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Classical Dynamics of the Hydrogen Atom and Muonium Trapped in Diamond Clusters: A Direct Ab-initio Dynamics Study

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Direct ab-initio dynamics calculations have been carried out for hydrogen and muonium (Mu) trapped in a $C_{10}H_{16}$ cluster model in order to elucidate qualitatively the finite temperature effect on f-value ($= |\Phi_H(0)|^2/|\Phi_{vac}(0)|^2$, where $|\Phi_{vac}(0)|^2$ is the contact spin density on H nuclei in vacuum and $|\Phi_H(0)|^2$ is one in the model cluster). In the dynamics calculations, a split-valence type basis set (31G) was used for the central hydrogen atom and a minimal basis set STO-3G for the cluster model. All atoms were treated as classical particles moving on the ab-initio full dimensional surface including all degrees of freedom calculated at the Hartree–Fock level. Three temperatures, 300, 600, and 1000 K, are chosen as simulation temperatures. The averaged f-values are obtained for each temperature by using MP2/3-21G* level. In addition, the f-value corresponding to 0 K is calculated by the static ab-initio MO calculation (i.e., without dynamics effect). The f-values for 0, 300, 600, and 1000 K were calculated to be 1.224, 1.211, 1.200, and 1.185, respectively, indicating that the f-value linearly decreases with increasing temperature. The f-value was simply expressed by the equation $f(T) = f(T = 0\text{ K})\,[1 - 0.325\times10^{-5}\,T]$. The present calculations indicated that the f-value is slightly affected by the thermal activation, the shift of f-value is small. This work is the first attempt to calculate the finite-temperature effect on the f-value at the ab-initio dynamics level.

There has been considerable interest in the trapping of hydrogen and muonium (Mu) atoms as impurities in semiconductors, particularly in diamond, silicon and germanium. Mu has one electron bound to the muon meson whose mass is 1/9 of hydrogen. The Bohr radius and ionization energy of Mu (0.5315 Å and 13.54 eV) are significantly close to those of hydrogen (0.5292 Å and 13.60 eV). Therefore, Mu behaves as an isotope of hydrogen.

Many theoretical works have been reported for muonium and hydrogen atoms trapped in several crystals. Sahoo et al. reported an ab-initio UHF calculation for the hydrogen (Mu) trapped in the diamond cluster.[1] They showed that the trapped muonium is localized in the tetrahedral interstitial space in diamond (T site). Esteicher et al. calculated the enhancement factor f expressed by

$$f = \frac{|\Phi_H(0)|^2}{|\Phi_{vac}(0)|^2}, \tag{1}$$

for the hydrogen atom trapped in several diamond cluster models, where $|\Phi_H(0)|^2$ is the contact spin density at nucleus in the solid and $|\Phi_{vac}(0)|^2$ is that in vacuum.[2] They obtained $f = 1.22$ for the hydrogen atom in $C_{10}H_{16}$ cluster, which is larger than that obtained from muon spin rotation (μSR) experiments, $f = 0.831$. They also examined the cluster size and the basis set effects on the spin density of muonium in a diamond cluster, and suggested that these dependencies are of secondary importance for the calculation of the f-value. Claxton et al. considered that the trapping of hydrogen in diamond occurs at the central point of the C–C bond in a diamond lattice if the C–C bond is extended by 0.6 Å.[3]

Hall and Mizukami calculated the f-value for the hydrogen trapped in $C_{10}H_{16}$ cluster by using the second-order perturbation method they developed.[4] They calculated the electrostatic potential around the trapped hydrogen by using HF/STO-3G method and considered the potential as the perturbation to the spin density of the hydrogen. The f-value was calculated to be 0.716, which is in good agreement with the experiment. They extended the second-order perturbation method to muonium trapped in MgO.[5] The calculated value agrees with experiments reasonably well.

Although the static structural and electronic properties have been thus studied extensively from a theoretical point of view, the dynamic properties are mostly unknown because there is no dynamics calculation of the hydrogen in the cluster. Finite-temperature effects on f-value are important in elucidating the essential feature of Mu in solid. The vibrational mode of trapped H atom (Mu) may couple strongly with the lattice phonon-mode at finite temperature, so that the electronic state of the H atom (Mu) would be perturbed by the dynamic effect. Holzschuh measured f-value of Mu trapped in Si and Ge solids. They showed that f-value decreases with increasing temperature.[6] Thus thermal activation seem to affect the contact spin density and f-value of the muonium.

In the present paper, we report the effect of finite temperature on the contact spin density of H atom (Mu) trapped in a diamond model cluster; we used a direct ab-initio dynamics method. Thermal nuclear motions of the diamond cluster and trapped hydrogen are discussed on the basis of theoretical results. It should be emphasized that the purpose of this study is not to calculate accurate values of contact spin density, but to elucidate qualitatively the temperature dependence of f-value. This work is the first attempt to calculate the finite-temperature effect at the ab-initio dynamics level.

Method of Calculations

Ab-initio MO Calculation. We have chosen a cluster model composed of $C_{10}H_{16}$ which corresponds to the one employed by Hall and Mizukami[4] and by Estreicher et al.;[2] see Fig. 1. The structure of the cluster model was fully optimized by the RHF energy-gradient method with STO-3G, 3-21G, and 6-31G* basis sets. The hydrogen-doped system, the cluster model plus the hydrogen, was also fully optimized by the UHF calculation. The basis sets of the central hydrogen were 3G, 21G, and 31G. Energetics calculations were carried out at the HF and MP2 levels of theory with STO-3G, 3-21G, and 6-31G* basis sets.[7]

Direct Ab-initio Dynamics Calculation. In general, the classical trajectory is performed on an analytically fitted potential energy surface as previously carried out by us.[8] However, it is not appropriate to predetermine the reaction surfaces of the present systems due to the large number of degrees of freedom ($3N-6=75$ where N is the number of atoms in the system). Therefore, in the present study, we applied the direct ab-initio trajectory calculation with all degrees of freedom. The details of the direct dynamics method are described elsewhere.[9]

Initial structures of both the free cluster and the hydrogen doped cluster models were chosen as the optimized ones. The trajectories are calculated at several temperatures defined by

$$T = \frac{1}{3Nk}\left\langle \sum_{i=1}^{N} m_i v_i^2 \right\rangle, \tag{2}$$

where N is number of atoms, v_i and m_i are velocity and mass of i-th atom, and k is Boltzmann's constant. The potential energy (total energy) and energy gradient was calculated at each time step. In the calculation of the classical trajectory, we assumed that each atom moves as a classical particle on a multi-dimensional potential energy surface. The equations of motion for n atoms in a molecule are given by Eqs. 3 and 4.

$$\frac{\mathrm{d}Q_j}{\mathrm{d}t} = \frac{\partial H}{\partial P_j}, \tag{3}$$

$$\frac{\partial P_j}{\partial t} = -\frac{\partial H}{\partial Q_j} = -\frac{\partial U}{\partial Q_j}, \tag{4}$$

where $j = 1-3N$, H is classical Hamiltonian, Q_j is the Cartesian coordinate of j-th mode, and P_j is conjugate momentum. These equations were numerically solved by the Runge–Kutta method. No symmetry restriction was applied to the calculation of the gradients in the Runge–Kutta method. The time step size was chosen by 0.20 fs, and a total of 2500 steps was calculated for each simulation. 10 snapshots of the trajectory are sampled at every 50 fs intervals and then the f-value is averaged for each temperature. The drift of the total energy is confirmed to be less than 0.1% throughout all steps in the trajectory. The momentum of the center of mass and the angular momentum around the center of mass are also confirmed to retain at the initial value of zero.

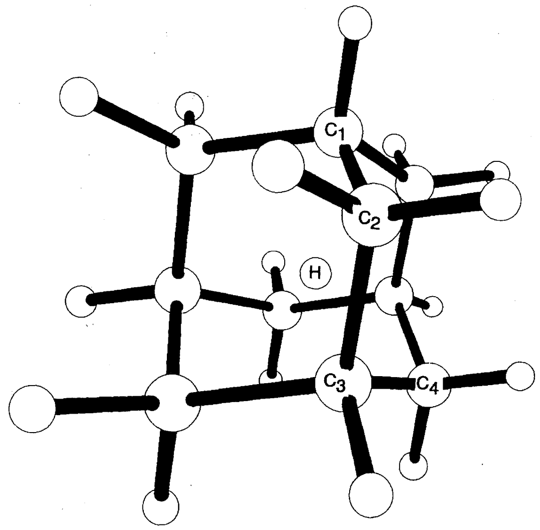

Fig. 1. Cluster model ($C_{10}H_{16}$) and trapping structure of the hydrogen (muonium). Parameters of the bond distances are $R_1 = r(C_1–C_2)$, $R_2 = r(C_2–C_3)$, $r_1 = r(C_1–H)$, and $r_2 = r(C_4–H)$. The angles are $\phi = \angle C_1–C_2–C_3$ and $\theta = \angle C_1–H–C_4$.

In direct ab-initio dynamics calculations, one generally requires a long CPU time and a large memory to generate even one trajectory. Due to this limitation, we used STO-3G basis set for the cluster model and 31G basis set for the trapped hydrogen (muonium), and the dynamics calculations were carried out at the HF level of theory throughout. This level of theory may be limited in a general computer facility. A CPU time was 7 d for one trajectory on a workstation (silicon Graphics, O_2).

Results

A. Ab-initio MO Study. Structure of the Cluster Model. First of all, the structure of the cluster model was determined by the RHF energy-gradient method. The optimizations were performed with STO-3G, 3-21G, and 6-31G* basis sets. As shown in Table 1, all calculations gave similar results for the structures of the cluster model and the hydrogen doped system. Hence, we will discuss the structures by using the results at the HF/6-31G* level of theory. The fully optimized structure had T_d symmetry and

Table 1. Optimized Structures of the Cluster Model (Model) and the Cluster Model + Hydrogen (Model+H) Calculated at HF Level
The bond distance and angles are in Å and in degrees, respectively.

Model	H	R_1	R_2	ϕ	r_1	r_2	θ
Model							
STO-3G		1.5468	1.5467	109.54			
3-21G		1.5418	1.5418	109.85			
6-31G*		1.5374	1.5374	109.73			
Model+H							
STO-3G	31G	1.5819	1.5818	109.75	1.5845	1.8254	125.3
3-21G	21G	1.5846	1.5837	109.84	1.5837	1.8305	125.3
6-31G*	31G	1.5744	1.5744	109.50	1.5746	1.8178	125.3

a C–C bond distance (R_1 and R_2) of 1.5468 Å. The angle of C–C–C (ϕ) was calculated to be 109.5°. The structures obtained agree with the experimentally observed one.[10]

Trapping Site of Hydrogen. The trapping structure of hydrogen in the $C_{10}H_{16}$ cluster model was optimized by the UHF/6-31G* energy-gradient method. As seen in Table 1, the C–C bond (R_1, R_2) in the cluster model was slightly elongated by trapping a hydrogen atom in the cluster (1.5744 vs. 1.5374 Å). It should be noted here that the hydrogen atom locates in a tetrahedral site (*T*-site) which is most stable in the cluster lattice: $r_1 = 1.5746$ Å and $r_2 = 1.8178$ Å and $\theta = 125.3°$. The trapping energy of the hydrogen was calculated to be a negative value (−5.8 eV), which means that the hydrogen is unstable in the cluster lattice.

The *f*-Value. The *f*-values for hydrogen in the cluster model were calculated by several levels of theory; the values are given in Table 2. All calculations gave larger values than 1.0: the HF/3-21G and HF/6-31G* calculations show that *f*-values are 1.221 and 1.242, respectively. In order to include the effect of electron correlation, MP2 calculations were carried out for the same systems. The *f*-value calculated by the MP2/3-21G calculation was $f = 1.224$, which is hardly changed. In contrast, significant lowering of *f*-value was observed for the MP2/6-31G*//HF/6-31G* calculation ($f = 1.070$). The spin density of the hydrogen in the cluster lattice is also calculated by a simple Mulliken population analysis to be 0.890, which suggests strongly that hydrogen behaves as a shallow spin donor in the lattice.

B. Direct Ab-initio Dynamics Study. Dynamics of Cluster Model. In this section, the finite-temperature effect on the *f*-value was studied by using the direct ab-initio dynamics calculations. Firstly, a trajectory calculation for the neutral cluster was performed to obtain the structure at the finite temperature. The calculation was run at a constant temperature from the optimized structure of $C_{10}H_{16}$. We chose 300 K for a simulation temperature and 0.01 ps for a bath relaxation time. The profile of the trajectory is given in Fig. 2. The potential energy of the system fluctuated greatly (See Fig. 2A), but its averaged value was close to a constant value during the simulation. Two bond distances (R_1 and R_2) are plotted as a function of time in Fig. 2B. The bond distances oscillated mutually in the range from 1.50 to 1.61 Å at 300 K. The angle of C–C–C (ϕ) was also fluctuated with the amplitude of ca. 4° in the neutral system as clearly seen in Fig. 2C. These results indicate that the lattice has a non-rigid structure at 300 K.

Table 2. *f*-Values Calculated by Several Methods

Method	Model	H	*f*-value	
HF	STO-3G	3G	1.225	present work
HF	STO-3G	31G	1.221	present work
HF	3-21G	21G	1.224	present work
HF	6-31G*	31G	1.242	present work
MP2	3-21G	21G	1.224	present work
MP2	6-31G*	31G	1.070	present work
HF	4-31G	31G	1.24	Ref. 2
HF	3-21G	21G	1.23	Ref. 2
HF	3-21G*	21G	1.28	Ref. 2
H-M[a)]	STO-3G	3G	0.716	Ref. 5

a) Second order perturbation method developed by Hall and Mizukami.

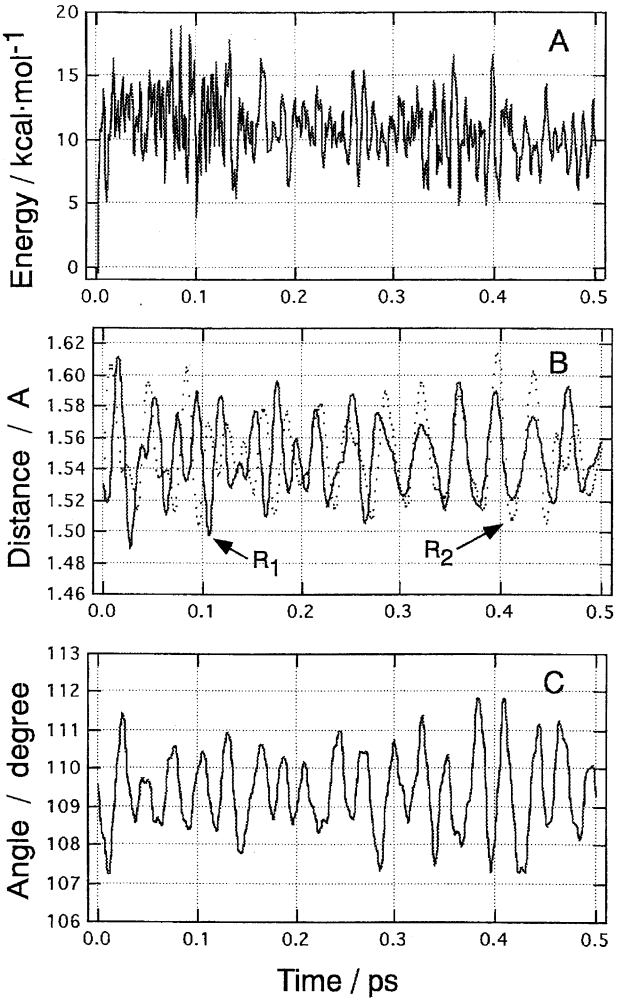

Fig. 2. A trajectory for the cluster model plotted as a function of simulation time. The simulation was carried out at 300 K. (A) the potential energy of the system, and (B) interatomic distances, R_1 and R_2, and (C) the angle ϕ versus time.

Dynamics of Hydrogen in the Cluster Model. The dynamics of muonium and atomic hydrogen in the model cluster have been examined at 300, 600, and 1000 K by similar calculations. As a sample trajectory of Mu, the result for 300 K is given in Fig. 3. The potential energy of the system calculated as a function of time is plotted in Fig. 3A. Even at 300 K, the potential energy fluctuated strikingly from 15 to 25 kcal mol^{-1}. The position of hydrogen defined by the distances (r_1 and r_2) and the angle (θ) was varied in the lattice (Figs. 3B and 3C). The fluctuation of distances was composed of two different parts: One has a vibration period of ca. 0.05 ps and the other is ca. 5.7 fs. The angle θ also vibrated as shown in Fig. 3C. These oscillations are caused by a vibrational mode-coupling between the lattice phonon-mode activated by thermal energy and the translational mode

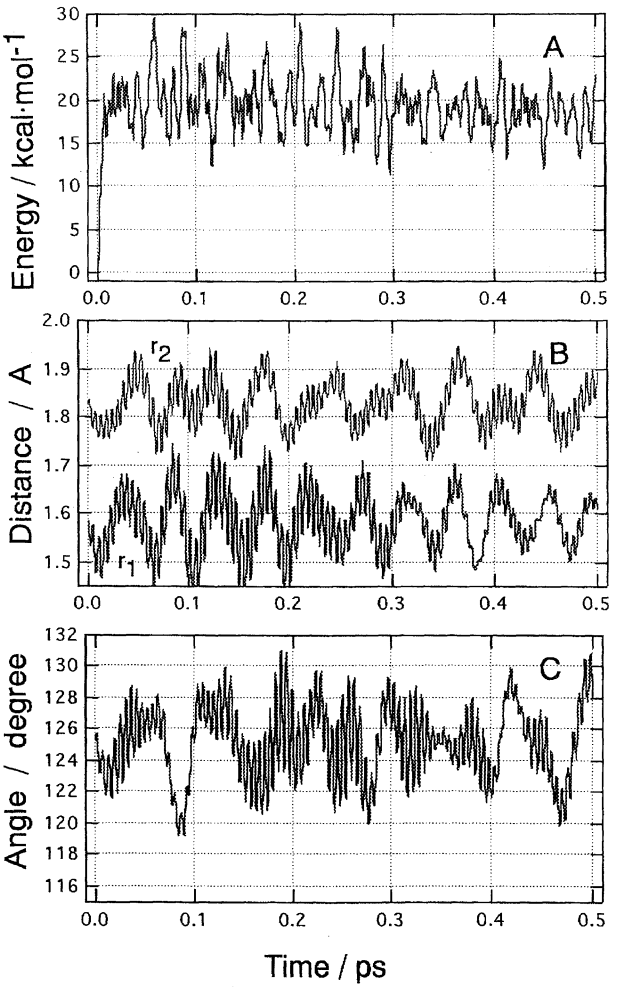

Fig. 3. A sample trajectory for Mu in $C_{10}H_{16}$ cluster model plotted as a function of reaction time. (A) the potential energy of the system, and (B) distances, r_1 and r_2, and (C) angle θ versus time.

of hydrogen in the lattice.

In order to elucidate the dynamics of Mu in more detail, an expanded view of Fig. 3 is given in Fig. 4 together with the results of the hydrogen trapped in the same temperature. In Fig. 4, the solid and dotted lines indicate the results of Mu and H, respectively. As seen in Fig. 4A, the potential energy of Mu was very close to that of hydrogen, although a slight shift of the energy is found at several points. The time dependence of the position of Mu (r_1 and r_2) was much different from that of the hydrogen: The position of Mu is changed very rapidly in comparison with that of the hydrogen because of the mass effect. The angle (θ) for Mu also vibrated more strikingly as a function of time.

Temperature Effect on *f*-Value. Similar dynamics calculations were carried out for both 600 and 1000 K. The tendencies of the results for these temperatures were very similar to those of 300 K. For each temperature, the contact spin densities were calculated by using the geometry at each sampling time, which is selected by 0.05 ps interval from 0.0 to 0.5 ps. The *f*-value was then averaged by these contact spin densities for each temperature. The calculated *f*-values

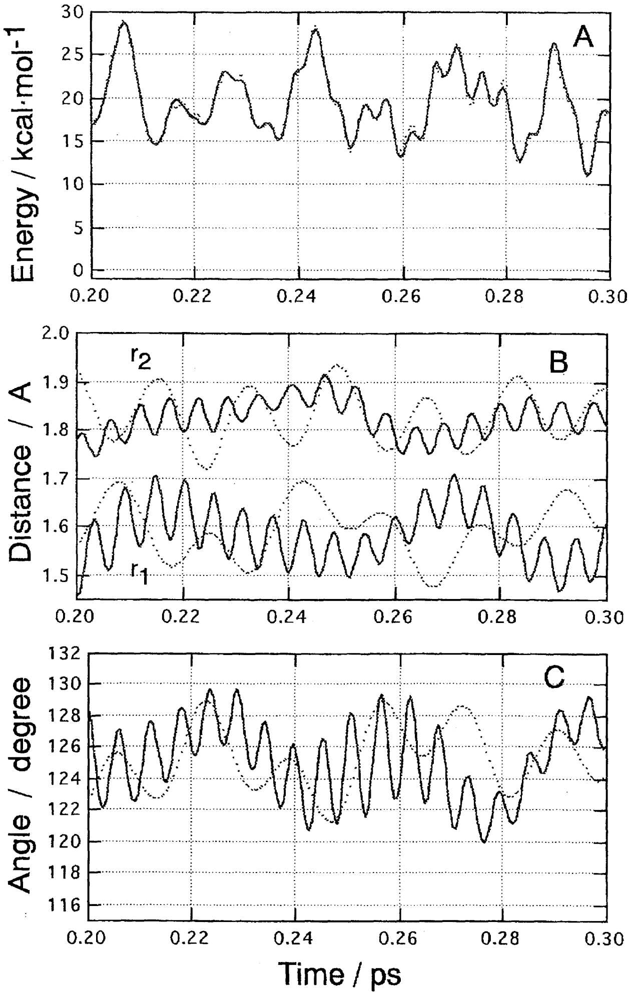

Fig. 4. Expanded view of Fig. 3. Solid and dashed lines indicate vlaues for Mu and hydrogen, respectively. The simulation was carried out at 300 K.

are plotted in Fig. 5. The value at 0.0 K was calculated by the static ab-initio MO calculation described in the previous section. The *f*-value is slightly affected by the thermal activation and decreases linearly with increasing temperature. The spin density estimated by a simple Mulliken population analysis and fermi contact term (FCT) are given in Table 3. The spin density decreases as well as FCT, suggesting that diffusion of unpaired electrons of Mu to the lattice atoms

Table 3. Temperature Dependence of Fermi Cantact Term (FCT in a.u), Spin Densities, Charges, and *f*-Values of Hydrogen Trapped in $C_{10}H_{16}$ Cluster Model, and the Hyperfine Frequencies (in GHz) for Hydrogen Atom (ν(H)) and Muonium (ν(Mu)) Trapped in the Cluster

T/K	FCT[a]	Spin dens.[a]	Charge	f−value	ν(H)	ν(Mu)
0	0.3057	0.8900	+0.265	1.224	1.738	5.462
300	0.3025	0.8820	+0.254	1.211	1.720	5.405
600	0.2998	0.8757	+0.247	1.200	1.704	5.356
1000	0.2959	0.8645	+0.248	1.185	1.683	5.289

a) Fermi contact term and spin density of hydrogen atom in vacuo are calculated to be 0.2488 a.u. and 1.0, respectively.

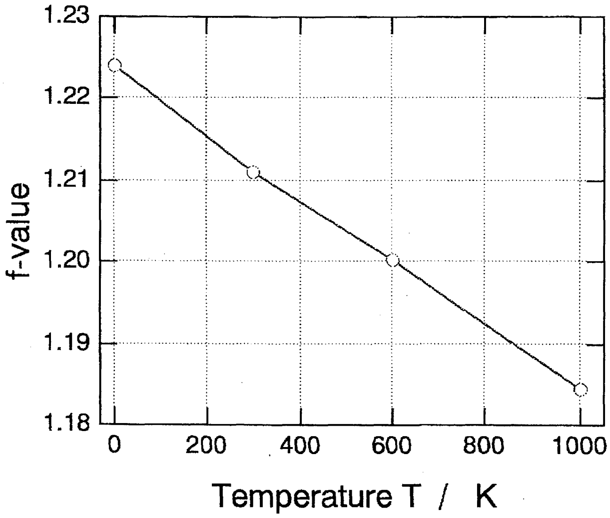

Fig. 5. The f-value of hydrogen (Mu) calculated by the direct ab-initio dynamics method. The simulation temperatures were 300, 600, and 1000 K. The f-value at 0 K was calculated by ab-initio MO method.

is enhanced by thermal activation. The hyperfine coupling frequencies for both hydrogen atom and Mu trapped in the cluster are given in Table 3. Both values decrease linearly as a function of temperature.

Discussion

A. Temperature Dependence of the Contact Spin Density. Firstly, we would emphasize that the purpose of this study is not to calculate the accurate f-values, but to elucidate qualitatively the finite temperature effect on the f-value for H atom (Mu) trapped in diamond model cluster. In the present study, the direct ab-initio dynamics calculation is applied to the dynamics of H atom (Mu) trapped in the diamond cluster. This work is the first attempt to elucidate the finite-temperature effect of H atom (Mu) in diamond.

As clearly seen in both Fig. 5 and Table 3, the f-value and contact spin density of hydrogen are slightly dependent on temperature. The contact spin density (Fermi contact term) calculated at temperature of 0.0 K (i.e, without thermal effect) is 0.306 a.u and the f-value is 1.224. At 1000 K, the contact spin density is lowered to be 0.296 a.u. The f-value also decreases linearly with increasing temperature ($f = 1.1845$ at 1000 K). Temperature dependence of f-value derived from the present calculations is simply expressed by a linear relation

$$f(T) = f(0)[1 - 3.22 \times 10^{-5}\, T], \qquad (T = 0.0\text{—}1000\ \mathrm{K}) \qquad (5)$$

where T is temperature and $f(0)$ is f-value at $T = 0.0$ K. Thus the f-value is affected by thermal activation, although the shift of the f-value is quite small. The influence on the f-value is due to the fact that the hydrogen (Mu) collides, striking the lattice-wall at high temperature. This may cause large spin electron transfer from the hydrogen (Mu) to the lattice atoms, so that the decrease of the contact spin density occurs as temperature increases.

The above result may be easily explained in terms of a Debye model.[11] According to the Debye model, the contact spin density is expressed by

$$\left(|\Phi_{\mathrm{H}}(0)|^2\right)_{T=T} = \left(|\Phi_{\mathrm{H}}(0)|^2\right)_{T=0}\left[1 - C\left[\frac{T}{\Theta_{\mathrm{D}}}\right]^4 \int_0^{\Theta_{\mathrm{D}}/T} \frac{x^3}{\mathrm{e}^x - 1}\mathrm{d}x\right], \qquad (6)$$

where Θ_{D} is the Debye temperature and C is a coupling constant. The averaged calorimetric Debye temperature of diamond is measured experimentally by 1860 K.[12] By using high temperature approximation, the temperature dependence of f-value at high temperature range is given by

$$f(T) = f(0)\left[1 - \frac{C}{3}\frac{T}{\Theta_{\mathrm{D}}}\right]. \qquad (7)$$

The f-value decreases linearly with increasing temperature. This linear relation is consistent with the present results. However, the quantitative feature at low temperature is somewhat different. At very low temperature, the integral part in Eq. 6 is $\pi^4/15$, so that the f-value becomes a constant value.

$$f(T) = f(0)\left[1 - \frac{\pi^4 C}{15}\left(\frac{T}{\Theta_{\mathrm{D}}}\right)^4\right] \approx f(0) \qquad (8)$$

Thus $f(T)$ should approach to $f(0)$ according to T^4 order as temperature lowers, but the temperature dependence of $f(T)$ in the present study has a linear relation at very low-temperature. This discrepancy originated from the classical treatment of quantum particles in the trajectory calculation.

Holzschuh observed temperature dependence of f-value of muonium in Si and Ge lattices by using muon spin rotation (μSR) experiment.[6] The observed f-value decreases with increasing with temperature and the variation is according to the Debye model (high temperature). The present calculation is consistent with their experimental feature, although the feature at very low temperature is slightly different.

B. Comparison with the Previous Studies. As shown in Table 2, all ab-initio MO calculations indicate that the f-value of Mu (hydrogen) trapped in $C_{10}H_{16}$ cluster model is much larger than the experiment ($f = 0.831$) except for Ref. 4 (H-M). In 1986, Estreicher et al. calculated f-value at the HF level. Their calculated values are 1.22 at the HF/4-31G level and 1.26 at the HF/4-31G level, which are also larger than experimental value ($f = 0.86$). In the present study, the static ab-initio HF calculations of the f-values gave the similar values (1.221 at the HF/3-21G level and 1.242 at the HF/6-31G*//HF/6-31G* level). In contrast, it was shown that the MP2 calculation with a medium class basis set (6-31G*) gave a significantly lowering of f-value ($f = 1.070$). The calculation with more large wave-function may provide a more accurate f-value. However, the purpose of this study is not to calculate accurate values of contact spin density, but to elucidate qualitatively the temperature dependence of f-value. Hence the level of theory used in the present study should be enough to elucidate a qualitative feature of thermal effect.

An experiment shows that Mu trapped in *T* site in diamond is inserted to C–C lattice at high temperature (> 1000 K) to form the C–H–C insertion form. However, the present calculation did not give the bond insertion form C–H–C. This is due to the fact that the bond insertion form in $C_{10}H_{16}$ cluster is much more unstable than that at *T*-site. The bond insertion form may be formed only in the large diamond cluster. Our preliminary calculation with the large clusters (we used $C_{30}H_{40}$ cluster model but at the semiempirical PM3 level and a long simulation time up to 20 ps) indicates that the hydrogen attacks the carbon atom at 2000 K to form C–H bond, although the C–H–C bond insertion form was not obtained.[13] Therefore more large cluster and longer simulation time would be required to study the bond C–H–C insertion.

C. Concluding Remarks and Future Work. We have introduced several approximations to calculate the potential energy and to treat the reaction dynamics. Firstly, we assumed that the hydrogen behaves as a classical particle in the multi-dimensional potential energy surface including all degrees of freedom. The quantum effect was not considered in the present calculations. This may cause slight changes of the *f*-value at very low temperature and of the dynamics of hydrogen in lattice. However, it may be currently impossible to treat the full dimensional quantum dynamics of Mu in diamond because of the many degrees of freedom of this system. Secondly, we assumed HF/STO-3G ($C_{10}H_{16}$) and 31G(H) multi-dimensional potential energy surface in the trajectory calculations throughout. The dynamics calculation with more accurate wave function may provide deeper insight in the detailed dynamics.

The present calculation shows that the *f*-value decreases with increasing temperature. This is consistent with the experiment.[6] However, the shift of *f*-value in the calculation was very small. This difference may be also caused by the small cluster size. Therefore, larger clusters would be required to obtain more quantitative values. Despite the several assumptions introduced here, the results enable us to obtain valuable information on the finite temperature effect on the *f*-value of the hydrogen (Mu) in diamond lattice.

In this work, we have considered only the muonium (hydrogen) trapped in $C_{10}H_{16}$ cluster. However, it is possible to simulate the dynamics for the atoms in other semiconductors. In order to expand the present model to the other trapping systems, the dynamics calculation of Mu in a Silicon lattice is now in progress.

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