The Dependence on Lattice Parameter in the Rotational Potential of the Methane Molecule in Argon Matrix

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Abstract

The rotational potential of methane molecule dispersed in rare gas matrix is expressed by 3rd, 4th, and 6th orders of orientational functions both in face-centered cubic lattice and in hexagonal lattice. We reformulate the angular variation of this potential using the angle about the (100), (−110), or (111) axis, so that we could see the rotational motion more directly. The most stable state is discussed among the typical orientations. In addition, the dependence on the separation between the tetrahedral molecule and neighboring rare gas atoms is derived in the orientational potential. From the potential analysis, we could not specify the optimum value of the separation shifted by the local lattice deformation. Also we compute the rotational energy in terms of one particle approximation, and compare the result in fcc lattice with the observation.

1. Introduction

Rare gas solid forms face-centered cubic (fcc) lattice structure in lower temperature. The distance between the nearest neighbors, R_x, in solid Ar or Kr is 0.3755 nm or 0.4992 nm[1], respectively. In phase II (the partially disordered phase) of solid CH_4, the centers of molecules construct the fcc lattice. In this phase, R_x is 0.4172 nm[2]. The value is intermediate between that of Ar and Kr. Next, in the system containing the isolated methane molecule replaced with a rare gas atom, the lattice around the tetrahedral molecule should be slightly deformed due to the mismatch of effective molecular size. The relaxation to the more stable state by shift of atomic positions gives rise to the change of the orientational potential, which is sensed by the central molecule. We evaluate the R_x-dependence of the interaction between the rotating molecule and the adjacent rare gas atoms. The orientational potential is usually described by Euler angles, or three rotational angles. Therefore, it is not easy to catch the actual motion using them, so that we establish the expressions in terms of a single angle. This formulation must facilitate the study of the R_x-dependence. The variation of potential can be depicted

as a function of the angle and the intermolecular distance. It is computed in fcc lattice and also in hexagonal closest packing (hcp) structure. We search the most probable orientation. Finally, we calculate the rotational energy under the derived field strength to investigate the effect of lattice deformation.

2. Computational Method

The rotational Hamiltonian of the molecule in the field from neighboring atoms is set up under the single particle approximation as a function of Euler angles $\omega = \{\alpha, \beta, \gamma\}$ [3] as follows:

$$H = K(\omega) + V_{346}(\omega) \tag{1}$$

where K is the kinetic part, and the rotational potential is expressed as

$$V_{346}(\omega) = \alpha_3 u_1(\omega) + \beta_4 V_4(\omega) + \beta_6 V_6(\omega) \tag{2}$$

Here, u_1 is the first component of 3rd order of tetrahedral potential. This corresponds to one component of octopole. The function V_4 or V_6 has the octahedral symmetry. It is normalized as

$$\int d\omega \, |V_j(\omega)|^2 = 8\pi^2 \quad (j = 3,4,6) \tag{3}$$

Table 1. The field strength in the 3-rd, 4-th, and 6-th order at three values of R_x. (B: rotational constant, 0.652 meV)

R_x/nm	α_3/B	β_4/B	β_6/B	β_6/β_4
3.700 (fcc)	0.0	17.86	-21.96	-1.230
(hcp)	-26.02	4.63	-15.63	-3.38
3.755 (fcc)	0.0	13.22	-16.14	-1.221
(hcp)	-19.02	3.43	-11.49	-3.35
3.800 (fcc)	0.0	10.33	-12.58	-1.218
(hcp)	-14.66	2.68	-8.95	-3.34

Table 2. The potential at the specific orientations in three values of R_x.

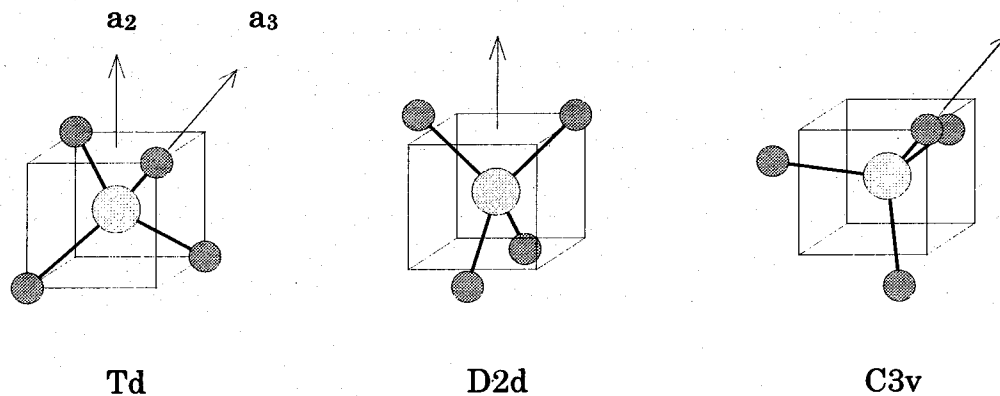| R_x/nm	V_{346}/B (T_d)	V_{346}/B (D_{2d})	V_{346}/B (C_{3v})
3.700 (fcc)	-25.60	68.31	-59.36
(hcp)	-68.48	44.58	-33.47
3.755 (fcc)	-18.53	50.26	-43.76
(hcp)	-50.07	32.70	-24.57
3.800 (fcc)	-14.37	39.18	-34.15
(hcp)	-38.89	25.54	-19.18

Fig. 1. Typical orientations of the tetrahedral molecule. A cube represents the octahedral field. The arrow a_2 is two-fold axis and a_3 is three-fold axis in the molecule.

and the function u_1 is given by

$$u_1(\omega) = \sqrt{7} \cdot V_3(\omega) \qquad (4)$$

The expansion coefficient α_3, β_4 or β_6 in (2) gives the field strength[4] of each order. This can be estimated by atom-atom pair wise potential. We use the values in exp-6 type of potential given by Bartell between proton in CH_4 and Ar atom[2]. In three values of R_x, these coefficients in fcc and in hcp lattices are given in Table 1. In the former lattice, cubic symmetry produces $\alpha_3 = 0$. In the latter, the 3rd order term contributes mainly, and the ratio β_6/β_4 is quite large. This ratio is related with the stable orientation[5] in the potential.

3. Computational Potential

The potential is evaluated at representative three orientations (T_d, D_{2d}, C_{3v}) as shown in Table 2. One member of each orientation is illustrated in Fig.1. The most stable is C_{3v} in fcc lattice and T_d in hcp. Moreover, we may say that the potential increases under the expansion of lattice for C_{3v} orientation. Both lattices have the same tendency. In contrast, for D_{2d} orientation it decreases probably due to the large relaxation from the high tension in unstable rotational state[6].

The potential consists of three terms as in (2). Because the rotational functions of this equation are described in term of three angles $\{\alpha, \beta, \gamma\}$, generally it is not easy to see how to rotate. By the combination of three successive rotations, we can find a definite type of rotation about the certain axis. In Table 3, the explicit expressions of octopole moments u_τ ($\tau = 1 \sim 7$) are given, and V_4, V_6 are also expressed in Table 4. It is convenient to investigate the rotational motion when we use a single angle θ in shifting from one orientation to other. It is possible to reformulate the equation in rotating about, e.g. (001), (-110), or (111) axis. We derive new expressions as shown in Tables 5 and 6. From the table, we can say that the 3rd order of function u_τ is reflected on 3-fold symmetry especially for the rotation about (111)

Table 3. The 3rd order of tetrahedral functions expressed by $\{\alpha, \beta, \gamma\}$.

$$u_1(\{\alpha, \beta, \gamma\}) = \frac{1}{2}[\cos\beta(1-3\cos^2\beta)\cdot\sin 2\alpha\cdot\sin 2\gamma + 2\cos 2\beta\cdot\cos 2\alpha\cdot\cos 2\gamma]$$

$$u_2(\{\alpha, \beta, \gamma\}) = \frac{\sqrt{15}}{8}[-\sin\beta(1+\cos^2\beta)\cdot\sin 2\alpha\cdot\cos 3\gamma - \sin 2\beta\cdot\cos 2\alpha\cdot\sin 3\gamma$$
$$+ \sin\beta(1-3\cos^2\beta)\cdot\sin 2\alpha\cdot\cos\gamma - \sin 2\beta\cdot\cos 2\alpha\cdot\sin\gamma]$$

$$u_3(\{\alpha, \beta, \gamma\}) = \frac{\sqrt{15}}{8}[\sin\beta(1+\cos^2\beta)\cdot\sin 2\alpha\cdot\sin 3\gamma - \sin 2\beta\cdot\cos 2\alpha\cdot\cos 3\gamma$$
$$+ \sin\beta(1-3\cos^2\beta)\cdot\sin 2\alpha\cdot\sin\gamma + \sin 2\beta\cdot\cos 2\alpha\cdot\cos\gamma]$$

$$u_4(\{\alpha, \beta, \gamma\}) = -\frac{\sqrt{15}}{2}\sin^2\beta\cos\beta\cdot\sin 2\alpha$$

$$u_5(\{\alpha, \beta, \gamma\}) = \frac{\sqrt{15}}{8}[\sqrt{\frac{3}{5}}\{\sin\beta(1+\cos^2\beta)\cdot\sin 2\alpha\cdot\sin 3\gamma + \sin 2\beta\cdot\cos 2\alpha\cdot\sin 3\gamma\}$$
$$+\sqrt{\frac{3}{5}}\{\sin\beta(1-3\cos^2\beta)\cdot\sin 2\alpha\cdot\cos\gamma - \sin 2\beta\cdot\cos 2\alpha\cdot\sin 3\gamma\}]$$

$$u_6(\{\alpha, \beta, \gamma\}) = \frac{\sqrt{15}}{8}[\sqrt{\frac{3}{5}}\{\sin\beta(1+\cos^2\beta)\cdot\sin 2\alpha\cdot\sin 3\gamma - \sin 2\beta\cdot\cos 2\alpha\cdot\cos 3\gamma\}$$
$$-\sqrt{\frac{3}{5}}\{\sin\beta(1-3\cos^2\beta)\cdot\sin 2\alpha\cdot\sin\gamma + \sin 2\beta\cdot\cos 2\alpha\cdot\cos\gamma\}]$$

$$u_7(\{\alpha, \beta, \gamma\}) = \frac{1}{2}[\cos\beta(1-3\cos^2\beta)\cdot\sin 2\alpha\cdot\cos 2\gamma - 2\cos 2\beta\cdot\cos 2\alpha\cdot\sin 2\gamma]$$

Table 4. The 4th or 6th order of octahedral function expressed by $\{\alpha, \beta, \gamma\}$.

$$V_4(\{\alpha, \beta, \gamma\}) = \frac{1}{32}[7(8-40\sin^2\beta+35\sin^4\beta)+35\sin^4\beta\cdot(\cos 4\alpha+\cos 4\gamma)$$
$$+5(8-8\sin^2\beta+\sin^4\beta)\cdot\cos 4\alpha\cdot\cos 4\gamma - 20\cos\beta(2-\cos^2\beta)\cdot\sin 4\alpha\cdot\sin 4\gamma]$$

$$V_6(\{\alpha, \beta, \gamma\}) = \frac{\sqrt{13}}{128}[(16-168\sin^2\beta+378\sin^4\beta-231\sin^6\beta)$$
$$-21(10\sin^4\beta-11\sin^6\beta)\cdot(\cos 4\alpha+\cos 4\gamma)$$
$$+7(16-104\sin^2\beta+134\sin^4\beta-33\sin^6\beta)\cdot\cos 4\alpha\cdot\cos 4\gamma$$
$$-56(1-10\cos^2\beta+11\cos^4\beta)\cos\beta\cdot\sin 4\alpha\cdot\sin 4\gamma]$$

axis. Similarly, V_4, V_6 are related with 4-fold symmetry typically in the case of (001) axis.

The variation of the rotational potential V_{346} in (2) at $R_x = 0.3755$ nm is illustrated as rotating about two-fold axis a_2 (Fig.2 (a)) or three-fold axis a_3 (Fig.2 (b)). Through rotating by 45° about a_2 the orientation moves from T_d to D_{2d} while by 60° about a_3 from T_d to C_{3v}. After moving in the latter case, the potential makes lower in fcc than in hcp. At another values of R_x, it changes in the same way. In this stage, we cannot fix the optimum R_x.

Actually, we need to compute the lattice energy to check precisely the stable orientation and the intermolecular distance. Now, the computation is reserved

Table 5. One-dimensional rotation in three-dimensional 3rd order of rotator functions.

	(001)axis	(111)axis	(−110)axis
u_1	$\cos 2\theta$	$\frac{1}{9}(5+4\cos 3\theta)$	$\frac{1}{8}(5\cos\theta+3\cos 3\theta)$
u_2	0	$\frac{2\sqrt{15}}{27}(-1+\cos 3\theta)$	$-\frac{\sqrt{30}}{32}(3\sin\theta-\sin 3\theta)$
u_3	0	$\frac{2\sqrt{15}}{27}(-1+\cos 3\theta)$	$-\frac{\sqrt{30}}{32}(3\sin\theta-\sin 3\theta)$
u_4	0	$\frac{2\sqrt{15}}{27}(-1+\cos 3\theta)$	$\frac{\sqrt{15}}{8}(\cos\theta-\cos 3\theta)$
u_5	0	$-\frac{2\sqrt{3}}{9}\sin 3\theta$	$\frac{\sqrt{2}}{32}(5\sin\theta+9\sin 3\theta)$
u_6	0	$-\frac{2\sqrt{3}}{9}\sin 3\theta$	$-\frac{\sqrt{2}}{32}(5\sin\theta+9\sin 3\theta)$
u_7	$-\sin 2\theta$	$-\frac{2\sqrt{3}}{9}\sin 3\theta$	0

Table 6. One-dimensional rotation in three-dimensional 4th or 6th order of rotator functions.

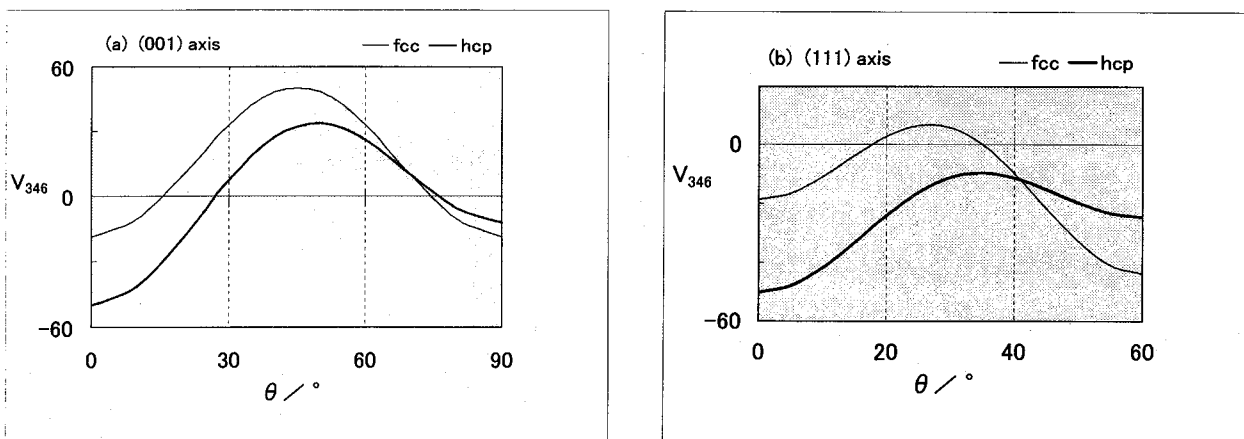|	(001)axis	(111)axis	(−110)axis
$\frac{V_4}{3}$	$\frac{1}{12}(7+5\cos 4\theta)$	$\frac{1}{27}(7+20\cos 3\theta)$	$\frac{1}{192}(7+140\cos 2\theta+45\cos 4\theta)$
$\frac{V_6}{\sqrt{13}}$	$\frac{1}{8}(1+7\cos 4\theta)$	$\frac{1}{243}(96+70\cos 3\theta+77\cos 6\theta)$ $\frac{1}{1024}(338+105\cos 2\theta+350\cos 4\theta+231\cos 6\theta)$	

Fig. 2. The potential V_{346} versus the rotational angle about (001) axis as shown in (a), and about (111) axis in (b). The initial angle $\theta = 0°$ corresponds to T_d orientation both in fcc and hcp lattices.

here. For, as mentioned above, whether the potential increases or decreases depends on the main orientation in the case of lattice expansion, and therefore, the various types of rotation contribute the rotational energy.

4. Computational Energy

We have calculated the rotational energy levels as a function of three coefficients α_3, β_4 and β_6 by solving the eigenvalue problem using the rotational Hamiltonian (1). Table 7 indicates the energy at three R_x's. The value is given as the difference from the ground level. At smaller R_x, the rotational energy is reduced due to the restriction in rotation. As the intermolecular distance increases, the energy rises. This corresponds to approaching to the free rotation.

In fcc lattice, the lowest value is really not far from $2B$, which is the first excited state in free rotation. The other R_x gives the similar behavior. In hcp lattice, because of the rather big value of α_3, the energy becomes smaller. The value at larger R_x also enhances except for the third energy in Table 7.

5. Conclusion

It is quite useful to expand the rotational potential in terms of the function with definite symmetry. The coefficients in crystal field are evaluated in different lattice parameters. The expression by only one angle is derived in the function with tetrahedral or octahedral symmetry. The stable orientation in the field is investigated. Also, we calculate the energy levels in the field strength estimated using atomic pair potential between proton and the surrounding rare gas atom. As a result, the dependence on R_x is given in fcc and hcp lattices. We compare with experimental

Table 7. The R_x-dependence in the rotational energy.

R_x/nm	$\Delta E/B$		
3.700　(fcc)	1.122	2.627	3.842
(hcp)	0.116	0.175	13.473
3.755　(fcc)	1.239	2.894	4.192
(hcp)	0.479	0.743	8.460
3.800　(fcc)	1.360	3.181	4.547
(hcp)	0.984	1.652	6.760

results by inelastic neutron scattering from the mixed system of methane molecule in rare gas matrix[7]. In this measurement, the peaks are found at 0.91, 2.2, 2.6 meV. These values certainly come from the system in fcc lattice. The values are rather larger than computed results as a whole. The system containing the ammonium ion in alkali halide lattice[8] also should have the comparable lattice deformation.

References

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