



## *In situ* low-temperature Raman studies of iodine molecules confined in the one-dimensional channels of AlPO<sub>4</sub>-5 crystals



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### ABSTRACT

We have performed *in situ* low-temperature Raman spectroscopy studies on iodine molecules confined in the one-dimensional (1D) round channels of AlPO<sub>4</sub>-5 (AFI) crystals. Polarized Raman measurements show that the Raman intensity of individual iodine molecules parallel to channel axis (termed lying molecules) increases more than that of iodine molecules perpendicular to channel axis (termed standing molecules) upon cooling temperature down to  $-196$  °C. This suggests that an orientation transformation of individual iodine molecules has occurred to increase the population of iodine molecules lying along channel axis as temperature decreases. Consequently, the corresponding Raman mode shows a redshift due to the enhancement of intermolecular interaction. This low-temperature induced orientation transformation is observed to recover when heated back to room temperature, indicating that orientation of iodine molecules confined in this porous medium can be modulated reversibly at a molecular level by cooling temperature down.

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## 1. Introduction

Manipulating, controlling atoms/molecules and constructing the desirable nanostructures, which possess outstanding properties have been drawn much attention by scientists in physics and chemistry [1–8]. These interests of scientific research are driven not only by the aspiration to understand the basic physical and chemical process in the microscopic field but also by the considerable diversities of promising potential applications in nanoscience and nanotechnology. So far, many efforts have been made to manipulate the microscopic atoms and molecules in a controllable way. For example, laser technology and electrostatic field have been employed to control the orientation of molecules [1–4]. Simultaneous STM and TEM can be used to fabricate golden nanowires with excellent quantum conductance behavior [5,6]. In addition, self-assembly on crystalline substrates also provide a powerful method for fabricating well-ordered nanostructures, which have implications in material science, chemistry and biology [7,8].

In recent years, numerous experimental and theoretical studies focus on assembling ordered atomic/molecular array using one-dimensional (1D) porous materials, such as SWCNTs, metal organic frameworks (MOFs) and zeolites [9–12]. AlPO<sub>4</sub>-5 (AFI), a kind of aluminophosphate zeolites, is constructed by corner-sharing AlO<sub>4</sub> and PO<sub>4</sub> tetrahedral and has ordered 1D parallel channels with round cross-section [7.3 Å × 7.3 Å], which are accessible to many small atoms and molecules [13]. The high structural stability and 1D porous framework make AFI an ideal template to fabricate and stabilize atomic/molecular aggregates in the unique confinement environment. It has been found that the confined guests exhibit many novel behaviors due to spatial confinement and interactions between the guests and the host frameworks. Selenium has been confined into the nanochannels of AFI and shows helical chain-like structure [14]. The smallest SWCNTs could grow in linear channels of AFI, which exhibit extraordinary electrical properties at low temperature [15,16]. The structures and dynamical behaviors of 1D hydrogen-bonded water nanostructures in AFI have also been reported in several works [17,18].

Iodine, as a representative diatomic molecule, has attracted much attention of scientists in recent years [19,20]. The structure of iodine species reconstructs in AFI channels and exists in the state of

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neutral iodine chains and individual iodine molecules, which have no counterpart in bulk phase [21]. Most recently, it has been found that the confined iodine species can be manipulated further by high external pressure [22,23]. Pressure modifies the confinement environment, forces the orientation of individual iodine molecules to channel axis direction and elongates the iodine chains.

Temperature, serving as an important tuning parameter, has a great influence on the structures and properties of substances. Previous reports show that the structure and dynamic behavior of molecules in confinement environment are closely related to temperature [24,25]. For example, the confined water molecules in the 1D channels of SWCNTs construct spontaneously 1D polygonal ice nanotubes or core-sheath ice structures at low temperatures, which are depending on the diameters of SWCNTs [24]. Besides, a special ladder-like structure of oxygen molecules has been obtained in a microporous metal-organic solid at 90 K by Kitaura and co-workers [25]. So far, few papers are dedicated to study structural transformation of iodine at low temperature, especially for iodine species in confinement environment [26–28]. Our knowledge on the structures and dynamic behaviors of the confined iodine molecules at low temperature is still limited. Thus, we explore the influence of low temperature on the structures of confined iodine species in AFI using Raman spectroscopy combined with polarized Raman measurements in this work. Our finding is that the orientation of individual iodine molecules is controllable and these molecules rotate to lie along channel axis direction as temperature decreases. This orientation transformation is reversible when heated back to room temperature. Such transformation has never been observed in bulk material of iodine. This suggests that the porous medium with one-dimensional channels, which can accommodate iodine, is very important in manipulating and controlling the orientation of individual iodine molecules. We propose that the new finding will have important applications in low-temperature-sensitive nanoscale devices.

## 2. Experimental details

AlPO<sub>4</sub>-5 (AFI) single crystals were synthesized under hydrothermal conditions by using triethylamine (TEA) as organic template agent [29]. Then, the as-synthesized AlPO<sub>4</sub>-5 crystals were calcined at 580 °C under O<sub>2</sub> atmosphere for 48 h to remove the TEA molecules in the channels. I@AFI were obtained using a vapor diffusion method [21,22]. A small quantity of iodine solids were used for preparing the I@AFI samples with low iodine filling density, while excess iodine solids were used for I@AFI samples with high iodine filling density. The samples with low and high iodine filling density show light red color and red color, respectively. Raman spectra were recorded using a Renishaw spectrometer equipped with a microscope with a spot size of about 5 μm at an excitation wavelength of 514.5 nm. *In situ* polarized Raman measurements were performed in VV configuration (shown in Fig. 2(a)). The polarization of incident laser and Raman scattering signal are both parallel to y axis direction. The polarization angle  $\theta$  is defined as the angle between the y axis direction and the c axis direction. Temperature was monitored through a programmable heating-cooling stage. Liquid nitrogen was used for cooling and the lowest temperature reached during the measurements was –196 °C.

## 3. Results and discussions

We chose I@AFI samples with different iodine filling densities to perform *in situ* low-temperature Raman measurements. Fig. 1(a) shows the temperature-dependent Raman spectra of I@AFI with low iodine filling density. A band, which is assigned to the individual iodine molecules confined in AFI channels, can be clearly

seen at about 209 cm<sup>-1</sup> at 20 °C and its second-order band is observed at about 417 cm<sup>-1</sup> [30]. As reported previously, the Raman spectrum of confined iodine is closely related to the population of iodine molecules in the nanochannels [31,32]. High iodine filling density increases the population of iodine molecules and decreases the separation between neighboring molecules. As a result, the confined iodine molecules in the channels of AFI will connect with each other side by side to form chain-like structures. Thus, the Raman spectrum at 20 °C shown in Fig. 1(b) is obviously different from that in Fig. 1(a). The band at around 170 cm<sup>-1</sup> is characteristic of iodine chains and the other two bands at around 203 cm<sup>-1</sup> and 209 cm<sup>-1</sup> can be attributed to individual iodine molecules [21,22,30]. The redshift in the Raman mode of individual iodine molecules compared with vapor iodine (214 cm<sup>-1</sup>) is due to the significant interaction from neighboring iodine molecules and AFI framework [31,32]. According to our previous Raman measurements at ambient condition [22], the Raman bands at 203 cm<sup>-1</sup> and 209 cm<sup>-1</sup> in I@AFI samples with high iodine filling density are attributed to iodine molecules parallel to channel axis direction (termed lying iodine molecules) and perpendicular to channel axis direction (termed standing iodine molecules). The intensity of Raman band at 203 cm<sup>-1</sup> due to lying iodine molecules is very weak at 20 °C (Fig. 1(a)), when the iodine filling density is low. We have carried out the Energy Dispersive Spectroscopy (EDS) analyses of I@AFI with low and high iodine filling density to roughly estimate the mass percent of iodine in I@AFI samples (Fig. A1). The mass percent of iodine in I@AFI with high iodine filling density is about 11.9%, while that in I@AFI with low iodine filling density is only about 5.1%. We find that the experimental method of preparing I@AFI samples and the profile of Raman spectrum of I@AFI with high iodine filling density at ambient condition is similar with those in a previous literature by Ye and co-workers [33]. The TG analysis in that work shows the iodine content is about 9.8%. Thus, we believe that the mass percent for high iodine filling density is about 10%–12% and that for low iodine filling density is about 5%.

Here, we first focus on the temperature induced transformations of the individual iodine molecules. As the temperature decreases, the Raman bands become sharper and stronger gradually. Similar Raman intensity enhancement upon cooling temperature down has also been observed in the Raman studies of iodine molecules in the channels of AlPO<sub>4</sub>-11 (AEL) crystals and iodine-doped poly(vinyl alcohol) films [28,34]. In the I@AFI with high iodine filling density, the 203 cm<sup>-1</sup> band due to lying iodine molecules shifts to 201 cm<sup>-1</sup> at –196 °C, while the position of band due to standing iodine molecules at 209 cm<sup>-1</sup> is temperature independent. In the I@AFI with low iodine filling density, the slightly asymmetric band at 209 cm<sup>-1</sup> splits and evolves into two bands at 201 cm<sup>-1</sup> and 209 cm<sup>-1</sup> at –196 °C, corresponding to the vibrations of lying iodine molecules and standing iodine molecules, respectively. On the low frequency side, a weak Raman band due to iodine chains appears at –196 °C. Note that the Raman band due to lying iodine molecules becomes stronger than the other one due to standing iodine molecules at –196 °C in I@AFI with both low and high iodine filling density. Such Raman changes indicate that structural transformations have happened between the standing and the lying iodine molecules in the channels of AFI crystals as temperature decreases. Upon heating back to room temperature, the Raman changes are reversible, suggesting the temperature-induced transformations of iodine molecules in I@AFI are reversible.

In previous studies, polarized Raman spectroscopy has been widely used to explore the geometric arrangement of species in confinement environment. It has been found that the intensity of iodine molecules parallel to channels axis in AEL shows a maximum in VV 0° configuration and decreases gradually as the polarization angle increases from  $\theta = 0^\circ$  to  $\theta = 90^\circ$ , while that of iodine

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