**Hydrogen/Deuterium Adsorption and Absorption Properties On and In Palladium Using a Combined Plane Wave and Localized Basis Set Method**

**Hiroki Sakagami,[[1]](#endnote-1) Masanori Tachikawa,1 and Takayoshi Ishimoto1**

Correspondence to: Takayoshi Ishimoto (E-mail: *tishimo@yokohama-cu.ac.jp*)

**ABSTRACT**

Detailed information on the H/D isotope effects for adsorption on the surface and absorption in the bulk is important for understanding the nuclear quantum effect. To achieve this purpose, we developed a new theoretical approach, namely, the combined plane wave and localized basis set (CPLB) method. By using the multi-component quantum chemical method, which takes into account the quantum effect of proton or deuteron, with localized part in CPLB method, direct analysis of H/D isotope effect about adsorption and absorption is achieved. In this study, we performed a theoretical investigation of the H/D isotope effects for adsorption on a Pd(111) surface and absorption in bulk Pd. We clearly showed H/D isotope effect on geometry during adsorption and absorption. Our developed CPLB approach is a powerful tool for analyzing the quantum nature of H/D in surface, bulk, and inhomogeneous systems.

**Introduction**

The behavior of H on surfaces has attracted extensive attention in various fields including astrophysics, material physics, and catalytic chemistry. For example, the mobility and tunneling diffusion of H on various types of ice have been analyzed to elucidate the origin of the interstellar medium.1,2 Further, the adsorption of H on graphite has been studied to understand the bonding nature of H to covalent substrates.3 In addition, the interaction between H and transition metals is a crucial factor in chemical and physical processes. The adsorption and diffusion properties of H on metal surfaces are some of the important phenomena for not only fundamental physics but also catalytic activity.4–7 Ferrin *et al.* calculated the adsorption and diffusion energies of H on various transition metal surfaces.4

As a popular example for analyzing the interactions between metals and H, Pd has been used in many experimental and theoretical studies due to the unique H adsorption/absorption and catalytic properties.8–12 Using scanning tunneling microscopy, Mitsui *et al.* observed that H binds to face-centered-cubic (fcc) sites on Pd(111) in the low temperature range (around 50 K).8 The theoretical work of Løvvik and Olsen also found that H was stably adsorbed on fcc sites.10 Powell and Kirkpatrick measured the diffusion coefficient of H on a Pd surface.11 In this analysis, D substitution for H was used to obtain detailed information on the different behavior of H and D, and the diffusion coefficient of H was determined to be larger than that of D.11 Jin *et al.* observed that the adsorption and desorption energies of H are smaller than those of D using a high vacuum microbalance.9 These experimental results clearly indicated that the adsorption of D on the Pd surface is stronger than that of H.

Further, Pd is well known to absorb H at ambient temperature.13–21 Contrary to the trend for adsorption on the Pd surface, the absorption energy of H is larger than that of D in the Pd bulk.19 For the diffusion coefficient of H inside bulk Pd, an inverse H/D isotope effect has been observed, where the diffusion of D is faster than that of H.7,21 Furthermore, differences in lattice expansion during H and D absorption have been observed for not only for bulk Pd21 but also for Pd nanoparticles.17,18 However, geometrical differences induced by H and D have only been observed experimentally in bulk Pd. Although the geometrical parameters for adsorption, such as Pd–H/D distances, are expected to be different and Koitaya *et al.* have reported H/D geometrical differences during surface adsorption on Rh(111),22 to the best of our knowledge, experimentally observed geometrical differences for the adsorption of H and D on Pd surfaces have still not been reported.

Generally, H/D isotope effects are induced by the differences in the quantum nature of protons and deuterons. The quantum effects can be clarified using parameters such as the zero-point energy, nuclear tunneling, and vibrational excitation for the discussion of H/D isotope effects. To analyze the H/D isotope effects theoretically, the difference in the zero-point vibrational energy (ZPVE) based on the harmonic approximation is often used, as this difference originates from the mass difference between H and D. The harmonic ZPVE approach is sometimes sufficient for a rough discussion of the H/D isotope effects on parameters such as the adsorption and absorption energies. In fact, Caputo and Alavi highlighted the necessity of the harmonic ZPVE correction to describe the absorption energy of H in bulk Pd.23 However, it is difficult to reproduce the lattice parameter difference induced by H and D absorption using only the framework of the harmonic ZPVE correction. In this sense, a direct treatment of the quantum effects of protons and deuterons would be indispensable for analyzing and discussing the geometrical differences induced by H and D, including lattice expansion and local geometrical changes, or by strong electron and nuclear coupling such as the interaction between a metal and H.

For the direct treatment of proton and deuteron quantum effects, we developed the multicomponent molecular orbital and density functional theory (MC\_MO and MC\_DFT) approaches, which are based on localized orbitals (LOs).24–26 Using this method, it is possible to describe the geometrical and electronic structure changes induced by H and D. Although this method has potential for investigating the H/D isotope effects for adsorption and absorption on and in Pd, the calculation of large systems, such as those defined by periodic boundary conditions (PBCs), is not realistic. In contrast, the plane wave (PW) approach is a powerful tool for calculating surface and bulk models using PBCs. However, the direct treatment of the quantum effects of protons based on the PW approach as well as the MC\_MO and MC\_DFT method has not yet been developed because of the difficulty of the high accurate calculations required to describe small geometrical and electronic structure differences induced by H and D.

To achieve the necessary accuracy for analyzing the H/D isotope effects for adsorption and absorption on and in Pd, we proposed the combined plane wave and localized basis set (CPLB) method.27 In this method, a highly accurate calculation based on the MC\_MO or MC\_DFT approach is used to describe the quantum effects of protons and deuterons directly using a cluster model. Conversely, the electronic structure of the surface or bulk system is calculated using the PW approach. The combination of both approaches enables us to realize a detailed analysis of the H/D isotope effects for adsorption and absorption.

Herein, we first explain the framework of our developed CPLB method. We then describe our analysis of the H/D isotope effect for adsorption on the Pd(111) surface using our developed CPLB method. Further, the absorption energy and geometrical changes induced by the H/D isotope effect for absorption in bulk Pd are also detailed.

**CPLB Calculation**

**Theoretical Background**

****Here, we briefly describe the concept of the CPLB method.27 As an example, the calculation procedure for H adsorbed on a Pd(111) surface is illustrated in Fig. 1. The total energy of the whole system (*E*(PW, whole)), which consists of H adsorbed on the Pd(111) surface model, is calculated using PW-based electronic structure calculations. The energy of adsorbed H surrounded by Pd atoms (*E*(PW, cluster) and *E*(LO, cluster)) is calculated using both PW- and LO-based electronic structure calculations for cluster models of adsorbed H. Based on these values, the total energy of the CPLB method (*E*(CPLB)) is calculated using Eq. (1), which provides sufficient accuracy by including both delocalized electronic structure and protonic quantum effects.

Figure 1. Schematic illustration of the CPLB approach for H adsorption on a Pd(111) surface. The small and large balls were treated using the PW and LO methods, respectively.

 (1).

The gradient of the CPLB method, such as the gradient with respect to nuclear coordinates, can be obtained using the gradient for each energy, as follows;

 (2).

Using this scheme, we developed a geometry optimization algorithm for the CPLB method. The H absorption energy and various properties were also calculated via the same procedure.

**Computational Details**

For the PW-based electronic structure calculations, we used the Vienna ab initio simulation package (VASP)28,29 with the projector-augmented wave method.30,31 The Perdew–Burke–Ernzerhof approximation with a generalized gradient approximation32 was used for the exchange and correlation functionals. The cut-off energy was set to be 400 eV.

The surface structure for H/D adsorption was modeled based on the supercell and consisted of 3 atomic layers with 16 atoms in each layer. To calculate the surface model based on the PBCs, 4 × 4 × 1 k-points were sampled using the Monkhorst–Pack grid method.33 The bulk structure for H/D absorption consisted of 108 atoms based on a 3 × 3 × 3 model of the unit cell, and 4 × 4 × 4 k-points were sampled.

To account for the quantum effects of protons and deuterons, the MC\_DFT method26 was applied to the LO-based electronic structure calculations using the modified Gaussian16 program package.34 The LanL2DZ basis set with an effective core potential35–37 was used for electrons. The single s-type Gaussian-type function, , was used for each protonic and deuteronic basis function. The  values for protons and deuterons were set to the standard values of 24.1825 and 35.6214, respectively.38 The B3LYP level of theory39,40 was used for the LO-based electronic structure calculations.

All of the geometry optimization calculations were performed under the concept of the CPLB scheme, as shown in Eq. (2)

**Results and Discussion**

**H/D Adsorption on the Pd(111) Surface**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Table 1. Adsorption energy (*E*ad) and geometrical parameters for H/D adsorption on a Pd(111) surface. *r*(Pd–X) and *R*(Pd–X) denote the vertical distance between the Pd surface and X and the nearest-neighbor Pd–X distances, respectively. | | | | |
| Method | X | *E*ad (eV) | *r*(Pd–X) (Å) | *R*(Pd–X) (Å) |
| Conven-tional PW | H | -2.725 | 0.845 | 1.820 |
| D | -2.749 | 0.845 | 1.820 |
| (H - D) | 0.024 | 0.000 | 0.000 |
| CPLB | H | -2.683 | 0.800 | 1.802 |
| D | -2.698 | 0.785 | 1.796 |
| (H - D) | 0.015 | 0.015 | 0.006 |

We analyzed the H/D adsorption properties on a Pd(111) surface. In this calculation, a H atom was placed on a fcc site on the Pd(111) surface. As a conventional PW approach, the harmonic ZPVE correction was used to analyze the differences in H and D adsorption after geometry optimization. During the geometry optimization, the atomic positions in the bottom (3rd) layer were fixed, whereas those in the other (1st and 2nd) layers and that of adsorbed H were relaxed. The adsorption energy and optimized parameters of adsorbed H and D are listed in Table I.

The H adsorption energy on the Pd(111) surface was defined as follows;

 (3),

where *E*ad is the H adsorption energy on the Pd(111) surface, *E*tot is the total energy of H adsorbed on the Pd(111) surface, and *E*surf and *E*H are the total energies of the Pd(111) surface model and the H atom, respectively. A negative *E*ad value means that H is stably adsorbed on the Pd surface. The H absorption energy before the harmonic ZPVE correction was −2.807 eV, which agrees very well with previous theoretical results.4 After the harmonic ZPVE correction, the adsorption energies of H and D on the Pd(111) surface were −2.725 and −2.749 eV, respectively. We clearly found a difference in the H and D adsorption energies, even using the harmonic ZPVE correction. The adsorption energy of H is lower than that of D, which corresponds to the experimentally observed trend.9 Our CPLB method, which used the MC\_DFT approach for the LO part, gave a H adsorption energy of −2.683 eV, which was lower than the D adsorption energy (−2.698 eV). Thus, both the conventional PW method and our CPLB method including nuclear quantum effects gave the same trend for the H/D isotope effect on the adsorption energy.

In the optimized adsorption structure of H on Pd(111) obtained using conventional PW-based first-principle calculations, the nearest-neighbor Pd–H distance was 1.820 Å, whereas the perpendicular distance between H and the surface plane was 0.845 Å. These values are in reasonable agreement with the previous theoretical results.4 Further, the conventional PW method gave the same optimized structures with both H and D. Although no direct observations of geometrical differences for H/D adsorption on the surface have been reported, covalent Y–H bonds are expected to be longer than the corresponding Y–D bonds41 owing to the anharmonicity of the potential.

Next, we analyzed the adsorption structures of H and D on Pd(111) obtained by CPLB coupled with MC\_DFT. Using this approach, the nearest-neighbor Pd–H distance (1.802 Å) was longer than that of Pd–D (1.796 Å). The distance between H and the Pd surface was also approximately 0.005 Å longer than in the case of D. Thus, a clear geometrical difference was observed for H/D surface adsorption as well as the covalent Y–H and Y–D bonds.41 In addition, we found a significant difference in the atomic charge around H and D, where the amount of electrons around a deuteron is larger than that around a proton. These results indicate that our developed CPLB approach is a powerful tool for analyzing the H/D isotope effects for various phenomena on the surface, such as adsorption, desorption, diffusion, and catalytic reactions.

**H/D Absorption in Bulk Pd**

****Next, we analyzed H/D absorption in bulk Pd. In this study, we focused on the octahedral (O) site as a H absorption site because stable absorption at the O site has been reported in both experimental and theoretical studies.17,18,21 To analyze the H/D isotope effects on the geometry and absorption energy, we placed one H or D atom in the O site in a bulk Pd structure consisting of 108 atoms.

Figure 2. Schematic illustration of the CPLB approach for H absorption in a bulk Pd system. The gray balls in the cluster were fixed during optimization in the PW and LO calculations as a buffer region.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Table 2. Absorption energy (*Eabs*) and geometrical parameters for H/D absorption in the octahedral site of the Pd108 bulk model. *r*(Pd–X) and *R*(Pd–Pd) denote the nearest-neighbor Pd–X and Pd–Pd distances, respectively, for the octahedral site containing X. | | | | |
| Method | X | *E*ad (eV) | *r*(Pd–X) (Å) | *R*(Pd–Pd) (Å) |
| Conven-tional PW | H | -0.122 | 1.998 | 2.826 |
| D | -0.099 | 1.998 | 2.826 |
| (H - D) | -0.023 | 0.000 | 0.000 |
| CPLB | H | -0.146 | 2.051 | 2.901 |
| D | -0.092 | 2.050 | 2.899 |
| (H - D) | -0.054 | 0.001 | 0.002 |

At a fixed lattice size following cell size optimization for Pd108, the atomic positions after H/D absorption were optimized for Pd108–H using the CPLB optimization scheme. The optimized structures for H absorption in the O site of Pd108 obtained by the conventional PW approach are shown in Fig. 2. This model is regarded as the -phase of the Pd–H system, as Dekura *et al.* observed a local interaction between Pd and H without a large expansion of the lattice parameter.13 For H absorption in Pd108, the nearest-neighbor and next-nearest-neighbor Pd–H distances for H in the O site became 0.024 and 0.015 Å longer, respectively, than those in the bulk Pd before H absorption (1.974 and 3.419 Å).

In the CPLB calculation, the 6 atoms near the H atom were considered for the LO part of the calculation, as shown in Fig. 2. The nearest-neighbor Pd atoms to H were optimized in the CPLB calculation The geometrical parameters for H/D absorption in the O site obtained by CPLB method are listed in Table II. For absorption at the O site, the nearest-neighbor Pd–H distance (2.051 Å) was 0.001 Å longer than that of Pd–D (2.050 Å). We clearly observed that the Pd–H distance is longer than the Pd–D distance after H/D absorption in the O site. In addition to this difference in the Pd–H/D distances, we observed a geometrical difference, as indicating by the Pd–Pd distance surrounding the absorbed H/D atom. That is, the Pd–Pd distance around the O site with absorbed H was 0.002 Å longer than that with absorbed D. Experimentally, the lattice parameters of the Pd–H system have been found to be longer than those of the Pd–D system.21 Although the experimental result was obtained for the -phase of the Pd–H/D system, our calculated result clearly reproduced the same tendency for the difference in lattice parameters after H and D absorption.

It is well known that an absorbed H/D atom will occupy an O site in bulk Pd23 because the absorption energies of O and tetrahedral (T) sites are stable and unstable, respectively. We also analyzed the H/D absorption energies in the O site under the framework of the CPLB method. The H adsorption energy in bulk Pd was defined as follows;

 (4)

where *E*abs is the H absorption energy in the Pd108 bulk model, *E*tot is the total energy of H absorbed in Pd108, and *E*bulk and  are the total energies of the Pd108 bulk model and a H2 molecule, respectively. Using the conventional PW approach, the H absorption energy in the O site was -0.050 eV stable than the D absorption energy. After the harmonic ZPVE correction, the absorption energies of H and D in the O site of Pd108 were -0.122 and -0.099 eV, respectively. The CPLB calculation gave absorption energies of H and D in the O site of Pd108 of -0.146 and -0.092 eV, respectively. Thus, the same trend was obtained using both the conventional PW method with the harmonic ZPVE correction and the CPLB method with the nuclear quantum effect.

**Conclusions**

In this study, we theoretically investigated the H/D isotope effects for adsorption on a Pd(111) surface and absorption in a bulk Pd system. We introduced a CPLB approach that combined PW and LO methods to include the effects of both the surface or bulk system and accurate treatment of the local electronic structure. In addition, the quantum effects of protons and deuterons were taken into account in the LO approach based on MC\_DFT. In the surface and bulk models, the adsorption and absorption energies of H obtained by CPLB with MC\_DFT were smaller and larger, respectively, than those of D, similar to the results obtained using the PW method with the harmonic ZPVE correction. Although the conventional PW method cannot reproduce the geometrical differences induced by H/D, our CPLB method clearly shows the H/D isotope effects on geometry during the adsorption and absorption processes. For H/D adsorption on the Pd(111) surface, the distance in the vertical direction was longer for Pd–H than for Pd–D. Thus, a H/D geometrical isotope effect for adsorption was theoretically observed for the first time using our CPLB method, although there have been no direct observations of geometrical changes induced by H/D adsorption. For H/D absorption in the Pd108 system, which is an -phase model of bulk Pd, we also found a longer distance for Pd–H than for Pd–D. In addition, the Pd–Pd distance surrounding the absorbed H was longer than that surrounding the absorbed D. This result was in good agreement with experimentally observed differences in the lattice parameters after H/D absorption. Based on these results, our developed CPLB approach is expected to be a powerful tool for analyzing the quantum nature of H/D in surface, bulk, and inhomogeneous systems.

**Acknowledgments**

This work was supported by JSPS KAKENHI Grant Numbers JP18K05035 and JP19H05062 (TI) and 18H01945 and 19H05063 (MT). The computations were carried out using the computer resources offered under the category of General Projects by the Research Institute for Information Technology, Kyushu University and Research Center for Computational Science (RCCS), Okazaki, Japan.

**Keywords:** CPLB method, nuclear quantum effect, metal-hydrogen interaction, H/D isotope effect, inhomogeneous structure

**References and Notes**

1. B. Senevirathne, S. Andersson, F. Dulieu, and G. Nyman, *Mol. Astrophys.* **2017**, *6*, 59-69.
2. K. Kuwahata, T. Hama, A. Kouchi, and N. Watanabe, *Phys. Rev. Lett.* **2015**, *115*, 133201.
3. T. Zecho, A. Güttler, X. Sha, B. Jackson, and J. Küppers, *J. Chem. Phys.* **2002**, *117*, 8486-8492.
4. P. Ferrin, S. Kandoi, A. U. Nilekar, and M. Mavrikakis, *Surf. Sci.* **2012**, *606*, 679-689.
5. D. R. Mullins, B. Roop, S. A. Costello, and J. M. White, *Surf. Sci.* **1987**, *186*, 67-74.
6. S. C. Wang and R. Gomer, *J. Chem. Phys.* **1985**, *83*, 4193-4209.
7. G. Sicking, *J. Less-Common Met.* **1984**, *101*, 169-190.
8. T. Mitsui, M. K. Rose, E. Fomin, D. F. Ogletree, and M. Salmeron, *Surf. Sci.* **2003**, *540*, 5-11.
9. Y. Jin, M. Hara, J. L. Wan, M. Matsuyama, and K. Watanabe, *J. Alloys Compd.* **2002**, *340*, 207-213.
10. O. M. Løvvik and R. A. Olsen, *Phys. Rev. B* **1998**, *58*, 10890-10898.
11. G. L. Powell and J. R. Kirkpatrick, *Phys. Rev. B* **1991**, *43*, 6968-6976.
12. H. Conrad, G. Ertl, and E. E. Latta, *Surf. Sci.* **1974**, *41*, 435-446.
13. S. Dekura, H. Kobayashi, R. Ikeda, M. Maesato, H. Yoshino, M. Ohba, T. Ishimoto, S. Kawaguchi, Y. Kubota, S. Yoshioka, S. Matsumura, T. Sugiyama, and H. Kitagawa, *Angew. Chem. Int. Ed.* **2018**, *57*, 9823-9827.
14. H. Kimizuka, S. Ogata, and M. Shiga, *Phys. Rev. B* **2018**,*97*, 014102.
15. K. Brownsberger, M. Ahart, M. Somayazulu, C. Park, S. A. Gramsch, and R. J. Hemley, *J. Phys. Chem. C* **2017**, *121*, 27327-27332.
16. R. B. Schwarz, H. T. Bach, U. Harms, and D. Tuggle, *Acta Mater.* **2005**, *53*, 569-580.
17. T. Ishimoto, M. Tachikawa, M. Yamauchi, H. Kitagawa, H. Tokiwa, and U. Nagashima, *J. Phys. Soc. Jpn.* **2004**, *73*, 1775-1780.
18. T. Ishimoto, M. Tachikawa, M. Yamauchi, H. Kitagawa, H. Tokiwa, and U. Nagashima, *Chem. Phys. Lett.* **2003**, *372*, 503-507.
19. T. B. Flanagan and W. A. Oates, *Annu. Rev. Mater. Sci.* **1991**, *21*, 269-304.
20. S. Majorowski and B. Baranowski, *J. Phys. Chem. Solids* **1982**, *12*, 1119-1127.
21. J. E. Schirber and B. Morosin, *Phys. Rev. B* **1975**, *12*, 117-118 (1975).
22. T. Koitaya, S. Shimizu, K. Mukai, S. Yoshimoto, and J. Yoshinobu, *J. Chem. Phys.* **2012**, *136*, 214705.
23. R. Caputo and A. Alavi, *Mol. Phys*. **2003**, *101*, 1781-1787.
24. T. Ishimoto, M. Tachikawa, and U. Nagashima, *Int. J. Quantum Chem.* **2009**, *109*, 2677-2694.
25. T. Udagawa and M. Tachikawa, *J. Chem. Phys.* **2006**, *125*, 244105 (2006).
26. M. Tachikawa, *Chem. Phys. Lett.* **2002**, *360*, 494-500 (2002).
27. T. Ishimoto and H. Kai, *Int. J. Quantum Chem.* **2018**, *118*, e25452 (2018).
28. G. Kresse and J. Furthmüller, *Phys. Rev. B* **1996**, *54*, 11169-11186 (1996).
29. G. Kresse and J. Hafner, *Phys. Rev. B*1993**,** *47*, 558-561.
30. G. Kresse and J. Joubert, *Phys. Rev. B* **1999**, *59*, 1758-1775.
31. P. E. Blöchl, *Phys. Rev. B* **1994**, *50*, 17953-17979 (1994).
32. J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865-3868.
33. H. J. Monkhorst and D. J. Pack, *Phys. Rev. B* **1976**, *13*, 5188-5192.
34. Gaussian 16, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.
35. P.J. Hay, and W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 270-283.
36. W. R. Wadt and P. J. Hay, *J. Chem. Phys.* **1985**, *82*, 284-298.
37. P.J. Hay, and W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 299-310.
38. T. Ishimoto, M. Tachikawa, and U. Nagashima, *Int. J. Quantum Chem.* **2006**, *106*, 1465-1476.
39. P. J. Stephens, F. J. Devlin, C. F. Chabalowski, and M. J. Frisch, *J. Phys. Chem.* **1994**, *98*, 11623-11627.
40. A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648-5652.
41. V. W. Laurie and D. R. Herschbach, *J. Chem. Phys.* **1962**, *37*, 1687-1693 (1962).

1. *Hiroki Sakagmi, Masanori Tachikawa, and Takayoshi Ishimoto*

   *Graduate School of Nanobioscience, Yokohama City University, 22-2 Seto, Kanazawa-ku, Yokohama 236-0027, Japan* [↑](#endnote-ref-1)