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High pressure Raman spectroscopy of H_2O-CH_3OH mixtures WEN-PIN HSIEH, YU-HSIANG CHIEN, Academia Sinica — Complex intramolecular interactions and the hydrogen-bonding network in H_2O-volatile mixtures play critical roles in many dynamics processes in physical chemistry, biology, and Earth and planetary sciences. We used high pressure Raman spectroscopy to study the pressure evolution of vibrational frequencies and bonding behavior in H_2O-CH_3OH mixtures. We found that the presence of low CH_3OH content in H_2O increases the transition pressure where water crystallizes to ice VI, but does not significantly change the pressure where ice VI transforms to ice VII. Furthermore, the stiffening rates of C-H stretching frequencies $d\omega/dP$in CH_3OH significantly decrease upon the crystallization of water, and the softening rates of the O-H stretching frequencies of ice VII are suppressed over a narrow pressure range, after which the frequencies of these modes shift with pressure in ways similar to pure CH_3OH and ice VII, respectively. Such complex pressure evolution of Raman frequencies along with pronounced variations in Raman intensities of CH_3OH within the sample, and the hysteresis of the water-ice VI phase transition suggest pressure-induced segregation of low content CH_3OH from ice VII.

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