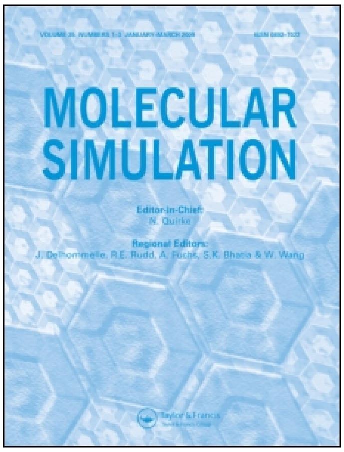

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Mechanism of Molecular Diffusion in Ice Crystals

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Mechanism of Molecular Diffusion in Ice Crystals

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We used molecular dynamics (MD) simulations to investigate the diffusion of O_2, N_2, CH_4, and CO_2 in a crystal of ice Ih. The results show that the diffusion mechanism for the molecules differs significantly from the interstitial mechanism that applies to small atoms such as helium. The air molecules hopped between stable sites by a new mechanism called the breaking-bond mechanism in which hydrogen bonds in the lattice are broken. The diffusion coefficients determined from the MD calculations are several orders of magnitude larger than the estimates under the assumption of the interstitial mechanism. We conclude that the repulsive interactive between the air and water molecules in ice is the dominant factor governing the diffusion mechanism.

Keywords: Molecular diffusion; Ice Ih; Molecular dynamics; Air molecules; Hydrogen bond

INTRODUCTION

Ice Ih is ordinary ice consisting of water molecules linked together by hydrogen bonds in a hexagonal framework with a very open structure [1]. A variety of molecules can be accommodated into the spaces in the lattice. The properties of such accommodated molecules, particularly gas molecules, are relevant to questions in subjects as diverse as geophysics, astronomy, and biology [2–4]. The diffusion of gas molecules is one of the primary topics in these research fields. Using Raman scattering of natural ice crystals recovered from the Antarctic ice sheet, Ikeda *et al.* [2] were able to study the diffusion phenomena of N_2 and O_2 molecules in ice. The results documented a process that cannot be observed on a laboratory time scale [3].

Small atoms such as He, Ne, and Ar in an ice lattice diffuse by the interstitial mechanism. Ikeda-Fukazawa *et al.* [5] performed molecular dynamics (MD) simulations of diffusion of He in ice Ih and found that the atom hops from one stable site to the adjacent stable site through a bottleneck in the energy barrier (Fig. 1). Ice Ih has two crystallographically non-equivalent interstitial sites designated Tu (uncapped trigonal) and Tc (capped trigonal) (Fig. 2). The Tu site is the stable site for the atoms. The diffusion process can be decomposed into two contributions: diffusion along the *c* axis (i.e. hops from one Tu site to an adjacent Tu site), and diffusion in *a*–*b* plane (i.e. hops from one Tu site to another Tu site through an adjacent Tc site).

The diffusion coefficient D at temperature T is proportional to $\exp(-Q/RT)$, where Q is the activation energy for a hop from a stable site to an adjacent site, and R is the gas constant. The potential barrier ΔE between the stable sites can be used as a measure of Q. The value of ΔE is calculated from the potential energies of the gas molecule in the lattice. The variation of the potential energy for a gas molecule during a hop parallel to the c-axis (i.e. Tu → Tu) in Fig. 3a is much less than that for a hop perpendicular to the *c*-axis (i.e. Tu → Tc → Tu) in Fig. 3b. The potential barrier ΔE is taken as the difference between the maximum and minimum energies. Figure 4 shows measured and calculated values of D and ΔE for various gas molecules. The data on D for He, Ne, and Ar (the open triangles) are from the literature [6–8]. Since the D values for O_2, N_2, CH_4, and CO_2 in ice are too small to measure directly, no experimental data have previously been reported. If the diffusion mechanism of these molecules is the interstitial mechanism, the D values

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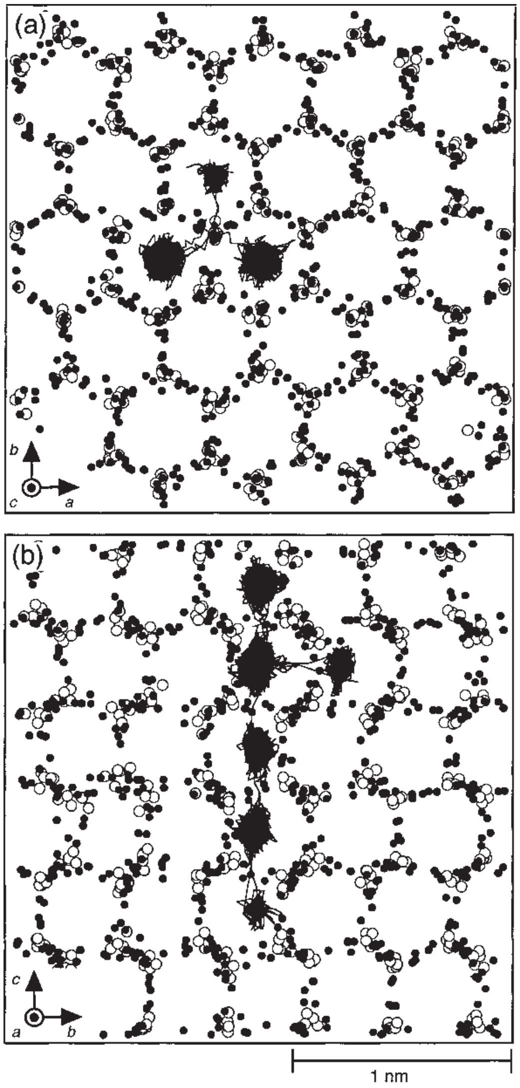

FIGURE 1 Trajectory of He for 560 ps at 270 K [5]. Projections are along (a) the *c* axis, and (b) and *a* axis. The open and solid circles are the initial positions of the O and H atoms in the ice lattice. The solid line is the trajectory of the center of He.

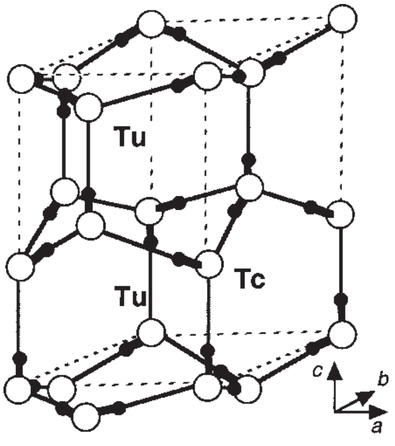

FIGURE 2 Crystallographic structure of ice Ih. The open and solid circles are the sites of the O and H atoms, respectively. The Tu interstitial site is centered in an open channel along the *c*-axis, whereas the neighboring Tc interstitial site is midway between H_2O molecules aligned along the *c*-axis.

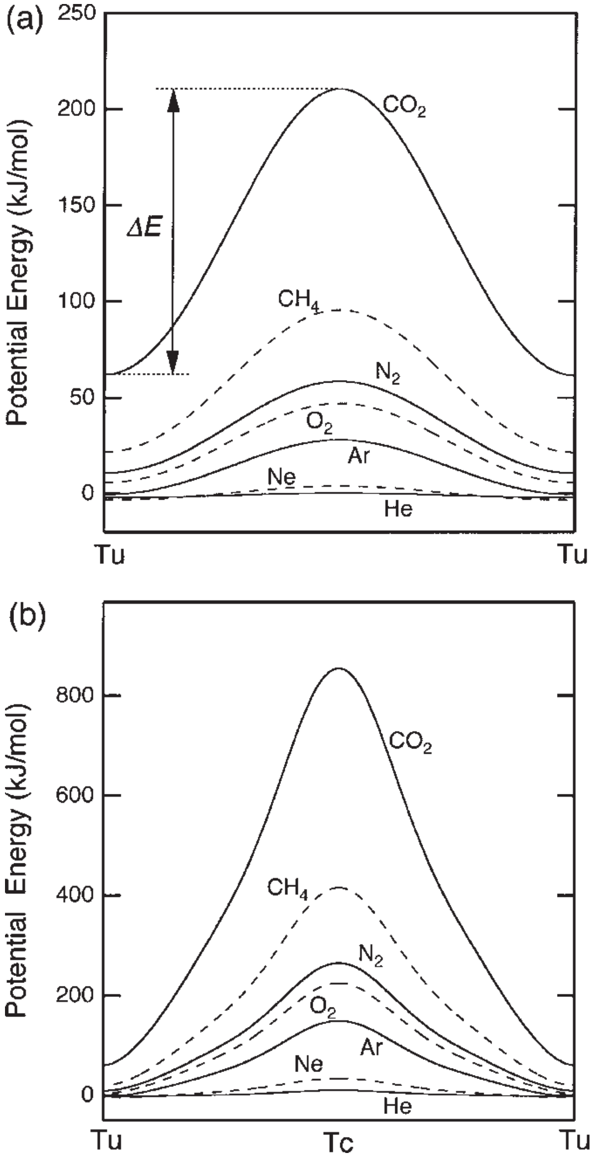

FIGURE 3 Variation of potential energy for various gas molecules during hops (a) parallel to the *c*-axis (i.e. Tu → Tu) and (b) perpendicular to the *c*-axis (i.e. Tu → Tc → Tu).

are assumed to be proportional to the ΔE value [9]. By extrapolating the fitting line to larger values of ΔE for O_2, N_2, CH_4, and CO_2, the values are estimated to be the values showed by the open circles in Fig. 4. The estimated values are at least several orders of magnitude smaller than those for the small atoms. However, such values are inconsistent with the results from the Raman spectroscopic study [2].

To investigate the diffusion mechanism of the air molecules in ice crystals, we did MD simulations of the diffusion of O_2, N_2, CH_4, and CO_2 in ice. The high potential energies for the molecules at the Tu site (i.e. Fig. 3a and b) suggests that the site is not a stable site for these molecules. Because the space of the Tu site is not large enough for these molecules, repulsive interactions dominate the interaction between the gas and water molecules in the Tu site. The MD

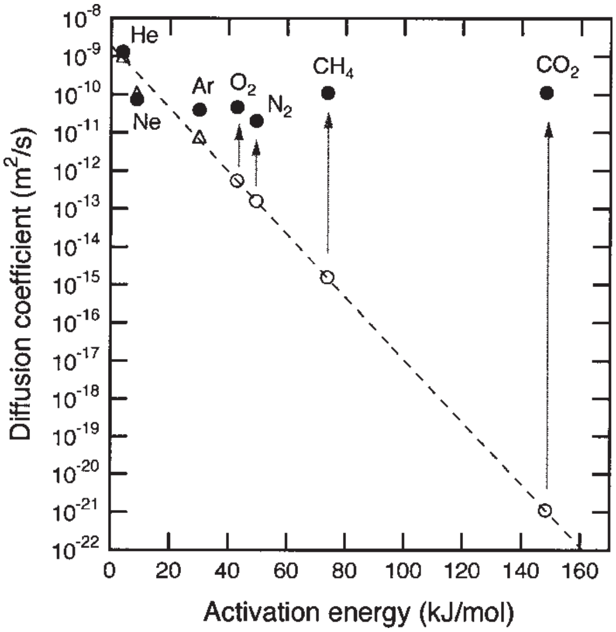

FIGURE 4 Relation between diffusion coefficient D and potential barrier ΔE for various gas molecules. Conditions are 270 K and one atom. The open triangles are the experimental data from the literature [6–8]. The open circles are the estimates under the assumption of the interstitial mechanism. The solid circles show the present results.

simulation is useful for investigating the stable site and the trajectory of the diffusion hops in the crystal.

MD CALCULATIONS

We used an atom–atom potential model, Kawamura potential model [10]. The Kawamura potential model has two-body interactions for all atom pairs and a three-body force. The two body interactions (i.e. Coulomb, short-range repulsion, van der Waals interactions, and covalent bond potentials) are given by

$$u_{ij}(r_{ij}) = \frac{z_i z_j e^2}{r_{ij}} + f_0(b_i + b_j)\exp\left(\frac{a_i + a_j - r_{ij}}{b_i + b_j}\right) - \frac{c_i c_j}{r_{ij}^6} + D_{1ij}\exp(-\beta_{1ij} r_{ij}) + D_{2ij}\exp(\beta_{2ij} r_{ij}) + D_{3ij}\exp\left\{-\beta_{3ij}\left(r_{ij} - \overset{*}{r}_{ij}\right)^2\right\}, \quad (1)$$

where r_{ij} is the distance between atoms i and j, and f_0 is a constant for unit adaptations between these terms. The z, a, b, and c are parameters of each atom type, and D_{ij}, b_{ij} and $\overset{*}{r}_{ij}$ are the parameters for intra-molecular interactions. The three-body force is used to constrain the intra-molecular angle (e.g. the H—O—H angle in water molecule). The three-body force is given by

$$u_{jij}(\theta_{jij}, r_{ij}) = -f_k[\cos\{2(\theta_{jij} - \theta_0)\} - 1]\sqrt{k_1 k_2}, \quad (2)$$

where

$$k_i = \frac{1}{\exp\{g_r(r_{ij} - r_m) + 1\}}. \quad (3)$$

θ_{jij} is the intra-molecular angle, and f_k and q_0 are parameters. The k_i defines the effective range of the three-body force. The potential parameters are listed in Table I. N_2 and O_2 are modeled as molecules with three point charges, because of neutral molecules [11]. The parameters were determined empirically by constraining the model to the experimental properties (e.g. crystallographic structure, density, dynamical motions, and vibrational energy) [5].

TABLE I Potential parameters used in the present simulations

	z	*Weight*	*a* (*Å*)	*b* (*Å*)	*c* (*kcal*$^{0.5}$ *Å*^{3} *mol*$^{-0.5}$)		
Two-body interactions							
O (H_2O)	−0.680	16.00	1.8345	0.136	24.200		
H (H_2O)	0.340	1.01	0.1156	0.036	0.000		
O (O_2)	0.366	16.00	1.6190	1.610	21.225		
N (N_2)	0.662	14.01	1.3970	0.135	21.480		
C (CH_4)	−1.200	12.01	2.1500	0.130	31.000		
H (CH_4)	0.300	1.01	0.0350	0.100	0.000		
C (CO_2)	−0.600	16.00	1.8300	0.135	30.800		
O (CO_2)	0.400	12.01	0.2100	0.100	0.000		
	D_{1ij} (*kcal/mol*)	b_{1ij} ($Å^{-1}$)	D_{2ij} (*kcal/mol*)	b_{2ij} ($Å^{-1}$)	D_{3ij} (*kcal/mol*)	b_{3ij} ($Å^{-2}$)	r^{*}_{3ij} (*Å*)
O—H group	−1314.0	2.77	0.0	2.2	10.7	6.60	1.110
O—O group	86154.84	5.913	−1629.32	1.512			1.6
N—N group	78691.87	5.796	−2525.07	1.248			1.6
C—H group	−1510.0	2.500	10290.58	5.0			
C—O group	92457.0	5.84	−6435.9	2.92			
	f_k (*J*)	q_0 (*deg*)	r_m (*Å*)	g_r (*Å*)			
Three-body interations							
H—O—H group	1.32×10^{-4}	99.50	1.39	9.7			
H—C—H group	1.31×10^{-4}	104.50	1.35	7.0			

We used a fundamental cell of ice Ih consisting of 360 water molecules in 45 unit cells. The structure of ice Ih as determined by X-ray diffraction [12] was used for the initial arrangement of oxygen atoms. The hydrogen atoms were randomly distributed at the double potential minimum between the O atoms according to the ice rules [13]. To equilibrate the fundamental cell, the MD code was run for 60 ps (picoseconds). Then, an air molecule was put in the ice cell. For the initial coordinates, the center of the air molecule was put in the center of the Tu site. The fundamental cell had three-dimensional periodic boundary-conditions.

The MD calculations were performed using the program MXDORTO developed by Kawamura [14]. The velocity Verlet algorithm [15] and the Ewald method [16] were used for atomic motions and for electrostatic interactions, respectively. The time step used in the calculations was 0.4 fs (femtoseconds). Temperature was maintained at 230, 240, 250, 260, and 270 K, whereas the pressure was kept at 0.1 MPa.

RESULTS AND DISCUSSION

We found that the diffusion path of CO_2 differs significantly from that of the interstitial mechanisms. In the interstitial mechanism, the diffusing molecule hopes from the Tu site to an adjacent Tu site without distorting the lattice (see Fig. 1). However, the simulation instead shows the migrating of the CO_2 molecule from a position between two formerly-occupied lattice O atoms, hereafter referred to as the B site, to an adjacent B site by pushing aside H_2O molecules in the ice lattice. Figure 5 shows the trajectory of the center of mass of the CO_2 molecule at 270 K for a period of 10.64 ns (nanoseconds) in the projections along the *c*, and *a* axes.

Figure 6 is a snapshot of the CO_2 molecule in the B site. The water molecular marked by the arrows have been pushed aside by the CO_2 molecule. The stable B site for the CO_2 molecule is in a gap created by the moving of the two water molecules, a site that was formerly the center of the O—O bond. This site is the point with minimum potential energy for the CO_2 molecule in the distorted lattice. The repulsive interaction between the CO_2 and H_2O molecules distorts the structure of the ice lattice and breaks a hydrogen bond. This type of diffusion mechanism, hereafter the breaking-bond mechanism, has not been observed for any other crystal. The reason it has not been observed in other crystals might be related to the requirement that the intermolecular bonds be weak, a requirement satisfied by the relatively weak hydrogen bonds in ice. The simulations showed that O_2, N_2, and CH_4 also diffused by the breaking-bond mechanism.

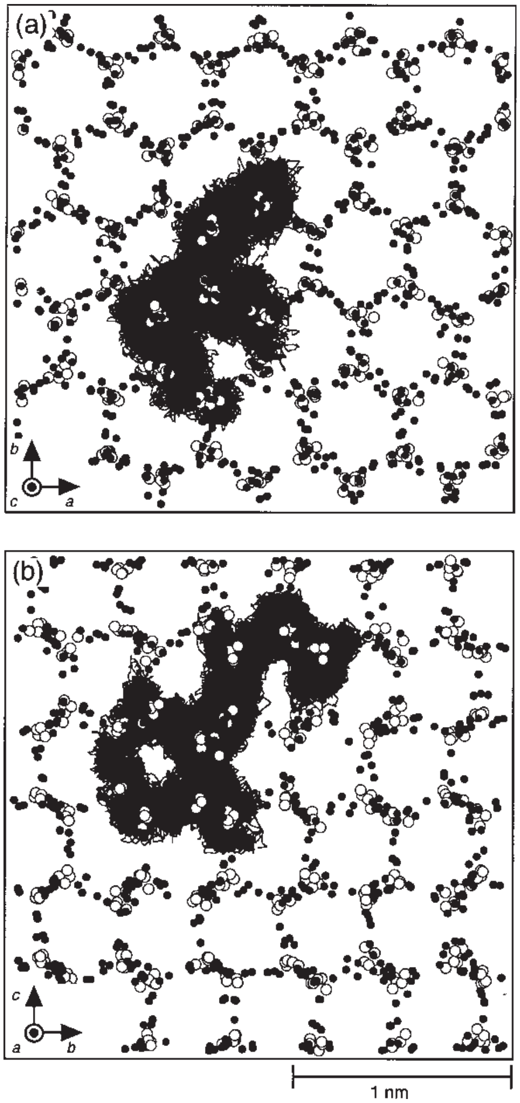

FIGURE 5 Trajectory of CO_2 for 10.64 ns at 270 K. Projections are along (a) the *c* axis, and (b) the *a* axis. The open and solid circles are the initial positions of the O and H atoms in the ice lattice. The solid line is the trajectory of the center of mass of CO_2.

Figure 7 shows the trajectories of a CO_2 molecule and the nearby H_2O molecules in the ice lattice as the CO_2 hop from one B site to an adjacent B site. The H_2O molecules (O_1 and O_2 in Fig. 7) with the proton without hydrogen bond are displaced from their original positions in the lattice. Due to the remaining hydrogen-bonds with the surrounding H_2O molecules, the displaced H_2O molecules are pushed towards their original positions. When one of the displaced H_2O molecules (O_1) returns to its original position, the CO_2 molecule migrates to the adjacent B site and the H_2O marked by O_3 is displaced from the lattice site. This process can then repeat as the CO_2 molecule migrates through the ice.

We now use the hopping frequency from the simulations Γ to estimate the diffusion coefficient. The diffusion coefficient of an accommodated

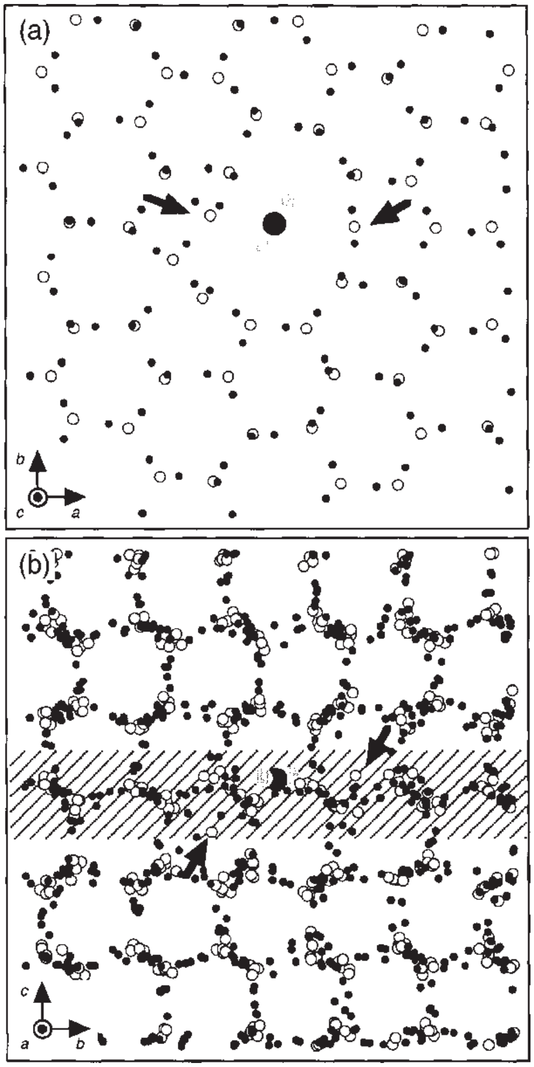

FIGURE 6 Snapshot of ice with a CO_2 molecule at 10.08 ps. The open circles are O atoms, the solid back circles are H atoms, and the solid gray circles are the CO_2 molecule. Projections are along (a) the *c* axis, and (b) the *a* axis. The plotted depth along the *c* axis in (a) is the hatched region in (b).

molecule in one direction is given by [17]

$$D = \alpha \lambda^2 \Gamma, \qquad (4)$$

where λ is the hop distance in the direction, and α is the number of equivalent paths for a forward hop. For a forward hop in the a–b plane, two equivalent pathways into an adjacent site exist. For a forward hop along the *c* axis, the channel of two equivalent exist splits into three equivalent pathways. Thus, the value of α is equal to 1 for both directions. The hop distance λ along the *c* axis is $c/4$ and that in the a–b plane is $a/2$. The hop frequency Γ is given by N/t, where N is the number of the observed hops during the time period of the calculation t (i.e. 10.64 ns). Using Eq. (4), the average values of D for CO_2 at 270 K for diffusions parallel and perpendicular to the *c* axis are calculated to be 7.1×10^{-11} and $1.5 \times 10^{-10}\ \mathrm{m^2/2}$, respectively. The standard deviations of the coefficients are 1.0×10^{-11} and $1.5 \times 10^{-11}\ \mathrm{m^2/s}$, respectively.

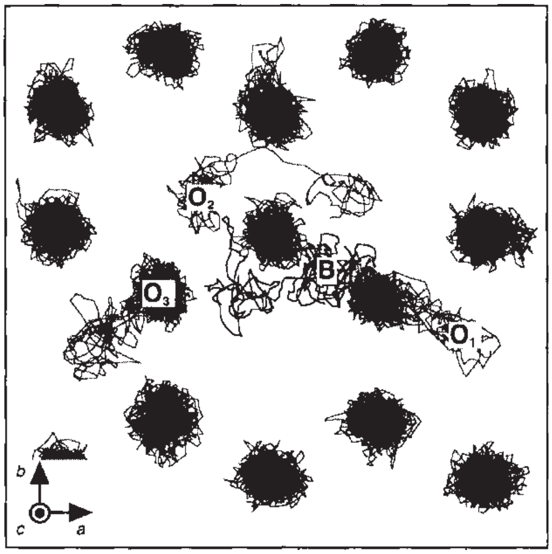

FIGURE 7 Trajectories of H_2O molecules (the gray lines) in the lattice during a hop of CO_2 (the black line) from a B site to an adjacent B site. Projections are along the *c* axis.

Figure 8 shows the temperature dependence of D for CO_2. The open squares and triangles show the coefficients for diffusion parallel and perpendicular to the *c* axis, respectively. The solid circles

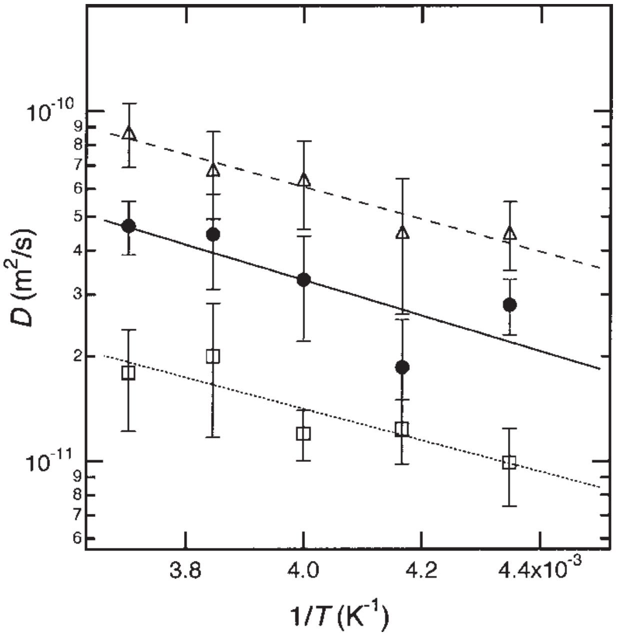

FIGURE 8 Temperature dependence of diffusion coefficient D of CO_2. The open squares and triangles show the coefficients of diffusion parallel and perpendicular to the *c* axis, respectively. The solid circles are the average values. The dotted, dashed, and solid lines show the fitting lines of the coefficients for diffusions parallel and perpendicular to the *c* axis and of the averaged coefficients, respectively.

TABLE II Parameters for diffusion coefficients

	Diffusion along c-axis		*Diffusion in a−b plane*		*Average*	
	Q (kJ/mol)	*D_0 (m^2/s)*	*Q (kJ/mol)*	*D_0 (m^2/s)*	*Q (kJ/mol)*	*D_0 (m^2/s)*
O_2	8.7	9.1×10^{-10}	8.9	4.3×10^{-9}	9.7	3.5×10^{-9}
N_2	4.2	7.4×10^{-11}	7.1	8.1×10^{-10}	5.1	2.0×10^{-10}
CH_4	45.8	2.4×10^{-2}	34.4	6.2×10^{-4}	37.5	1.5×10^{-3}

show the average diffusion coefficients. The diffusion coefficient at temperature T is fit to

$$D = D^0 \exp\left(-\frac{Q}{RT}\right), \tag{5}$$

where D^0 is a constant. The fit values of Q and D^0 are 18.9 kJ/mole and $4.5 \times 10^{-7}\,\mathrm{m^2/s}$ for the diffusion parallel to the c axis, 13.1 kJ/mole and $5.8 \times 10^{-8}\,\mathrm{m^2/s}$ for the diffusion perpendicular to the c axis, and 14.7 kJ/mol and $9.1 \times 10^{-8}\,\mathrm{m^2/s}$ for the average coefficient. The values for O_2, N_2, and CH_4 are listed in Table II.

The Q values for CH_4 are larger than those for the other molecules for the following reason. For diffusion with the breaking-bond mechanism, the strength of the hydrogen bond in the lattice and the localized vibrational motion of the accommodated molecule in the lattice determine the activation energy. Therefore, as the strength of the hydrogen bond does not depend on the type of the accommodated molecule, the localized vibrational motion of the accommodated molecule in ice determines the difference in the activation energy. The strong coupling between the localized low-frequency vibrations of the air molecules and the lattice vibration govern the breaking and reforming of the hydrogen bonds in the lattice. The low-frequency vibrations of the air molecules in the ice lattice can be decomposed into two contributions: the localized translational motion of the center of mass, and the rotational oscillation about this center. The latter does not occur for a spherical molecule such as CH_4. Therefore, the activation energy of CH_4 is higher than the uni-axial molecules such as O_2, N_2, and CO_2.

The solid circles in Fig. 4 show the D values determined from the MD calculations at 270 K. The values are higher than the estimates under the assumption of the interstitial mechanism (i.e. the open circles). The difference between the estimate and the present result increases with an increase in the molecular size. For example, the calculated diffusion coefficient is 11 orders of magnitude higher than the interstitial estimate for the CO_2 molecule. The molecular-type dependence for the diffusion with the breaking-bond mechanism (i.e. O_2, N_2, CH_4 and CO_2) is small because the strength of the hydrogen bond is the dominant factor for the diffusion coefficient, and this is independent of molecule type. For the interstitial mechanism, the potential barrier between the stable sites is the dominant factor governing the diffusion coefficient. Therefore, the estimates under the assumption of the interstitial mechanism are extremely small in comparison with the D values determined from the MD calculations.

CONCLUSIONS

We performed MD simulations of the diffusion of air molecules (O_2, N_2, CH_4, and CO_2) in an ice crystal, and observed the hops of these air molecules from a stable site to an adjacent site. The results show that the stable site for these molecules is the B site and the diffusion mechanism is the breaking-bond mechanism. The molecules migrate between the stable sites by breaking the hydrogen bonds in the lattice. We conclude that the repulsive interaction between the air and water molecules is the dominant factor governing the diffusion mechanism.

The diffusion coefficients determined from the MD calculations are larger than the estimates under the assumption of the interstitial mechanism. This result implies that the diffusion coefficients of the greenhouse gases (CO_2 and CH_4) in polar ice sheets are higher than the previous estimates. The result has important implications for reconstructions of the paleoatmosphere from polar ice cores.

Acknowledgements

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