

Poster Presentation

MS49.P08

Phase Transition and Polymerization of Acetonitrile under High Pressure

H. Zheng^{1,2,3}, K. Li^{1,2,3}, G. Cody¹, C. Tulk³, J. Molaison³, W. Yang^{4,5}, I. Ivanov⁶, M. Guthrie¹, H. Mao^{1,2,5}

¹Carnegie Institution of Washington, Geophysical Laboratory, Washington, D.C., United States, ²Center for High Pressure Science and Technology Advanced Research, Beijing, China, ³Oak Ridge National Laboratory, Spallation Neutron Source, Oak Ridge, TN, United States, ⁴HPSynC, Geophysical Laboratory, Carnegie Institution of Washington, Argonne, IL, United States, ⁵Center for High Pressure Science and Technology Advanced Research, Shanghai, China, ⁶Oak Ridge National Laboratory, Center for Nanophase Materials Sciences, Oak Ridge, TN, United States

Successful application of high pressure on synthesis of organic polymer, including the conducting polymer and super hard materials depends on the knowledge of reaction mechanism. The evolution of crystal structure under high pressure especially the structure close to transition pressure is crucial to conclude the reaction mechanism. Nitriles represent a large class of interstellar molecules and are the potential source of amino acids. Understanding its behavior at extreme conditions has gained increasing attention recently. Acetonitrile (CH₃CN), the simplest organic compound with C≡N triple bond, can act as a model system for studying the pressure induced polymerization. The phase transition of acetonitrile under high pressure has been studied extensively.[1-3] However, it is still controversial and there is no any detailed discussion about its polymerization mechanism under high pressure. Here, we report the in-situ high pressure Raman spectra and powder neutron diffraction results on CD₃CN, which indicates a minor phase transition at 5 GPa. The neutron diffraction shows that CD₃CN keeps the orthorhombic phase from 1.66 GPa to 20.58 GPa which is very close to the reaction pressure. The weak hydrogen bonding CD...N arranges the molecule into 3-dimensional framework which can be treated as two sets of diamond like structures interpenetrating with each other. Interestingly, the observed N...D distance is 1.984 Å at 20.58 GPa, shorter than the van der Waals distance of N...H (2.75 Å) by 28%. The van der Waals separation is often taken as a reference distance for the molecular instability. Thus, a hydrogen transfer process during the polymerization can be concluded. This deduction is also supported by the solid state NMR and FTIR results of the recovered polymerized CH₃CN (p-CH₃CN) from high pressure. In addition, the atomic pair distribution function and Raman spectra indicate the p-CD₃CN or p-CH₃CN has a random packed layer structure with nano-graphene lattice.

[1] K. M. Yenice, S. A. Lee, *J. Raman Spectrosc.*, 1996, 27, 835-840, [2] A. Olejniczak, A. Katrusiak, *J. Phys. Chem. B*, 2008, 112, 7183-7190, [3] C. Ma, F. Huang, X. Wu, H. Cui, F. Li, H. Zhu, Q. Zhou, Q. Cui, *RSC Adv.*, 2013, 3, 1509-1513

Keywords: high pressure, polymerization, neutron diffraction