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Exploring the versatile reactivity of the F⁻ + SiH₃Cl system on a full-dimensional coupled-cluster potential energy surface

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ABSTRACT

We develop a full-dimensional analytical potential energy surface (PES) for the F^- + SiH₃Cl reaction using ROBOSURFER for automatically sampling the configuration space, the robust [CCSD-F12b + BCCD(T) - BCCD]/aug-cc-pVTZ composite level of theory for computing the energy points, and the permutationally invariant polynomial method for fitting. Evolution of the fitting error and the percentage of the unphysical trajectories are monitored as a function of the iteration steps/number of energy points and polynomial order. Quasi-classical trajectory simulations on the new PES reveal rich dynamics resulting in high-probability $S_N 2$ (SiH₃F + Cl⁻) and proton-transfer (SiH₂Cl⁻ + HF) products as well as several lower-probability channels, such as $SiH_2F^- + HCl$, $SiH_2FCl + H^-$, $SiH_2 + FHCl^-$, $SiHFCl^- + H_2$, $SiHF + H_2 + Cl^-$, and $SiH_2 + HF + Cl^-$. The Walden-inversion and front-side-attack-retention $S_N 2$ pathways are found to be competitive, producing nearly racemic products at high collision energies. The detailed atomic-level mechanisms of the various reaction pathways and channels as well as the accuracy of the analytical PES are analyzed along representative trajectories.

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I. INTRODUCTION

Recent experimental and theoretical investigations have provided deep insights into the atomic-level dynamics and mechanisms of bimolecular nucleophilic substitution (S_N2) at the carbon (C) center,¹⁻¹⁸ revealing various reaction pathways, such as direct rebound, direct stripping, ion-dipole pre- or post-reaction complex formation, hydrogen-bonded complex formation, front-side complex formation,9 and roundabout1 Walden inversion as well as front-side attack and double inversion.⁴ In addition to carbon center, S_N2 reactions can also occur at the silicon (Si) center;¹⁹⁻³ however, much less is known about the Si-centered $S_{\rm N}2$ reactions than the widely studied C-centered analogues. Therefore, following some early electronic structure work on the F⁻ + SiH₃F and Cl⁻ + SiH₃Cl systems,^{11,19–27,30,31} we recently investigated the stationary points and various product channels characterizing the X^{-} + SiH₃Y [X, Y = F, Cl, Br, I] reactions using high-level explicitly correlated *ab initio* methods.³² Even if carbon and silicon are valence isoelectronic, ab initio computations reveal qualitatively dif-

ferent potential energy profiles for C- and Si-centered systems. The well-known Walden inversion transition state (TS) is a minimum and the front-side attack TS is submerged at Si center, which may result in very different dynamics at C and Si centers, for example, the submerged front-side TS may undermine the stereospecificity at Si. Furthermore, the Si-H bond is significantly weaker than C-H, which may facilitate proton transfer, hydride ion substitution, or other alternative product channels at Si-centered reactions. Despite the fact that one may expect very complex dynamics in the case of Si-centered ion-molecule reactions, to the best of our knowledge, only a few reaction dynamics investigations have been performed for such systems^{27,33,34} and no analytical potential energy surface (PES) is available.

In the present study we develop a global full-dimensional analytical coupled-cluster-quality PES for the F⁻ + SiH₃Cl reaction, which surface allows efficient dynamics investigations. The PES development is carried out utilizing our ROBOSURFER program system³⁵ for automatic sampling of the configuration space and the permutationally invariant polynomial method^{36,37} for fitting the





ab initio energy points. The new PES is then used for quasi-classical trajectory (QCT) computations, which reveal the atomic-level mechanisms of the title reaction. We focus on the details of the PES development and the different reaction pathways uncovered by the present simulations. We are particularly interested in the ratio of the inversion and retention channels and their mechanisms. Furthermore, we pay special attention to unexpected product channels, which may be revealed by the dynamics simulations. In Sec. II, we describe the computational details including initial data sampling, fitting procedure, automatic PES development as well as QCT initial and final conditions. In Sec. III, the results on the stationary point properties and accuracy of the analytical PES, reaction probabilities, cross sections, and representative trajectories showing the atomic-level mechanisms of the different channels are presented and discussed. The paper ends with summary and conclusions in Sec. IV.

II. COMPUTATIONAL DETAILS

The PES development started from an initial set of *ab initio* energy points obtained by random alternations of the geometries of the stationary points, reactants, and products. We used the permutationally invariant polynomial method^{36,37} for fitting and the PES was iteratively improved by the ROBOSURFER program package,³⁵ which runs QCT simulations, manages *ab initio* calculations, and adds new points to the fitting set automatically. The quality of the PES was monitored by the frequency of the unphysical trajectories and by the fitting errors in the chemically relevant regions at each iteration. After the PES was found to be sufficient, final QCT simulations were performed, and reaction probabilities and integral cross sections were calculated.

A. Initial fitting set

The initial fitting set is obtained by randomly displacing the Cartesian coordinates of 11 stationary points (minima: WMIN, FSPreMIN, FSPostMIN, *anti-* and *syn-*FBHMIN, *anti-* and *syn-*ClBHMIN and ClDHBMIN, transition states: FSTS, FDITS, and ClDITS) in the 0–0.32 Å interval and randomly scattering the reactants and the bimolecular products (SiH₃Cl + F⁻, SiH₃F + Cl⁻, SiH₂Cl⁻ + HF, SiH₂F⁻ + HCl, SiH₂FCl + H⁻, SiH₂ + FHCl⁻, and SiHFCl⁻ + H₂) around each other with a center of mass distance of 2–10 Å and then randomly displacing their Cartesian coordinates as well in the 0–0.32 Å interval. We generated 500 randomly modified versions of each reference geometry for a total of 9000. Not all energy calculations converged for these geometries, so the size of the initial fitting set was slightly smaller, 8934 points.

All the *ab initio* computations are performed by the Molpro program package.³⁸ We used a combination of the explicitly correlated coupled-cluster singles and doubles (CCSD-F12b)³⁹ and the Brueckner coupled cluster⁴⁰ perturbative triples [BCCD(T) – BCCD] with the augmented correlation consistent triple-zeta basis set, aug-cc-pVTZ,⁴¹ AVTZ for short,

$$(CCSD-F12b + BCCD(T) - BCCD)/aug-cc-pVTZ.$$
 (1)

We chose this composite method because in a previous study of our research group it was found that the commonly used CCSD(T)-F12b, which is a gold standard in electronic structure calculations, misbehaves in some cases of highly distorted geometries, resulting in deep holes on the PES, which is detrimental to QCT simulations.⁴² It was also found that the misbehavior of CCSD(T)-F12b is due to the breakdown of the (T) perturbative part of the calculation and that by using the abovementioned composite method deep holes on the PES can be avoided more effectively.⁴²

B. Fitting procedure

The r_{ij} spatial distance of atoms *i* and *j* is the Euclidean norm of the difference of their Cartesian coordinate vectors $(\mathbf{x}_i \text{ and } \mathbf{x}_j)$: $r_{ij} = \|\mathbf{x}_i - \mathbf{x}_j\|$. We define a Morse variable, y_{ij} , as an exponentially transformed version of the distance, r_{ii} , as

$$y_{ij} = e^{-\frac{r_{ij}}{a}},\tag{2}$$

in which the damping parameter *a* controls the asymptotic behavior of the PES. In our case, we chose the value of *a* to be 3 a_0 (a_0 is the Bohr radius).

The PES is expressed as a polynomial in terms of the Morse variables in a way that it is invariant to the interchanges of like-atoms (for details, see Refs. 36 and 37). It uses all transformed interatomic distances, a total of 15 for the F^- + SiH₃Cl system. The fifth-order expansion requires 3292 coefficients and 10810 coefficients are needed for the sixth-order expansion.

A weighted least-squares method was used to calculate the fitting coefficients, denoted by vector **c**,

$$\mathbf{c} = (\mathbf{W}\mathbf{A})^{+}\mathbf{W}\mathbf{b},\tag{3}$$

where **b** is the vector of *ab initio* energies, **W** is a diagonal matrix containing the weights, and the *i*-th row of matrix **A** is obtained by evaluating the permutationally invariant polynomial basis^{36,37} at the corresponding geometry expressed as Morse variables, \mathbf{y}_i , i.e.,

$$\mathbf{A} = \begin{bmatrix} \mathbf{p}^{\mathrm{T}}(\mathbf{y}_{1}) \\ \mathbf{p}^{\mathrm{T}}(\mathbf{y}_{2}) \\ \vdots \\ \mathbf{p}^{\mathrm{T}}(\mathbf{y}_{n}) \end{bmatrix}, \qquad (4)$$

The **(WA)**⁺ denotes the pseudoinverse of the matrix product **WA**. The weight of the *i*-th geometry is defined as

$$W_{ii} = \frac{w_a}{E_{\text{rel},i} + w_a} \frac{w_b}{E_{\text{rel},i} + w_b}$$
(5)

based on its energy relative to the energy of the global minimum $(E_{\text{rel},i})$. The values of parameters w_a and w_b are set to 0.15 and 0.5 E_h , respectively.

The energy of a given geometry can be obtained on the PES by taking the dot product of the coefficients and the polynomial basis evaluated at the geometry written in Morse variables,

$$E_{\text{PES}}(\mathbf{y}) = \mathbf{c} \cdot \mathbf{p}(\mathbf{y}). \tag{6}$$

C. PES development

The initial dataset of 8934 geometries served as the starting point for our iterative PES development using the ROBOSURFER



FIG. 1. Evolution of the quality of the PES during the development. Percentage of unphysical trajectories as a function of PES iterations (top) and root-mean-square fitting errors in the chemically relevant region as a function of the fitting set size (bottom). The chemically relevant region is divided into two parts, between –68.7 and 26 kcal/mol (lower region) and between 26 and 120 kcal/mol (higher region) with respect to the energy of the reactants.

program package, which was recently developed by our group.³⁵ Our strategy was to run 1000 trajectories at a collision energy of 1 kcal/mol with different impact parameters ranging from 0 to 12 a_0 , incrementing by 0.5 a_0 . Once the quality of the PES was deemed sufficient, as indicated by a frequency of unphysical trajectories below 1%, the collision energy was raised to 10 kcal/mol. The collision energy was gradually increased from 10 to 80 kcal/mol in increments of 10 kcal/mol. The range of impact parameters was consistent throughout the energy increase, and the number of trajectories remained fixed at 1000.

Figure 1 illustrates the evolution of the PES quality over the development process, represented by the change in percentage of unphysical trajectories and by the change in root-mean-square fitting errors (RMSEs) in the chemically relevant energy regions, which are divided into lower and higher parts and span from -68.7 to 120 kcal/mol relative to the reactants. The results are displayed as a function of the number of PES iterations and the size of the fitting set, respectively. Initially, we employed a fifth-order polynomial, and the maximum target collision energy of 80 kcal/mol was reached after 237 iterations. During this time, the size of the fitting set increased to 14 586 points. Starting with an RMSE of 0.5 kcal/mol in the lower and 1.2 kcal/mol in the higher regions, the fitting errors grew rapidly as the fitting set expanded, surpassing 2.5 kcal/mol in the lower and 5.5 kcal/mol in the higher part of the relevant PES regions. We continued the development with a sixthorder fitting function, following the previous strategy, varying the

J. Chem. Phys. **158**, 224303 (2023); doi: 10.1063/5.0153083 Published under an exclusive license by AIP Publishing collision energies between 1 and 80 kcal/mol. This time, the fitting errors were initially much smaller, a few tenths of kcal/mol, and finally the RMSE reached only around 1.5 kcal/mol even in the higher energy region. The PES development was completed after 342 iterations and the final fitting set consisting of 19 470 geometries.

We considered a trajectory unphysical if its final step resulted in at least four fragments. This evaluation method is referred to as the geometric method in Fig. 1. We also calculated the percentage of unphysical trajectories based on energy conservation as a comparison. If any step along a trajectory differs in total energy, i.e., the sum of the kinetic contributions and potential energy, by more than 10^{-5} % from the initial step, we declare the trajectory unphysical. The frequency of unphysical trajectories remained below 1% according to both methods up to a collision energy of 80 kcal/mol on the final PES.

In order to assess the multi-reference character of the configurations used for the fitting, we plot the distributions of the T_1 -diagnostic values⁴³ in Fig. 2. As Fig. 2 shows, virtually all the T_1 values are below 0.02 in the lower-energy region and even in the energy range of 26–120 kcal/mol, relative to the reactants, only a few T_1 values exceed 0.02, indicating that the use of the singlereference methods is adequate to properly describe the chemically relevant configuration space of the title reaction. We assume that the excited electronic states do not compromise the description of the ground state PES because, even at the most problematic regions, ${}^1SiH_2 + FHCl^-$ (ground state) vs ${}^3SiH_2 + FHCl^-$ (excited state)



FIG. 2. Distributions of the T_1 -diagnostic values of the CCSD-F12b/AVTZ wavefunctions at the configurations used for the fitting in the chemically relevant region. The chemically relevant region is divided into two parts, between -68.7 and 26 kcal/mol (lower region) and between 26 and 120 kcal/mol (higher region) with respect to the energy of the reactants. The bin size is 0.0002.

and SiH₃ + FCl⁻ (ground state) vs SiH₃⁻ + FCl (excited state), the energy difference between the two electronic states is about 20 kcal/mol.³² Furthermore, we note that the SiH₃ + FCl⁻ channel is highly endothermic [$\Delta E_e(\Delta H_0) = 76.7(74.0)$ kcal/mol], thus it does not play any role in the present dynamics study.

D. QCT simulations

QCT simulations were performed on the final PES with collision energies of 1 and 5 kcal/mol and up to 40 kcal/mol in steps of 5 kcal/mol for the title reaction. The vibrational energy of the polyatomic reactant, SiH₃Cl, was set to its zero-point energy using normal mode sampling⁴⁴ and its rotational energy was set to zero. The orientation of the reactants was randomly rotated at the beginning of each simulation. The impact parameter, b, was varied from 0 with increments of 0.5 a_0 to b_{max} , where all trajectories resulted in nonreactive collisions. The value of b_{max} was 25, 17, 14, 12.5, 11.5, 11, 10.5, 10, and 9.5 *a*⁰ for the collision energies of 1, 5, 10, 15, 20, 25, 30, 35, and 40 kcal/mol, respectively. The initial center of mass distance was set by $\sqrt{x^2 + b^2}$, where x was set to 40 a_0 for collision energies of 1 and 5 kcal/mol and 25 a0 for higher collision energies to ensure that the initial distance was always greater than b_{max} . For each impact parameter and collision energy, 5000 trajectories were run using the velocity Verlet algorithm^{45,46} with a time step of 3 \hbar/E_h . This resulted in a total of 1 255 000 simulations, which were terminated when the maximum atom-atom distance exceeded the initial maximum interatomic distance by at least 1 a_0 .

The integral cross section (ICS) denoted by σ is a function of collision energy (E_{coll}). The ICS can be calculated as

$$\sigma(E_{\text{coll}}) = 2\pi \int_{b=0}^{b_{\text{max}}} bP(E_{\text{coll}}, b) db,$$
(7)

where $P(E_{coll}, b)$ represents the reaction probability at a given E_{coll} and *b*. We calculated the integral cross section for each product channel by numerically integrating using the trapezoidal rule.

Two kinds of zero-point energy constraints are used. A trajectory fulfills the soft vibrational constraint if the sum of the classical vibrational energies of the products reaches the sum of the harmonic zero-point energies of the PES-optimized products of the corresponding reaction. The hard constraint requires that the vibrational energy of each product fragment individually be at least its zeropoint energy. In the case of a single polyatomic (at least diatomic) fragment, the soft and hard constraints become equivalent.

E. Categorization of product channels

We categorized the product geometries based on connectivity by performing membership checks between their adjacency lists and the permutationally invariant sets of the adjacency lists of the reference geometries. The adjacency of two atoms, *i* and *j*, was determined by their spatial distance being less than the sum of their covalent radii, $d_i + d_j$, plus a constant *c*. The covalent radii for hydrogen, fluorine, and chlorine were taken as 0.31, 0.57, and 1.02 Å, respectively, based on the paper of Cordero *et al.*,⁴⁷ and the constant *c* is defined to be 0.80 Å. For the covalent radius of silicon, we used a slightly higher value, 1.60 Å, than the reported. These values were chosen such that the connectivity of the reference geometries corresponds to our chemical intuition while categorizing most of the product geometries. It is worth noting that there are other combinations of atomic radii and *c* that perform just as well as the one we used.

Figure 3 depicts the adjacency lists as nested lists of ordered atomic indices of the neighboring atoms. As an example, two cases are shown, the reactants and the proton-abstraction products. Despite the fact that permutations of hydrogen atoms result in six chemically equivalent geometries, the set of adjacency lists is typically smaller. For the reactants, all permutations of hydrogens result in the same connectivity. On the other hand, in the case of proton abstraction, a set of three different adjacency lists can be created.

The computational time of an adjacency list from spatial coordinates depends on the square of the number of atoms and the cost of generating the invariant set of the adjacency lists of a reference geometry in larger systems primarily depends on the permutational symmetry. Although generating the invariant set of a reference geometry is a one-time operation and in the case of smaller systems, like F^- + SiH₃Cl, it is negligible. We used Python for the implementation and represented the adjacency lists as standard tuples of tuples of integers and the invariant sets as standard sets of these nested tuples. The advantage of this representation is that a set membership check in Python has constant time complexity, O(1).⁴⁸ This feature becomes more relevant in systems with higher permutational symmetry.



FIG. 3. Permutationally invariant sets of adjacency lists of reactants (left) and $SiH_2CI^- + HF$ products (right), with indices of hydrogens of 0, 1, 2 and indices of silicon, fluorine, and chlorine of 3, 4, and 5, respectively.

A shortcoming of a purely connectivity-based categorization is that multiple product channels can share the same connectivity. For instance, in our study, halide ion substitution can be divided into inversion and retention mechanisms. To differentiate between these reactions, we employed a vector projection method that was previously reported by our research group.⁴⁹

The identification of a product with three fragments is much less straightforward than for a product with two fragments. This is because, in the case of two fragments, the termination condition of the simulation ensures that the fragments are sufficiently separated. However, with a three-fragment product, two of the fragments may be close to each other and, if the simulation were to continue, other chemical reactions might have occurred. It is also possible that in a strongly excited vibration, the elongated bond is not detected, or in a vibrationally distorted structure extra connections can appear, resulting in unidentified geometries. We solved these problems by propagating the unidentified products, which may be unphysical or just highly distorted, and the three-fragment ones by a few thousand steps, and then, in the case of a "better trajectory step," the original spatial and velocity coordinates were replaced. A "better trajectory step" means the first trajectory step of a two-fragment geometry instead of a previously three-fragment or unidentified one, or the first three-fragment geometry instead of an unidentified product. If an unidentified product is followed by three- and then two-fragment geometries, the first two-fragment geometry is chosen.

III. RESULTS AND DISCUSSION

A. Schematic PES

Figure 4 presents the reaction channels of the SiH₃Cl + F^- system, along with the relative energies of the stationary points and products that were calculated using the [CCSD-F12b + BCCD(T) – BCCD]/AVTZ composite coupled-cluster level of theory as well as calculated on the PES. The system exhibits a diverse reactivity, resulting in a variety of products that are sometimes formed through multiple mechanisms.

The chloride ion substitution is the most exothermic reaction [$\Delta E_e(\Delta H_0) = -48.1(-47.3)$ kcal/mol], leading to SiH₃F + Cl⁻. The Walden minimum (WMIN) with a large classical (adiabatic) negative energy, -68.7(-67.3) kcal/mol, reveals a barrierless inversion and the front-side attack transition state (FSTS) corresponds to a retention mechanism with deep negative barrier, -54.0(-53.2) kcal/mol. Overall, a mixture of retention and inversion products is expected even at low collision energies.

In the analogous carbon-centered system, $CH_3Cl + F^-$, a double inversion mechanism is responsible for the retention products at collision energies significantly lower than the barrier height of the front-side attack substitution.⁴ According to Ref. 4, double inversion involves a partial proton abstraction, where the HF moves around the central atom, leading to the formation of an inverted transition state, [FH–CH₂Cl]⁻. This transition state then rearranges into an inverted back-side attack structure, ultimately resulting in the formation of the retention products through Walden inversion. We discovered the silicon analog of this transition state, FDITS, which possesses the same symmetry as the carbon-centered one.³² Their classical(adiabatic) relative energies are also compara-

ble, 16.1(13.6) kcal/mol,³² for the carbon-centered double inversion TS and 14.7(14.5) kcal/mol for FDITS.

The proton abstraction is barrierless and exothermic with $\Delta E_e(\Delta H_0) = -7.9(-9.1)$ kcal/mol, meaning the SiH₂Cl⁻ + HF reaction channel opens at low collision energies. It is worth noting that the proton abstraction on the CH₃Cl + F⁻ PES is an endothermic process with $\Delta E_e = 29.2$ kcal/mol.⁴

The hydride ion substitution, SiH₂FCl + H⁻, is a direct reaction and is classically athermic within chemical accuracy and adiabatically slightly exothermic [$\Delta E_e(\Delta H_0) = -0.1(-2.9)$ kcal/mol]; therefore, this channel is expected to open at low collision energies. It may compete with chloride substitution because they arise from the decomposition of the same set of stationary points.

Many indirect reaction channels are observed. The most significant of them is the hydrogen-chloride formation, SiH₂F⁻ + HCl, which competes with chloride substitution via a barrierless proton abstraction by the leaving ion. The reaction is exothermic with $\Delta E_e(\Delta H_0) = -4.8(-7.2)$ kcal/mol.

The second-most exothermic reaction is the two-fragment hydrogen molecule production, SiHFCl⁻ + H₂, with $\Delta E_e(\Delta H_0)$ = -39.5(-43.0) kcal/mol. Molecular hydrogen can be formed by two main mechanisms. The simpler mechanism is when the hydride ion substitution is followed by proton abstraction by the leaving ion. The other, more complex mechanism begins with the formation of HCl, which in itself is an indirect reaction, followed by the formation of a dihydrogen-bonded complex, ClDHBMIN, with classical(adiabatic) relative energies of -18.4(-19.7) kcal/mol. During a classically endothermic but adiabatically athermic process [$\Delta E_e(\Delta H_0) = 5.1(0.1)$ kcal/mol], this deep negative energy minimum breaks into three parts, SiHF, H₂ and Cl⁻, and finally the SiHF and Cl⁻ fragments unite. These relative energies also imply that there is a three-fragment hydrogen molecule formation channel that opens at low collision energy. The hypothesized [FH-HSiHCl]⁻ minimum as the analog of ClDHBMIN could not be optimized, thus the HF and H₂ formation channels are not connected.

The endothermic $[\Delta E_e(\Delta H_0) = 15.9(14.0) \text{ kcal/mol}]$ mixed bihalide ion formation, SiH₂ + FHCl⁻, is possible by two mechanisms, with the decomposition of the *anti*- or *syn*-FBHMIN complex, which is formed after the proton abstraction of the fluoride ion, or by the decomposition of the *anti*- or *syn*-ClBHMIN, the complex that is formed after HCl production. The relative energies of these complexes are comparable, -22.8(-22.3) kcal/mol for *anti*and *syn*-FBHMIN, -19.3(-20.3) kcal/mol for *anti*-ClBHMIN and -19.8(-20.8) kcal/mol for *syn*-ClBHMIN.

At high collision energies, the formation of another threefragment product, SiH₂ + HF + Cl⁻, was observed through the decomposition of either SiH₂Cl⁻ following proton abstraction or the bihalide ion in the case of SiH₂ + FHCl⁻. However, the PES does not reproduce the *ab initio* reaction energies for SiH₂ + HF + Cl⁻ with near chemical accuracy, as the direct *ab initio* $\Delta E_e(\Delta H_0)$ values are 39.6(36.2) kcal/mol, whereas the PES gives 32.2(28.8) kcal/mol. Nevertheless, this product channel plays a minor role below $E_{coll} = 40$ kcal/mol.

Figure 5 compares the PES and direct *ab initio* composite coupled-cluster classical reaction energies of the reactions shown in Fig. 4. The PES reaction energies vary from -48.4 to 16.0 kcal/mol with an RMSE of only 0.26 kcal/mol.



FIG. 4. Schematic PES of the $SiH_3CI + F^-$ reactions, depicting the structures and relative energies (in kcal/mol) of the known stationary points (without boxes) and the main products (within boxes). The classical *ab initio* energies are obtained at the [CCSD-F12b + BCCD(T) - BCCD]/AVTZ level and the harmonic zero-point vibrational corrections of the adiabatic energies are calculated using the CCSD(T)-F12b/AVTZ method.



FIG. 5. Comparison of the classical reaction energies of the main product channels calculated on the analytical PES and by direct composite coupled-cluster theory.





The RMSE values of the zero-point vibrational energies of the PES-optimized minima, transition states, and the products compared to the CCSD(T)-F12b/AVTZ energies, optimized at the same coupled-cluster level of theory, are 88, 220 and 86 cm⁻¹, respectively (Fig. 6). Based on these comparisons, the PES describes the seven most important product channels within chemical accuracy.

In Fig. 7, two-dimensional scans of the PES are given along the Si–F and Si–Cl distances at WMIN and FSTS keeping the other coordinates fixed at the stationary-point values. As Fig. 7 shows, in both cases the contour plots are smooth, providing another evidence of the good quality of the analytical PES.



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FIG. 7. Two-dimensional contour plots of the analytical PES along the Si–F and Si–CI distances at WMIN and FSTS keeping the other coordinates fixed at the stationary-point values

B. Reaction probabilities

Figure 8 shows the reaction probability of each product channel as a function of impact parameter at different collision energies. The maximum impact parameter ranges from 25 a_0 at a collision energy of 1 kcal/mol, to 11.5 a_0 at a collision energy of 20 kcal/mol, and finally 9.5 a_0 at a collision energy of 40 kcal/mol. The system demonstrates a high total reactivity, with over 95% between impact parameters of 0 and 14 a_0 at a collision energy of 1 kcal/mol. However, as the collision energy increases, the total reactivity decreases. At 40 kcal/mol, the total reactivity at b = 0 is about 76%, which is still high. The primary contributors to the total reactivity are the chloride substitution, proton abstraction, and HCl production reactions. The combined probability of the remaining five observed reactions is comparable to the probability of HCl production.

At collision energy of 1 kcal/mol, the probability of chloride substitution is about 80% at an impact parameter of 0, which decreases linearly until it reaches 50% at an impact parameter of 22 a_0 . Beyond that point, the probability drops rapidly before reaching the maximum impact parameter of 25 a_0 . Between 20 and 40 kcal/mol, the opacity function of the chloride substitution shows no significant collision energy dependence as the b = 0 reactivity decreases from 63% to 57%. Proton abstraction favors higher impact parameters. At $E_{\text{coll}} = 1$, 20, and 40 kcal/mol, its opacity functions show maxima, 33%, 35%, and 26%, at b = 16, 7, and 6.5 a_0 , respectively.

The opacity function of HCl production is almost flat at $E_{\rm coll} = 1$ kcal/mol, showing a slight preference for smaller impact parameters. At b = 0, the reaction probability is about 0.5% and varies proportionally with the chloride substitution up to $b_{\rm max}$. At higher collision energies, the b = 0 probabilities are higher, 3% and 5% at $E_{\rm coll} = 20$ and 40 kcal/mol, respectively, but the maximum impact parameter of this reaction does not reach the total $b_{\rm max}$. There is no HCl production beyond b = 8.5 a_0 at $E_{\rm coll} = 20$ kcal/mol and higher.

The hydride substitution prefers higher collision energies and lower impact parameters as the b = 0 probabilities at $E_{coll} = 20$ and 40 kcal/mol are 0.4% and 1% and the maximum impact parameter in this energy range turned out to be 4.5 a_0 . At $E_{coll} = 1$ kcal/mol, the probability of hydride substitution is negligible.

The FHCl⁻ formation channel cannot open at low collision energies due to its endothermicity. At $E_{coll} = 20$ kcal/mol, only a handful of those trajectories are observed at lower impact parameters (5000 trajectories were run at each *b*). The opacity function at $E_{coll} = 40$ kcal/mol varies proportionally with proton abstraction and shows a maximum of 0.2% at $b = 5.5 a_0$.



FIG. 8. Opacity functions of the SiH₃Cl + F^- reactions obtained at different collision energies. The probability function of other reactions (upper row) means the combined probabilities of the reactions in the lower row without the HCl production. Total reactivity refers to the sum of the probabilities of the eight indicated reactions.

The H₂ production channel has a low probability, despite being the second-most exothermic reaction. Its opacity functions at different collision energies have a similar shape to those of the HCl production but are always lower. At $E_{coll} = 1$ kcal/mol, the b = 0probability is around 0.2%–0.3%. At higher collision energies, E_{coll} = 20 and 40 kcal/mol, the maximum reaction probabilities, 1.5% and 1.9%, are observed between b = 0 and 1.5 a_0 in both cases, showing a clear preference for low impact parameters. The maximum impact parameter at $E_{coll} = 1$ kcal/mol is 21 a_0 , whereas at $E_{coll} = 20$ and 40 kcal/mol it drops dramatically to 6.5 and 5 a_0 , respectively.

The opacity function of SiHF + $H_2 + Cl^-$ does not depend on the impact parameter at $E_{coll} = 1$ kcal/mol, showing a constant reaction probability below 0.05% up to $b = 24 a_0$. Similar to the SiHFCl⁻ + H_2 reaction, the three-fragment H_2 producing reaction also changes its preference to low impact parameters at higher collision energies.

Finally, the very endothermic SiH₂ + HF + Cl⁻ reaction channel does not open at low collision energies. At $E_{coll} = 40$ kcal/mol, the b = 0 reaction probability is about 0.15%.

Figure 9 shows the opacity functions of the chloride substitution divided into inversion and retention. At $E_{coll} = 1$ kcal/mol, the probability of inversion is almost constant, between 50% and 60%, up to b_{max} , while the retention shows a linear decline starting from 18%. The opacity functions at $E_{coll} = 20$ kcal/mol have a similar shape at lower impact parameters, but beyond $b = 4.5 a_0$ the inversion appears to be more preferred. At $E_{coll} = 40$ kcal/mol below $b = 5 a_0$, the retention is the dominant mechanism, but for higher impact parameters the inversion becomes more favored.

C. Integral cross sections

Figure 10 shows the excitation functions of the SiH₃Cl + F⁻ reactions, which is the ICS as a function of collision energy, up to $E_{coll} = 40$ kcal/mol with different vibrational energy constraints, and Fig. 11 presents the excitation functions of the chloride ion substitution divided into inversion and retention mechanisms.

The cross section of the chloride substitution decreases monotonically with the collision energy. For $E_{coll} = 1$ kcal/mol, σ is greater



FIG. 9. Opacity function of the chloride ion substitution divided into inversion and retention at different collision energies.

than 1000 a_0^2 , while for $E_{\text{coll}} = 40$ kcal/mol it drops below 70 a_0^2 . This significant decline is mainly caused by the drop of the maximum reactive impact parameter at larger collision energies. Due to the exothermicity of the reaction, the chloride substitution does not violate the vibrational energy constraint even at low collision energies. At lower collision energies, inversion dominates, whereas at high collision energies racemization occurs. Between $E_{coll} = 1$ and 40 kcal/mol, the ICS of the inversion decreases by a factor of 27, and the ICS of the retention decreases by a factor of 3.5.

The excitation function of the proton abstraction has a similar shape as that of the chloride substitution, but much lower, $\sigma = 370$ and 290 a_0^2 without and with soft vibrational energy constraint, respectively, at the lowest E_{coll} . The decrease of the ICS is mainly caused by the decrease of the maximum reactive impact parameter. On the other hand, with the hard constraint, the function is approximately constant at around $\sigma = 50 a_0^2$. The reason for the difference between the hard and soft constraint values is that a significant part of the energy was transferred to the vibrational energy of one of the two polyatomic fragments, which may compensate the zero-point energy (ZPE) violation of the other product in the soft case.

The ICS of the HCl formation is the largest at $E_{coll} = 1$ kcal/mol at around 4.7 a_0^2 . At higher collision energies, over E_{coll} = 20 kcal/mol, the σ settles around 1.5 a_0^2 . The decrease in smaller collision energies is due to decrease in the maximum reactive impact parameter, but at higher collision energies the reaction does not depend on the impact parameter that much.

The ICS of the hydride substitution increases monotonically as a function of the collision energy. The reaction opens at the lowest collision energies, reaching $\sigma = 0.25 a_0^2$ at $E_{coll} = 40$ kcal/mol. It is an almost athermic reaction, but surprisingly the ratio of the vibrational constraint violating trajectories is negligible over $E_{\rm coll} = 10$ kcal/mol.

The FHCl⁻ production channel opens at 16.0(13.6) kcal/mol classically(adiabatically) on the PES. The excitation function shows a constant, almost negligible, σ between $E_{coll} = 15$ and 25 kcal/mol, but at higher collision energies σ grows linearly up to $\sigma = 0.17 a_0^2$ at $E_{coll} = 40$ kcal/mol. The effect of soft vibrational constraint is not significant beyond $E_{coll} = 25$ kcal/mol energies; however, the hard constraint halves the ICS.

The excitation function of H₂ production has a similar shape to that of HCl production with smaller σ values. At $E_{coll} = 1$ kcal/mol, the ICS is 1.3 a_0^2 , which drops to 0.4 a_0^2 at $E_{coll} = 5$ kcal/mol remaining relatively constant at higher collision energies, with or without the soft constraint. With the hard vibrational constraint applied, the cross section remains between 0.08 and 0.27 a_0^2 throughout the entire energy range with a slight preference for higher collision energies.

Without vibrational energy constraint, the three-fragment H₂ production shows a flat excitation function, with σ around 0.1 a_0^2 , between 5 and 40 kcal/mol collision energies and a maximum, $\sigma = 0.3 a_0^2$, at $E_{\text{coll}} = 1$ kcal/mol.

The SiH₂ + HF + Cl⁻ reaction opens at 32.2(28.8) kcal/mol classically(adiabatically) on the PES; accordingly, the excitation function is zero throughout the lower collision energy range, but beyond E_{coll} = 30 kcal/mol, the ICS without energy constraint grows quickly, reaching 0.07 a_0^2 at $E_{coll} = 40$ kcal/mol. Almost all SiH₂ + HF + Cl⁻ trajectories violate the vibrational energy constraints.

D. Reaction mechanisms

From the multitude of simulations carried out on the final PES, we chose 30 trajectories propagated at $E_{coll} = 40$ kcal/mol, five for each two-fragment product channel, to represent the most significant mechanisms, as well as to perform a trajectory-based error analysis by comparing the direct ab initio and PES energies of the geometries along the trajectories. We quantify the maximum absolute errors (MAEs) in addition to the root-mean-square errors (RMSEs) to account for the possibility that, during the simulation, the errors may be relatively low for most geometries but spike at some distorted structures. In the supplementary material, Figs. S1-S30 show the representative trajectories with snapshots of the key steps of the mechanisms and Figs. S31-S36 show the errors of the trajectories recalculated on the previous PES iterations.

Based on the representative trajectories, the final potential energy surface (PES 342) provides a near-chemically accurate



FIG. 10. Excitation functions of the SiH $_3$ Cl + F⁻ reactions obtained without as well as with soft and hard ZPE constraints.

description of the chloride substitution, with an average RMSE of 1.0 kcal/mol. For proton abstraction, HCl production, hydride substitution, and FHCl⁻ production, the average RMSEs are around 2 kcal/mol. The average RMSE for H₂ production is somewhat higher at 3.3 kcal/mol, which is comparable to the accuracy of conventional direct dynamics techniques that use density functional theory.⁵⁰ The chloride substitution trajectories showed no MAE exceeding 5 kcal/mol, with MAEs ranging between 2.3 and 4.9 kcal/mol. However, other trajectories suffered from larger error peaks. For proton abstraction, the MAE for four

trajectories ranged from 5.3 to 7.4 kcal/mol, while one trajectory had a significantly higher MAE of 18.4 kcal/mol at the point of collision between the reactants (Fig. S7). For HCl production, hydride substitution, FHCl⁻ production, and H₂ production, the average MAEs were 7.9, 8.3, 12.2, and 18.2 kcal/mol, respectively, mainly at the product sides of the trajectories. It is hard to predict the effect of the short but high error peaks on the reliability of the results in the case of these low probability channels. Nevertheless, as Fig. 12 shows, the PES reproduces well the qualitative features of the potential energy curves along the trajectories.

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FIG. 11. Integral cross sections of the inversion and retention products of the chloride ion substitution (top) and the ratio of the retention products as a function of collision energy (bottom) without vibrational energy constraints.

It is worth noting that in the later stages of the sixth-order development, beyond PES 325, no significant improvements were observed in the RMSEs and MAEs, as shown in Figs. S31–S36. In fact, for the hydride substitution trajectories, the RMSEs and MAEs were slightly increasing rather than decreasing. Additionally, considering that the global fitting errors showed a monotonic increase with the size of the fitting set, as shown in Fig. 1, we concluded that further development with the same strategy using sixth-order fitting would only have decreased the overall quality of the PES.

Figure 12 presents snapshots of representative trajectories featuring the most common as well as other interesting, unexpected mechanisms that are characteristic to the title system and likely to occur in similar silicon-centered systems and showing the potential energies as a function of propagation time. To obtain a more comprehensive understanding of these mechanisms, numerous other trajectories that were propagated at $E_{coll} = 1$ and 40 kcal/mol were animated and visually inspected.

The reactant sides of the selected representative trajectories were very similar due to the identical initial center of mass distances and collision energies. Upon starting the simulations, the reactants collide after ~0.2 ps. The zero-point vibrational energy of SiH₃Cl is 16.8 kcal/mol and, in accordance with the virial theorem, the potential energy oscillates around half of the ZPVE at the beginning of each simulation.

As seen in Figs. 8 and 9, the most prominent reaction is the halide substitution, with high probabilities for both inversion and retention. Simple, direct examples of Walden inversion and retention are shown in the top row of Fig. 12, where short-lived back-side and front-side attack complexes precede inversion and retention,

respectively. The lifespan of these complexes is significantly longer at low collision energies. Trajectory animations revealed that even at large impact parameters at $E_{coll} = 1$ kcal/mol, most collisions, including those that did not result in halide substitution, were started with the formation of a back-side attack complex due to WMIN being by far the most stable stationary point. This explains the high and nearly constant probability of inversion up to the maximum impact parameter at this collision energy (Fig. 9). If the initial orientation of the reactants was not favorable to the back-side attack complex formation, the silvl chloride molecule would rotate accordingly. This reorientation at small impact parameters results in energy transfer to the F-Si-Cl bond bending, increasing the likelihood of backside attack complex transformation into a front-side one. It was also found that at the lowest collision energy and at high impact parameters, reactant reorientation leads to the formation of more rotationally excited and less vibrating back-side attack complexes with a lower tendency to transform into front-side attack structures, giving an explanation to the linear decrease in the probability of halide substitution with retention as a function of impact parameter at $E_{\text{coll}} = 1$ kcal/mol. On the other hand, at $E_{\text{coll}} = 40$ kcal/mol, there is no sufficient time for the reactants to reorient before the collision occurs. Consequently, the stereochemistry of the products depends mainly on the impact parameters and attack angles. At smaller impact parameters, a direct front-side collision is more probable than a back-side collision, leading to the preference for retention with rebound mechanism. Conversely, at higher impact parameters, the stripping mechanism becomes dominant. We observed a few instances of double inversion following proton abstraction, in which the SiH₂Cl⁻ ion inverts its configuration before the return of the HF. It occurs if the WMIN is formed after this step, although it is common to form a front-side complex instead, resulting in inverted products. Additionally, the self-inversion of the highly vibrationally excited SiH₃F at high collision energy is also possible.

After halide substitution, HCl production can occur due to proton abstraction of the leaving ion. Figure 12(d) presents an example of this process. Trajectory animations revealed that the formation of ClBHMIN and ClDHBMIN complexes in the exit channel is common, particularly at low collision energy. These complexes can influence scattering angles or lead to hydrogen production via the mechanism depicted in Fig. 12(h).

At $E_{coll} = 1$ kcal/mol, the ClDHBMIN decomposition is the primary mechanism for hydrogen molecule production, leading to SiHFCl⁻ + H₂ and SiHF + H₂ + Cl⁻. At $E_{coll} = 40$ kcal/mol, a competing mechanism for SiHF + H₂ + Cl⁻ arises from the H₂ elimination of vibrationally excited SiH₃F following halide substitution. At high collision energies, the proton abstraction of the hydride ion is the primary mechanism of the SiHFCl⁻ + H₂ production [Fig. 12(g)].

The hydride ion substitution generally occurs through a direct mechanism, which involves the decomposition of a distorted $[F-SiH_3-Cl]^-$ complex [Fig. 12(e)]. Due to its low inertia, the hydride ion can easily be deflected by the remaining SiH₂FCl molecule and often leaves in a random direction.

At high collision energies and large impact parameters, the direct mechanism for proton abstraction is favored [Fig. 12(c)], while at low collision energies and impact parameters, the indirect mechanism through back-side attack complex formation in the entrance channel is dominant. FBHMIN is commonly observed in



FIG. 12. Snapshots of representative trajectories of the SiH₃Cl + F^- reactions and comparison of the direct *ab initio* and PES energies along the trajectories.

the exit channels of proton abstraction, which influences the product scattering. Additionally, FBHMIN formation is a crucial step in FHCl⁻ production at high collision energies [Fig. 12(f)].

IV. SUMMARY AND CONCLUSIONS

Moving beyond the widely studied C-entered $S_N 2$ reactions, we develop the first, high-level *ab initio* analytical PES for a Si-centered reaction, $F^- + SiH_3Cl$, using ROBOSURFER for sampling the configuration space,³⁵ a CCSD(T)-F12b/aug-cc-pVTZ-quality composite

method⁴² utilizing the robust Brueckner (T) term for energy computations, and the permutationally invariant polynomial method^{36,37} for fitting. We show the evolution of fitting errors and the percentage of unphysical trajectories during the PES development. We have found that a sixth-order fit provides chemical accuracy (RMSE around 1 kcal/mol) while the ratio of the unphysical trajectories is below 1%. We note that keeping the RMSE low was challenging for the title reaction, presumably due to the many open product channels involving three-body breakups as well. Nevertheless, the analytical PES reproduces the stationary point properties very well, in most cases with less than 0.5 kcal/mol deviations from the direct

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ab initio data. QCT simulations on the new PES reveal very complex dynamics and unexpected product channels for the F⁻ + SiH₃Cl reaction. In addition to halogen substitution and proton abstraction, which are also widely studied at C centers, HCl, H⁻, FHCl⁻, H₂, $H_2 + Cl^-$, and $HF + Cl^-$ formations are also found in the case of the Si-centered title reaction, showing that the ion-molecule reactions are much more complex at Si centers than at the analogous C central atoms. Furthermore, an interesting feature of the Si-centered reactions is that the front-side attack transition state is submerged, thus the retention may compete with Walden inversion at Si centers. Indeed, our simulations reveal substantial amount of front-side attack reactivity and the F⁻ + SiH₃Cl reaction tends to produce almost racemic products as the collision energy increases. Based on trajectory animations, we have provided a detailed description of the atomic-level mechanisms of the various reaction channels. Moreover, a unique feature of our work is that we have carefully and thoroughly analyzed the accuracy of the PES energies along many representative trajectories. In the case of the high-probability channels, the analytical PES quantitatively reproduces the features of the direct ab initio coupled-cluster potential energy curves, whereas for the low-probability channels the agreement is only qualitative. Similar detailed comparisons of the PES and direct ab initio energies are very rare in the literature, the present study may inspire others to perform this kind of evaluation. Furthermore, the present work may help and motivate future theoretical and experimental investigations on Si-centered ion-molecule reactions, which may be more challenging and chemically rewarding than those performed at C centers.

SUPPLEMENTARY MATERIAL

See the supplementary material for accuracy of the PES along representative trajectories as well as for codes for PES evaluation utilizing Refs. 36 and 37.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Attila Á. Dékány: Data curation (lead); Formal analysis (lead); Investigation (lead); Methodology (lead); Visualization (lead); Writ-

DATA AVAILABILITY

The data that support the findings of this study are available as supplementary material and from the corresponding author upon reasonable request.

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