



# Covalent symmetrization of the hexagonal networks of trimesic acids at high pressure



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## ABSTRACT

The covalent symmetrization of the hexagonal networks of 1,3,5-trimesic acids under compression was studied applying inelastic Raman spectroscopic scattering in the pressure range 0–7.6 GPa. The first pressure induced phase transition, resulted from representative warping of trimesic acids network plane, was observed when compression met 0.4 GPa. Above approximately 1.9 GPa, as reflected in our Raman data, intra-plane hydrogen bonds became covalent and proton became homogeneous. Further compression beyond 7.6 GPa led to a significant loss of long-range order, marked by amorphization. Pressure-induced transformation and its mechanisms, exhibited in our experiment, reflect a characteristic structural transition of symmetric trimesic acids resulted from the effect of hydrogen-bonding interaction.

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## 1. Introduction

Hydrogen bond, one of the most important directional intermolecular interactions, plays a vital role in tuning molecular conformation, molecular aggregation, and the function of a vast number of chemical systems ranging from inorganic to biological. With ongoing developments in various subjects, including mineralogy, material science, general inorganic and organic chemistry, super-molecular chemistry, biochemistry, molecular medicine, and pharmacy [1], the research of hydrogen bonds is growing rapidly in depth as well as in breadth. In recent years in particular, the effects of pressure on the molecular systems with hydrogen bonds have attracted great attention, since pressure is a thermodynamic parameter of paramount importance for calibrating and understanding chemical equilibria and chemical kinetics, thus vital to the study of condensed matter physics.

Being an archetypal molecule, formic acid and its three-dimensional polymerizations of formic acid under high pressure and its mechanism of proton transfer have been proposed before [2,3]. Allan has determined the high-pressure crystal structures of ethanol and acetic acids, including the positions of the hydrogen atoms [4]. Moreover, the studies of the effect of high pressure on unsaturated compounds molecule systems (e.g. acetylene, butadiene and propylene) and the aromatics derivatives (e.g. terphenyl) have been reviewed to illustrate the perspectives of phase

transition at ultrahigh pressures [5,6]. To achieve a full understanding of the effect of pressure on different polymorphs of the same compounds, related compounds and crystal structures, as well as phase transitions, have been discussed [7–10]. These studies are important to unveil the bonding mechanism of interrelated polymers, understand the correlation between structural properties, offer potential guidance for crystal engineering, and more generally, are vital to predict the effect of pressure on crystal structure, reactivity of molecular solids, and the degree of planarization geometry from a puckered molecule [11–18].

Trimesic acid (benzene-1,3,5-tricarboxylic acid, TMA) was a widely studied molecule, in part due the low-density hydrogen-bonded networks and non-covalent interactions materials of solid state compounds it can form [19]. In crystals, trimesic acid was a molecule which predictably forms intricate networks with intriguing supra-molecular properties (catenation or interpenetration, polymorphism and inclusion) as a consequence of its molecular symmetry and complementary hydrogen-bonding capabilities [20]. As a result, the two-dimensional, the three-dimensional arrangement of the networks formed by hydrogen bonding between TMA molecules, have been investigated by several researchers [21–25]. It has been suggested that trimesic acid, the monomer of poly(trimesic acid), exhibits unusual features in polymerization as it has three symmetrical carboxyl group which can readily undergoes molecular associations through variable hydrogen bonds not only between the TMA molecules, but also in the interior of the molecule. Since hydrogen-bonding interactions have proven to be sensitive to compression and the two-dimensional network comprising large open rings at ambient

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condition [26], it is absolutely essential to do research about the effect of pressure on structural transformations of trimesic acid [5].

We have therefore carried out in-situ high-pressure Raman investigation of TMA up to 7.6 GPa and reported the structural transitions leading to the phase change of trimesic acids in this article. Our analysis indicates that at approximately 1.9 GPa the hydrogen bonds within the plane become symmetric. At this point the substance becomes non-molecular, and the conformer distinction disappears, accompanied by the occurrence of covalent symmetrization. At higher pressures, TMA transforms gradually to a polymeric amorphous phase.

## 2. Experiment

Samples of 1,3,5-benzene-tricarboxylic acids were obtained from Sigma Aldrich A.R and were well-preserved before utilization. Apparatus for producing ultrahigh-pressure were Mao-Bell diamond anvil cell (DVC) with 500  $\mu\text{m}$  diameter of diamond anvil. A sheet of T301 steel, constituting a sealing device for generating super high pressure, with thickness of 250  $\mu\text{m}$  were used as gasket material. Having compressed the gasket to 80  $\mu\text{m}$  thickness, a superhigh pressure cell with a diameter of 200  $\mu\text{m}$  was created by drilling compressed gasket with a shaped tetragonous Tungsten carbide needle. In order to form high pressure experimental environment, appropriate amount of long strip shape sample was added to drill the cell under photics microscope. Owing to its Linear Correlation of the pressure-induced shifts of R1 lines of Ruby, Ruby powder whose diameters are roughly 10  $\mu\text{m}$  were used as calibration standard to precisely monitor pressure in the cavity in real-time. In this experiment, pressure transmitting medium were not applied for the reason that intervals of R1 fluorescence lines shifts of Ruby were invariant. Hence, the effects of non-hydrostatic pressure can be neglected in this study. The ranging of experimental pressure is 0–7.6 GPa on account of the Raman spectra. Raman spectra were recorded by confocal laser microscopy Raman spectrometer of Reni Shaw in via. Incentive wavelength light of Spectra Physics 160M laser was 514.5 nm and the output power of the laser was 8 mW connected to LEICA DMLM microscope system with 5 times amplification objective lens. Laser beam, accordingly, can accurately focus on the samples in the high pressure chamber and the 50–4000  $\text{cm}^{-1}$  wave-number range of Raman spectra, which the integration time of spectra was 20 s, were recorded as well. All the experiments were carried out at room temperature.

## 3. Results and discussion

In order to investigate the structural transformation resulted from changes of molecular kinetic energy and potential energy, the high pressure in-situ Raman spectra within 0–7.6 GPa are collected. For observing the reversibility of the phase transition, Raman spec-

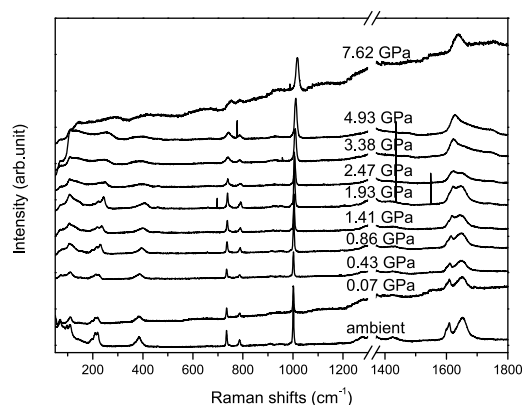


Fig. 1. Selected high-pressure Raman spectra of trimesic acid.

tra recorded comprise process of compression and decompression. The results show that there is no obvious difference between compression and pressure release process, except the pressure hysteresis effect. According to the characteristic Raman spectra, TMA are chemically stable under pressure until 7.6 GPa. Selected Raman spectra of 1,3,5-trimesic acid from 0 to 7.6 GPa are shown in Fig. 1.

### 3.1. Raman spectra under compression

It can be seen that the most significant Raman vibration mode under ambient condition are O=C–O and C–O–H stretching vibration, benzene ring breathing vibration, symmetric stretching vibration of C=O, C–O–H asymmetric stretching vibration, O–C=O wagging vibration, COOH out-of-plane vibration, and C–C symmetric stretching mode. Detailed attribution of Raman vibrational modes are presented in Table 1. On account of the effect of the filter, Raman spectroscopic information with wavenumber below 50  $\text{cm}^{-1}$  is missed. Additionally, we fail to observe any Raman vibrational mode in the vicinity of 1332  $\text{cm}^{-1}$  owing to the high intensity of diamond Raman peak. Overall, with the increase of pressure, accompanied by the disappearance of fractional Raman vibrational modes, the linear width of the Raman spectrum gradually broadens, making it difficult for the position of the Raman peak to be resolved.

### 3.2. Frequency–pressure relationship of trimesic acid

#### 3.2.1. Raman spectra of TMA in the pressure region of 0–0.4 GPa

At atmospheric pressure, all the Raman vibrational modes can be calculated using factor group analysis. Most of the peaks are in accord with the results of the previous measurements, demonstrating the coherence of the structural information with former studies [26]. According to previous report, the basic structure of TMA was

Table 1  
Observed frequencies ( $\text{cm}^{-1}$ ) of Raman active modes of trimesic acid with assignments and their slope of frequency–pressure curve,  $d\nu/dP$  ( $\text{cm}^{-1}/\text{GPa}$ ).

Frequency ( $\text{cm}^{-1}$ )	Assignment		$d\nu/dP$ ( $\text{cm}^{-1}/\text{GPa}$ )					
	Ambient	0.42 GPa	1.93 GPa	PhaseI	PhaseII	PhaseII'	PhaseIII	
1652	1651	1646		$\nu_2(\text{C}=\text{O})$	–2.1	–8.2	–2.1	–1.0
1609	1611	1623		$\nu_2(\text{C}-\text{O})$	5.2	8.2	8.1	–0.5
1001	1002	1006		$\nu_2(\text{C}-\text{C})\gamma(\text{COOH})$	1.5	2.8	2.7	2.1
787	787	791		$\tau(\text{C}_6\text{H}_6)$	–0.3	5.3	3.7	–3.1
735	735	738		$\varpi(\text{O}-\text{C}=\text{O})$	0.2	3.0	1.6	2.0
385	387	406		$\nu_2(\text{C}-\text{O}-\text{H})$	3.9	19.5	12.3	–17.8
219	223	243		–	8.2	17.3	14.0	11.2
210	212	223		$\delta(\text{COOH})$	1.2	6.9	8.1	11.8
109	110	108		Lattice	2.1	–4.9	2.7	2.2
69	77	–		Lattice	15.6	–	–	–

$\nu_a$ : anti-symmetric stretching,  $\nu_s$ : symmetric stretching;  $\delta$ : out-of-plane;  $\varpi$ : wagging;  $\gamma$ : rocking;  $\tau$ : ring distortion.

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