Supplementary materials for

Multiple Guest Occupancy in Clathrate Hydrates and Its Significance to Hydrogen Storage

Dong-Yeun Koh,[a] Hyery Kang[a] and Huen Lee*[a,b]

[a]Department of Chemical and Biomolecular Engineering, KAIST, Daejeon 305-701, Republic of Korea

[b]Graduate School of EEWS, KAIST, Daejeon 305-701, Republic of Korea

*To whom correspondence should be addressed. E-mail : hlee@kaist.ac.kr

Table of Contents

S1. Experimental Methods

Figure S1 Raman spectra according to the molar ratio of 1-methylpiperidine, where single and multiple hydrogen occupancy instances are shown

Figure S2 Time-resolved Raman spectra of the 0.5 mol% 1-methylpiperidine product. Within 24 hours, a full tuning effect is observed.

S1. Experimental Method

Synthesis of clathrate hydrate samples

Deionized water of ultrahigh purity was supplied from Merck (Germany) and the 1-methylpiperidine, 2-methylpiperidine, 3-methylpiperidine and 4-methylpiperidine samples were supplied by Sigma-Aldrich Inc. H_2 gas with a purity of 99.9995mol% was supplied by Special Gas (Korea). Powdered ice (~200μm) was mixed with an appropriate amount of solid MPDs in liquid nitrogen (LN_2). These solid-solid mixtures were pressurized with H_2 up to 12 MPa at 77K. The reactors were then placed in a temperature-controlled bath at 240K. The pressure of each system became stable at around 58 MPa after 6-24hr. Under this temperature and pressure condition, pure hydrogen hydrate could not be formed without a promoter. The reactor was kept in a 240K bath for 3 days. Reactor was quenched in LN_2 and simultaneously the pressure was released to atmospheric pressure for further spectroscopic analysis.

Characterization methods: PXRD, Raman Spectroscopy

For Raman measurements the Horiba Jobin Yvon LabRAM HR UV/Vis/NIR high resolution dispersive Raman microscope was used in which a CCD detector is equipped and cooled by liquid nitrogen. The excitation source was an Ar-ion laser emitting a 514.53 nm line. The laser intensity was typically 30 mW. Samples were kept at 77 K during Raman measurements. For variable temperature experiment, LINKAM unit was used to control the sample temperature.

The PXRD patterns were obtained using Rigaku D/max-IIIC diffractometer with CuKα as a light source (λ=1.5406 å) at a generator voltage of 40 kV and a generator current of 300 mA. Low-temperature stage attached to XRD kept the working temperature to 90K and step scan mode of 0.01^{o}/3s was applied.

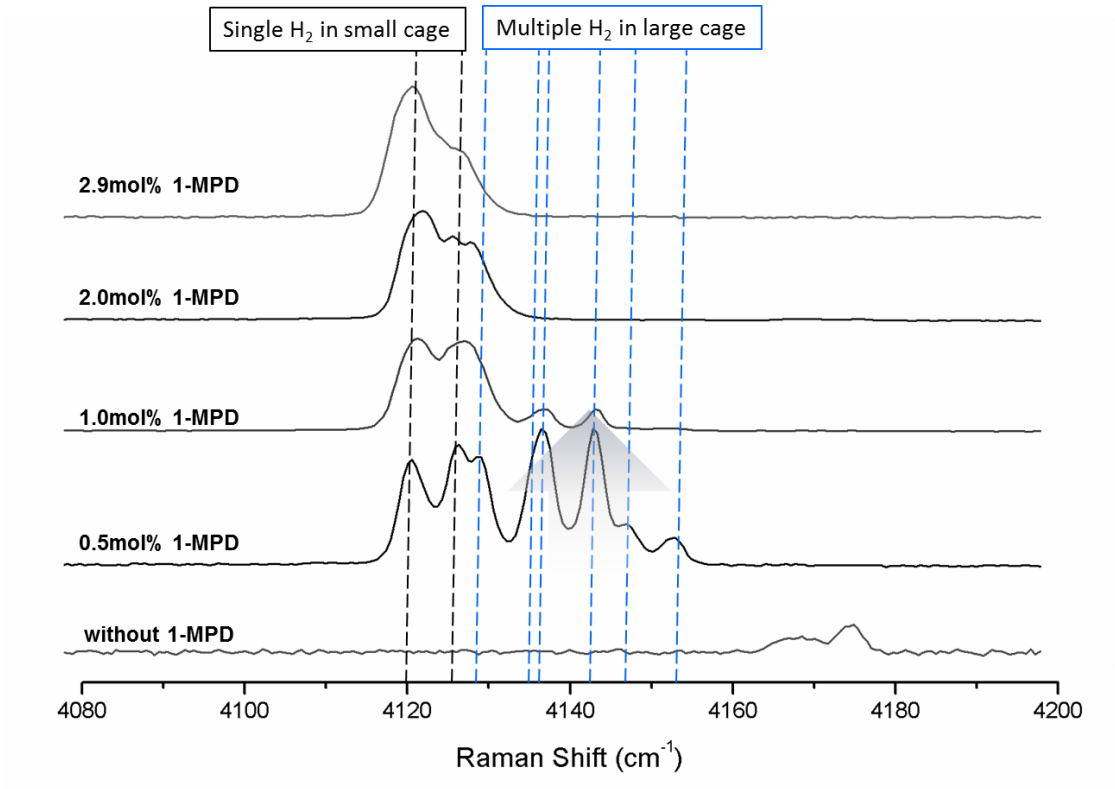

Figure S1. Raman spectra according to the molar ratio of 1-methylpiperidine, where single and multiple hydrogen occupancy instances are shown

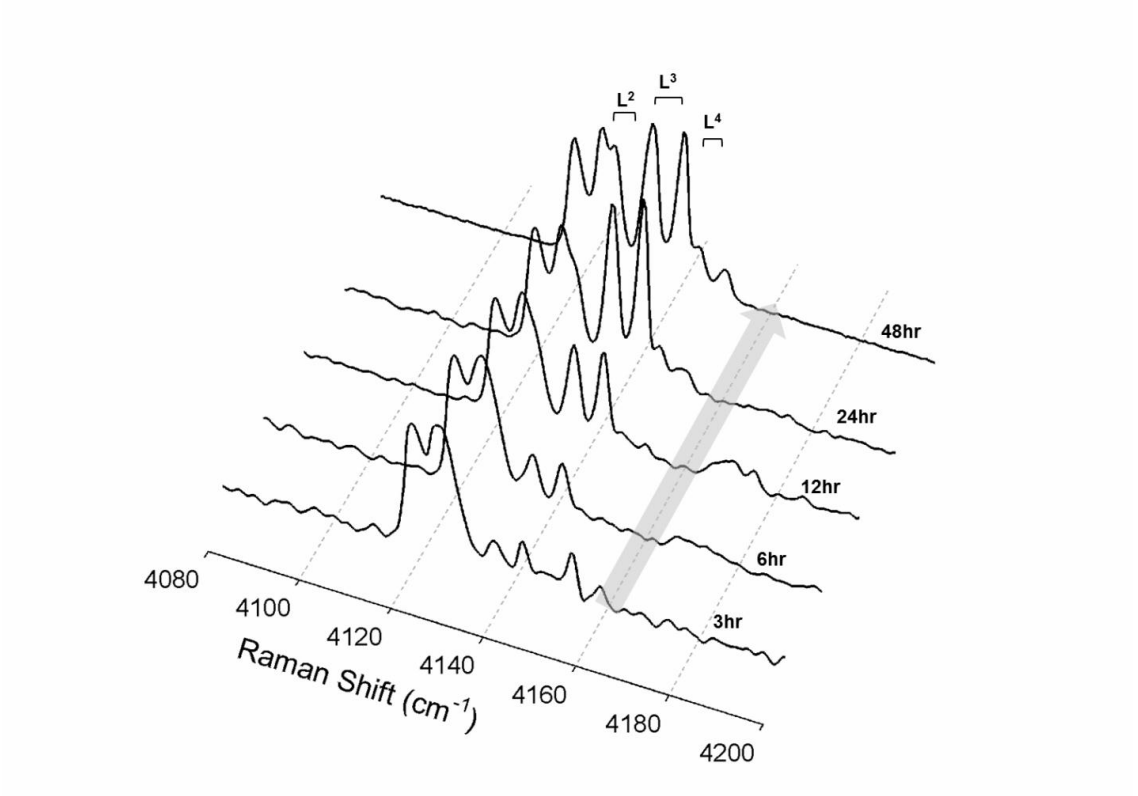

Figure S2. Time-resolved Raman spectra of the 0.5 mol% 1-methylpiperidine product.

Within 24 hours, a full tuning effect is observed.