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Dynamic Reaction Coordinate Analysis: An Application to \( \text{SiH}_4 + \text{H}^- \rightarrow \text{SiH}_5^- \)

**Abstract**

An ab initio classical trajectory method, the dynamic reaction coordinate (DRC) method based on ab initio electronic structure calculations, is applied to a study of the chemical reaction \( \text{Si}^- + \text{H}^- \rightarrow \text{SiH}_5^- \). Both side attack (C2v symmetry) and front attack (C3v symmetry) of \( \text{H}^- \) on \( \text{SiH}_4 \) are examined. To analyze the nature of the intramolecular vibrational energy transfer, the DRC and its corresponding momentum are mapped onto normal modes of both reactant and product systems. These analyses show that Berry pseudorotation occurs repeatedly in the \( \text{SiH}_5^- \) produced by the side attack, whereas the SN2 reaction \( \text{H}^- + \text{Si}^- \rightarrow \text{Si}^- + \text{H}^- \) often occurs upon front attack depending on the initial relative velocity.

**Disciplines**

Chemistry

**Comments**

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Dynamic Reaction Coordinate Analysis: An Application to SiH₄ + H⁻ → SiH₅⁻

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An ab initio classical trajectory method, the dynamic reaction coordinate (DRC) method based on ab initio electronic structure calculations, is applied to a study of the chemical reaction SiH₄ + H⁻ → SiH₅⁻. Both side attack (C₂ᵥ symmetry) and front attack (C₃ᵥ symmetry) of H⁻ on SiH₄ are examined. To analyze the nature of the intramolecular vibrational energy transfer, the DRC and its corresponding momentum are mapped onto normal modes of both reactant and product systems. These analyses show that Berry pseudorotation occurs repeatedly in the SiH₅⁻ produced by the side attack, whereas the SN₂ reaction H⁻ + SiH₄ → SiH₄ + H⁻ often occurs upon front attack depending on the initial relative velocity.

I. Introduction

Pentacoordinated silicon anions have been the subject of both experimental¹⁻⁵ and theoretical⁶⁻¹⁷ interest, due to their implication in a variety of chemical reactions. Of particular interest has been the nature of isomerization of such species by the Berry pseudorotation process¹⁸ and the manner in which pseudorotation affects reactivity. Since the barrier to pseudorotation is generally much smaller than the well corresponding to SiH₄ + X⁻ → SiH₃X⁻, pseudorotation within the well can have an impact on the subsequent chemistry. The equilibrium structure of the simplest pentacoordinated silicon anion, SiH₅⁻, is trigonal bipyramidal. Berry pseudorotation (Figure 1) proceeds from one trigonal bipyramidal arrangement to another through a tetragonal transition state with a 2 (3) kcal/mol barrier at the second-order perturbation theory (Hartree–Fock) level of theory.¹¹ This process of pseudorotation from trigonal bipyramid through the transition state may be used as a prototype to study the dynamical behavior of SiH₅⁻. A particularly interesting question is what is the nature of the intramolecular vibrational energy transfer between the initial approach of H⁻ (that presumably becomes the Si–H stretching motion) and the pseudorotation?

There are many ways in which an H⁻ may approach SiH₄. However, three attack orientations upon a highly symmetrical SiH₄ are side, front, and back attack as shown in Figure 2. Due to the molecular symmetry, these attacks may occur in six, four, and four equivalent ways, respectively. The expected products are SiH₅⁻ (addition) in side or front attack, SiH₄ + H⁻ (SN₂) in front attack, and SiH₃⁻ + H₂ (abstraction) in back attack. It should be noted that, in the addition reaction, the H⁻ anion is likely to occupy an equatorial position in side attack vs an axial position in front attack (see Figure 2). In this paper, we study the side and front attack cases.

When a chemical reaction is studied in quantum chemistry, typically stationary points, i.e., reactant, product, and transition state geometries, are located and then the character of these stationary points is determined by normal mode analysis. Once these stationary points have been characterized, the reaction path may be followed, using the intrinsic reaction coordinate (IRC)¹⁹


Figure 1. Illustration of Berry pseudorotation.

method, from transition state to both reactants and products. More detailed dynamic information may be obtained by determining the reaction path Hamiltonian.²⁰ The vibrational normal modes can be defined systematically along the reaction path by diagonalizing the Hessian matrix of energy second derivatives after projecting out the gradient vector (the reaction coordinate direction). This approach probes small vibrational displacements transverse to the minimum energy path. Recently, Hirano et al.²¹,²² proposed useful methods that make use of vibration mixing and vibration mapping to describe a vibrationally interacting system using reactant and product normal modes. Their scheme suggests that the correlation diagram connecting normal modes from reactant to product is helpful in the same manner as a molecular orbital (MO) diagram because those modes belonging to different symmetry representations cannot mix with each other throughout the reaction. These are all, however, static analyses in the sense that they examine static features of a potential surface which governs the molecular dynamical process.

For the examination of dynamical aspects of a reaction directly with ab initio wave functions, one can turn to the dynamic reaction coordinate (DRC) approach.²³⁻²⁵ The DRC
II. Methods of Calculation

*Ab initio* MO calculations are performed for the reaction, SiH$_4$ + H$^-$ $\rightarrow$ SiH$_5^-$, with the 6-31++G(d,p) basis set, using the restricted Hartree–Fock (RHF) method. It has previously been shown$^{9-11}$ that the effect of correlation on this reaction is small enough that RHF calculations provide a qualitatively reasonable picture. The equilibrium geometries are located for reactants and product, and normal mode analysis is performed for both structures. For both side attack ($C_2v$ symmetry) and front attack ($C_3v$ symmetry) paths, energy profiles are calculated as a function of the Si–H$^-$ distance such that the other geometrical parameters are optimized under symmetry constraints.

DRC calculations are performed for both side and front attack processes at the same computational level. As initial conditions, it is assumed that an H$^-$ attacks equilibrium SiH$_4$ along the principal axis of symmetry of the reaction system, i.e., $C_3v$ and $C_2v$ symmetry in side and front attack cases, respectively. With these conditions, the reaction system is constrained to the initial symmetry, because the DRC calculation is based on Newton’s equations, so the initial symmetry must be retained. Thus, these processes can be described only in terms of the totally symmetric coordinates. It should be noted that due to this symmetry constraint Berry pseudorotation can only be initiated in a side attack (see Figures 1 and 2).

To analyze the process of energy transfer among vibrational modes, the DRCs and their conjugate momenta transformed into mass-weighted coordinates are mapped onto totally symmetric normal modes of the reactant (R) and product (P) as follows,$^{25}$

$$Q_i^A(t) = \sum_k (X_k(t) - X_k^A) \sqrt{m_k} \lambda_{ik}^A$$
$$P_i^A(t) = \sum_k \dot{X}_k(t) \sqrt{m_k} \lambda_{ik}^A \text{ (A = R or P)}$$

where $Q_i^A$ and $P_i^A$ are the $i$th normal coordinate and its conjugate momentum, respectively, $X_k$ and $\dot{X}_k$ are the $k$th Cartesian coordinate and corresponding velocity, respectively, $X_k^A$ is the $k$th Cartesian coordinate of the equilibrium geometry (R or P), $\lambda_{ik}^A$ is the $k$th component of the $i$th normal mode, $m_k$ is the atomic mass corresponding to $X_k$, and $N$ is the number of atoms in the reaction system. Then, we have two representations, $(Q_i^R(t), P_i^R(t))$ and $(Q_i^P(t), P_i^P(t))$, for the DRC trajectory. The former shows harmonic vibrations when $X(t)$ stays in the region around $X^R$ while the latter shows harmonic vibrations when $X(t)$ approaches the region of $X^P$.

All calculations are performed using the electronic structure program package, GAMESS.$^{28}$

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A. Potential Energy Surface of Reaction System. Figure 3 shows energy profiles as a function of the Si–H$^-$ distance, $r$, along the (a) $C_2v$ (side attack) and (b) $C_3v$ (front attack) optimized path, respectively. The energies are given relative to the dissociation limit (SiH$_4$ + H$^-$). The energy minimum points at $r = 1.52$ Å in (a) and $r = 1.63$ Å in (b) correspond to the product, SiH$_5^-$. As is shown in these figures, the former profile has both an energy minimum and maximum between separated
reactants and the product, while the latter is downhill to product, with a very flat region around \( r = 3 \) Å. In order to examine the effect of electron correlation, we also performed MP2 calculations at the RHF optimized geometry of the product, the minimum (\( r = 4.46 \) Å) and maximum (\( r = 2.42 \) Å) points (side attack), and the geometry optimized at \( r = 3 \) Å (front attack). The calculated energy values relative to that of the dissociation limit are given in Table 1. The RHF and MP2 surfaces are quantitatively a bit different but qualitatively similar. Thus, in this study, the DRC at the HF level is expected to be sufficient to obtain a qualitative analysis of the dynamics.

A normal mode analysis at the energy maximum and minimum points on the side attack path shows that those structures correspond to a second-order saddle point (two imaginary modes) and a transition state, respectively. Both structures have a nontotally symmetric mode with an imaginary frequency that breaks the \( C_2 \) symmetry in a direction toward the front attack path. This suggests that the side attack path is unfavorable, so that when the \( H^- \) anion approaches SiH\(_x\) from the side, the \( H^- \) turns away from the side attack path. Only when the initial relative velocity of \( H^- \) and SiH\(_x\) is sufficiently large can the \( H^- \) attack along the side direction before turning aside.

In the initial stage of the DRC calculations, the \( H^- \) is located at 7 Å away from the Si in both attack cases. The potential energies for the initial structures are calculated to be \(-0.3\) and \(-0.4\) kcal/mol in side and front attacks, respectively. For the side attack, the reaction system needs more than 8.8 (=8.5 + 0.3) kcal/mol (see Table 1) to cross the maximum. In contrast, for a front attack, the reaction system in principle needs no kinetic energy because the energy profile is downhill to product as shown in Figure 3b. Four initial kinetic energies are studied for each attack direction: 9, 10, 11, and 13 kcal/mol for the side attack and 1, 3, 5, and 7 kcal/mol for the front attack. The time step is taken as 0.1 fs, and a trajectory of >400 fs is calculated in every case.

### B. Normal Modes of Reaction System

Table 2 gives the symmetry representation, vibrational frequency (cm\(^{-1}\)), and period (fs) of each normal mode in SiH\(_4\) (\( T_d \) symmetry) and SiH\(_5^-\) (\( D_{3h} \) symmetry). In SiH\(_4\), modes with low frequency (\( L_2, L_3, L_5, L_6, \) and \( L_9 \)) are primarily \( H^-\!-\!Si^-\!-\!H \) bending, and modes with high frequency (\( L_1, L_4, L_5, \) and \( L_6 \)) are primarily \( Si^-\!-\!H \) stretching. In SiH\(_5^-\), the five highest frequency modes are \( Si^-\!-\!H \) stretches, with \( L_1 \) and \( L_2 \) being primarily axial stretches and \( L_3, L_5, \) and \( L_6 \) being primarily equatorial stretches. Modes \( L_4, L_5, L_6, L_{11}, \) and \( L_{12} \) are dominated by \( Hax^-\!-\!Si^-\!-\!Heq \) bending motions, whereas \( L_9 \) and \( L_{10} \) correspond to the \( \text{Hax}^-\!-\!Si^-\!-\!Heq \) bend as reported by Gordon et al.\(^{11}\)

The molecules SiH\(_4\) and SiH\(_5^-\) have 9 and 12 normal modes, respectively. When the \( H^- \) anion approaches SiH\(_x\), the supermolecule \((H^-\!-\!\cdot\!\cdot\!\cdot SiH_x)\) acquires a symmetry that depends on the direction of \( H^- \) approach (giving a subgroup of the original \( \text{SiH}_x \) \( T_d \) symmetry). Since the supermolecule is composed of six atoms, it has 12 normal modes even when two fragments are so separated that they have no interaction with each other.

Based on the vibrational correlation method proposed by Hirano et al.,\(^{21,22} \) the 12 modes of the supermolecule can be understood as a combination of modes of \( H^- \) and SiH\(_x\). When the interaction of \( H^- \) and SiH\(_x\) is weak (or they are well-separated), nine modes originate from SiH\(_x\) and three modes originate from \( H^- \) translations and SiH\(_x\) translations or rotations. Note that the latter three modes have zero eigenvalues. One of these three is the mode resulting in \( \text{H}^-\!-\!\cdot\!\cdot\!\cdot \text{SiH}_x \) collision, \( L_{col} \). The mode \( L_{col} \) can be expressed as\(^{31,22} \)

\[
L_{col} = \left( \frac{m_X}{m_{5,\text{SiH}_x} + m_H} \right)^{1/2} T_{\text{SiH}_x} - \left( \frac{m_{\text{SiH}_x}}{m_{5,\text{SiH}_x} + m_H} \right)^{1/2} T_{H^-}\quad (3)
\]

where \( m_X \) is the mass of fragment X and \( T_{X,Z} \) is a translation of X along the \( z \)-axis in mass-weighted coordinates\(^{32} \) (it is assumed that the two fragments collide with each other along the \( z \)-axis). Naturally, all modes should be classified according to symmetry representations of the supermolecule. Note that, in the supermolecule, the degenerate modes in SiH\(_x\) are split depending on the direction of \( H^- \) approach even when the fragments are far enough apart that their frequencies remain the same.
In these DRC calculations, the normal modes of both reactant and product are adopted as coordinate basis vectors to describe molecular dynamics, i.e., two coordinate systems are prepared for the description. The origins of these coordinate systems are located at the starting point, where $H^-$ is 7 Å separated from the equilibrium SiH$_4$, and at equilibrium SiH$_5^-$. The supermolecule normal modes ($H^-\cdot\cdot\cdot$SiH$_2$) are employed as basis modes for the reactants. Since the reaction system never loses its symmetry during the DRC calculation, the reaction process can be described only in terms of totally symmetric coordinates, i.e., totally symmetric normal modes. Of course, the set of totally symmetric normal modes in the $(C_2\nu)$ side attack is different from that in the $(C_3\nu)$ front attack. In the following, basis modes of the side and front attack are separately described with illustrations.

1. Side Attack. In the side attack, there are five totally symmetric normal modes. Thus, this process is described in a five-dimensional configuration space. Parts a and b of Figure 4 show the basis modes for the reactants and product, respectively. The superscripts R and P denote reactant and product, respectively. In Figure 4a, the distance between $H^-$ and Si is scaled for convenience. The positive direction of each mode is indicated by the arrows. The numbering of the normal modes is the same as that given in Table 2, and $L_{col}^R$ is defined in eq 3. According to Table 2, the basis modes originate from $A_1, E,$ and $T_2$ modes in SiH$_4$ and $A_1'$ and $E'$ modes in the product. $L_2^R, L_4^R, \text{and } L_5^R$ in the reactant and $L_2^P, L_4^P, \text{and } L_5^P$ in the product originate from degenerate modes.

In the initial stage of a DRC calculation, the reaction system is located at the origin ($Q^R(0) = 0$) and has kinetic energy only in the direction of $L_{col}^R (P^R(0) = 0$ when $i = \text{col})$ in the reactant coordinate space. As the $H^-$ approaches SiH$_4$, the other modes in Figure 4a ($L_1^R, L_3^R, L_6^R, \text{and } L_7^R$) may be excited by acquiring energy from $L_{col}^R$. When mode $L_2^R$ is excited, it leads to Berry pseudorotation.

When this process is described using the coordinate system of the product (Figure 4b), as $H^-$ approaches SiH$_4$, the reaction system approaches the origin. The initial kinetic energy in this case is distributed among all product modes, $L_1^P, L_3^P, L_5^P, L_6^P,$ and $L_7^P$. The momentum of each mode is determined in
2. Front Attack. In the front attack, we have four totally symmetric normal modes to describe the process. Parts a and b of Figure 5 show these basis modes in the reactants and product, respectively. The basis modes originate from $A_1$ and $T_2$ modes (Table 2) in SiH$_4$ and $A_1'$, $A_2'$, and $A_3''$ modes in the product. In the reactant, $L_8^R$ and $L_9^R$ originate from degenerate modes ($T_2$). Note that, since the splitting of degenerate modes is different, $L_4^R$ and $L_7^R$ in the reactant are different from those in the side attack case (compare those in Figure 5a with those in Figure 4a).

As noted for the side attack, the reaction system starts from the origin in the direction of $L_{col}^R$ in the reactant coordinate space. As H$^-$ approaches SiH$_4$, modes $L_4^R$, $L_5^R$, and $L_9^R$ (Figure 5a) may be excited. When $L_4^R$ and $L_9^R$ are excited, an SN$_2$ reaction can occur. In the product coordinate system (Figure 5b), $L_4^P$ denotes the movements leading to the SN$_2$ reaction. Thus, it is of interest to examine the interactions among $L_{col}^R$, $L_4^P$, and $L_9^R$ in the reactant and to examine the motions along $L_9^P$ in the product.

C. DRC Analysis. 1. Side Attack. Figure 6 shows the potential energy changes along the DRC trajectory in the side attack; the initial kinetic energy is taken to be (a) 9, (b) 10, (c) 11, and (d) 13 kcal/mol. Since the DRC method conserves the total energy, the sum of potential and kinetic energy is constant. As an example, the kinetic energy change is also shown in case a. The bottom of the potential energy well (global minimum) is $-12.8$ kcal/mol (Table 1). This is indicated by the dashed line in Figure 6.

In the first stage, the potential energy decreases slowly over 25–30 fs depending on the initial velocities and then starts to increase rapidly. In this stage, the H$^-$ approaches SiH$_4$ from $r = 7$ Å to $r = 4$ Å in Figure 3a. It should be noted that, in the absence of symmetry constraints, the reaction system would lose $C_2$ symmetry in this region as discussed earlier and deviate from the side attack path. For case a after about 20–35 fs, the potential attains a maximum of 9 kcal/mol and then hardly changes beyond $\sim 100$ fs.

In case (a), the potential fluctuations settle down around 0 kcal/mol and show only slight vibrational motion after that. This means that the reaction system cannot cross the maximum in Figure 3a and is again separated into two fragments, i.e., H$^-$ and SiH$_4$. As was described in the previous section, the reaction system needs more than 8.8 kcal/mol to cross the maximum. However, dynamically, some energy will be transferred to the other vibration modes through vibrational interactions. So, the kinetic energy of 9 kcal/mol is not enough to cross over the pass. In the other cases (b)–(d), after crossing over the pass.
of about 10 kcal/mol, vibrational structure can be seen in the potential profiles. Thus, the reaction system crosses over the pass and comes into the well of SiH$_5^-$.

Next, consider the DRC analysis in terms of the basis modes of the reactant given in Figure 4a. Figure 7 shows changes of those normal coordinates along the DRC trajectory. Each part of Figure 7 corresponds to parts (a)–(d) of Figure 6, respectively. In this coordinate system, the reaction system is initially located at the origin, and is deformed into the positive direction of L$_{coi}^R$. Around $t = 50$ fs (or $Q_{coi}^R = 8$ bohr amu$^{1/2}$), the other modes begin to fluctuate. For case a, corresponding to the smallest input of kinetic energy, $Q_{coi}^R$ decreases sharply after 80 fs. For cases (b)–(d), after about 50–70 fs, $Q_{coi}^R$ fluctuates around $Q_{coi}^R = 10$ bohr amu$^{1/2}$ (see also Figure 6). In this period, for (b)–(d) some of the initial translational energy is used for the geometrical deformation of SiH$_4$ to that in SiH$_5^-$. In case (a), due to the insufficient kinetic energy, the H$^-$ is scattered ($Q_{coi}^R$ decreases with a constant rate after that). It should be noted that, in case (a), the vibrational modes of SiH$_2$ obtain a small amount of energy from the H$^-$ attack and show some vibrational motion after the scattering.

In the other cases, i.e., (b)–(d), all modes show a large fluctuation. The most characteristic feature is the fluctuation of the pair of modes $L_i^R$ and $L_j^R$ with a constant ratio. As noted above, L$_i^R$ in Figure 4a corresponds to Berry pseudorotation. So, in the SiH$_5^-$ complex produced by the side attack, Berry pseudorotation appears to occur repeatedly. Judging from parts (b)–(d) of Figure 7, another trigonal-bipyramidal geometry connected by pseudorotation is located at about ($Q_i^R$, $Q_j^R$) = (−3, 4).

Since pseudorotation is an SiH$_5^-$ mode, the above dynamics can be seen directly in terms of the product basis modes given in Figure 4b. Parts (a)–(d) of Figure 8, corresponding to parts (a)–(d) of Figure 7, illustrate the changes of those normal coordinates along the DRC trajectory. In the initial stage, all coordinates go toward zero, meaning that the reaction system goes toward equilibrium SiH$_5^-$. For cases (b)–(d) after approaching the origin, each mode exhibits a fluctuation about 0, with some fluctuations (e.g., $L_0^P$) being quite large. In addition, it can be verified that the fluctuations of $L_0^P$ (Berry pseudorotation) causes changes of the vibrational center of this mode periodically between $Q_0^P = 0$ and 3 bohr amu$^{1/2}$. Thus, this complex oscillates between two equilibrium structures.

In summary, Berry pseudorotation occurs continuously within the well of SiH$_5^-$ produced by the side attack of H$^-$, and thus, SiH$_5^-$ is very active dynamically.

2. Front Attack. Figure 9 shows changes in the potential energy along the DRC trajectory for the front attack; the kinetic energies initially given to the system are (a) 1, (b) 3, (c) 5, and (d) 7 kcal/mol. As before, the dashed line indicates the global minimum corresponding to the product. The potential energy decreases gradually over about 50–100 fs, whereupon it falls into the product well. The larger the initial velocity is, the faster the reaction system drops into the well. Since the reaction system may deviate from the optimized path, it does not necessarily arrive at the bottom of the well.

After entering the well, each trajectory undergoes violent fluctuations of the potential energy. The larger the initial velocity, the more violent the fluctuation. The potential often goes beyond the dissociation limit. After about $t = 300$ fs, the fluctuations of the potential energy moderate, and the trajectory settles into slight vibration around zero in cases (a) and (b). In case (d), the fluctuation of the potential energy also acquires a constant rhythm after about $t = 300$ fs, but the magnitude of the fluctuations is large and the center of the vibration is not at the origin. The results for (a) and (b) suggest that the reaction system leaves the well (an H$^-$ departs from SiH$_3$), and SiH$_3$ acquires a slight vibrational energy. However, these profiles
Figure 7. Changes of normal coordinates of the reactant along the DRC trajectory in side attack. Each part of (a)-(d) corresponds to parts (a)-(d) of Figure 6, respectively.

Figure 8. Changes of normal coordinates of the product along the DRC trajectory in side attack. Each part of (a)-(d) corresponds to parts (a)-(d) of Figure 6, respectively.

do not provide sufficient information to determine which H (the initial approaching H− or an H in SiH₄) departs. This will be clear from our normal mode mapping analysis, discussed below.

Parts (a)-(d) of Figure 10 show fluctuations of the normal coordinates of the reactant along the DRC trajectories, corresponding to parts (a)-(d) of Figure 9, respectively. These
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Figure 9. Potential energy changes along the DRC trajectory in front attack; the initial kinetic energy is (a) 1, (b) 3, (c) 5, and (d) 7 kcal/mol. The dashed line shows the potential energy well (global minimum).

Figure 10. Changes of normal coordinates of the reactant along the DRC trajectory in front attack. Each part of (a)–(d) corresponds to parts (a)–(d) of Figure 9, respectively.

Figures show that the reaction system goes in the direction of $L_{coi}^R$ initially. At $Q_{coi}^R \approx 10$ bohr amu$^{1/2}$, the system enters the domain of $\text{SiH}_5^-$ and the other modes start to fluctuate. In case (a), with just 1 kcal/mol kinetic energy, all coordinates except $Q_{coi}^R$ settle to zero after the initial fluctuations ($t > 300$ fs) and $Q_{coi}^R$ decreases with a constant rate. These results suggest that with very small kinetic energy input, the initial approaching $H^-$ is scattered through a dynamic interaction with
SiH₄ over 200 fs (t ≈ 100–300 fs). When the starting kinetic energy is increased to ≥3 kcal/mol (parts (b)–(d) of Figure 10), different behavior is observed.

As described in the previous section, the characteristic modes leading to the Sₙ₂ reaction are L₇R and L₈R in the reactant and L₈R in the product. The L₇R mode in Figure 5a corresponds to a reverse umbrella motion (H₃) in SiH₄. In equilibrium SiH₅⁺, Si is located in the plane of the H₂ umbrella. Thus, as the H⁻ approaches SiH₄, the SiH₅⁺ moiety feels a force in the positive L₇R direction, resulting in vibrational excitation of the L₇R mode. As shown in parts (b)–(d) of Figure 10, the reaction system undergoes a L₈R vibrational motion at around Q₈R = 1.2 bohr amu⁻¹/₂ at ~250 fs. This corresponds to the geometry of equilibrium SiH₅⁺. Note that the movement of Q₈R is in phase with that of Q₇R. When the reaction system goes beyond the dissociation limit in L₇R, the system leaves the well of the product and the two fragments, i.e., H⁻ and SiH₄, separate. When dissociation occurs in L₈R, the system leaves the well in the normal phase of the SiH₅⁺ and Berry pseudorotation can occur in the L₈R mode. In both cases, the system leaves equilibrium SiH₅⁺ at about 300 fs, although Q₇R and Q₈R have changed their signs. This can be understood by examining Figure 5b: the two H atoms exchanged in the Sₙ₂ reaction have antisymmetric motions in L₇R and L₈R. In case (c), the reaction system remains within the SiH₅⁻ well over 400 fs. As expected, the fluctuation of the L₇R mode is large. In case (d), the profiles are qualitatively similar to those for case (b) (the Sₙ₂ reaction). However, the deviation of the coordinates from zero is very loose. In addition, each coordinate has some vibrational structure. This may indicate that the reaction system forms a loosely bound complex, exhibiting a large amplitude motion around the well.

For examination of the dynamics of the H⁻–SiH₄ complex in case (d), we performed DRC calculations over a much longer (1200 fs) time period. Figure 12 shows the resulting changes in the normal coordinates of (a) the reactant, (b) the product, and (c) changes in two Si–H distance, r₁ and r₂, along the DRC trajectory. Here, r₁ denotes the distance from the initial approaching H⁻ and r₂ denotes that from the H₂ in the opposite side. These figures show that, although the complex attempts to separate into H⁻ and SiH₄, the complex again unsuccessfully attempts to escape the well. Note that H₂ (r₂) lengthens to almost 5 Å away from Si at 390 fs. Around 1 ps, the complex again unsuccessfully attempts to escape the well.

In summary, either scattering of the approaching H⁻ or an Sₙ₂ reaction may occur by a front attack with a small initial relative velocity. In some cases, this mode of attack forms a loosely bound complex around the SiH₅⁻ well.

IV. Conclusion

In this paper, dynamical aspects of the reaction SiH₄ + H⁻ → SiH₅⁻ are studied by the DRC method based on ab initio MO calculations. To clarify the energy transfer mechanism, the DRC and its conjugate momentum are mapped onto both reactant and product normal modes. This analysis shows that, under side attack, the initial translational energy is transferred to the L₇R mode of SiH₅⁻ and Berry pseudorotation can occur...
Figure 12. Changes in the normal coordinates of (a) the reactant and the product, and (c) changes in two Si–H distances $r_1$ and $r_2$, along the DRC trajectory over 1200 fs for case d in Figure 9; $r_1$ denotes the distance from the initial approaching H$^+$; $r_2$ denotes the distance from the H in the opposite side.

continuously within the SiH$_3^-$ well. Under front attack, scattering of the initial approaching H$^+$ or an $\text{Si}_2$ reaction occurs, depending on the initial relative velocity. In some cases, the reaction system forms a loosely bound complex around the well.

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References and Notes

(32) In this paper, all normal modes are represented in the mass-weighted coordinate.

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