively. For such studies on proton dynamics and its influence on molecular structure under pressure, Infrared (IR) spectroscopy is the preferred technique because of the difficulty with structural methods, viz. X-ray/neutron, to monitor hydrogen positions at high pressures (even deuteration can vary wavefunctions and dynamics). However, high pressure IR investigations using diamond anvil cells demand a high brilliance of the probing beam to be focused on a spot of the order to tens of microns. Synchrotron radiation is the ideal source for IR microscopy and therefore a new IR lab for comprehensive condensed matter research and an IR beamline have been developed at Indus-1 synchrotron source. Hence, both the works of development of the IR beamline and initiating the studies on proton dynamics were taken up in parallel and are described in this paper.

**Development of IR beamline:**
The high brightness of synchrotron radiation in the infrared region as compared to the thermal sources comes from the very small size of the source and the directional property of the emitted radiation (narrow emission angles). The spectrum of a bending magnet radiation is uniform in the horizontal plane of emission. But in the vertical plane, it is strongly wavelength dependent and the cross section of the ‘fan’ emitted is systematically filled with higher wavelength condensed matter as one moves away from centre (Fig.1). For wavelengths significantly longer than the critical wavelength ($\lambda_c = 61$ Å, i.e. ~ 202 eV for Indus-1) of the storage ring, the characteristic angle $\theta_c$ depends upon the wavelength $\lambda$ as $\sim (\lambda/\rho)^{1/3}$, where $\rho$ is the radius of curvature of electron trajectory. Hence an optimization of the acceptance angle becomes crucial to extract the high wavelength infrared components from the storage rings.

![Fig. 1: (Top to bottom) Extracted beam profiles (cross section) as calculated for $\lambda = 50$ µm at Indus-1 with 35 mrad beamport opening; focussed spot (nearly 300 µm)](image)

Indus-1 commissioned in 1999, operates at 100 mA beam current with beam lifetime of ~1.8 hours. The IR beamline is installed at the 10° port of dipole (DP-4) and integrated with a FTIR end-station (Fig. 2). The first mirror can be conveniently placed close to the beamport so that the radiation can be

![Fig. 2: (top to bottom) Optical layout of beam extraction and transport upto the experimental station of beamline - showing IR microscopy for high pressure, cryogenic system, FTIR interferometer, Liq. He Bolometer detector etc.](image)
collected over a large vertical and horizontal emission angle, which makes it possible to obtain both horizontal and vertically polarized IR radiation from the source, which is very difficult to obtain from a thermal source. With the acceptance angle of 35 mrad, vertical collection of radiation covering the complete mid infrared region became possible at Indus-1.

An analysis of the 100% gold reflection lines shows that for synchrotron source, the signal to noise ratio (SNR) depicts relatively much smaller decline as compared to the thermal source, upon reducing the microscopic aperture. This gives nearly an order of magnitude higher signal to noise ratio for smaller focused spots. Various other developments have been carried out at the experimental station, which make it a unique national facility for in-situ high pressure, low temperature, imaging and polarization dependent IR measurements (Fig. 2).

The above efforts are well complemented with the development of a very high resolution (~ 0.0012 cm⁻¹) IR lab at BARC for spectroscopic studies of molecules and transient species in absorption (using normal and indigenously developed long path cell) and transmission (using electrodeless discharge lamps and hollow cathodes) modes.

**High pressure studies of molecular crystals**

Colourless single crystals were grown by slow evaporation from an aqueous solution containing stoichiometric ratios of glycine and oxalic acid. The samples were characterized using single-crystal XRD, neutron diffraction, Raman and IR spectroscopy.

For IR studies, an indigenously developed clamp type symmetric DAC was used with an IR microscope coupled to Bruker Vertex 80V FTIR equipped with various sources and beamsplitters, installed at the experimental station of IR beamline at Indus-1. LN₂-cooled MCT detector was used for the complete mid-IR range. All the studies were initially carried out using thermal source, which was followed by using the synchrotron source in some of the cases. Polycrystalline sample in CsI matrix along with a couple of ruby balls was loaded in a 150 μm hole of a tungsten gasket preindented to a thickness of ~60 μm for absorption studies.

Pressure calibration was done using ruby fluorescence.

High pressure Raman studies were carried out in an existing facility, based on confocal micro Raman setup in back scattering geometry, configured around Jobin-Yvon (HR 460) spectograph. Mao Bell DAC was used for Raman and support studies using XRD. The results are well complemented with first principles molecular dynamics simulations using VASP code.

**Proton Migration in OAD**

Oxalic acid dihydrate, an important molecular solid in crystal chemistry, ecology and physiology, is being studied for nearly 100 years now. The most debated issues regarding its proton dynamics have arisen due to an unusually short hydrogen bond between the acid and water molecules (dO₁---Ow ~ 2.43 Å, ∠O₁HOw ~ 177°). In O₁-Ht---Ow, the acceptor Ow (oxygen atom of water) also acts as a donor for the carbonyl group of subsequent OA molecule, forming a chain, −C-O₁-Ht---Ow-Hw−O₂=C-. The alternate hydrogen bonded chain causes a net decrease in O---O through the well known cooperativity effect of hydrogen bonds. Due to this enhanced strength, the initial beliefs, which date back to 1930s, of observing a proton transfer state of oxalic acid dihydrate at ambient conditions were ruled out by a number of studies in subsequent decades. Though, X-ray and neutron studies have also been reported under pressure, hydrogen atom positions could not be unambiguously determined which could affirm the thermodynamic conditions for proton motion.

Using combined in-situ spectroscopic studies and first-principles simulations at high pressures, we found that the structural modification associated with this hydrogen bond is much more significant than ever assumed [1]. Initially, under pressure, proton migration takes place along this strong hydrogen bond at very low pressures of 2 GPa (Fig. 3). This results in the protonation of water with systematic formation of hydronium ion and dianionic oxalate, thus reversing the hydrogen bond hierarchy in the high pressure phase II (Fig. 3). The resulting hydrogen bond between hydronium ion and carboxylic group shows remarkable strengthening under pressure, even in the pure ionic phase III as seen from the softening and dampening...
of the v1 hydronium mode (Fig. 3). The oxalic acid molecule also shows various changes due to transition from neutral to dianionic species, for example vanishing of Fermi resonance between C-O and C=O as observed from the merging of the two IR modes into one band. The loss in the cooperativity of H-bonds leads to another phase transition at ~9 GPa through reorientation of other hydrogen bonds. High pressure phase IV is stabilized by a strong hydrogen bond between the dominant CO2 and H2O groups of oxalate and hydronium ions respectively. The findings suggest that oxalate systems may provide useful insights on proton transfer reactions and assembly of simple molecules under extreme conditions.

![Image](https://example.com/image.png)

**Fig.3:** (top) Asymmetrization of H-bond on proton transfer, (bottom) High pressure IR spectra shows (a) softening of O-H stretch modes, (b) vanishing of OH signatures from OA and (c) evolution of H3O+' IR mode

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**Hydrogen bond symmetrization aiding supramolecular assembly in GO**

Glycinium oxalate (GO), the simplest amino-acid-carboxylic acid complex crystallizes in monoclinic structure with space group P2_1/c and four formula units per unit cell (Z=4). It possesses a nearly linear and strong O3-H7---O6 hydrogen bond \((d_{0--0} \approx 2.54 \text{ Å}, d_{H--0} \approx 1.65 \text{ Å} \text{ and } \angle \text{HOH} = 177^\circ)\) between semioxalate molecules in a columnar arrangement along the \(b\)-axis (Fig. 4). These semioxalate (HC2O4) columns hold the head to tail linked glycine (NH2CH2COOH) sheets in the \(ac\)-plane via other hydrogen bonds to form the three dimensional network. We have studied the proton dynamics of this strong O3-H7---O6 hydrogen bond under pressure, beyond the symmetrization limit up to ~ 20 GPa [2].

Under compression when the proton moves close to the mid-point of a very strong hydrogen bond O-H---O, the system becomes highly anharmonic leading to OH instability and resulting in remarkable dampening of vOH (stretching) mode (~2360 cm\(^{-1}\) for GO) (Fig. 4). A large red shift of ~ 250 cm\(^{-1}\) up to 2.5 GPa in vOH mode (from theory and ambient reflectance) and a substantial reduction in the O3---O6 distance \((d_{O3---O6} < 2.5 \text{ Å}, \text{see Fig. 4})\) implies that this hydrogen bond is strengthened under pressure and is on the verge of approaching symmetrization limit. The bond parameters obtained from MD calculations (total 12000 equilibrated configurations, in 1 femto-second time steps used at each pressure to generate the dynamical picture) show that the spread of proton distribution reduces with pressure and shifts towards the bond mid-point. The large softening of vOH mode, as approximated by a power law fit \((v \sim [A(P_e-P)]^{0.5})\) for the soft mode gives \(P_e \sim 8.15 \text{ GPa}\) as the pressure corresponding to vOH mode instability. At pressures close to 10 GPa, the distance between oxygen atoms, \(d_{O3--O6}\) continuously reduces to ~2.4 Å, accompanied by an increase in the covalent bond length \((d_{O3-H7})\), decrease in the hydrogen bond length \((d_{H7--O6})\). However, \(\angle \text{HOH}\) remains close to ~180°. The probability of crossing the mid-point through proton hopping increases with pressure and is already significant at ~10 GPa. This implies proton sharing between the closely overlapped potential minima in which the proton hops between the two
sites, which mimics the proton being at the midpoint. The consequent proton sharing between the two semioxalates would result in the emergence of neutral oxalic acid like spectral features, which have also been confirmed from the Raman and infrared modes.

We also note a relative increase in the background of the observed IR band profile above 2 GPa (See Fig.4). Such broad envelopes, resembling a continuum arise due to large νOH dampening and ride over the background of various other fundamentals. Its centroid shifts to lower frequencies (up to ~1000 cm⁻¹ at 18 GPa), at an increased rate above 8 GPa and the extent of this band crosses the lowest 600 cm⁻¹ mark to enter even in the far IR regions at higher pressures. Above 12 GPa, the evolution of broad envelopes in N-H stretching regions, behavior of N-H---O H-bonds and the observed transition in glycine conformation from bent to planar have suggested the formation of a supramolecular assembly in GO assisted by N1-H4---O4=C3 interactions at high pressures where glycine hammocks (in ac-plane) are tied to the infinite symmetric H-bonded oxalate poles (b-axis).

**Novel phase transitions in BGO**

Bis(glycinium)oxalate, another organic complex of glycine and oxalic acid family has a very short and strong O-H---O hydrogen bond (H---O=1.3 Å, O---O=2.461 Å) between glycinium and oxalate ions. Our high pressure studies of BGO indicate structural transformations across 1.6 and 4.5 GPa due to reorientation of H-bonds [3]. The appearance of Raman active modes in the IR spectra (Fig. 5) and vice versa above 1.6 GPa confirms that glycine molecules have become non equivalent leading to loss of centre of symmetry (implies breakdown of principle of mutual exclusion) and hence a non centrosymmetric high pressure phase. Softening followed by discontinuous shift of νO-H mode suggest that, in the high pressure phase above 1.6 GPa, though relatively weaker compared to that in the parent phase, yet strong O-H---O bonds exist. Further, high pressure dielectric studies suggest that the pressure induced transition results in a possible ferroelectric phase above 1.6 GPa, whereas low temperature spectroscopic and single crystal X-ray studies indicate that there is no phase transition occurring at low temperatures.
Conclusion
To summarize, we have studied proton dynamics of strong hydrogen bonds under pressure in glycine and oxalic acid family of complexes and set up various state-of-the-art national experimental facilities for IR spectroscopic studies covering a wide scientific domain. The findings of different high pressure studies carried on these crystals suggest that these systems can be the model systems to understand proton dynamics as they have depicted all the three and rare events of proton transfer across the barrier (relevant to enzymatic catalysis), a symmetric hydrogen bonded state (relevant to water transport in earth’s crust and basic physics) and hydrogen bond reorientation inducing phase transformation to a possible ferroelectric state at moderate pressures.

Contributors
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References