Anomalous aggregation state of deuterium molecules in the nanoscale pores of a metal organic framework

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The behavior of hydrogen molecules adsorbed onto the nanospace of porous materials is of great interest but is poorly understood. Here we show direct visualization of deuterium molecules adsorbed on isoreticular metal organic frameworks (IRMOF-1) at 77 K using reverse Monte Carlo simulation based on first principle molecular dynamics simulation and neutron diffraction. Results show that the two types of adsorption sites around a ZnO_4 cluster are almost fully occupied by the deuterium molecules but that other sites are not fully occupied. Moreover an interesting information about the aggregation state of deuterium molecules was directly obtained from the deuterium–deuterium partial pair distribution function. Namely, the average distance of deuterium molecules adsorbed onto IRMOF-1 is slightly longer than that in a solid state but much shorter than that in the corresponding gas state. © *2010 American Institute of Physics*. [doi:10.1063/1.3490625]

I. INTRODUCTION

Hydrogen shows promise as a next-generation energy source from the perspective of CO_2 emissions and renewal energy. Various kinds of hydrogen storage materials have been examined for the realization of small and lightweight hydrogen storage systems. Porous materials are the most common potential candidates as hydrogen storage materials because they can physically adsorb hydrogen molecules under a low heat of adsorption. Recently, metal organic frameworks (MOFs), which are formed by metal oxide clusters with organic linkers, have attracted a great deal of interest lately because of their large surface areas.[1] In particular, isoreticular MOFs (IRMOFs) have been investigated by a number of researchers with respect to their hydrogen (deuterium) adsorption properties.[2–5] Rosi *et al.*[2] reported that IRMOF compounds are capable of adsorbing a large amount of hydrogen at 78 K and room temperature. They also reported an inelastic neutron scattering spectra for adsorbed hydrogen in IRMOF-1 (MOF5), whose structure is shown in Fig. 1, and showed that sites around the zinc oxide cluster and the 1,4-benzenedicarboxylate (BDC) hexagonal linker are available during hydrogen adsorption. Later, Yildirim and Hartman[4] performed neutron diffraction measurements at 3.5 K and reported the presences of four deuterium adsorption sites. Namely, three of them are different sites around the zinc oxide cluster and these sites are termed Cup site, ZnO_3 site, and ZnO_2 site, respectively. The other site is the top of the hexagonal linker, which was termed Hex site.[4] However, these measurements were performed below the solidification temperature for deuterium. From a practical application standpoint it is necessary to determine the adsorption sites in their temperature range for gaseous adsorption. In this work, therefore, the deuterium adsorption sites in IRMOF-1 were investigated at 77 K using a pair distribution function technique derived from the Fourier transformation of a structure factor obtained by neutron diffraction. The pair distribution function directly provides the correlation distances between atoms but only yields one-dimensional information. Therefore, reverse Monte Carlo (RMC) modeling,[6] a well-established and effective method of constructing three-dimensional atomic arrangements of crystalline and disordered materials, and molecular dynamics simulation were used in order to determine the adsorption sites.

The results show interesting information about not only the adsorption sites but also the aggregation state of D_2 molecules adsorbed onto IRMOF-1 under 1 MPa D_2 pressure. That is, unusually-short D_2-D_2 distance, which corresponds to that in a gas state under about 50-fold pressure, is observed in the deuterium–deuterium partial pair distribution function.
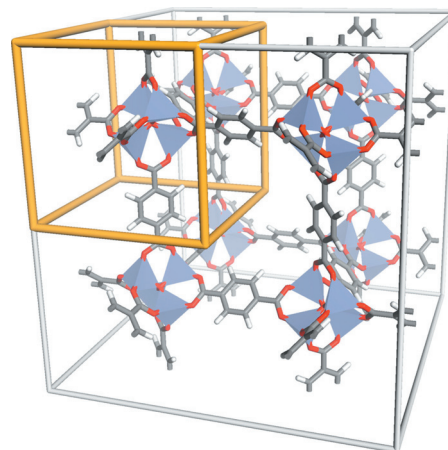

FIG. 1. (Color) Structure of IRMOF-1 (Ref. 16). The small cube corresponds to the unit structure in Fig. 7(a).

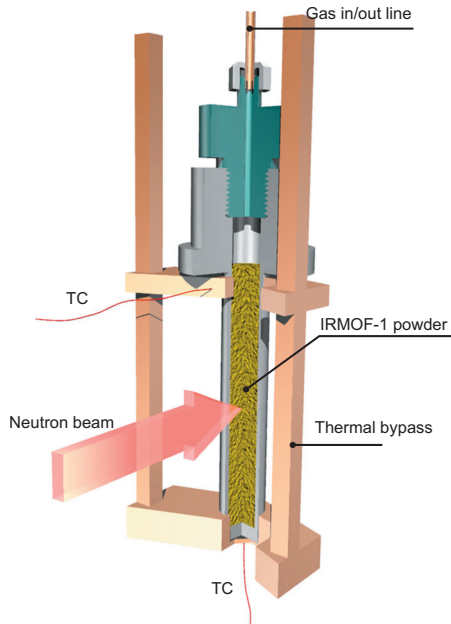
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FIG. 2. (Color) Schematic diagram of container for neutron diffraction measurements.

II. EXPERIMENTAL PROCEDURE

A. Sample preparation

A deuterated IRMOF-1 sample was prepared in the same way as reported in Ref. 16. That is, a mixture of $Zn(NO_3)_2 \cdot 4H_2O$ and deuterated BDC was dissolved in a distilled N,N′-diethylformamide, and the solution was heated at 353 K for 24 h in a closed vessel. A crystalline d-IRMOF-1 powder was obtained in 90% yield.

B. Neutron diffraction experiments

The neutron diffraction measurements were carried out in the high intensity total scattering spectrometer installed at the pulsed neutron source of the High Energy Accelerator Research Organization (KEK, Tsukuba, Japan). A pressure-resistant cylindrical container made of Ti–Zr neutron zero-scattering alloy with an inner diameter of 8.0 mm and a wall thickness 1.0 mm was used. A schematic diagram of the container is shown in Fig. 2. The top of the container was cooled using a helium cryostat. A thermal bypass made of copper was attached to the top and bottom of the container in order to reduce the temperature differential between them. Two thermocouple sensors were located at the top and bottom of the container and the maximum temperature difference was within 3 K. Deuterium gas was loaded through a l/16 in. external diameter stainless steel tube that was connected to the top of the container.

The neutron diffraction measurements were performed on the IRMOF-1 powder sample at 77 K under vacuum and 1 MPa D_2 pressure. Under the latter condition, the scattering from D_2 gas going into the spaces between the powder particles is not negligible. Thus the scattering intensity of D_2 gas under 1 MPa pressure was also measured at 77 K and subtracted from the scattering intensity of the IRMOF-1 powder measured under 1 MPa D_2 pressure to account for

the filling factor of the IRMOF-1 powder. The amount of deuterium adsorption in the IRMOF-1 sample was evaluated from the pressure change, and the deuterium molecule to Zn ratio was determined to be $D_2/4Zn=16.0(1)$, which agrees well with that obtained by a Sieverts' type apparatus.

The structure factors, $S(Q)$, where $Q=4\pi \sin \theta/\lambda$ (2θ is the scattering angle and λ the neutron wavelength), were derived by the application of various corrections for the background absorption[7] and multiple scattering,[8] as well as via normalization using a vanadium rod.

$S(Q)$ was analyzed by the Faber–Ziman definition[9] as follows:

$$S(Q) = \frac{I(Q) - \{\langle b^2 \rangle - \langle b \rangle^2\}}{\langle b \rangle^2}, \tag{1}$$

and

$$\langle b^2 \rangle = \sum_i c_i b_i^2, \quad \langle b \rangle = \sum_i c_i b_i, \tag{2}$$

where c_i and b_i are the concentration and the coherent scattering length for neutron diffraction of the component atoms i, respectively. The pair distribution function, $g(r)$, can be derived from the Fourier transformation of $S(Q)$ as follows:

$$g(r) = 1 + \frac{1}{2\pi^2 r\rho} \int_0^{Q_{min}} Q(S(Q)-1)\sin QrdQ, \tag{3}$$

where ρ is the average number density of the atoms.

The $g(r)$ for an IRMOF1 compound is written as a weighted sum of ten partial pair distribution functions, $g_{i-j}(r)$:

$$g(r) = \sum_{i,j} w_{i-j} g_{i-j}(r). \tag{4}$$

Here w_{i-j} is the weighting factor, defined as:

$$w_{i-j} \frac{c_i c_j b_i b_j}{\langle b \rangle^2}. \tag{5}$$

Due to the deuterium adsorption, the number of partial pair distribution functions is fatally increased to 15. However, only the pair correlations related to adsorbed deuterium molecules (D^{ad}–Zn, D^{ad}–O, D^{ad}–C, and D^{ad}–D^{hex} and D^{ad}–D^{ad} pairs, here D^{ad} stands for adsorbed deuterium molecules and D^{hex} for deuterium atoms belonging to the hexagonal linker in IRMOF-1) were required to investigate the D_2 adsorption sites in the IRMOF-1 compound. Sum of the weighting factors of these pair correlations are 0.625 for the IRMOF-1 powder measured under 1 MPa D_2 pressure. The other 0.375 is a constituent of the host IRMOF-1, and then we can remove its contribution and obtain a pair distribution function related to adsorbed deuterium molecules, $g^{D_2}(r)$, as follow:

$$\begin{aligned} g^{D_2}(r) = [g(r)(\text{at 1 MPa } D_2) - 0.375 \\ \times g(r)(\text{under vacuum})] \times 1.6. \end{aligned} \tag{6}$$
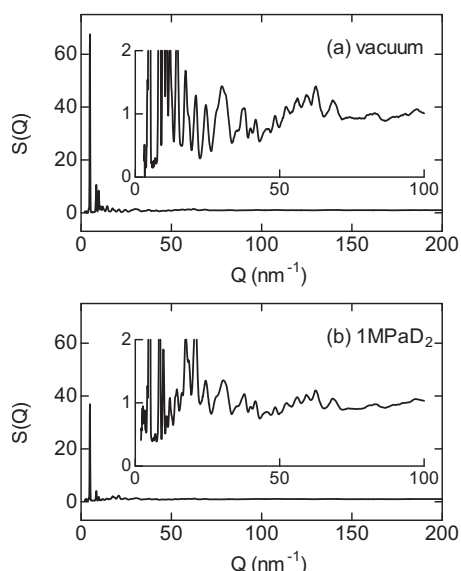
FIG. 3. Total structure factors, S(Q), for the IRMOF1 powder measured at 77 K (a) under vacuum and (b) at 1 MPa D_2 pressure covering the full Q-range, and enlarged illustrations in the region below 100 nm^{-1}.

III. RESULTS AND DISCUSSION

A. Neutron diffraction

Figure 3 shows the total structure factors, $S(Q)$, for the IRMOF-1 powder measured at 77 K under vacuum and at 1 MPa deuterium pressure. The pair distribution functions, $g(r)$, which were derived from the Fourier transformation of these total structure factors with a Q_{max} of 200 nm^{-1}, are compared in Fig. 4. Here the $g(r)$ curve for the IRMOF-1 powder measured under vacuum is multiplied by the factor 0.375 for comparison. Both $g(r)$ curves have two peaks at 0.107 nm and 0.136 nm and these peaks mainly correspond to C–D^{hex}, C–O, and C–C correlations, respectively. On the other hand, a new sharp peak is observed at 0.07 nm in the $g(r)$ curve after deuterium loading that corresponds to D^{ad}–D^{ad} correlations. The coordination number, calculated from the area under the peak, was 1.0(3). This result indicates that all deuterium adsorbed onto IRMOF-1 are in the form of molecules. Moreover, difference in the $g(r)$ curves before and after the deuterium loading can be seen above 0.25 nm and these correspond to the pair correlations related
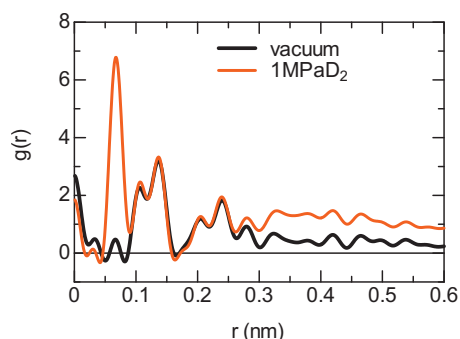

FIG. 4. (Color) Pair distribution functions, $g(r)$, for the IRMOF1 powder measured at 77 K under vacuum and at 1 MPa D_2 pressure. The $g(r)$ curve for the IRMOF1 powder measured under vacuum is multiplied by the factor 0.375 for comparison.
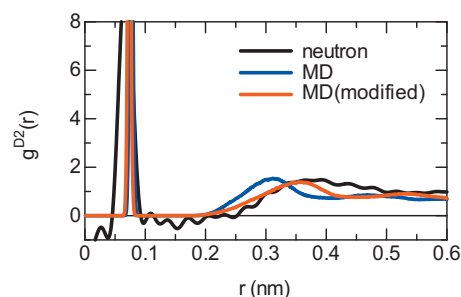

FIG. 5. (Color) The pair distribution function related to the adsorbed D_2 molecules, such as D^{ad}–Zn, D^{ad}–O, D^{ad}–C, and D^{ad}–D^{hex} D^{ad}–D^{ad} correlations, obtained by using Eq. (6) (black line). Neutron-weighted sum of partial pair distribution functions related to D_2 molecules (D^{ad}–Zn, D^{ad}–O, D^{ad}–C, D^{ad}–D^{hex}, and D^{ad}–D^{ad} correlations) as calculated by MD simulation (blue and red lines).

to the adsorbed D_2 molecules, such as D^{ad}–Zn, D^{ad}–O, D^{ad}–C, and D^{ad}–D^{hex} D^{ad}–D^{ad} correlations. The pair distribution function related to adsorbed deuterium molecules, $g^{D_2}(r)$, which was obtained by using Eq. (6), is presented in Fig. 5.

B. First principle molecular dynamics (FPMD)

The neutron diffraction results directly give the precise pair correlations between D_2 molecules and constituent atoms of IRMOF-1. However, additional information is needed in order to elucidate the deuterium adsorption sites because the neutron pair distribution function is one-dimensional information. We performed FPMD simulations based on density functional theory (DFT) (Ref. 10) local density approximations[11,12] in order to obtain information about adsorption states (such as dissociation of molecular) as well as adsorption sites. In the FPMD simulations, a super cell with a=b=c=1.8151 nm and $\alpha=\beta=\gamma=60°$ was used, and 106 atoms (Zn: 8, O: 26, C: 48, D^{hex}:24) were located at the positions reported by Eddaoudi *et al.*[16] The deuterium molecules (32 molecules, D_2/4Zn=16.0) were put randomly in the unit cell as a gas phase. The FPMD simulations were performed using the projector augmented-wave[15] method calculation package, VASP,[13,14,21,27] with $1 \times 1 \times 1$ k-point meshes. Here, the atomic weight of hydrogen atoms was changed to 2.014 for them to become deuterium atoms. The plane wave energy cut-off and convergence energy conditions were determined as 400 eV and 0.1 meV, respectively. The FPMD calculations were performed using NVT (the constant entity-number/volume/temperature) ensemble at 77 K for more than 35 000 steps with an integral time of 0.2 fs. To obtain an average result, FPMD calculations were executed five times using different initial configurations of deuterium molecule positions and over 200 000 total MD steps were used to analysis.

The partial pair distribution functions related to the deuterium molecules (D^{ad}–Zn, D^{ad}–O, D^{ad}–C, D^{ad}–D^{hex}, and D^{ad}–D^{ad} correlations) were calculated using the configuration of deuterium molecules. Here, each correlation peak was broadening using Gaussian function with $\sigma=0.05$. The neutron-weighted sum of these functions is compared in Fig. 5 (blue line) with the experimental results. The difference at around 0.3–0.4 nm between two curves is thought to be due
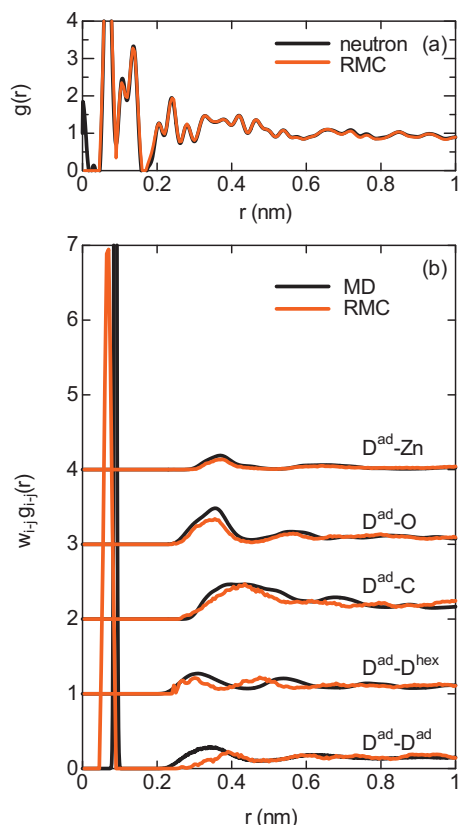
FIG. 6. (Color) (a) Pair distribution functions, $g(r)$, observed by neutron diffraction for IRMOF-1 measured at 1 MPa D_2 pressure, compared with the neutron diffraction $g(r)$ functions calculated from the RMC model (red line). (b) Partial pair distribution functions $g(r)$ calculated from the MD, compared with those calculated from the RMC model (red lines).
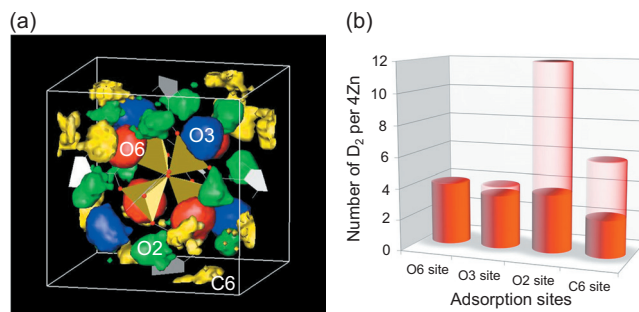

FIG. 7. (Color) (a) Isosurface plots of deuterium molecules adsorbed on the IRMOF-1 derived from the RMC configuration. The average density distribution of deuterium molecules was divided into 0.05-nm-sided cubes. (b) The occupancy rates for deuterium molecules at each adsorption site. Four, 4, 12, and 4 sites per 4 Zn for O6, O3, and O2, respectively.

to an over-binding of the hydrogen adsorption energies based on DFT calculations. Because the hydrogen adsorption energy of benzene based on DFT was 9.75 kJ/mol, which was larger than the experimental value of graphite (4.99 kJ/mol).[17] Therefore, we needed to correct for the correlation distances of the FPMD results and the correction factor was determined to be 1.15. The modified function is also plotted in Fig. 5 (red line). Moreover, it can be confirmed that the deuterium molecules do not dissociate but keep molecular state in the adsorption process. This result is agreed with that obtained from $D^{ad}-D^{ad}$ coordination number of neutron pair distribution function.

C. RMC simulation

In order to elucidate the adsorption sites of deuterium molecules in IRMOF, the RMC simulation was applied. RMC simulation was carried out by using a self-written code. A simulation box containing 3392 atoms (Zn: 256, O: 832, C: 1536, D^{hex}: 768) with periodic boundary conditions was used. First, an RMC configuration of host IRMOF-1 was constructed by fitting the model $g(r)$ to the neutron $g(r)$. Here the crystal structure of IRMOF-1, reported by Eddaoudi *et al.*,[16] was used as a starting configuration. Maximum movement for each atom was set to 0.002 nm to keep the initial structure. The neutron $g(r)$ for IRMOF-1, calculated from the RMC model, is plotted by the red line in Fig. 6.

Next, the adsorption sites of D_2 molecules were determined. The previously constructed configuration of Zn, O, C, and D^{hex} atoms in IRMOF-1 was used, and these atoms were fixed in the RMC simulation. Namely, only deuterium molecules were moved. Recently, not only experimental data but also classical molecular dynamics simulation results are used in order to improve the reliability of the RMC modeling.[22–26] Here the RMC simulation was performed referencing the FPMD simulation result. Namely, the configuration of deuterium molecules, obtained by FPMD simulation, was used as an initial configuration. Moreover, the RMC model was fitted not only to the neutron $g(r)$ but also to the partial pair distribution functions obtained from the FPMD simulation results. The closest distances between two atoms ($D^{ad}-Zn$, $D^{ad}-O$, $D^{ad}-C$, and $D^{ad}-D^{hex}$) were determined to be 0.25 nm.

The total and partial $g(r)$ curves, calculated from the RMC model, are plotted in Fig. 6, and compared with the total $g(r)$ curve obtained by neutron diffraction and the partial pair distribution functions obtained by FPMD simulation. Excellent fits as shown were obtained for the total $g(r)$ curves, along with goodness-fits with the partial $g(r)$ curve.

Figure 7(a) shows the density isosurface plots. Here, the average density distribution of deuterium molecules was divided into 0.05 nm-sided cubes and density isovalue plots (1.5×10^{-5} molecules/nm^{-3}) are presented in the figure. Four high density regions, indicated by different colors (red, blue, green, yellow), are clearly observed around the ZnO_4 cluster and the hexagonal linker. We term these sites the O6 site, O3 site, O2 site, and C6 site, respectively, based on the $D^{ad}-O$ coordination number. In the previous study,[4] these sites correspond to the Cup site, ZnO_3 site, ZnO_2 site, and Hex site, respectively. This result shows that the O6 and O3 sites are considerably occupied and that the deuterium molecules are located at these site positions. On the other hand, the O2 and C6 sites are comparatively empty and the deuterium molecules are distributed around these site positions. In Fig. 7(b), the occupancies for deuterium molecules in each adsorption site are presented. Indeed, the O6 and O3 sites are almost fully occupied by the deuterium molecules. These results are consistent with the calculated adsorption energy for the O6 and O3 sites, which are larger than that for O2 and C6 sites. On the other hand, the O2 and C6 sites are not fully

occupied. The occupancy state for O2 sites is attributable to the interaction between deuterium molecules. That is, the average O6–O2 and O3–O2 distances calculated from the RMC model are 0.36 nm and 0.34 nm, respectively, which are shorter than the average D^{ad}–D^{ad} distances. Consequently, repulsion between deuterium molecules is considerable, and they influence the site occupancy of O2 sites. Therefore, only one-third of the sites are occupied, despite the presence of O2 sites in large numbers.

The C6 sites are about half empty. Unlike the O2 sites, the average O6–C6 and O3–C6 distances are more than 0.46 nm and hence the repulsion between deuterium molecules is weak. Therefore, the occupancy state for C6 sites is thought to be attributable to the relatively-small adsorption energy. Sagara *et al.*[18] reported that adsorption energy for C6 sites is 5.27 kJ/mol. This value is comparable with the experimental value for the hydrogen adsorption energy on graphite (4.99 kJ/mol) (Ref. 17) and smaller than that for other adsorption sites.

The RMC model shows interesting information related to the state of D_2 molecules adsorbed onto IRMOF-1. Namely, the D^{ad}–D^{ad} partial pair distribution function (shown in Fig. 6) has a broad peak around 0.4 nm. This result indicates that the average intermolecular distance of adsorbed deuterium molecules is about 0.4 nm. It is shorter than that in a critical state but close to those in solid states.[19,20] Such D_2–D_2 distance surprisingly corresponds to that in a gas state under about 50 MPa at 77 K conditions.

IV. CONCLUSIONS

The adsorption sites of deuterium molecules onto IRMOF-1 were investigated at 77 K, using RMC modeling, based on the associated neutron diffraction data and molecular dynamics simulation. The results show that the O6 and O3 sites are almost fully occupied by the deuterium molecules but the O2 and C6 sites are not. The occupancy state for these sites is dependent not only on the adsorption energy but also on the extent of repulsion between deuterium molecules. Moreover, the results also show that the average distance between deuterium molecules adsorbed onto IRMOF-1 is slightly longer than that in solid phase but shorter than that in a gas state under 1 MPa at 77 K conditions. Namely, the deuterium molecules are concentrated in a very dense state. Since the motions of deuterium molecules are constrained by the nanospace concurrent with adsorption energy, such irregular states of deuterium molecules occurs in IRMOF-1.

This suggests that the nanoscale control of three-dimensional framework structures allow an increase in the amount of adsorption. We believe strongly that the method used in this study is useful in investigating the behavior of adsorbed molecules.

[1]M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe, and O. M. Yaghi, Acc. Chem. Res. **34**, 319 (2001).
[2]N. L. Rosi, J. Eckert, M. Eddaoudi, D. T. Vodak, J. Kim, M. O'Keeffe, and O. M. Yaghi, Science **300**, 1127 (2003).
[3]J. L. C. Rowsell, A. R. Millward, K. S. Park, and O. M. Yaghi, J. Am. Chem. Soc. **126**, 5666 (2004).
[4]T. Yildirim and M. R. Hartman, Phys. Rev. Lett. **95**, 215504 (2005).
[5]F. M. Mulder, T. J. Dingemans, H. G. Schimmel, A. J. Ramirez-Cuesta, and G. J. Kearley, Chem. Phys. **351**, 72 (2008).
[6]R. L. McGreevy and L. Pusztai, Mol. Simul. **1**, 359 (1988).
[7]H. H. Paalman and C. J. Pings, J. Appl. Phys. **33**, 2635 (1962).
[8]I. A. Blech and B. L. Averbach, Phys. Rev. **137**, A1113 (1965).
[9]T. E. Faber and J. M. Ziman, Philos. Mag. **11**, 153 (1965).
[10]W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
[11]D. M. Ceperley and B. Alder, Phys. Rev. Lett. **45**, 566 (1980).
[12]J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
[13]G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993).
[14]G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).
[15]P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994).
[16]M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe, and O. M. Yaghi, Science **295**, 469 (2002), and supporting information.
[17]L. Mattera, F. Rosattelli, C. Salvo, F. Tommasini, U. Valbusa, and G. Vidahi, Surf. Sci. **93**, 515 (1980).
[18]T. Sagara, J. Klassen, and E. Ganz, J. Chem. Phys. **121**, 12543 (2004).
[19]d_{solid}(14.15K)=0.0763g/cc. $dist_{H-H}$=0.395mn. $d_{critical}$(33.25K) =0.0310g/cc. $dist_{H-H}$=0.533nm.
[20]Encyclopaedia Chimica, ed. Editorial Committee of Encyclopaedia Chimica (Kyoritsu shuppan, Tokyo, 2001), Vol. 5, p. 48 (in Japanese).
[21]G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).
[22]L. Pusztai, O. Pizio, and S. Sokolowski, J. Chem. Phys. **129**, 184103 (2008).
[23]L. Pusztai, I. Harsányi, H. Dominguez, and O. Pizio, Chem. Phys. Lett. **457**, 96 (2008).
[24]L. Pusztai, H. Dominguez, O. Pizio, and S. Sokolowski, J. Mol. Liq. **147**, 52 (2009).
[25]R. Vácha, T. Megyes, I. Bako´, L. Pusztai, and P. Jungwirth, J. Phys. Chem. A **113**, 4022 (2009).
[26]V. Mile, L. Pusztai, H. Dominguez, and O. Pizio, J. Phys. Chem. B **113**, 10760 (2009).
[27]The FPMD simulations have been performed using the ab-initio total-energy and molecular dynamics program VASP (Vienna ab-initio simulation program) developed at the Institut fur Material-physik of the Universitat Wien.