High-pressure polymorphism of the electrochemically active organic molecule Tetrahydroxy-p-benzoquinone

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Abstract

The structural and chemical response of tetrahydroxy-p-benzoquinone to isothermal compression to near 20 GPa have been studied using powder x-ray diffraction and vibrational spectroscopy. Compression beyond 11.5 GPa resulted in the appearance of several new peaks in the x-ray patterns, changes in the peak distribution and intensities, as well as the disappearance of features observed at lower pressures, which when coupled with concomitant changes in the infrared spectrum are indicative of a phase transition. Further analysis of the infrared spectra suggest this phase transition results in an increase in the anharmonicity of the system. Raman spectroscopic experiments indicate the high-pressure phase to be highly photosensitive and easily polymerized.

Key words: High-pressure, diamond anvil cell, spectroscopy

I. Introduction

The study of electrochemically active organic molecules for use in advanced batteries has garnered considerable attention recently as a result of the pervasive need for high-performance energy storage devices. Within this field, tetrahydroxy-p-benzoquinone (THQ) and alkali metal salts of THQ are of particular interest as a result of recent studies in which a battery was produced from a lithium salt of THQ ($\text{Li}_4\text{C}_6\text{O}_6$) [1,2] and was shown to have good electrochemical performance [2]. THQ can be readily isolated in high-yield from natural plant products [3-6], making it a green, renewable material for advanced batteries. The electrochemical properties of THQ were first documented by Souchey et al.[7] and subsequent studies have demonstrated and derived the mechanism of the efficient reversible charge transfer process of THQ and several of its alkali metal salts [2,8-11].

With application of pressure, some charge transfer complexes with differing donor and acceptor molecules have been shown to undergo a neutral to ionic phase transition associated with the electron transfer [12]. Charge-transfer complexes of only one molecular species are known [12]; such materials are characterized by short non-bonded C to O distances which readily permit electronic mixing of π -bonded orbitals and are often chromophoric molecules. Self complexation in THQ was suggested first from the x-ray diffraction [13] and then directly from the mechanisms derived for the charge transfer process [8-11]. However, the high-pressure behavior of charge transfer molecules which undergo self-complexation has not been previously studied and as such a high-pressure study on THQ seems warranted.

The molecular structure of THQ, shown in Figure 1, was determined by Klug [13] from single crystal data and refined with an R value of 0.079. During this refinement, the material was discovered to be a dihydrate, with a resulting chemical stoichiometry of $\text{C}_6(\text{OH})_4\text{O}_2 \cdot 2 \text{H}_2\text{O}$. The compound crystallizes in the monoclinic space group $\text{P2}_1/\text{c}$ with $a = 5.266 \pm 0.002 \text{ \AA}$, $b = 5.118 \pm 0.002 \text{ \AA}$, $c = 15.502 \pm 0.008 \text{ \AA}$ and $\beta = 103.89 \pm 0.02^\circ$. Each unit cell of THQ consists of two centrosymmetric quinone molecules and water molecules. An extensive intermolecular hydrogen bonding network was noted, as is shown in Figure 1, which results in individual chains of water and quinone molecules arranged in a layered structure. Additionally, each quinone molecule is hydrogen bonded to the nearest chain of water molecules. Interestingly, the quinone molecule was found to be nearly planar with C=O distances of $1.229 \pm 0.005 \text{ \AA}$ and C=C

distances of 1.342 ± 0.005 Å, which are significantly shorter than is observed in other charge transfer molecules [13] and suggestive of strong charge transfer through self-complexation.

Here, the *in-situ* isothermal x-ray diffraction and vibrational spectroscopic studies of the behavior of THQ to pressures near 20 GPa as a function of pressure are reported. The primary experimental motivations were to examine the structural and chemical response of THQ under compression, to search for possible structural transitions in the material and determine changes to the normal modes of vibrational in an effort to better understand if self-complexation can be enhanced at high-pressure. In the course of the experiments, evidence of a first order phase transition from the $P2_1/c$ space group to the $C2/c$ space group was observed near 12 GPa, as indicated by concomitant changes in the x-ray diffraction and vibrational spectra. The analysis of the x-ray diffraction patterns and infrared spectra collected in a compression sequence to near 20 GPa, followed by decompression studies revealed the polymorphic phase transition to be reversible with a moderate hysteresis.

II. Experimental Methods and Analysis

Polycrystalline Tetrahydroxy-p-benzoquinone (THQ, $C_6(OH)_4O_2 \cdot 2 H_2O$) was obtained from Sigma-Aldrich with a purity of 99% and used without further purification. Multiple diamond anvil cells were loaded using the following parameters for each interrogation technique (i.e. X-ray diffraction and spectroscopy). First, the black polycrystalline sample was mechanically ground into a fine powder with a ruby mortar and pestle and then approximately 150 micrograms of THQ and a ruby sphere with an approximate diameter of 25 microns were placed into the sample compartment. The sample compartment was made from a rhenium gasket, which was preindented to an average thickness of 80 microns with a 200 micron hole drilled into the indentation via electron discharge machining. A neon pressure-transmitting medium was loaded into the sample chamber using a high-pressure gas loading vessel previously described [14]. The *in-situ* pressure was monitored using ruby manometry in all experiments, which correlates the shifts of the R_1 and R_2 lines of ruby to a well-defined equation of state [15] and has an estimated precision of ± 0.1 GPa at room temperature.

Raman spectroscopy was performed at room temperature (298K) using an in-house designed 180-degree back scattering spontaneous Raman spectrometer. Briefly, samples were excited using a laser diode pumped solid-state laser operating at a wavelength of 514 nm, an

average power of 20 mW, and a laser spot diameter of ~ 4 microns. Raman scattering emitted from the samples were focused into and dispersed by a 500 mm focal length imaging monochromator equipped with a 1200 grooves/mm grating and the resulting signal was detected by a thermoelectrically cooled CCD camera. The full width at half maximum (FWHM) spectral resolution of the detection system was $\sim 1.1 \text{ cm}^{-1}$. Synchrotron-based infrared measurements were performed at beamline U2A of the National Synchrotron Light Source of Brookhaven National Laboratory. Extensive detail of the optical layout and specifics of this beamline is available [16]. Infrared absorption spectra were collected at room temperature (298K) between 500 and 4000 cm^{-1} , although the use of Type Ia anvils limited the amount of useful information below 1000 cm^{-1} owing to the multiple absorptions of the diamond anvils in this spectral region. A spectral resolution of 4 cm^{-1} was used over an average collection time of 12 minutes. The contribution of the diamond anvils to the spectra was removed by normalizing the spectra to a background spectra obtained from an empty diamond anvil cell. Frequencies were extracted using the peak fitting feature of OriginPro v 8.1.

Room-temperature (298K) isothermal angle dispersive X-ray diffraction experiments were conducted using a focused synchrotron beam at beamline 12.2.2 of the Advanced Light Source and at beamline 16BM-D of the Advanced Photon Source. The x-ray beam with a wavelength of 0.041 nm was collimated to $15 \mu\text{m} \times 15 \mu\text{m}$; the x-ray diffraction pattern was collected for an average collection time of approximately 90 seconds per pressure point. The lattice structural parameters were determined from the diffraction patterns using the JADE 9.0 software package. The starting crystallographic structure was obtained from the ambient crystal structure of Klug [13]. The refinement of the atomic positions with pressure was not attempted, due to the large number of atoms per unit cell coupled with the limited number of diffraction peaks. The resulting volume data was analyzed using a third-order Birch-Murnaghan (BM) equation of state [17].

IV. Results and Discussion

A. Properties at ambient pressure

At ambient pressure, the observed powder x-ray diffraction pattern for THQ indexes similar to the previously reported structure [13]. Due to thermal expansion, the structural parameters refined in this work are slightly larger than those previously reported [13] as is

summarized in Table I. Figure 2b shows the results of indexing the data from this study with the refined unit cell. Limited information on the normal modes of vibration of THQ was found in the literature, but the vibrational spectra of THQ collected during this study under atmospheric conditions have some similarities to that previously observed for the parent molecule of 1,4-benzoquinone [13, 18-21]. With twenty-two atoms per molecular unit of THQ, sixty unique normal modes of vibration are dictated for THQ at ambient pressure. In this study, thirty-eight vibrational maxima were noted between the Raman and infrared spectra. Table II presents a summary of the observed spectral lines, along with the likely molecular motions associated with the vibrational features. The mode Grüneisen parameters, γ_i , have been calculated for the Raman and Infrared data of Phase I and Phase II using previously defined equations [22]. The Grüneisen parameters of several modes associated with ring motions are, on average, double that of other modes, suggesting the THQ ring becomes easily compressed and deformed under application of pressure, while the low values for the other modes implies they are less sensitive to pressure. The bands associated with the O-H stretching modes show slightly negative Grüneisen parameters and as such are contributing negatively to thermal expansion and are highly flexible.

B. High Pressure Transition

Representative x-ray diffraction patterns presented in Figure 2 generally reveal small changes with compression to pressures near 11.5 GPa. Compression beyond 11.5 GPa resulted in the appearance of several new peaks in the x-ray diffraction patterns, changes in the peak distribution and intensities, as well as the disappearance of features observed at lower pressures. LeBail crystallographic analysis revealed the modifications can be attributed to a first-order phase transition from Phase I with $P2_1/c$ symmetry to Phase II with $C2/c$ symmetry. The $C2/c$ symmetry was identified using the pattern index setting in JADE 9.0. Results of the indexing are shown in Figure 2b. The lattice parameters of Phase II refined at 13.4 GPa are $a = 4.958 \pm 0.003$ Å, $b = 4.833 \pm 0.004$ Å, $c = 14.799 \pm 0.005$ Å and $\beta = 100.96 \pm 0.02$ °. As evidenced by the x-ray diffraction and infrared spectra, Phase II remains the kinetically favored structure at least to pressures which slightly exceed 20 GPa. The transition from Phase I to Phase II results in a nearly 10% decrease in volume and a decrease of nearly 0.3 Å in the c lattice vector (Figure 3b)

between 11.5 and 13.4 GPa (Figure 3). This degree of compressibility is not surprising, as the chains of quinone and water molecules lie nearly parallel to this axis at ambient pressure. In the Phase I low pressure structure, the chains of quinone and water molecules are offset resulting in an extensive network of non-symmetrical hydrogen bonds with varying lengths, as is shown in Figure 1b. Based upon several observations in the infrared spectra near the transition, the hydrogen bonds between the THQ and water molecules become increasingly anharmonic in Phase II as a result of continued application of pressure and it is hypothesized that the hydrogen bonding network begins to symmetrize. An increase in the anharmonicity of the system has been correlated with an increase in the strength of the hydrogen bond [24], which manifests in the infrared by anomalous shifts in vibrational bands, observation of symmetry-forbidden modes of vibration, and differing resonance phenomena. The negative Grüneisen parameters observed for the O-H modes also imply increasing anharmonicity, as well as the possibility of pressure induced amorphization. In comparison to the spectra of Phase I observed below 11.5 GPa, the width of the absorption band structure observed in Phase II in this spectral region significantly increased and its relative intensity became larger. The centroid of this peak red shifts to lower frequencies, at a near constant rate up to the phase transition near 12 GPa (Figures 4 and 5). Above the transition, the bandwidth increases significantly. Such broad spectral envelopes have been used as prime evidence of a strengthening of the hydrogen bond in low barrier hydrogen bonded systems close to symmetrization [24-27]. On average, the O-H vibrational modes of the THQ red shift nearly 20 cm^{-1} from ambient pressure to the transition. The extent of the red-shift has been correlated with the strength of the hydrogen bond [28], the proton donor-acceptor distance [29, 30] and the ionization potential of the proton acceptor [31]. Collection of the infrared spectra at high-pressure below 1000 cm^{-1} was limited due to the contributions from the diamond anvils, but the Raman spectra (Figure 6) collected as a function of pressure show that the O-H bending mode observed near 846 cm^{-1} at ambient pressure shifts to ca. 825 cm^{-1} near 12 GPa (Figure 7), providing further evidence for the increasing anharmonicity of THQ. A large degree of anharmonicity has been previously correlated to increased electron transfer rates in charge transfer molecules [32], which suggests Phase II may have better electrochemical properties than Phase I.

As evidenced by the x-ray diffraction and the vibrational spectra, Phase II remains the prevalent phase to pressures slightly above 20 GPa. Upon decompression, Phase II reverts to

Phase I, as indicated by the near complete recovery of the infrared and x-ray signatures of Phase I (Figures 2 and 4). The sample which had been used for Raman spectroscopy was not recoverable to the starting material, likely because of photochemical interaction with the laser used for spectral interrogation. This will be discussed further below. The recovery of the sample upon decompression when subjected to infrared and x-ray probes suggests the Phase I to Phase II transition involves only conformational changes in the molecules and hydrogen bonding network rather than atomic rearrangement due to the onset of chemistry. The x-ray diffraction patterns of Phase II are consistent with a C2/c structure with smaller lattice parameters (Figure 3) and a nearly 5% increase in density (Figure 8) over the pressure range studied. This transition can be regarded as a symmetrization of the more primitive P2₁/c space group. A number of details regarding the compression behavior of Phase II to near 20 GPa are worth noting. First, the equation of state beyond 12 GPa Phase II of THQ remains highly compressible. This compressibility seems to relate directly to geometry modifications of the molecular structure, as indicated by the general shift of the vibrational modes to higher frequency (Figures 5 and 7). The most notable exception to this general trend is the anomalous vibrational softening of the infrared active C=O stretching mode (ca. $\sim 1700\text{ cm}^{-1}$), which shows a decrease of nearly 40 cm^{-1} between 15 and 21 GPa. This shift not only suggests a weakening of the bond but also an intermolecular charge transfer interaction through self-complexation, which also has been observed in several other charge transfer molecules [13]. Additionally, after a smooth softening between 12 and 18 GPa, the band ca. 1550 cm^{-1} at 15.2 GPa begins to develop, gains intensity at the expense of the C=O band and results in bands with approximately equal intensity near 18.6 GPa. This behavior corresponds to a typical Fermi resonance, which has been commonly observed in hydrogen bonded materials [24, 33, 34].

Raman spectroscopic data collected over the pressure range studied (Figure 6) reveal a generalized broadening and loss of lines. This is particularly evident above the pressure of transition to Phase II, where the low frequency modes evolve into a few broad Raman bands. The loss of distinct Raman features and the irreversibility of these trends in direct contrast with the X-ray diffraction and Infrared spectroscopic measurements suggest the THQ undergoes a photochemically activated transition into a disordered polymer. Various members of the quinone family have been observed to undergo photochemically induced polymerization, most notably ubiquinone and plastoquinone, which are used for electron transport in photosynthetic and

mitochondrial processes [35]. It is thought that the onset of this reaction occurs with the generation of free OH[•] radicals. Additionally, it has been shown that p-benzoquinone, a parent molecule of THQ, has an n- π^* transition in the region from 350 to 520 nm, which overlaps the wavelength of the laser used for this study. For p-benzoquinone, the polymerization was found to occur very quickly with rates up to ½ kg of material per minute [36]. Further characterization of the material recovered from the Raman spectroscopic studies was attempted via x-ray and infrared investigations but analysis yielded little insight into the structure of the possible products. X-ray diffraction patterns confirmed the sample to be largely amorphous and infrared analysis revealed only smeared out broad features which could not be interpreted.

VI. Conclusions

A systematic study of the response of THQ to pressures slightly exceeding 20 GPa has been presented. The x-ray diffraction patterns and the infrared spectra revealed significant changes near 12 GPa which are consistent with a phase transition. Further information elucidated from the infrared spectra suggests the extensive hydrogen bonded network becomes highly anharmonic and possibly begins to symmetrize in response to increasing pressure. The high-pressure Phase II was found to remain the kinetically favored phase to pressures near 20 GPa. Anomalous vibrational softening of the infrared active C=O stretching mode, coupled with a Fermi resonance, suggests Phase II can also undergo strong charge transfer through self-complexation. Raman spectroscopic studies revealed Phase II to be strongly photochemically active and possibly undergo polymerization. Attempts to characterize the photochemically-induced product were attempted but interpretation was very challenging. Future studies could involve the use of small angle scattering, pair-distribution function analysis using neutron diffraction and/or x-ray photoelectron spectroscopy to obtain information about the chemical bonds and localized microstructure of polymerized THQ.

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Figure 1. (left) Molecular structure of THQ (b) Extended network of THQ showing the layered arrangement of molecules. Hydrogen bonds are shown in light blue. Dangling atoms have been removed for ease of viewing.

Figure 2. (a) Selected x-ray diffraction of THQ collected under pressure. The patterns are offset for clarity. The pattern collected upon decompression from 21.2 GPa is shown in light gray at the bottom of the chart. (b) Indexing of the low and high pressure phases of THQ

b

Figure 3. (a) Pressure-volume relationship of THQ upon compression (solid points) and decompression (open points), based on unit cell refinements using x-ray diffraction data. The lines indicate the 3rd order fit to the Birch-Murnaghan equation of state. (b) Pressure dependence of the lattice vectors of THQ upon compression (solid points) and decompression (open points) Points collected upon compression have been fit to third-order polynomials and the resulting line are shown to help guide the eye. (c) Pressure dependence of the beta angle (Phase I) and alpha angle (Phase II) collected upon compression (solid points) and decompression (open points) Points collected upon compression have been fit to third-order polynomials and the resulting line are shown to help guide the eye.

Figure 3. Continued

Figure 4. Selected infrared spectra of THQ collected under pressure. The spectra are offset for clarity. The infrared active features observed at ambient pressure prior to compression are indicated as vertical black lines. The infrared spectrum collected upon decompression from near 20 GPa is indicated by 'd0.0 GPa'.

Figure 5. Pressure- induced IR peak shifts of THQ for Phase I (black squares) and Phase II (red circles). Linear fits to the compression data are shown to help guide the eye. Infrared peak positions collected upon decompression from near 21 GPa are shown as blue triangles. The solid vertical line indicates the region of the phase transition.

Figure 6. Selected Raman spectra of THQ collected under pressure to near 22 GPa. The spectra are offset for clarity.

Figure 7. Pressure- induced Raman peak shifts of THQ for Phase I (black squares) and Phase II (red circles). Linear fits to the compression data are shown to help guide the eye. The solid vertical line indicates the region of the phase transition.

Figure 8. Density of THQ derived from the volume for Phase I (black squares) and Phase II (red circles). Linear fits to the compression data are shown to help guide the eye. The solid vertical line indicates the region of the phase transition.

Table 1. Crystallographic data and details of measurement for THQ at ambient pressure, where ρ is the density, K_T is the isothermal bulk modulus obtained from the fit of the data to the 3rd order Birch Murnaghan equation, K_T' is the first order pressure derivative of the bulk modulus, and T is the temperature

	Klug [13]	This study (Phase I)
a (Å)	5.226	5.230(8)
b (Å)	5.118	5.126(3)
c (Å)	15.502	15.518(1)
β ($^\circ$)	103.89	103.8(5)
V (Å) ³	402.50	404.0(1)
ρ (g/cm ³)	1.717	1.71(1)
K_T (GPa)		42.3(7) GPa
K_T'		3.8(7)
T (K)	273	298

Table II. Raman and Infrared vibrational bands (in cm^{-1}) observed for Phase I of THQ at ambient pressure and Phase II at 12.5 GPa, compared with the previously identified lines of p-benzoquinone [21]. The γ values are the least-squares fit to the Grüneisen equation [22]. Molecular motions associated with the vibrational features are suggested based upon previous spectral assignments.

This study, Phase I				This study, Phase II				Dunn <i>et al.</i> [21]		Molecular Motion
IR	γ (IR)	Raman	γ (Raman)	IR	γ (IR)	Raman	γ (Raman)	IR	Raman	
		399	0.20					415		C=O bend
						430	-0.01		445	ring bend
		484	0.28			487	0.36	476		C=O bend
543	0.13					524	0.16	524		C=O bend
		589	0.20							ring deformation
614	0.50	605	0.45			631	-0.04	600	600	ring breathing
748	0.47					699	-0.08	745		ring breathing
		764	0.07						772	C-C stretch
805	0.25	825	0.34					797	797	out-of-plane ring distortion
887	0.16									O-H bend
		846	-0.03					903		O-H bend
		954	0.11					946		C-C stretch
1002	0.20								1014	C-O bend
		1065	0.28					1076		C-C stretch, O-H bend
1309	0.19							1313		O-H bend
1368	0.21							1366		C-C stretch, O-H bend
1419	-0.01			1414	0.02					O-H bend
		1466	0.12	1451	-0.23	1530	-0.50			O-H bend
1550	-0.01			1562	-0.16			1542		Combination $748 \text{ cm}^{-1} + 805 \text{ cm}^{-1}$
		1585	0.08	1564	0.10			1595	1594	C=C stretch
1610	0.06					1611	0.06		1614	C=C stretch
1661	0.13			1664	-0.11				1660	C=O stretch

		1666	0.13					1666		C=C stretch
1685	0.05	1689	-0.01	1702	-0.17	1690	0.01	1682	1687	C=C stretch
1727	0.06							1718	1717	C=O stretch
1910	0.07							1912		C=O stretch
1963	0.10							1967		C=O stretch
2960	-0.15							2990		H-bonded O-H stretch
3050	-0.07									H-bonded O-H stretch
3065	-0.13			3077 3179	-0.21					O-H stretch
3272	-0.03			3280	-0.25					O-H stretch
3359	-0.09			3384	-0.22			3315		O-H stretch
3431	-0.08			3483	-0.15					O-H stretch
3530	-0.05									O-H stretch