*Bull. Chem. Soc. Jpn.*, ***74***, *2279–2283 (2001)*

# The Surface Reaction Mechanism on Al(111)

**Tohru Nakajima and Koichi Yamashita***

Department of Chemical System Engineering, Graduate School of Engineering, University of Tokyo, Tokyo 113-8656

(Received February 26, 2001)

A surface reaction mechanism in the aluminum chemical vapor deposition (Al-CVD) method using dimethylaluminum hydride (DMAH) as the material gas has been studied using quantum chemical methods. Density functional theory (DFT) and a cluster model were used to calculate the potential energies and the structures of adsorbates and transition states of surface reactions. We have obtained the result that the hydrogen molecule and trimethylaluminum (TMA) are easily produced, while methane cannot be formed as a reaction product of Al-CVD because of the large barrier height, although the latter reaction path is thermodynamically accessible.

In our previous theoretical study,[1,2] we reported a reaction mechanism for chemical vapor deposition (CVD) using dimethylaluminum hydride (DMAH).[3–15] In particular, we treated the aluminum growth on aluminum surfaces, which is considered to be the main process in Al-CVD. Our conclusions were that i) a deposition of aluminum in Al-CVD using DMAH begins to occur by means of a dissociative adsorption of DMAH into methylaluminum hydride and the methyl group; ii) methylaluminum hydride dissociates to methylaluminum and atomic hydrogen on the surface with an activation energy of ~19 kcal/mol; iii) the volatile hydrogen molecule, methane and trimethylaluminum (TMA) are obtained as reaction products; iv) the activation energy for the dissociation of methylaluminum into the aluminum atom and the methyl group is lowered by movement of methylaluminum to a kink or a step on the surface,[2] where aluminum is deposited with a so-called islands structure. In contrast to these theoretical results, it was reported that volatile methane molecules were not observed as reaction products in the experimental study.[3,11–13] From the theoretical viewpoint, this discrepancy seems to arise from lack of explicit consideration for surface reactions between various kinds of admolecules produced by the dissociative adsorption of DMAH on the surface.

In this article, we present the origin of this discrepancy between the experimental and theoretical studies. Focusing on the surface reactions between admolecules, e.g. dimethylaluminum, methylaluminum, the methyl group and the hydrogen atom, we have obtained energy diagrams and transition states for several surface reactions, in which the hydrogen molecule, methane, dimethylaluminum, and trimethylaluminum are produced, by calculating potential energies and molecular structures of adsorbants and transition states of the surface reactions by means of quantum chemical methods.

## Computational Details

We employed Becke's three parameter hybrid method with nonlocal correlation provided by the Perdew 86 expression (B3P86).[16–18] The adopted basis set was the Los Alamos effective-core potential (ECP)[19–21] plus the double-zeta basis including polarization functions on aluminum atoms and the Dunning-Huzinaga full double-zeta basis[22] including polarization functions on carbon and hydrogen atoms. All the calculations were performed using the Gaussian 94 program.[23]

We employed the cluster model to represent the aluminum substrate surface. The upper surface of this model cluster forms the Al(111)-surface with face-centered cubic structure (fcc). The distance of closest approach between aluminum atoms was fixed at 2.863 Å, which is equal to the experimental lattice constant (4.049 Å) in the aluminum crystal. The distance between the surface and the second layers is 2.338 Å.[2] The assessments of cluster size and structure dependence were performed in the previous paper.[2] Among the model clusters dealt with in the paper,[2] we used the 7–3 cluster, which consists of seven aluminum atoms for the surface layer, and three for the second layer, because of the variety of adsorption sites expressed on the surface layer and a reduction of computational tasks. With this model cluster, we investigated adsorption of admolecules, transition states for the surface reactions and desorption of the reaction products.

Energy diagrams were obtained from the adsorption energies calculated for each admolecule separately in reactants and those for all the adsorbates in co-adsorption and transition states. In order to search transition states, we chose the newly formed bond lengths as the reaction coordinates and calculated the potential energies along these reaction paths.

In this study, we deal with the following surface reactions:

$$\mathrm{H_{ad} + H_{ad} \rightarrow H_{2ad} \rightarrow H_{2gas}}, \tag{1}$$

$$\mathrm{H_{ad} + CH_{3ad} \rightarrow CH_{4ad} \rightarrow CH_{4gas}}, \tag{2}$$

$$\mathrm{CH_{3ad} + AlCH_{3ad} \rightarrow Al(CH_3)_{2ad} \rightarrow Al(CH_3)_{2gas}}, \tag{3}$$

$$\mathrm{CH_{3ad} + Al(CH_3)_{2ad} \rightarrow Al(CH_3)_{3ad} \rightarrow Al(CH_3)_{3gas}}. \tag{4}$$

Subscripts ad and gas represent the adsorption state and the gas molecule, respectively. Other reactions were not considered because it is important to make it clear whether the hydro-

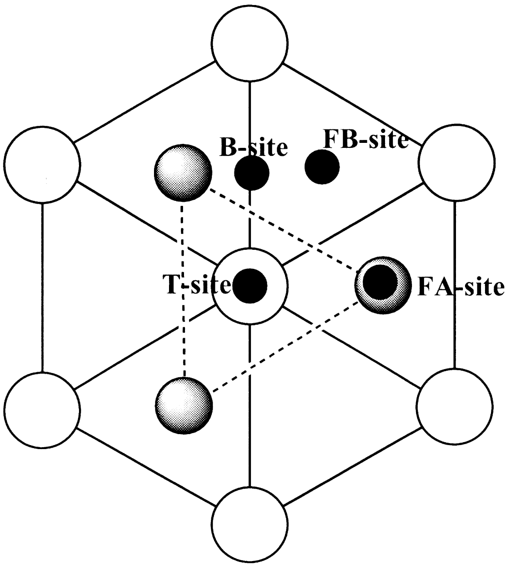

Fig. 1. Adsorption sites on the surface of 7–3 cluster, where T, B, FA and FB represent the terminal, bridge, three-fold A and three-fold B sites, respectively.

gen molecule, methane, and trimethylaluminum are the reaction products or not, although these molecules are considered to be the reaction products in some experimental studies.[3,9–13]

## Results and Discussions

As shown in Fig. 1, we have considered adsorption onto the following surface adsorption sites: the terminal (T), the bridge (B), the three-fold A (FA), and the three-fold B (FB) sites, where an aluminum atom of the second layer exists directly under the FA site but not under the FB site.

We summarize the adsorption energies of admolecules in Table 1. The most stable adsorption sites for the hydrogen atom, the methyl group, methylaluminum, and dimethylaluminum are FB, T, FA, and B sites, respectively. The adsorption energies of the hydrogen atom and dimethylaluminum are quite large (53.6–61.1 kcal/mol for the hydrogen atom and 61.5–67.3 kcal/mol for dimethylaluminum, respectively) as compared with those of the methyl group and methylaluminum. The energy differences in Table 1 were obtained with the lowest adsorption energy as a reference energy point for each admolecule. For the methyl group and methylaluminum, the energy differences change significantly depending on the adsorption sites, in particular, those on the FA site for the methyl group and those on the T site for methylaluminum are surprisingly high.

The reaction paths for the surface reactions among admolecules are described as follows: (i) reactant admolecules are well separated from each other on the most stable adsorption sites on the surface; (ii) they exist on the most stable neighboring sites by moving on the surface, except for the case of production of the hydrogen molecule, where the most stable adsorption sites of both admolecules (two hydrogen atoms) are the FB site and they cannot exist on the most stable neighboring sites simultaneously; (iii) the system comes to the transition state of the surface reaction; (iv) the products are adsorbed on the surface; (v) finally, the desorption of products occurs. The processes from (i) to (ii), from (ii) to (iv), and from (iv) to (v) imply the diffusion of admolecules, the surface reaction between admolecules, and the desorption of products, respectively. In particular, we focused on the surface reaction mechanism in the present paper and investigated these surface reac-

Table 1. Adsorption Energy of Admolecules on 7-3 Al Cluster (kcal/mol)

| Admolecule | Adsorption site[a)] | Adsorption energy | Energy difference[b)] |
|---|---|---|---|
| H | B | 55.4 | +5.6 |
| | FA | 53.6 | +7.5 |
| | FB | 61.1 | 0.0 |
| | T | 55.5 | +5.5 |
| $CH_3$ | B | 33.6 | +10.0 |
| | FA | 28.3 | +15.2 |
| | FB | 32.9 | +10.6 |
| | T | 43.5 | 0.0 |
| $AlCH_3$ | B | 45.0 | +4.1 |
| | FA | 49.0 | 0.0 |
| | FB | 43.3 | +5.8 |
| | T | 19.5 | +29.5 |
| $Al(CH_3)_2$ | B | 67.3 | 0.0 |
| | FA | 62.3 | +5.0 |
| | FB | 61.5 | +5.8 |
| | T | 65.2 | +2.1 |

a) B, FA, FB and T represent bridge, three-fold A, three-fold B and terminal sites, respectively.

b) These are calculated using each the adsorption energy on the most stable adsorption site as a reference point.

tions by using the model cluster adsorbing two adsorbates simultaneously. We have calculated total energies and adsorption structures with respect to the conditions described above, (i)–(v), along the reaction paths by the gradient-corrected DFT method,[16–18] which is widely used in theoretical studies as a practical quantum chemical tool.[24–26]

The energy diagrams along these reaction paths are illustrated in Fig. 2. The structures of the transition states of the surface reactions are shown in Fig. 3. In reaction (1), 4.3 and 14.2 kcal/mol are needed for two hydrogen atoms to approach each other on the most stable and closest adsorption sites and on the FB and T sites, respectively. The activation energy for the production of the hydrogen molecule is 13.4 kcal/mol for the surface reaction. In the transition state, the hydrogen atom above the FB site moves towards the one above the T site. The bond length (hereafter, the bond lengths between admolecules in transition states are defined by the distances between the hydrogen atom for atomic hydrogen, the carbon atom for the methyl group, and the aluminum atom for methylaluminum, dimethylaluminum and TMA) of the hydrogen molecule in the transition state is ~1.2 Å. The desorption of the hydrogen molecule seems to be quite easy because there is no necessity for desorption energy. On the other hand, the production of methane needs a large energy, specifically, the activation energy is 23.7 kcal/mol. In the transition state, the hydrogen atom above the FB site moves close to the methyl group existing just above the T site and the bond length between the methyl group and the hydrogen atom is ~1.5 Å. The desorption of methane needs no energy, as with that of the hydrogen molecule. However, we note that there could exist stable adsorption states of $H_2$ and $CH_4$, where the adsorption energies (the energy barriers for desorption) are sufficiently low, since it is difficult to reproduce weak interactions such as a dispersion force by the DFT methods used here.

In the case of the production of TMA, we should consider two kinds of elementary processes on the surface; the production of dimethylaluminum from methylaluminum and the methyl group, which is described in reaction (3), and that of TMA from dimethylaluminum and the methyl group, which is also given in reaction (4). From the energy diagram, it is found that reaction (3) proceeds easily without large activation energies. In the transition structure, the methyl group above the T site and methylaluminum above the FA site are situated with a bond length of ~2.5 Å. However, the desorption of dimethylaluminum needs an extremely high energy and dimethylaluminum is considered to be adsorbed on the surface. In reaction (4), which is the surface reaction between the product of reaction (3) and the methyl group, the activation energy is not so large and TMA is considered to be easily produced on the surface although it needs a slightly higher energy for reactant admolecules to approach each other onto the most stable neighboring adsorption sites. Dimethylaluminum remains above the B site and the methyl group moves from the T site towards the opposite direction for dimethylaluminum. In the transition

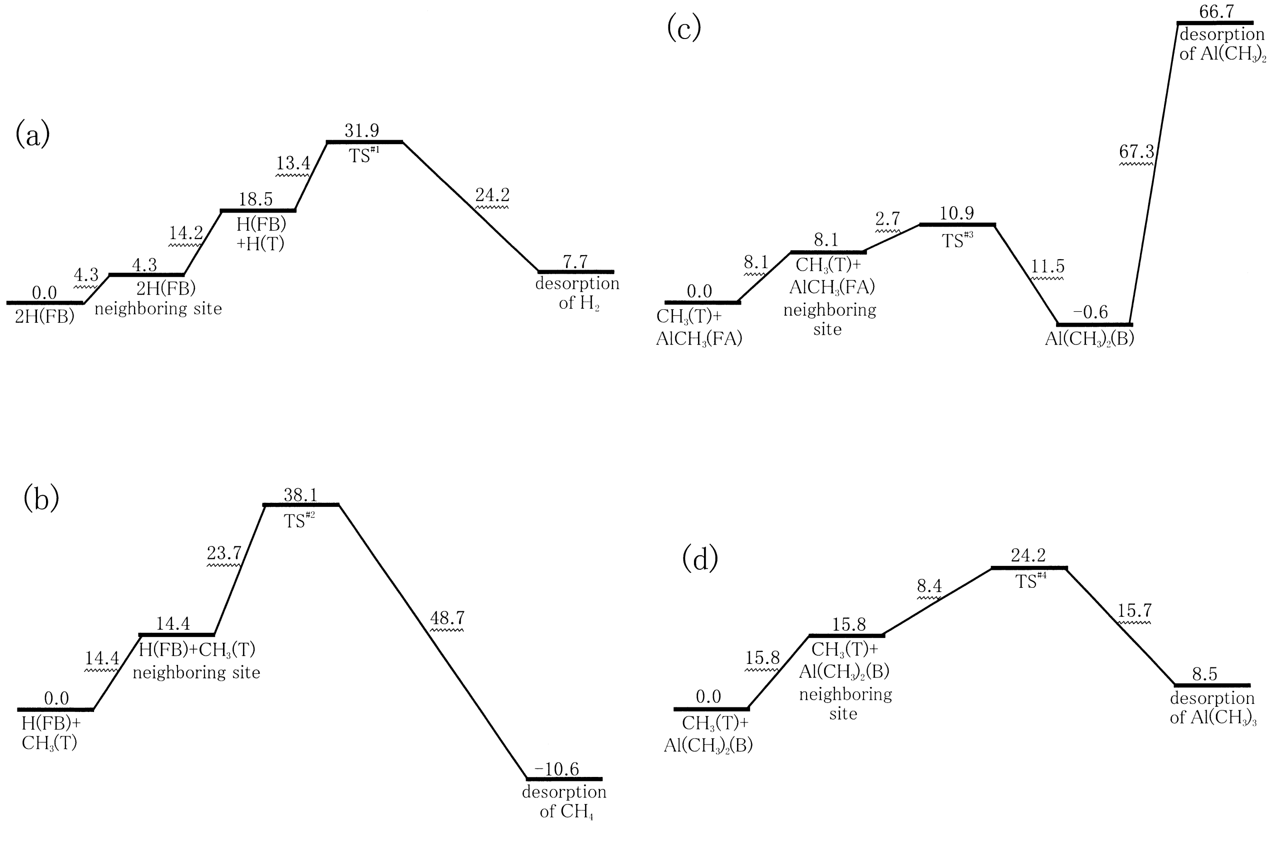

Fig. 2. Energy diagrams along the surface reactions (a) $H_{ad} + H_{ad} \rightarrow H_{2ad} \rightarrow H_{2gas}$, (b) $H_{ad} + CH_{3ad} \rightarrow CH_{4ad} \rightarrow CH_{4gas}$, (c) $CH_{3ad} + AlCH_{3ad} \rightarrow Al(CH_3)_{2ad} \rightarrow Al(CH_3)_{2gas}$, (d) $CH_{3ad} + Al(CH_3)_{2ad} \rightarrow Al(CH_3)_{3ad} \rightarrow Al(CH_3)_{3gas}$. Potential energies are given with those in reactant states as reference energy points, respectively. Energy differences, which are underlined, are also presented.

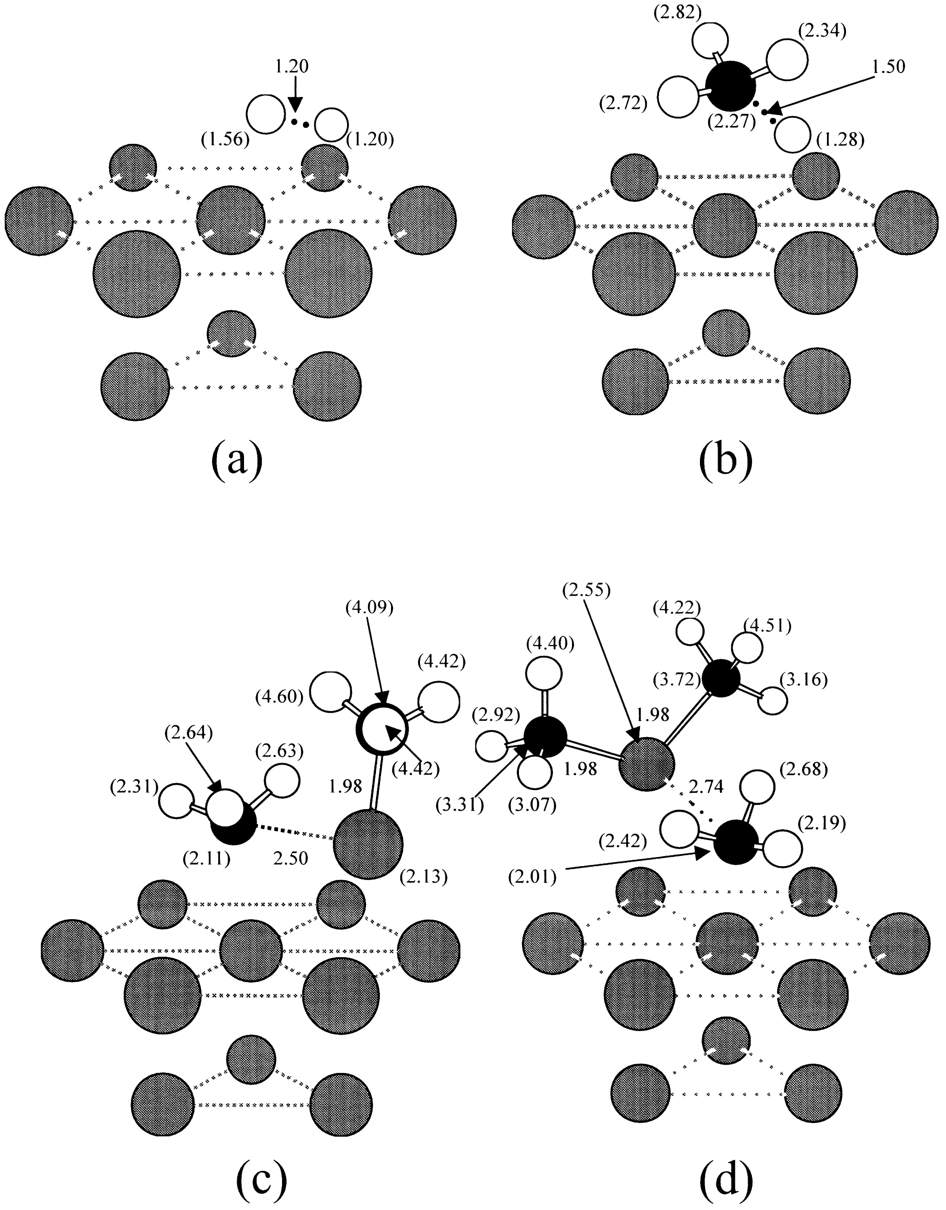

Fig. 3. Structures in transition states of surface reactions: (a) $H_{ad} + H_{ad} \rightarrow H_{2ad}$; (b) $H_{ad} + CH_{3ad} \rightarrow CH_{4ad}$; (c) $CH_{3ad} + AlCH_{3ad} \rightarrow Al(CH_3)_{2ad}$; (d) $CH_{3ad} + Al(CH_3)_{2ad} \rightarrow Al(CH_3)_{3ad}$. Bond lengths (Å) are presented. Distances from the surface (Å) are also given in parentheses.

state, the bond length between dimethylaluminum and the methyl group is ~2.7 Å. TMA is also stable against desorption from the surface.

In the previous study,[1,2] we have tentatively concluded that the volatile hydrogen molecule, methane, and TMA are easily formed as the reaction products in Al-CVD using DMAH, without any considerations of surface reactions. However, from the direct calculations with respect to the surface reactions, we may conclude in this article that the hydrogen molecule and TMA are easily produced. On the other hand, methane cannot be formed because of the high activation energy for the surface reaction. The tendency to produce hydrogen and TMA rather than methane is considered to be unchanging at temperatures (~200 °C) and pressures (~1 Torr) because of the large energy differences (~10 kcal/mol) between the activation energies. This conclusion is consistent with the recent experimental results in Al-CVD using DMAH.[12,13]

This work was partially supported by the Semiconductor Technology Academic Research Center (STARC). We are grateful to Professors H. Komiyama, Y. Shimogaki and Y. Egashira for their valuable comments and discussions. We also thank Doctors H. Ito and J. Aoyama for their useful discussions.

## References

1 T. Nakajima and K. Yamashita, *J. Mol. Struct. (THEOCHEM)*, **490**, 155 (1999).

2 T. Nakajima, T. Tanaka, and K. Yamashita, *Surf. Sci.*, **444**,

99 (2000).

3 D. R. Strongin and P. B. Comita, *J. Phys. Chem.*, **95**, 1329 (1991).

4 M. Hanabusa and A. Komatsu, *Appl. Phys. Lett.*, **65**, 1826 (1994).

5 M. Hanabusa, A. Oikawa, and P. Y. Cai, *J. Appl. Phys.*, **66**, 3268 (1989).

6 N. Takeyasu, Y. Kawano, E. Kondoh, T. Katagiri, H. Yamamoto, H. Shinriki, and T. Ohta, *Jpn. J. Appl. Phys.*, **33**, 424 (1994).

7 N. Zhu, T. Cacouris, R. Scarmozzino, and R. M. Osgood Jr., *J. Vac. Sci. Technol. B*, **10**, 1167 (1992).

8 E. Kondoh and T. Ohta, *J. Vac. Sci. Technol. A*, **13**, 2863 (1995).

9 K. Masu, M. Yokoyama, H. Matsuhashi, and K. Tsubouchi, *Appl. Surf. Sci.*, **79/80**, 237 (1994).

10 K. Tsubouchi and K. Masu, *J. Vac. Sci. Technol. A*, **10**, 856 (1992).

11 B. G. Willis and K. F. Jensen, Conference Proceedings ULSI XII, 29 (1997).

12 M. Sugiyama, Y. Shimogaki, H. Itoh, J. Aoyama, T. Yoshimi, and H. Komiyama, Proc. Symp. Fundamental Gas-Phase and Surface Chemistry of Vapor-Phase Materials Syntheses, Electrochemical Society, Pennington, U.S.A., **98-23**, 252 (1998).

13 M. Sugiyama, H. Itoh, J. Aoyama, H. Komiyama, and Y. Shimogaki, *Jpn. J. Appl. Phys.*, **39**, 1074 (2000).

14 M. Sugiyama, T. Nakajima, T. Tanaka, H. Itoh, J. Aoyama, Y. Egashira, K. Yamashita, H. Komiyama, and Y. Shimogaki, *Jpn. J. Appl. Phys.*, **39**, 6501 (2000).

15 M. Sugiyama, T. Iino, H. Itoh, J. Aoyama, H. Komiyama, and Y. Shimogaki, *Jpn. J. Appl. Phys.*, **38**, L1528 (1999).

16 A. D. Becke, *Phys. Rev. A*, **38**, 3098 (1988).

17 J. P. Perdew, *Phys. Rev. B*, **33**, 8822 (1986).

18 A. D. Becke, *J. Chem. Phys.*, **98**, 5648 (1993).

19 P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, **82**, 270 (1985).

20 W. R. Wadt and P. J. Hay, *J. Chem. Phys.*, **82**, 284 (1985).

21 P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, **82**, 299 (1985).

22 T. H. Dunning Jr. and P. J. Hay, "Modern Theoretical Chemistry," ed by H. F. Schaefer III, Plenum, New York (1976), p. 1.

23 M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. A. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, "Gaussian 94," Gaussian Inc, Pittsburgh PA, (1995).

24 L. Fan and T. Ziegler, *J. Am. Chem. Soc.*, **114**, 10890 (1992).

25 J. H. Jang, J. G. Lee, H. Lee, Y. Xie, and H. F. Schaefer III, *J. Phys. Chem. A*, **102**, 5298 (1998).

26 A. Gindulyte, L. Massa, L. Huang, and J. Karle, *J. Phys. Chem. A*, **103**, 11045 (1999).