

## Supporting Information

### **Experimental Observation of New phase, Determination of Loading-Path of Glassy State and Loading–Path Dependent Phase Transitions for Pyridine around Freezing Pressure via Raman modes in Low wavenumber**

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Figure S1. Raman spectra of the lattice phonon region measured during compression and decompression of direct crystalline pyridine.

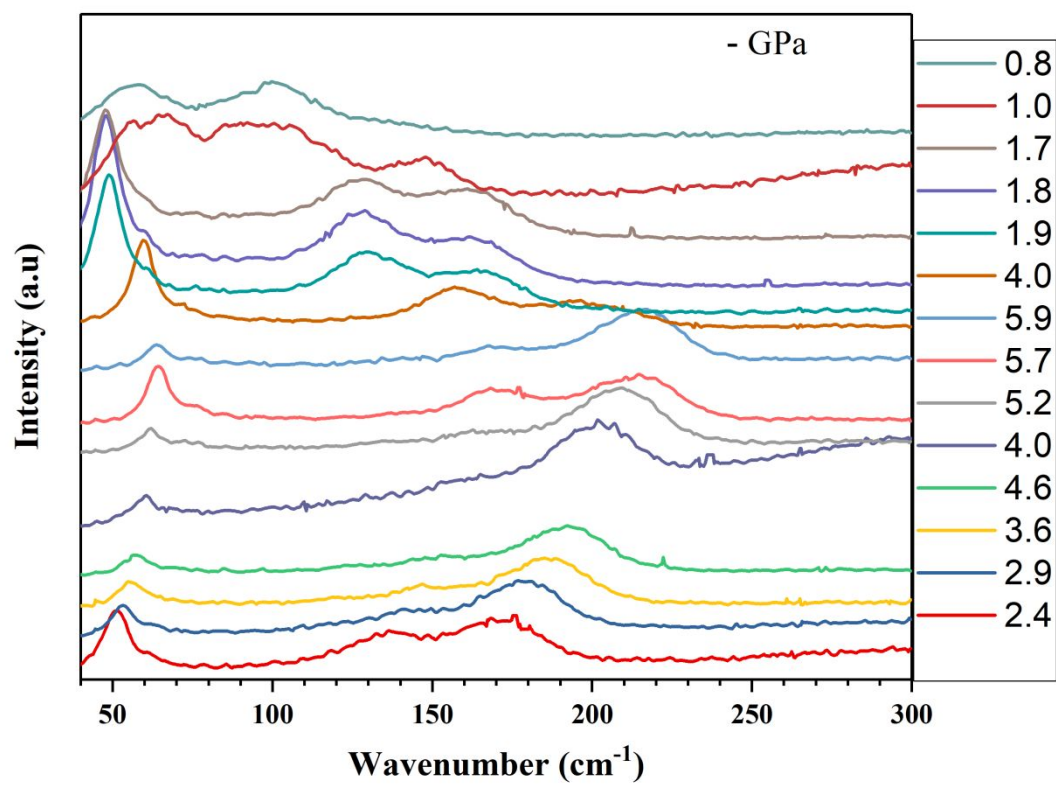


Figure S2. Low frequency Raman spectra of pyridine obtained by manual recrystalline measured during compression from 1.1 GPa up to 7.7 GPa and decompression down to 2.3 GPa. The symbols of “III” and “II” correspond to the phase III and phase II, respectively.

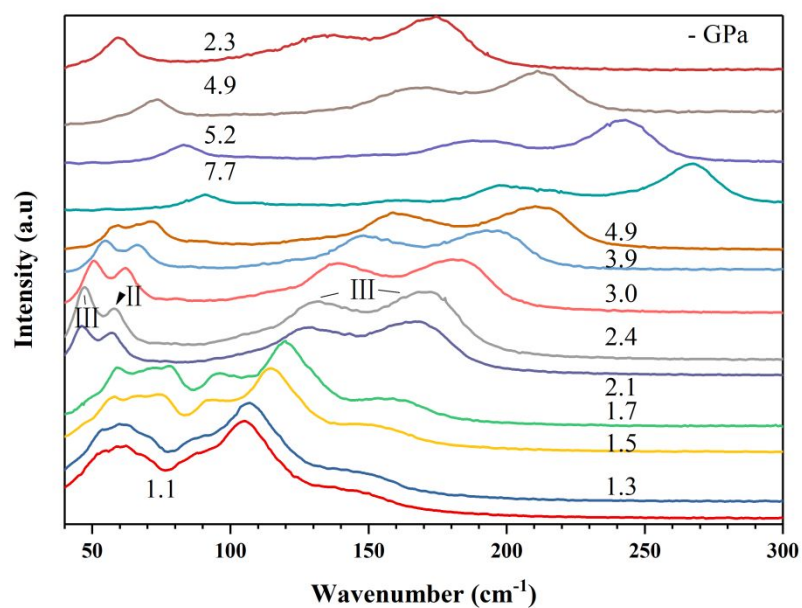


Figure S3 Low frequency Raman spectra measured during a spontaneous transition by staying for two days, where the pressure of chamber drops from 2.0 GPa and 1.9 GPa.

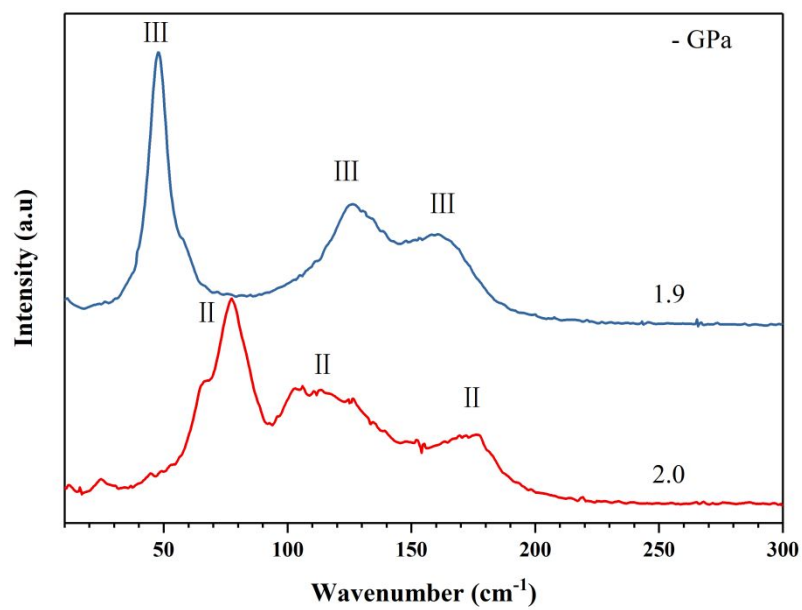


Figure S4 Low frequency Raman spectra of pyridine unloading from phase III to 1.3 GPa at different areas as remarked in the inset. Smooth area 1 is phase III, rough area 2, 3, 4 is phase II. Interface between smooth and rough is mixture of phase II and phase III.

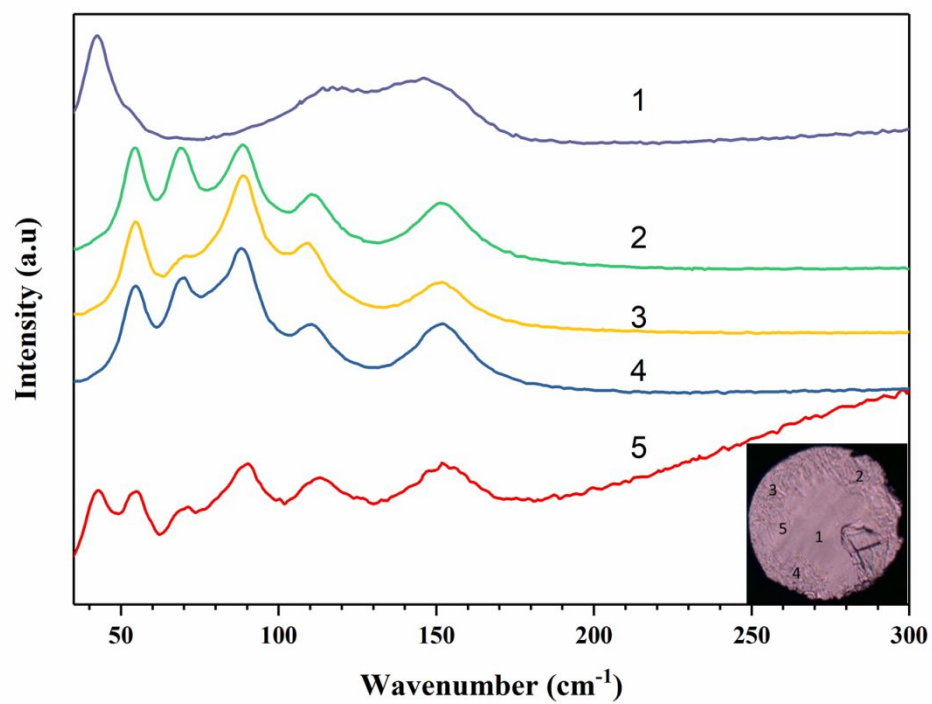


Figure S5 Pressure-dependent Raman shift of high density phase II pyridine at room temperature. Solid straight lines are linear fits to the data.

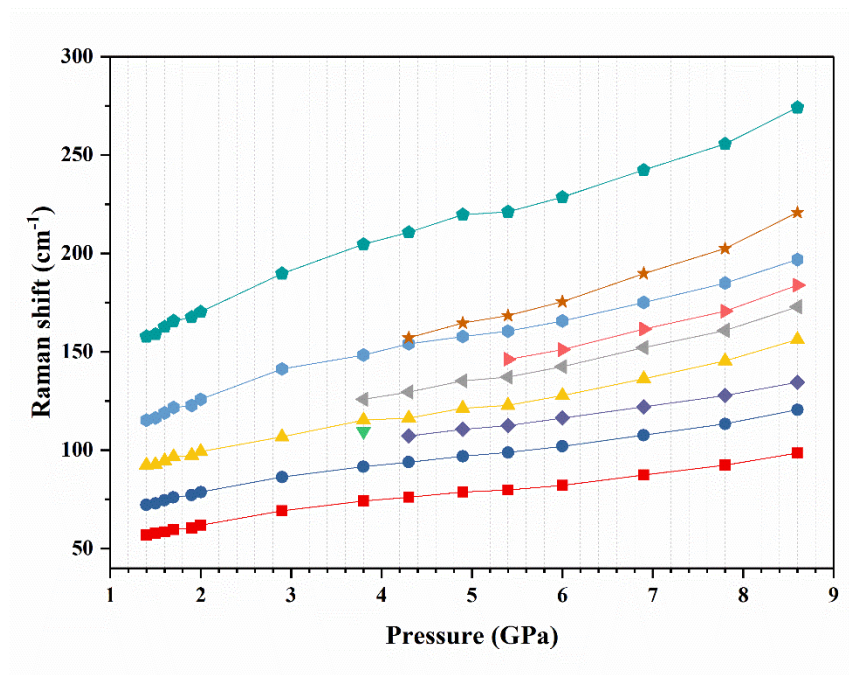


Figure S6 Comparison of Raman spectra at low frequency for pyridine under different conditions. Curve (a) corresponds to the manual recrystalline pyridine undergoing firstly loading and then unloading down to 1.3 GPa. Curves (c) and (b) are response to the manual recrystalline pyridine via loading at 1.0 GPa and 1.3 GPa, respectively. Curve (d) corresponds to the spontaneous recrystalline pyridine, but undergoing only loading to 1.0 GPa. Curves (e) and (f) correspond to the direct crystalline pyridine undergoing unloading with fast and slow speed, respectively.

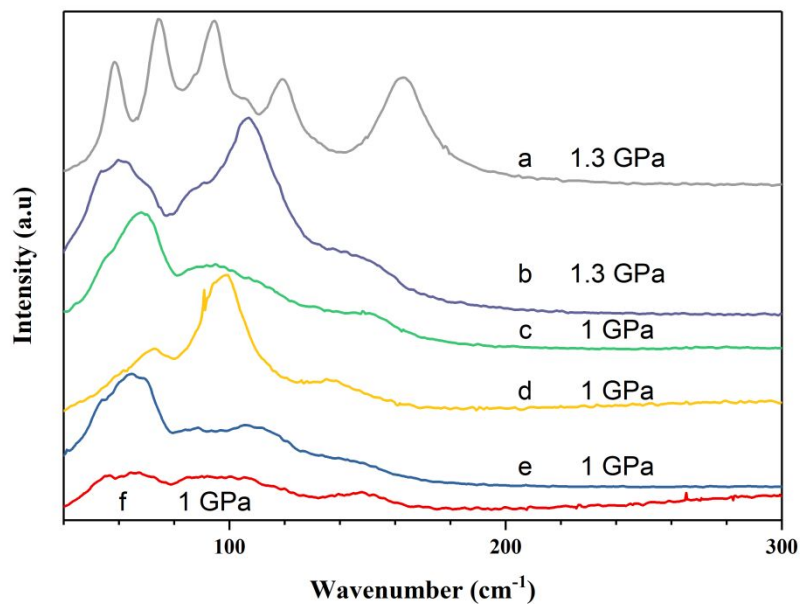


Figure S7 The simplified phase diagram of pressure-phase structure observed in compression (black right arrows), decompression (black left arrows) and staying for days (red arrows) at room temperature experiment. Arabic numerals indicate the pressure values and Roman numbers indicate the phases, where the transformations have been observed. Green dashed dotted line indicates solid liquid equilibrium. Dashed line indicates the crossed boundary of phases. Up dashed arrow indicates the transition of phase I - II at 2.1 GPa. There are five path of loading and unloading, where path a indicates direct loading from liquid to solid, path b indicates direct unloading from solid to liquid, path  $c_1$  indicates spontaneous recrystallization to stay the equilibrium for 2 days, path  $C_{2-1}$  indicates manual recrystallization by a unperceivable compression increment and then transformation into phase III by compression and path  $C_{2-2}$  which was the most completed path indicates manual recrystallization by a unperceivable compression increment, then transformation into the metastable state at 2.0-2.1 GPa and transformation into phase II' and finally transformation into new phases. The blue dense filled box indicates the pressure range of pyridine in metastable state in the path of  $C_{2-2}$ .

