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Diffusion on (110) Surface of Molecular Crystal Pentaerythritol Tetranitrate

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Abstract

Using classical molecular dynamics simulations, we investigate the diffusion mechanisms of admolecules on the (110) surface of molecular crystal pentaerythritol tetranitrate. Our results show that (1) admolecules are stable at off lattice sites, (2) admolecules diffuse along close-packed $\left[1\bar{1}1\right]$ and $\left[\bar{1}11\right]$ directions, and (3) admolecules detach from the surface at 350K and above. Based on the number of diffusion jumps as a function of temperature, we estimate the jump frequency to be $v = 1.14 \times 10^{12} e^{-0.08eV/kT}$ per second.

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The molecular crystal pentaerythritol tetranitrate (PETN), an energetic material, has both civilian and defense applications. For example, it is used in the treatment of cardiovascular diseases [1]. In the form of a powder, PETN is also effective in explosive ignition, and its performance in this application is known to be strongly related to the crystallite particle size, morphology, and surface area. As particles coarsen, effectiveness decreases. To make better use of the PETN powder, it is therefore critical to understand the physical mechanisms of mass transport that govern the coarsening process.

Experimental characterizations show that PETN particles are faceted and show a wide range of different morphologies [2]. From the theoretical perspective, kinetic Monte Carlo simulations can provide much insight into the coarsening of PETN particles [3], provided that the diffusion mechanisms and diffusion coefficients are known [4]. For simple processes, direct experimental characterization may be possible [5]. More often, kinetic processes are too complex or too fast to be experimentally observed. For inorganic materials such as metals, surface diffusion has been exhaustively investigated [6]. In contrast, the surface diffusion of molecular crystals has seldom been investigated by atomistic simulations [7].

Using classical molecular dynamics simulations, we investigate the diffusion mechanisms of admolecules on the PETN (110) surface, which is the thermodynamically most preferred surface. The atomic arrangement in each PETN molecule is shown in Fig. 1(a), and the body-centered-tetragonal (BCT) crystalline symmetry of PETN in Fig. 1(b). The projections of atomic positions along [100] and [001] directions [Fig. 1(c and d)] demonstrate how a molecule bonds to or connects with its neighbors. The two molecules in the unit cell of Fig. 1(c) differ in orientation by a ninety-degree rotation about the <001> direction. We use the COMPASS force field of Sun et al [8, 9] to describe the interactions of PETN atoms and molecules. This choice is based on the fact that the force field reproduces crystalline structure, sublimation energy, lattice constants, and elastic constants of PETN [9, 10]. This force field is also used in our recent studies of surface formation energies [3].

In preparation for finite temperature simulations, we have determined the lattice constants of PETN as a function of temperature through constant temperature and constant stress simulations of a perfect PETN crystal. The simulation cell consists of

$4\times4\times6$ unit cells (as shown in Fig. 1c) along [100], [010] and [001] directions, respectively; a perfect crystal is represented through periodic boundary conditions. The Ewald summation method is used for the calculation of electrostatic and van der Waals interactions. The temperature dependence of lattice constants is shown in Fig. 2.

Based on the finite temperature lattice constants, we construct a simulation cell for the surface diffusion studies. As shown in Fig. 3, an admolecule sits on the thermodynamically most preferred (110) surface. The horizontal dimensions of the simulation cell are eight molecular layers along [001] and 10 molecular layers along $[1\,\bar{1}0]$ directions; periodic boundary conditions apply to both of the horizontal directions. The vertical dimension, along the z-axis, is eight molecular layers in thickness. Atoms in the three bottom layers are fixed to their perfect lattice positions according to the lattice constants of finite temperature to mimic a large bulk under the surface. This thickness of the fixed region is larger than the cutoff distance of the short range interaction. However, long range interactions between surface atoms and those deeper under the surfaces are omitted here. We conjecture that such omission is reasonable because our focus is on molecular migration and therefore energy differences among various surface positions, which are generally insensitive to long range interactions. Three other molecular layers immediately above the fixed region are subjected to temperature control according to the Nosé-Hoover algorithm [11, 12], to maintain a constant temperature simulation. The other molecular layers rigorously follow Newtonian dynamics to avoid any artifacts from temperature control. The Newtonian equations are integrated using the velocity-Verlet algorithm [13] with an integration step of 0.5 fs. Since a free surface exists in our diffusion study, the three-dimensional Ewald summation method is modified by adding a correction term to remove the interaction force between the images of the simulation cell along the z-direction [14].

In all finite temperature simulations (at 100K, 150K, 200K, 250K, 300K, 350K, and 450K), the admolecule quickly relaxes to lower energy configurations, as marked by the large circle in Fig. 4(a), even though it starts from a lattice position. The accompanying quenching leads to the same relaxation, with an energy decrease of 0.13 eV. As an extension, we have checked the stable positions of dimers (two admolecules next to each other), and found that they prefer lattice positions, unlike monomers.

The dynamic trajectories of a single admolecule show that their diffusion is primarily along the $\left[1\bar{1}1\right]$ and $\left[\bar{1}11\right]$ directions on the (110) surface. Shown in Fig. 4 are trajectories of the admolecule over the period of 75 ps at 100K and 300K, respectively. Based on the trajectories, we derive the number of molecular jumps among stable positions, ignoring immediate backtrack jumps. At each temperature, there are five independent simulations, each lasting for 75 ps. At each moment, the molecular position is related to a stable position, indicated by the large circle in Fig. 4(a). The molecule is considered to have jumped to another position when it is within 0.35c of the new position and stays for more than 0.1 ps (typical atomic vibration period); c is the lattice constant along [001]. The critical separation of 0.35c corresponds to the distance between a lattice site and nearby stable off-lattice position of minimum energy; for reference, the distance between the two nearest stable positions is 1.10c. The average number of jumps per unit time (from high temperature simulations), together with error bars, is shown in Fig. 5 as a function of temperature. The fitted functional dependence on temperature is $\nu = 1.14 \times 10^{12} e^{-0.08eV/kT}$ per second

Finally, the admolecule detaches at 350K; that is, its upward displacement is larger than one inter-layer distance of 0.35c, as shown in Fig. 6. For the five independent simulations at 350K, the time it takes for the admolecule to detach varies. But in all cases, the admolecule detaches within 75 ps. At even higher temperature (450K), an admolecule first detaches from the surface as at 350K and subsequently evaporates. The detachment of admolecules at 350K, a little above room temperature, may lead to substantially faster diffusion and thereby may be responsible for the changes in the crystallite properties of PETN.

We note that the admolecule diffusion does not follow a typical pattern of vibration and jump, in contrast to adatom diffusion in metals. The admolecule gradually diffuses from one site to another (instead of suddenly jumping to another site), probably because the four legs of each admolecule switch from one substrate molecule to another. The coordinated motion facilitates the molecular diffusion, and we expect this pattern of gradual diffusion to be generic to molecular crystalline surfaces.

In summary, we have used force-field based molecular dynamics to investigate the diffusion mechanisms and estimate the jump frequency of an admolecule on the

PETN (110) surface. Our studies reveal four features. First, the admolecule is more stable at an off-lattice site than a lattice site by 0.13 eV. Second, the admolecule diffuses primarily along the $\left[1\bar{1}1\right]$ and $\left[\bar{1}11\right]$ directions on the (110) surface. Third, the jump frequency of the admolecule is $v = 1.14 \times 10^{12} e^{-0.08eV/kT}$ per second. Finally, the admolecule starts to detach at 350K.

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Figure Captions:

Fig. 1: (a) Atomic arrangement of a PETN molecule, (b) the BCT crystalline structure of PETN, and (c and d) projections of atomic positions along [100] and [001] directions. The lattice constants are *c* along [001] and *a* along [100] and [010] directions.

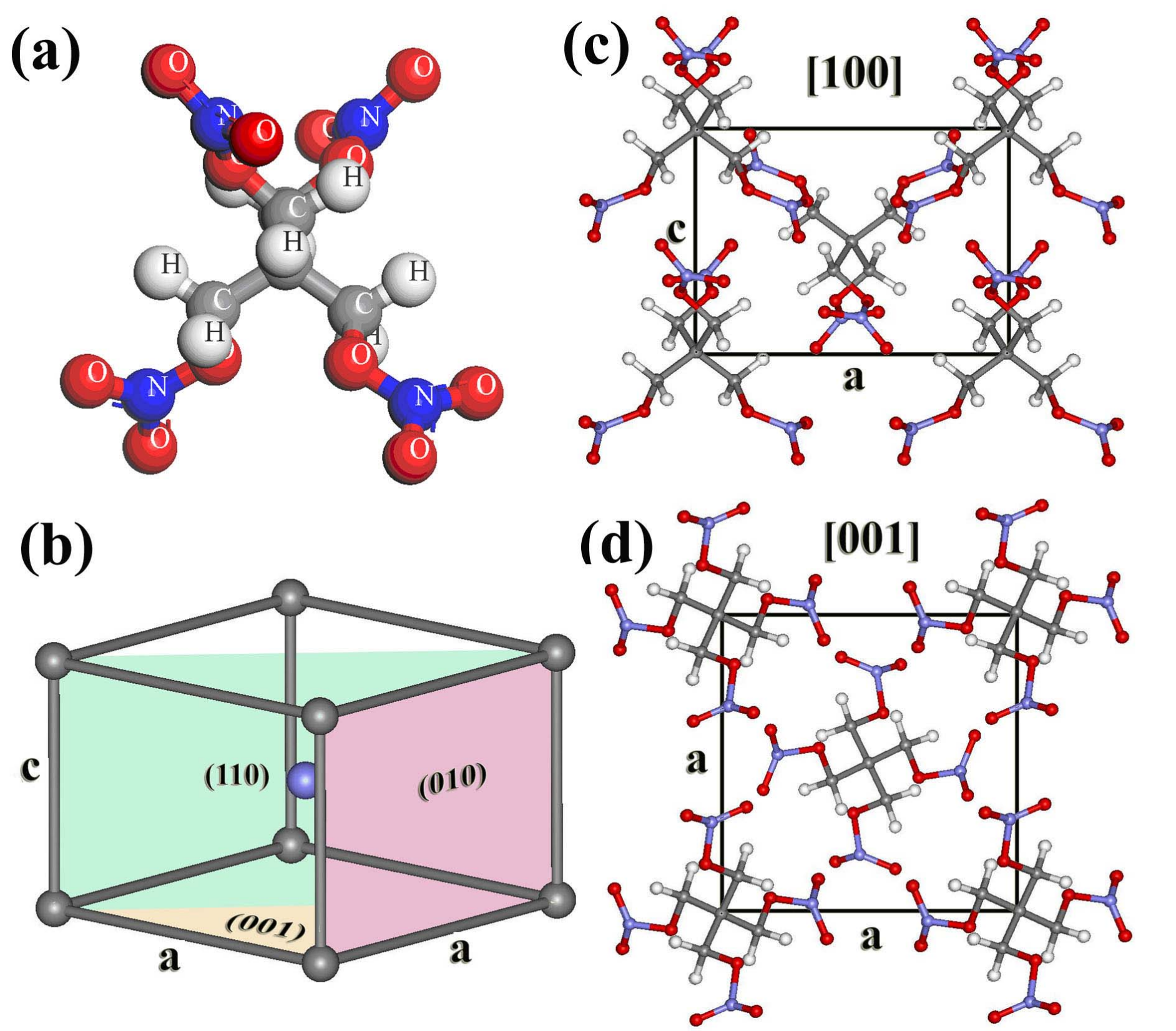
Fig. 2: Temperature dependence of lattice constants *a* (solid circles) and *c* (open circles), as defined in Fig. 1(b, c and d).

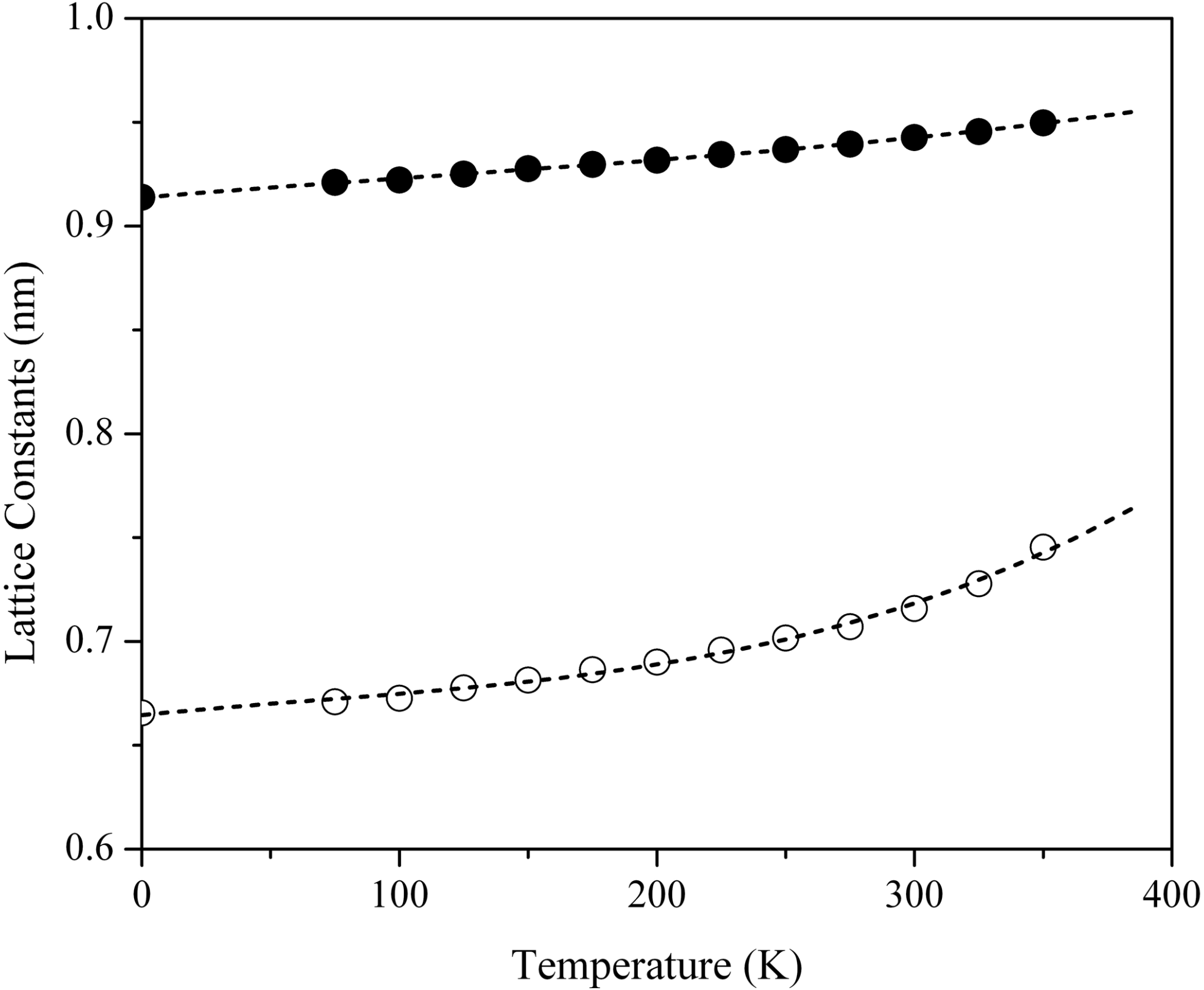
Fig. 3: Atomic configuration of a typical simulation cell.

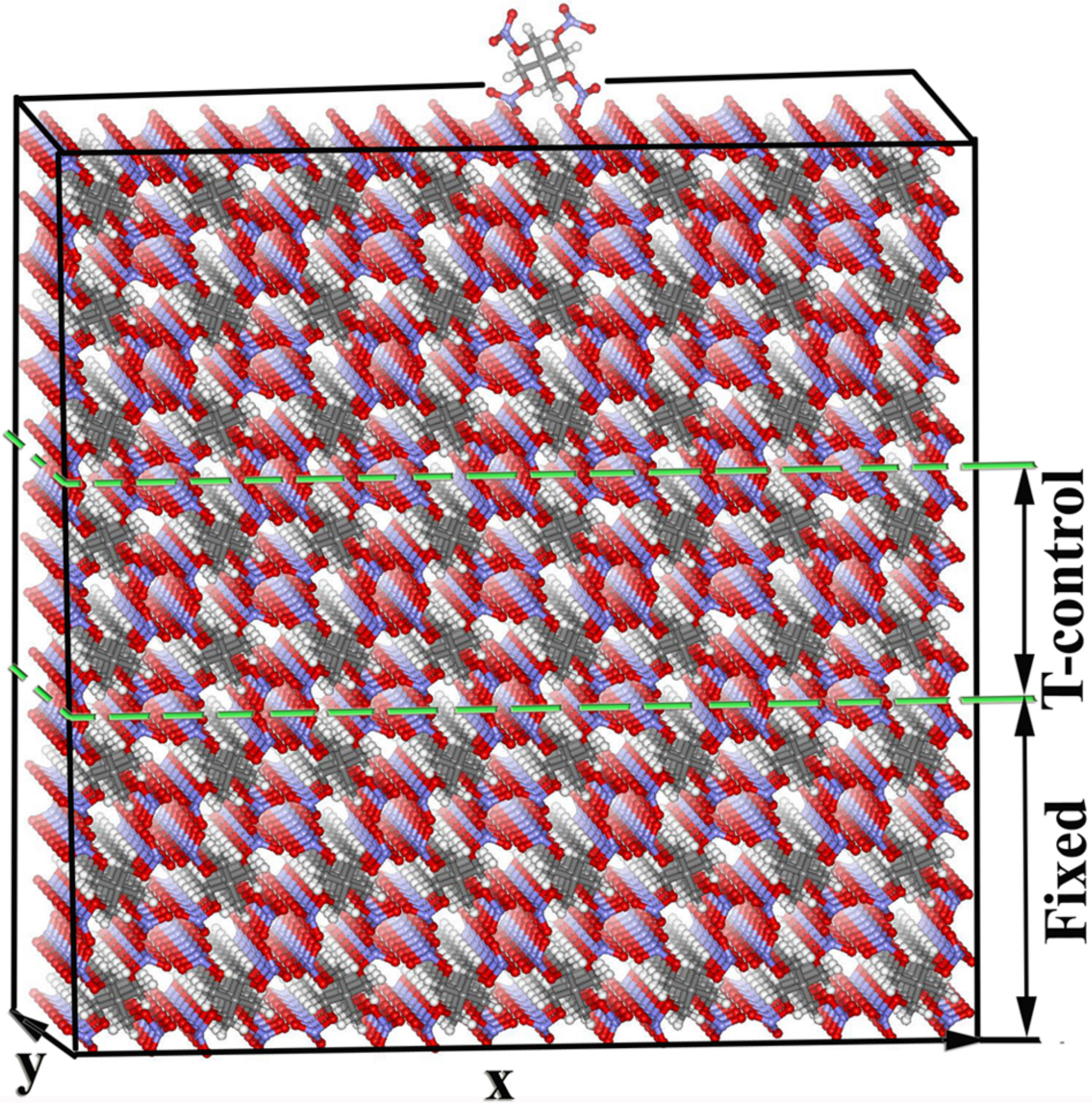
Fig. 4: Trajectories of the diffusing admolecule, or the center carbon in the admolecule to be precise, during 75 ps at low temperature 100 K (a) and the high temperature 300K (b). The solid circles represent molecules on top layer of surface, and the open circles represent molecules right on the surface.

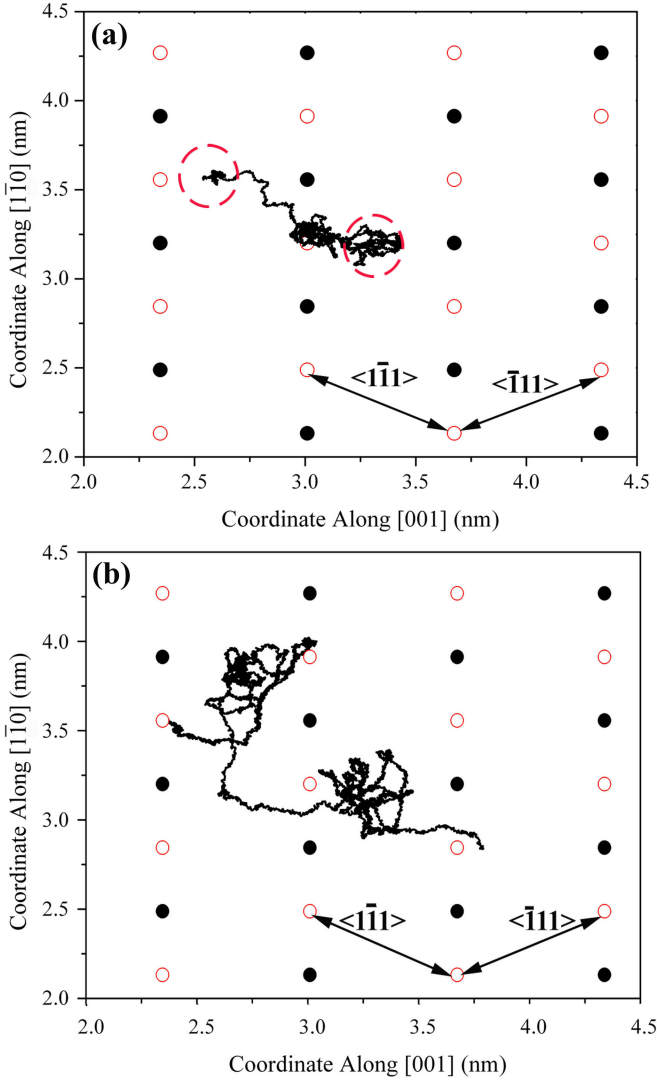
Fig. 5: Jump frequency of admolecule as a function of temperature. The melting temperature T_m is 414K [8].

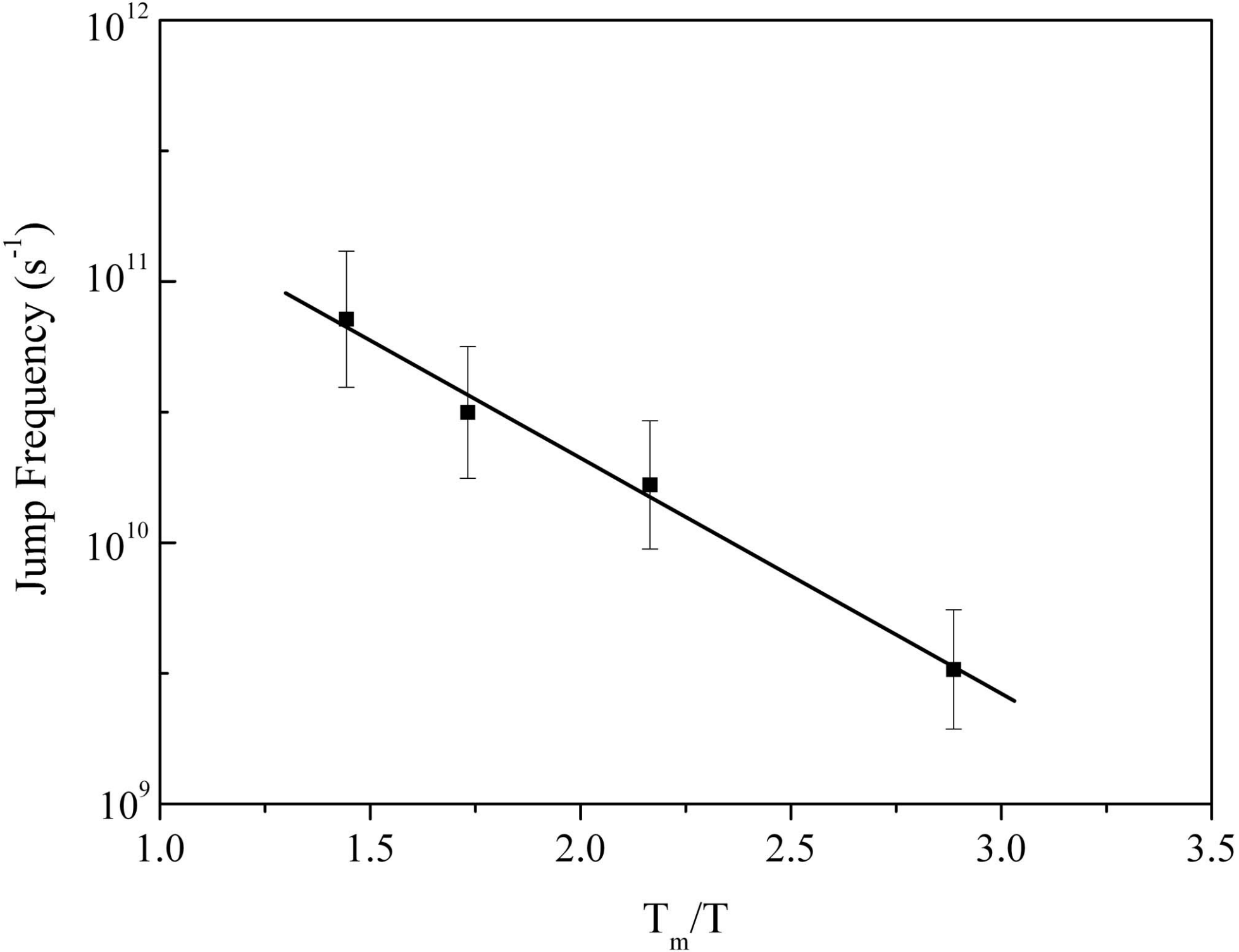
Fig. 6: Vertical displacement of the diffusing admolecule at 350K, as a function of time.

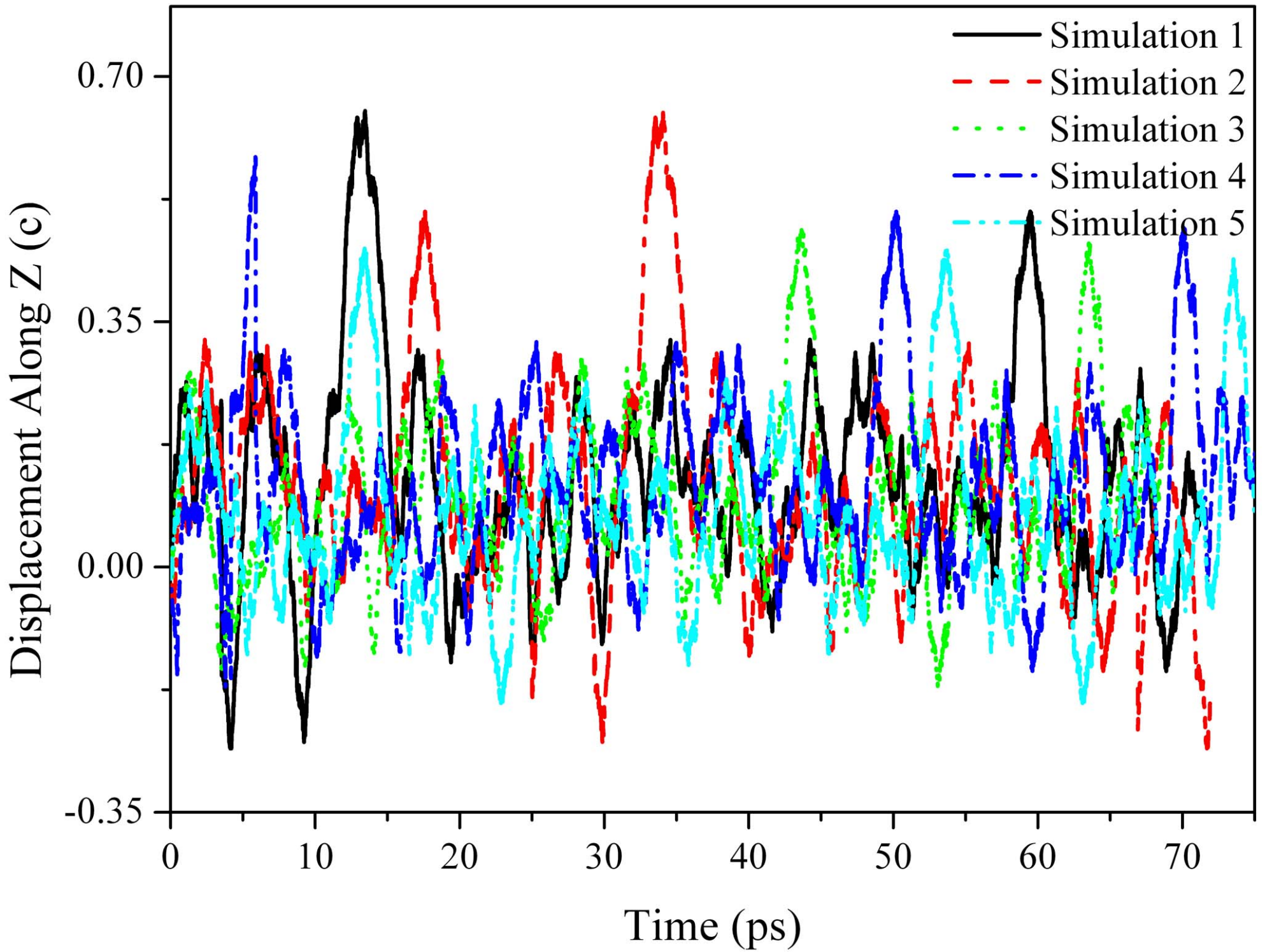

(a)
O
N
C
H
(b)
c
(110)
(010)
(001)
a
a
(c)
[100]
c
a
(d)
[001]
a
a


1.0
0.9
0.8
0.7
0.6
Lattice Constants (nm)
0
100
200
300
400
Temperature (K)


T-control
Fixed
y
x


(a)
(b)
Coordinate Along [1$\bar{1}$0] (nm)
Coordinate Along [001] (nm)
<1$\bar{1}$1>
<$\bar{1}$11>
2.0
2.5
3.0
3.5
4.0
4.5


Jump Frequency (s-1)
10^12
10^11
10^10
10^9
1.0
1.5
2.0
2.5
3.0
3.5
Tm/T


Simulation 1
Simulation 2
Simulation 3
Simulation 4
Simulation 5
0.70
0.35
0.00
-0.35
Displacement Along Z (c)
0
10
20
30
40
50
60
70
Time (ps)