Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information

High pressure Raman study on confined individual iodine molecules as molecular probes of structural collapse in $AlPO_4$-5 framework

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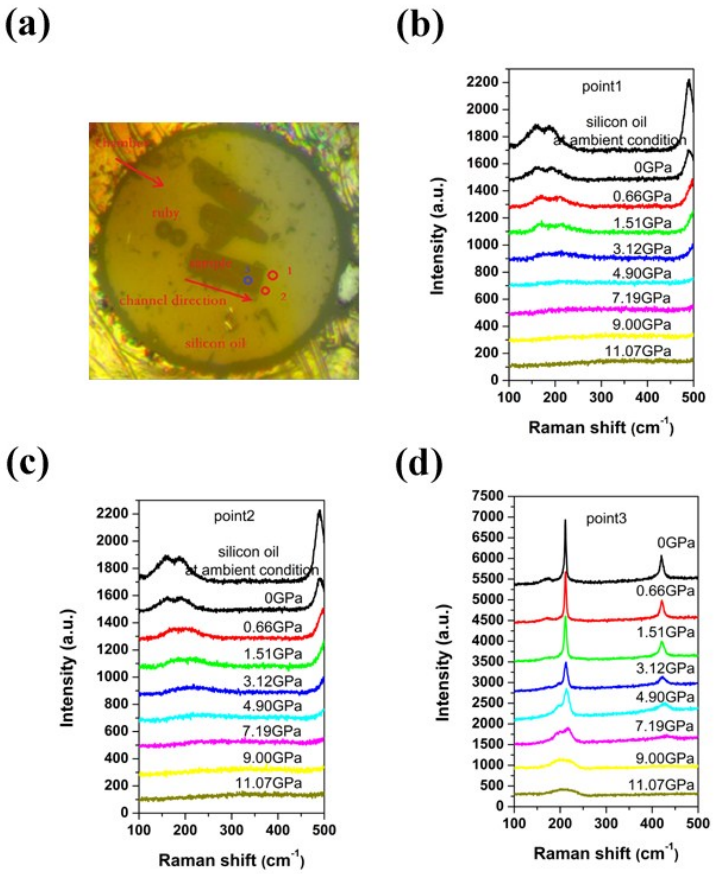

Fig. SP1 (a) Optical image of the sample chamber in the high pressure experiment. (b) and (c) Raman spectra under high pressures measured at point 1 and point 2 in the sample chamber. (d) Raman spectra under high pressures measured at point 3 on the sample.

We choose I@AFI sample which has similar dimension as that used to record high pressure Raman spectra shown in Fig.1 and carry out a parallel high pressure Raman experiment to measure whether Raman signals of iodine exist outside the sample upon increasing pressure. We focused on two points outside the end of I@AFI sample (point 1 and point 2) in the sample chamber as shown by the red circles and one point (point 3) on the sample as shown by the blue circle in Fig.SP1a. The corresponding Raman spectra are shown in Fig. SP1b, Fig.SP1c and Fig.SP1d. Fig. SP1d depicts a Raman change of confined iodine upon compression, which is consistent with that in Fig.1, while only Raman spectra of silicon oil can be observed in Fig. SP1b and Fig.SP1c in the studied pressure range and no Raman signals of iodine are found, suggesting that no iodine molecules leak out of the channels.

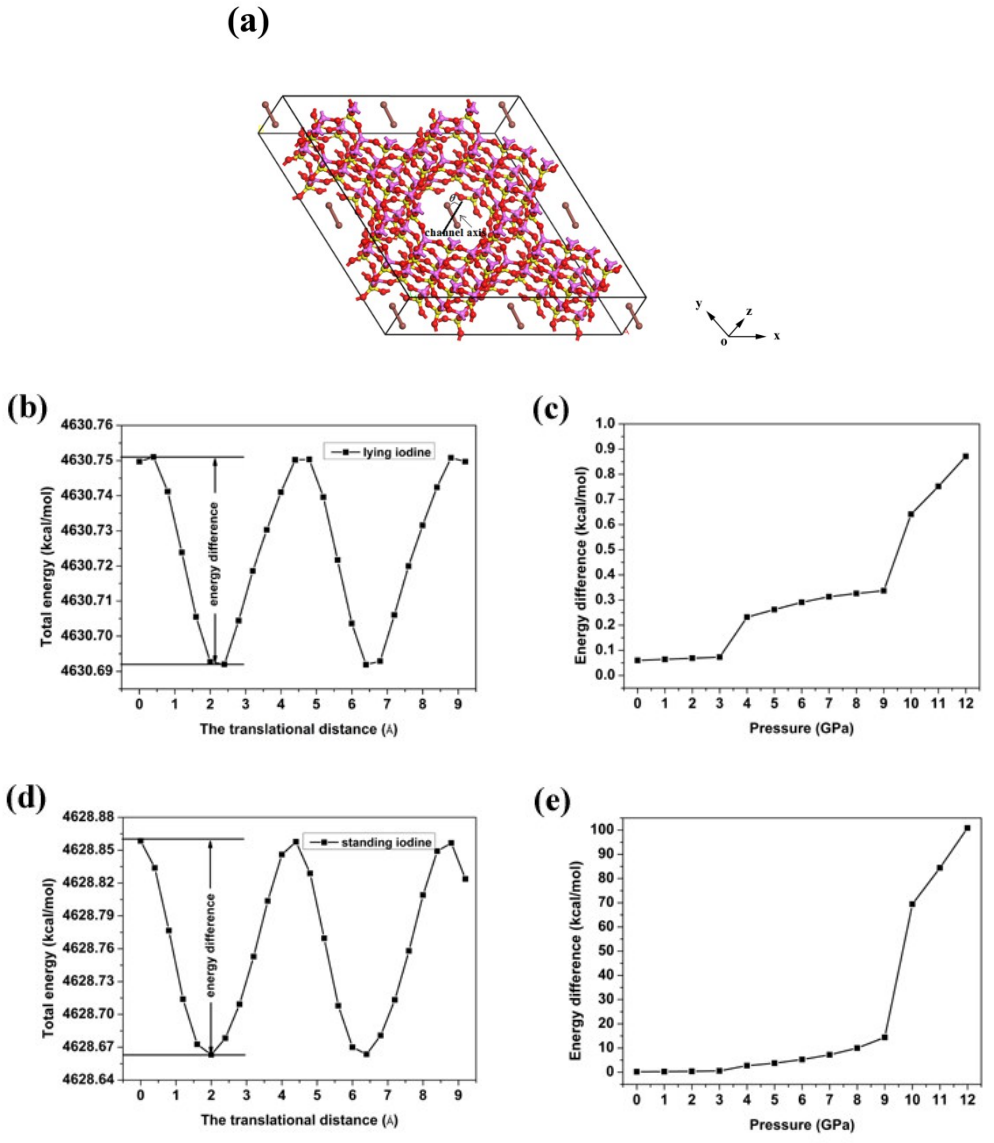

Fig. SP2 (a) The graphical representation of I@AFI system. A 1×1×2 super cell of AFI is constructed. One iodine molecule is put on the channel axis with a dip angle θ, which is defined as the angle between the bond direction in an iodine molecule and the channel axis direction. The atoms are colored as follows: pink for aluminum atoms, and yellow for phosphorus atoms, red for

oxygen atoms, purple for iodine atoms. (b) Total energy of I@AFI system obtained by moving lying iodine molecules (θ=0°) along channel axis direction at 0GPa. (c) The pressure dependent energy difference for lying iodine molecule in AFI channel at high pressures. (d) Total energy of I@AFI system obtained by moving standing iodine molecules (θ=90°) along channel axis direction at 0GPa. (e) The pressure dependent energy difference for standing iodine molecule in AFI channel at high pressures. The total energy of I@AFI system with one iodine molecule in the channel is calculated using the universal force field (UFF) implemented by the Forcite code in Materials Studio. During the calculation, the iodine molecules are moved along the channel axis with a step length of 0.4 Å.

We discuss whether the iodine molecules can leak out of AFI from the perspective of total energy of I@AFI system. Fig. SP2b and Fig. SP2d show the total energies of I@AFI system with lying iodine and standing iodine at 0GPa, respectively. We can see that both the total energies change periodically. The system needs more energy to conquer translational energy barrier if the lying iodine molecule or standing molecule is moved along channel axis direction. The translational barrier can be estimated by the energy difference as shown in the figures. We note that the energy difference for the system with standing molecules is much higher than that with lying molecules at 0GPa. Thus, it is much harder for the standing molecules to move along channel axis direction. Meanwhile, it can hinder the movement of lying molecules. Upon compression, the framework of AFI contracts and both the energy differences increase (Fig. SP2c and Fig. SP2e). That is to say, the translational movements of iodine molecules are more restricted under high pressures. Thus, the confined iodine molecules are not preferable to come out of the channels.

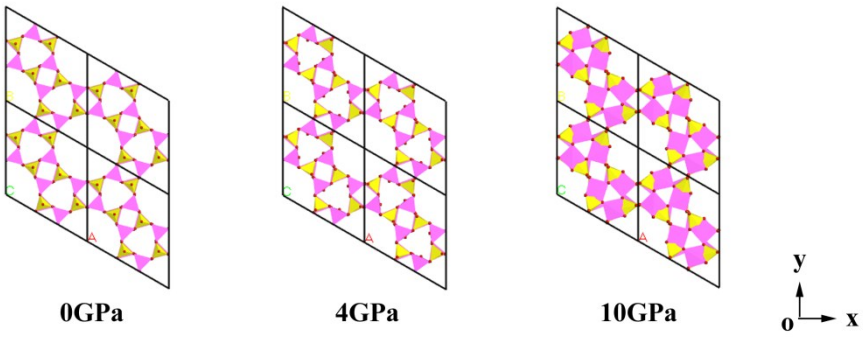

Fig.SP3 The graphical representations of cross-section transformation of AFI framework in the theoretical simulations at 0, 4 and 10GPa. The pink polyhedrons represent AlO_4 ($AlPO_5$ at 10GPa), and the yellow polyhedrons represent PO_4.

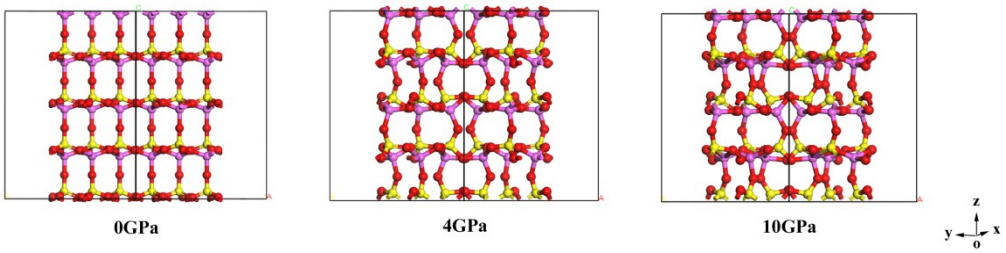

Fig.SP4 The graphical representations of structural transformation of AFI framework in the theoretical simulations at 0, 4 and 10GPa. The atoms are colored as follows: pink for aluminum atoms, and yellow for phosphorus atoms, red for oxygen atoms.