A MOLECULAR DYNAMICS (MD) STUDY OF METHANE IN SILICALITE-1: A NOVEL MØLLER-PLESSET POTENTIAL ENERGY SURFACE

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ABSTRACT

A novel methane/silicalite-1 potential function for MD simulations has been developed using quantum chemical calculations at a Møller-Plesset secondary level/ 6-31G* basis set. As an application a diffusion coefficient of 5.55x10^{-9} $m^2.s^{-1}$ and heat of adsorption of -5 kcal.mol^{-1} have been obtained for a concentration of one methane molecule per intersection and reasonably match with available studies. In contrary, methane-methane radial distribution functions reveal a first peak at 6.3 Å at the low loading (one molecule per intersection) and of 5.4 Å at the highest loading (four molecules per intersection) instead of the first peak at about 4 Å at all concentrations [14], and interpreted there as a consequence of methane-methane Lennard-Jones parameters use. It is, then, demonstrated that the appearance of the peak at 4.0 Å is caused primarily by an unbalance of the methane/methane and silicalite-1/methane pair potentials. With consistence, the present analysis exhibits favorable resident sites at various concentrations in the zigzag channel.

Keywords: ab initio calculation, potential, diffusion coefficient, methane, silicalite-1, MP2

INTRODUCTION

Proper description of diffusion in zeolite confines is of considerable importance in practice owing to their applications in technological industry and science [1,2]. In particular, ZSM-5 and its dealumina analogue known as silicalite-1 are widely used in various petrochemical processes, e.g., in conversion of methanol to gasoline [3]. In recent years, molecular dynamics (MD) simulation has become an essential tool for studying various diffusive guests in zeolites. In most cases, the dynamical results are in good agreement with values obtained from experimental techniques [4,5,6]. Notwithstanding a very few structural information is acknowledged.

According to our best knowledge, an initially available force-field for methane/zeolite systems were a five center models that treated each atom atomistically using a Lennard-Jones potential and a spherical one by Kiselev et al. [7], June et al. [8,9]. Annother simple model that treated methane as a sphere or united atom model was that of Goodbody et al. [10]. Most theoretical works often compare their calculated dynamical result of diffusion coefficients with PFG NMR values gauged by Caro et al. [11]. However, very few literature can be found with regard to structural information [12-]. Spherical methane diffusing in rigid and flexible silicalite-1 frameworks was investigated by Demontis et al. [12,13], while Nicholas et al. used an atomistic MM2 methane model [15] in the fixed lattice [14] through MD simulations. Also given in ref. [14] the similar LJ parameters to MM2 were extrapolated based on ref. [16] by Trouw. Another quantity that often is used in order to investigate the quality of a potential is the heat of adsorption and/or the Henry coefficient, as the one improved by Smit [17]. To date, another model has been developed by Engel et al. [18] as a sum of electrostatic, inductive, dispersive and repulsive interactions.

In prospect, the ab initio derived potential reliably demonstrates its usefullness in describing a proper arrangement of guest molecules inside the pore as recently we exhibited fruitful water constructions by means of an ab initio fitted model [19-]. In the same way, we employ the new ab initio based MP2 silicalite-1/methane interaction to investigate methane structural data. The results of first maxima of pair distribution functions between silicalite and methane consistently exhibit the first peaks centered at approximately 4 Å [12,14]. In contrast, the pertinent methane-methane pair functions displays a first broad peak at 6.4 Å at low loadings and at 5.4 Å at the highest loading (4 molecules per intersection) whereas the peaks appear at about

4 Å at various concentrations due to the methane-methane parameters used [12,14]. We accordingly stage a revision of methane structures based on the ab initio potential surface and eliminated the misleading methane-methane interaction effect for the first time.

NOVEL INTERMOLECULAR PAIR POTENTIAL

Table 1. Final optimization parameters for atom i of methane interacting with atom j in each channel of the silicalite-1 lattice. Subscripts sd and st denote sinusoidal (zig-zag) and straight channels, respectively. Energies in kcal.mol^{-1}, distances (r_{ij}) in Å and atomic net charges (q) in atomic units.

i	j	q_i	q_j	A (Å^{10} kcal.mol^{-1})	B (Å^{12} kcal.mol^{-1})	C (Å^{8} kcal.mol^{-1})
C	Si_{sd}	-0.87	-0.66	-7349979	35791283	484120
C	Si_{st}	-0.87	-0.66	-47973904	283370791	2316815
C	O_{sd}	-0.87	-0.66	1157607	-3234971	-113445
C	O_{st}	-0.87	-0.66	2281723	-7914489	-185328
H	Si_{sd}	0.43	0.165	652722	-1199457	-67753
H	Si_{st}	0.43	0.165	1386542	-2765365	-141278
H	O_{sd}	0.43	0.165	-13594	7620	5704
H	O_{st}	0.43	0.165	94594	-291945	-3738

Ab initio fitted silicalite-/methane potential based on the second-order Møller-Plesset perturbation (MP2) level with the extended 6-31G* basis sets is developed by fitting c. a. 150 data points into an analytical function:

$$\Delta E(\mathrm{m,s}) = \sum_{i}^{5}\sum_{j}^{288}\left\{\frac{A_{ij}^{ab}}{r_{ij}^{8}} + \frac{B_{ij}^{ab}}{r_{ij}^{12}} + \frac{C_{ij}^{ab}}{r_{ij}^{10}} + \frac{q_i q_j}{r_{ij}}\right\} \tag{1}$$

where 5 and 288 denote the numbers of atoms in a methane molecule (m) and the silicalite-1 (s) unit cell, respectively. The constants A_{ij}, B_{ij} and C_{ij} are fitting constants and r_{ij} is the distance between atom i of methane and atom j of silicalite-1. Also, q_i and q_j are the atomic net charges of atoms i and j in atomic units, approximated from the population analysis of the isolated molecules in the quantum chemical calculations. Superscripts a and b on the fitting parameters have been used to classify atoms in different environmental conditions, i.e., in the different channels. The methane-silicalite fitting parameters were listed in Table 1.

MOLECULAR DYNAMICS SIMULATIONS

The crystallographic silicalite-1 cell [24] has lattice parameters a = 20.07 Å, b = 19.92 Å and c = 13.42 Å, characterized by two types of channels with Pnma symmetry group. The structure has two types of channels shown in Figure 1: straight channel and zigzag channel respectively parallel to y- and x-axes, which are interconnected at the intersection. The diffusion along the z direction is possible only by alternating moves of the sorbate between these two channel segments. The simulation box is arranged by 1x1x2 units of silicalite-1 where the loading number (n_{ld}) is set to 1, 2, 3 and 4 methane molecules per intersection or correspondingly to 8, 16, 24, and 32 methane molecules per box.

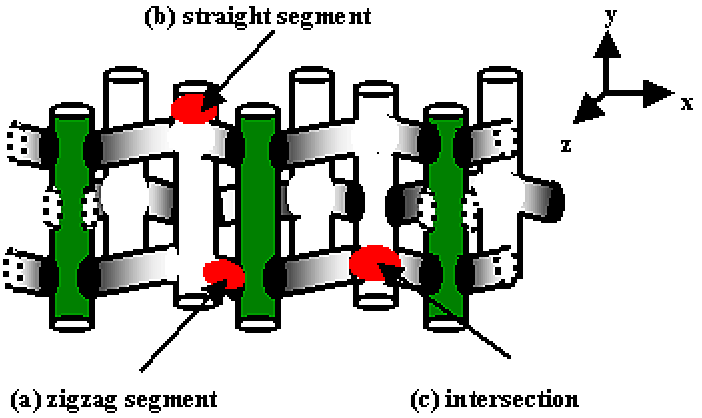

Figure 1. Schematic drawing of (a) zigzag, (b) straight segments, and (c) intersection of silicalite channels.

The time step of 1 fs was used to maintain the energy conservation at 298 K. Periodic boundary conditions have been applied. The MP2 methane/methane potential proposed by Rowley et al. [25] was used. The Ewald summation can be avoided in this system by an application of shifted force potentials because the total charge of the system is zero [26,27]. The evaluation part of each run corresponds to a trajectory length of 10 ns after a 0.5 ps thermalization period.

RESULTS AND DISCUSSION

The interaction energies of methane crossing the zigzag channel are respectively represented in Figure 2 where the insert depicts its configuration. Asymmetry in the curves is due to slight shifts of the minima from the origin (at s = 0 Å) indicating the model sensitivity, as a consequence of a configurational asymmetry. In addition, the results demonstrate that available FF models [10,12,17,18] are sufficiently satisfied with our ab initio silicalite-1/methane potential. A variant of the curve width indicates a unique characteristic of each model, hence, variety of interior potential surface.

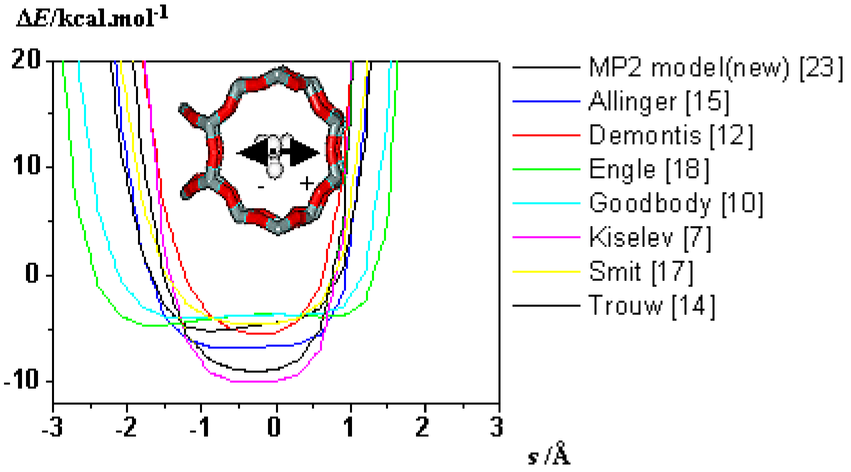

Figure 2. Interaction energies of methane at a configuration shown in the insert with silicalite-1 obtained by various models as a function of distance s.

In view of the fact that good data are available for comparison with respect to dynamical results obtained from simulations using various models [8,10,12-14,18] and in good agreement to available experimental data [11], the focus of the present study is, accordingly, on structural rather than dynamical properties.

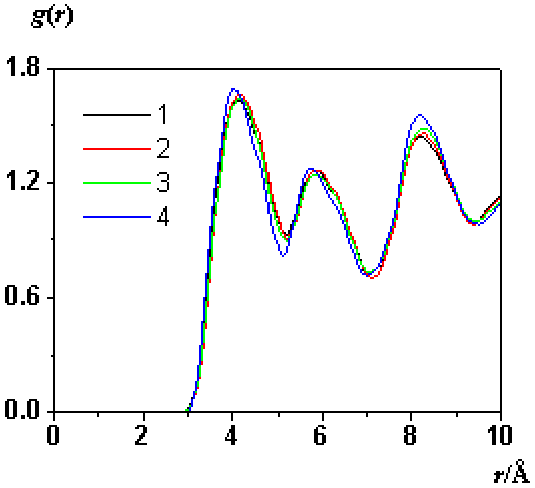

Figure 3. Radial distribution functions, g(r), from oxygen atoms of silicalite-1 surface to carbon atoms of methane molecule at various loadings (n_{ld}).

Figure 3 displays radial distribution functions (RDFs) between silicalite and methane from the oxygen atom on the surface to a center of mass of an methane molecule at various loadings. The RDFs approximately exhibit the same first sharp maxima around 4.2 Å, and second broad peaks centered at 5.8 Å. Due to the cylinder-like structure with the diameter of 8.2 Å of silicalite channels, methane molecules lying under the first maximum can be assigned to those moving along the middle of the channels as the distance is close to that of the channel centers. This information suggests the optimal route of diffusive methane molecule through the axis of silicalite-1 channels, which is similarly to that observed for diffusive water when $n_{ld} \leq 6$ [23]. The other peaks at about 6 Å and 8 Å are designated to those distances of carbon atoms to other oxygen atoms of the nearest 10-oxygen membered ring and of other adjacent rings, respectively. These findings are in excellent agreement with previous works [12,14].

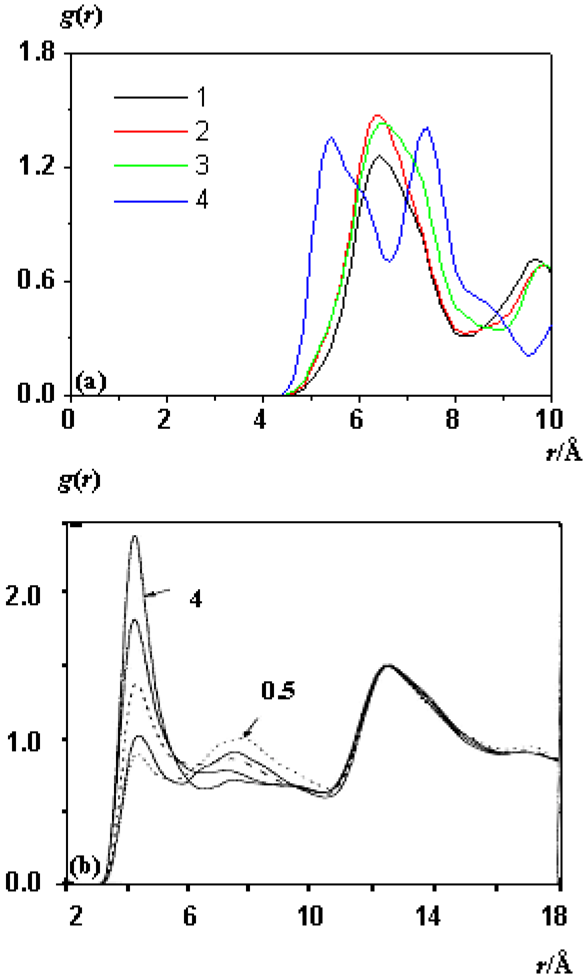

Figure 4. Radial distribution functions, g(r), from carbon atoms of methane molecules obtained in (a) this study and (b) ref. [14] at various loadings.

Further information can be attained as regards to guest-guest radial distribution function. As depicted in Figure 4a, the center of mass between methane molecules RDFs at various loadings. For comparison, the RDFs taken from ref. [14] are also shown in Figure 4b.

At the highest loading a distinct structure of the methane-methane structure has been observed. The plot conspicuously shows a first sharp peak at 5.4 Å with a first minimum at 6.6 Å, followed by the shoulder at 6.2 Å. The second sharp peak at 7.4 Å is shown up with the shoulder at 8.4 Å. In strikingly, other first peaks approximately occur at 6.3 Å for $n_{ld} \leq 3$. These facts indicate a significant alteration in their arrangement at the highest loading. As a transition concentration for methane residence sites when $n_{ld}>3$, the first broaden maximum at 6.4 Å is established with a minimum at 8.9 Å. The methane-methane RDFs for $n_{ld}\leq 2$ display the first apparent maxima at 6.4 Å and the according minimum at 8.2 Å.

In order to assign these first peaks, we examined various methane configurations. The results are plot in Figure 5. There is a clear tendency that methane molecules are designated to those sites between straight and zigzag channels, and suggested these two channels as most favorable occupation sites. In addition, the plots exhibit not only straight and zigzag channels but also the same zigzag segments as preferentially sitting resident sites. These residences concern the first peak and shoulder observed at the highest loading. The plots indicate other trends that the probability of methane locations at the intersection portion decreases and that at the straight channel increases with increasing loading. Note that the greatest advantage of the ab initio fitted model is the one-to-one correspondence between the ab initio and the fitted energies, our outcome is accordingly expected as one of high reliability.

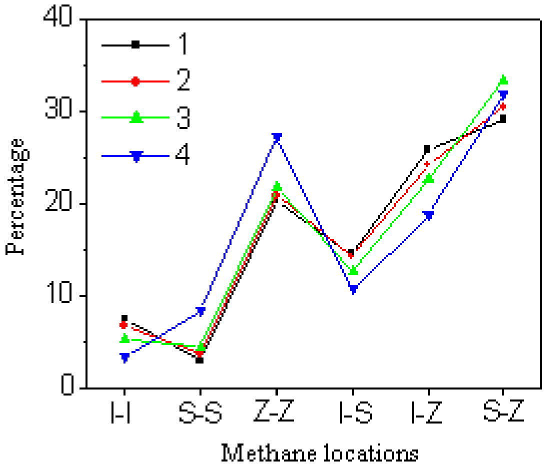

Figure 5. The relative residences of methane lied in the first peak of methane-methane RDFs at various loading; I, S and Z respectively referred to intersection, straight, and zigzag portions.

The self-diffusion coefficient in this study has been calculated according to the method described in ref. [28]. The obtained value of $5.53\text{x}10^{-9}$ $\text{m}^2.\text{s}^{-1}$ is in reasonable agreement with the one from PFG-NMR measurements [11], $1.0 \pm 0.2\text{x}10^{-8}$ $\text{m}^2.\text{s}^{-1}$ for one diffusive methane molecule per intersection.

The theoretical heat of adsorption $\langle H \rangle$ at $n_{ld}=1$ is obtained by following a definition:

$$\langle H \rangle = \langle U \rangle - RT \tag{4}$$

where R and T are the gas constant and temperature. $\langle U \rangle$ is an ensemble-averaged potential energy of the methane-silicalite interactions. The heat of adsorption calculated by ab initio model of -5 kcal.mol^{-1} agrees with experimental data of -4.8 and -6.7 kcal.mol^{-1} [29,30] and those obtained from previous models in a range from -4.3 to -5.8 kcal.mol^{-1} [8,10,12,14,18,31].

CONCLUSION

The significant contribution of this work is to reveal the importance of an ab initio fitted silicalite-1/methane model for the treatment of structural information. The dynamical results for self-diffusion coefficients are in satisfactory agreement to both experimental and theoretical data available. The reasonable agreement of activation energy and heat of adsorption with accessible data are presented. In consistency, a zigzag channel is preliminary favored for residences.

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