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Anharmonic coupling between fundamental modes in tetramethylurea

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In situ high pressure Raman spectra of tetramethylurea have been measured up to 25 GPa, liquid-solid and solid-solid phase transitions were detected at 0.2 GPa and 7.4 GPa, respectively. An unprecedented spectral phenomenon is the observation of a Fermi resonance between the fundamental modes. An exponential relationship between the intensity and the frequency difference was concluded. Pressure provides us a new way to study the correlation between Fermi resonance parameters.

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I. INTRODUCTION

Tetramethylurea (TMU) is a colorless mobile organic liquid with some unique physicochemical properties. It is an excellent solvent for a number of organic and inorganic substances; moreover, it has a high boiling point. Therefore, it is recognized as a suitable reaction solvent for many chemical reactions.^{1,2} Experimental and theoretical studies about pure liquid TMU and binary mixtures of TMU with other solvents have been reported.^{3–9} Due to the presence of the oxygen site and four methyl groups, the TMU molecule can be considered a suitable solute for probing hydrophobic as well as hydrophilic interactions.

Fermi resonance is the shifting of the energies and intensities of bands in infrared or Raman spectrum. It is a consequence of quantum mechanical mixing.^{10–12} Two conditions must be satisfied for the occurrence of Fermi Resonance: (1) The two vibrational states of a molecule transform according to the same irreducible representation of the molecular point group. In other words the two vibrations must have the same symmetry. (2) The transitions accidentally have almost the same energy. Fermi resonance often occurs between normal and overtone or combination modes, if they are nearly coincident in energy. As compared to the unperturbed levels, the energy difference between the two coupling modes increases, and the overtone or combination mode gains intensity from the fundamental mode. The two modes are describable as a linear combination of the parent modes.^{11,12} And Fermi resonance does not really produce additional bands in the spectrum. Normally, Fermi resonance comes into being between fundamental and overtone or combination modes;^{11–16} it has never been observed between two fundamental modes, as a result of not being satisfied in the symmetry and energy factors between the two non-degeneracy fundamental modes.

As independent thermodynamic parameters apart from those usually studied, such as temperature and chemical com-

position, pressure has been playing an increasingly important role in condensed matter physics.^{17–19} Pressure can be effective in shortening atomic distance, enhancing orbital overlap, and consequently it can modify crystalline structures and tuning interactions. Thus it is important external parameters that can tune the energy of the phonons and molecular symmetry. Several studies have been reported on molecular Fermi resonance induced by high pressure.^{20–22} However, they only concerned the coupling between combination and fundamental modes, and obviously relative intensity changes between the coupling modes in the compression process. To the best of our knowledge, the observation of pressure-induced Fermi resonance between fundamental modes has never been reported previously.

In recent years we have undertaken experimental investigations of dilute TMU-water solutions, with a special emphasis on the relationship between dilution and hydrogen bonding.²³ In this paper these studies are extended with the investigation of the pure liquid TMU under compression. And we found a pressure-induced anharmonic coupling effect between the fundamental modes in TMU, and the relationship between the frequency difference and intensity was analyzed.

II. EXPERIMENTAL METHODS

TMU was purchased from Sigma-Aldrich and used without further purification. The high-pressure cell used in this experiment was based on symmetric diamond anvil cell (DAC) having two diamonds with 400 μm culet size. The sample with a small ruby chip ($\sim 10\ \mu\text{m}$) was loaded in a 200 μm hole drilled in a 250 μm thick T301 gasket pre-indented to 80 μm thickness. The pressure calibration was done using ruby fluorescence.²⁴ Raman measurements were conducted with the Acton SpectraPro 2500i spectrometer equipped with a liquid nitrogen cooled CCD camera (Pylon: 100B). The 532 nm line of diode laser was employed to excite the sample. The spectral resolution was approximately $1\ \text{cm}^{-1}$. The laser power was 3.6 mW and the typical accumulation time for each spectrum was 30 s. Frequency calibration of the Raman spectrum was realized using the characteristic $520\ \text{cm}^{-1}$

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TABLE I. Frequencies of Raman bands and their assignments of TMU.^a

Raman shifts (cm ⁻¹)	Assignments
1639	C=O stretching (A)
1461	CH ₃ asym def (2A, B)
1432	CH ₃ sym def (A, B)
1410	CH ₃ sym def (A, B)
1143	CH ₃ rocking (A, 2B)
1110	CH ₃ rocking (A)
1061	CH ₃ rocking (A, B)
1021	NMe ₂ sym str (A)
916	NMe ₂ sym str, CH ₃ rocking (B)
784	CO o.o.p. def (B)
739	CN ₂ sym str, NMe ₂ sym str (A)
581	CO i.p. def (B)
557	CN ₂ scissoring, NMe ₂ scissoring (A)
415	NMe ₂ rocking (B)
289	CH ₃ torsion

^astr., stretching; def, deformation; i.p., in plane; o.o.p., out-of-plane; asym., asymmetry; sym., symmetry. A and B are the symmetry species for C₂ point group.

line of silicon. All measurements were performed under room temperature.

III. RESULTS AND DISCUSSION

A. Pressure induced phase transitions of TMU

The TMU molecule in the C₂ point group has 54 fundamental frequencies belonging to the symmetry species 27A and 27B. All of the 54 vibrations are infrared and Raman active, with polarized Raman bands for the 27A symmetric modes.²⁵ The ambient pressure Raman spectrum of TMU observed by us agreed well with those reported in the literature.²⁵ The most prominent Raman active modes are CH₃, C=O, and CN₂ stretching vibrations. And based on the DFT and normal coordinate calculations, their exact peak positions as well as the appropriate vibrational assignments are listed in Table I. The *in situ* Raman spectra of TMU were acquired up to 25 GPa at room temperature. The selected spectra are shown in Fig. 1. We also conducted Raman measurements

on decompression all the way down to ambient pressure, and the spectra are more or less similar to those of compression, the reversible Raman spectral also indicated that TMU is chemical stable up to 25 GPa.

As changes in response of the Raman mode with pressure is a good indicator of a possible phase transition,^{26,27} the Raman frequency shifts as a function of pressure are shown in Fig. 2, except the bands due to C=O vibrations, the frequencies of the vibrations change linearly with pressure, and a monotonous blueshift of the Raman modes is observed up to 25 GPa. At room temperature, a liquid-solid phase transition can be observed at 0.2 GPa by visual observations through a microscope in the Raman spectrometer. The spectral changes including missing and splitting of modes, appearance of new vibrational modes, and sudden changes in the slope of the frequency-pressure curve could be observed at about 7.4 GPa, so a solid-solid phase transition can be concluded at this pressure. On further compression, no obviously spectral evidence of phase transitions could be observed up to 25 GPa. We label the new solid phase below 7.4 GPa as phase I, and it transits to phase II in the pressure range of 7.4–25 GPa, we will analyzed the detailed spectral changes in each phase.

As shown in Fig. 1, the most interesting Raman bands are located at 1639 and 784 cm⁻¹, which are assigned as C=O stretching (A) and out-of-plane C=O deformation (B) mode, respectively. In the pressure range from ambient to 3 GPa, the two bands shift to lower wavenumber region, indicating that the C=O bond is lengthened with pressure. This is the result of the inter-molecular interactions, as TMU molecules do not form strong intermolecular hydrogen bonds, and a dipole-dipole coupling via the C=O bonds can occur in TMU dimer, as shown in scheme 1 (Fig. 3).²⁵ Under compression, the inter-molecular dipole-dipole interaction is enhanced, which induces the C=O bond lengthened with pressure. In the pressure range from 3 to 7.4 GPa, the 784 cm⁻¹ Raman band keeps its previous shift tendency. While a pressure-induced splitting phenomena could be observed for C=O stretching band at 3 GPa (Fig. 2). This phenomenon may be correlated with multi-intermolecular dipole interactions as shown in scheme 2 (Fig. 3). This interactions make a new C=O

FIG. 1. Selected high pressure Raman spectra of TMU from ambient to 25 GPa.

FIG. 2. The pressure dependence of Raman peak positions of internal vibrational modes. The dotted line represents the boundary of the two solid phases. The dots in different colors and symbols represent the different Raman peaks.

stretching band arise at a relative lower wavenumber region together with the intensity enhancement of new band. The co-existent of the two bands suggests that the dipole-dipole and multi-dipole interactions should be present in this pressure range. With the increase of pressure, the two C=O stretching bands shift to higher wavenumber region, and the original C=O stretching band decreases in intensity and finally disappears at 7.4 GPa, indicating that the multi-dipole interactions are the dominant intermolecular interactions. When the pres-

sure increases more than 7.4 GPa, only the new C=O stretching band is present in the entire compression process. The new intermolecular interaction in C=O bond is also a result of the new molecular packing geometry in phase 2.

B. Fermi resonance between fundamental modes

Another intriguing spectral observation is the Raman peaks located at 739 and 784 cm^{-1} , which are assigned as $\text{CN}_2 + \text{NMe}_2$ symmetry stretching and out-of-plane C=O deformation modes, respectively. The frequencies of the two bands at different pressure could be seen in Fig. 2. According to previous analyses, as a result of the intermolecular dipole-dipole interactions, the out-of-plane C=O deformation mode shifts to lower wavenumber region with the pressure. In contrast, the $\text{CN}_2 + \text{NMe}_2$ symmetry stretching vibration shifts to higher wavenumber region. Due to the different pressure-induced shift trends of the two bands, below 3.4 GPa, the frequencies of the two bands get close to each other with the increase of pressure. As shown in Fig. 4, the frequency difference decreases from 45 cm^{-1} at ambient pressure to 10 cm^{-1} at 3.4 GPa. When the pressure increases to 3.4–7.4 GPa, the two bands merge into one convolved band. When the pressure increases to 7.4 GPa, the out-of-plane C=O

Scheme 1

Scheme 2

FIG. 3. Dipole-dipole (Scheme 1) and multi-intermolecular dipole (Scheme 2) interactions in TMU.

FIG. 4. Plots of pressure dependence of frequency difference (solid circles) and intensity ratio (solid squares) of the out-of-plane C=O deformation to CN₂ + NMe₂ symmetry stretching modes.

deformation mode reappears at the lower wavenumber side of CN₂ + NMe₂ stretching band with a relatively higher intensity compared to its previous peak, as shown in Fig. S1(A) of the supplementary material.²⁸ We plotted the intensity ratio of out-of-plane C=O deformation to CN₂ + NMe₂ stretching mode in Fig. 4 (blue line). A significant increase in the value of intensity ratio can be observed at 7.4 GPa and the intensity decreases with further increasing pressure.

In this experiment, at 7.4 GPa, the reappearing intensity band of out-of-plane C=O deformation mode may be associated with an anharmonic coupling between two fundamental modes. Fermi resonance is found to occur frequently in many polyatomic molecules and is used to explain some characteristic features of Raman and infra-red spectra. Provided the two independent vibrations belong to the same symmetry species and commensurable in frequency, the vibrations will perturb each other, resulting in a mutual repulsion of the two levels and a mixing of eigenfunctions. For linear three-atom molecules such as CO₂ and CS₂ etc.,^{21,22} the symmetric-stretching fundamental and the bending first overtone have nearly coincident harmonic frequencies and the same symmetry, causing the resonance between the two modes which induces the weak overtone mode to gain intensity from the symmetric-stretching fundamental mode. While for aromatic materials such as benzene and biphenyl etc.,^{11,29,30} according to Wilson notion,³¹ the mixing between a binary combination $\nu_1 + \nu_6$ and ν_8 modes results in the observations of two bands with similar intensity at about 1600 cm⁻¹. For other polyatomic molecules with great number of atoms, due to the great number of active and non-active vibrational modes, it is difficult to assign a band to the Fermi resonance mode. Among the previous studies in Fermi resonance, it has never been found between fundamental modes, as a result of the symmetry and frequency requirements. Under the harmonic approximation the two dominant factors hinder the coupling of fundamental modes. Pressure is an effective external parameter to tune the molecular structure, and thus the typical frequency and the symmetry of vibrational modes can be tuned. Under the frequency require-

ments in Fermi resonance, the two non-degenerate modes participating in coupling should have commensurable frequencies. The application of hydrostatic pressure to the molecular system can induce changes of bond lengths and angles and normally make vibrational frequencies move to the higher region with the increase of pressure. If we need the frequency of the nearby fundamental modes get close in the compression process, a difference frequency-pressure relationship or a controversial pressure-induced frequency shift tendency is needed. In this situation, the presentation of some special inter-molecular interactions such as dipole-dipole or hydrogen bond interactions may be helpful for the frequency requirements. Under the symmetry requirement, the pressure-induced phase transition is beneficial for the Fermi resonance modes, due to the ability to lower the molecular symmetry.

As shown in Fig. 4, during the first compression process, the frequency difference of CN₂ + NMe₂ stretching and out-of-plane C=O deformation modes decreases with increasing pressure (black line). According to our previous analysis, the smaller the frequency difference is, the stronger the coupling effect in Fermi resonance is. However, the nearly constant value of the intensity ratio indicates that there is no coupling between the two fundamental modes below a pressure of 3.4 GPa. In the pressure range 3.4–7.4 GPa, the CN₂ + NMe₂ stretching and out-of-plane C=O deformation modes merge into one unresolved band, which cannot give any spectral evidence of coupling effects. From their frequency-pressure relationship, the frequency of the CN₂ + NMe₂ stretching and out-of-plane C=O deformation modes will have the same value at about 5 GPa, and the two peaks would swap their position in further compression. From the above analysis, it can be concluded that even though the frequency requirement is satisfied, we cannot observe the fundamental Fermi resonance in the pressure range from ambient pressure to 7.4 GPa. As TMU molecule belongs to C₂ point group, the symmetry of the two modes corresponds to A and B, respectively. In phase I, we believe that TMU molecule keeps its original C₂ symmetry, which fails to satisfy the symmetry requirement, thus we cannot observe the coupling effects between fundamental modes. When the pressure increases to 7.4 GPa, it transforms to phase II and the out-of-plane C=O stretching mode with a relative higher intensity is observed at the lower wavenumber region as a result of anharmonic coupling effects. Phase transition always associates with a lowering of the molecular point symmetry, and then the symmetries of the two bands are same, which satisfies the symmetry requirement of the two fundamental modes. From the above analysis, we can see that without the same symmetry, coupling between the two fundamental modes cannot be observed. Therefore, a pressure-induced phase transition is a key factor for the anharmonic coupling effects.

As shown in Fig. 4, in phase II, the intensity of out-of-plane C=O stretching mode drops significantly with pressure, there exists good linear positive correlation between frequency difference and external pressure in phase 2 (Eq. (1)). While there is strong nonlinear relationship between the intensity ratio and pressure, a single exponential decay curve fitting was done on the intensity ratio-pressure curve

line (Eq. (2)). The decay pressure is 3.46 for TMU.

$$\Delta\omega = k \cdot p, \quad (1)$$

$$I_F = I_0 \exp\left(\frac{-p}{t}\right). \quad (2)$$

$\Delta\omega$ is the frequency difference of the coupling bands and p is the external pressure. As $\Delta\omega$ is linearly proportional to the pressure, then the intensity ratio shows an exponential decay to $\Delta\omega$. t is the coefficient with a dimension of GPa, and the value of t in TMU is larger than that of traditional Fermi resonance materials such as benzene and biphenyl, whose values are 1.05 and 0.84, respectively, as shown in Figs. S1(B) and S1(C) of the supplementary material.²⁸ This phenomenon may be due to the different pressure-induced frequency shift speeds of Fermi resonance doubles, as a result of Fermi resonance happening between combined and fundamental modes for benzene and biphenyl.

The high pressure technique is a convenient way to tune the molecular structure which can realize the coupling between fundamental modes, and it is used not only for the mode assignments but also for the study of vibrational coupling mechanism between fundamental modes. Fermi resonance in the present case involves not isolated TMU molecules but the inter-molecular correlation effects in crystal.

IV. CONCLUSIONS

In this report, high pressure Raman spectra of TMU were carried out up to 25 GPa, a liquid-solid phase transition was detected at around 0.2 GPa, from the new arising of the internal mode. The spectral phenomena of C=O stretching band gave new information about the inter-molecular dipole-dipole interactions. More importantly, pressure-induced Fermi resonance between the fundamental modes was observed in phase II, an exponential relationship between the intensity and the frequency difference was analyzed. In conclusion, pressure may be an efficient way to tune the anharmonic coupling between fundamental modes.

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