Does the Cl + CH₄ \rightarrow H + CH₃Cl Reaction Proceed via Walden Inversion?

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Supporting Information

ABSTRACT: We report a chemically accurate global ab initio full-dimensional potential energy surface (PES) for the $Cl(^{2}P_{3/2}) + CH_{4}$ reaction improving the highenergy region of our previous PES [Czakó, G.; Bowman, J. M. *Science* **2011**, 334, 343– 346]. Besides the abstraction (HCl + CH₃) and the Walden-inversion substitution (H + CH₃Cl) channels, the new PES accurately describes novel substitution pathways via retention of configuration. Quasiclassical trajectory simulation on this PES reveals that the substitution channel opens around 40 kcal/mol collision energy via Walden inversion and the retention cross sections raise from ~50 kcal/mol. At collision energy of 80 kcal/mol, the retention pathways provide nearly 40% of the substitution cross section, and retention substitution may become the dominant mechanism of the Cl + CH₄ reaction at superhigh collision energies. The substitution probability can be as high as ~70% at zero impact parameter (*b*) and decreases rapidly with increasing *b*, whereas the abstraction opacity function is broad having 5–10% probability over a



larger *b*-range. The high-energy angular distributions show scattering into forward and backward directions for the abstraction (direct stripping) and face-attack Walden-inversion substitution (direct rebound) channels, respectively. Retention can proceed via edge- and vertex-attack pathways producing dominant sideways scattering because the breaking C–H or Cl–H bond is usually at a side position of the forming Cl–C bond.

1. INTRODUCTION

The reaction of chlorine atom with methane $(CH_4, CHD_3, etc.)$ has become one of the benchmark systems to study the dynamics of polyatomic chemical reactions.^{1–16} Recently many experimental and theoretical studies investigated the Cl + CH₄ \rightarrow HCl + CH₃ reaction and its isotopic variants, thereby uncovering vibrational and rotational mode specificity,^{1,3,6,8} testing the Polanyi rules,^{1,3,12} and mapping the angle-dependent barrier.⁷ Besides the above-mentioned hydrogen-abstraction channel, at high collision energies the substitution channel leading to H + CH₃Cl opens.^{4,17} The substitution reactions of methane with atoms are the prototypes of the well-known bimolecular nucleophilic substitution $(S_N 2)$ reactions proceeding with Walden-inversion mechanism. Even if halogen atoms are not nucleophiles, the mechanisms of the atom plus methane and S_N2 reactions are similar (i.e., the atom/nucleophile attacks the carbon atom and the hydrogen atom/leaving group departs from the opposite side of the collinear transition state while an umbrella motion inverts the configuration around the carbon center). While the dynamics and mechanisms of $S_{\rm N}2$ reactions have been widely studied, $^{18-27}$ there have also been a few investigations for the atom + methane substitution processes.^{28–35,4,17} Following the early experimental studies, potential energy surface (PES) developments,34-37 and trajectory simulations,^{34,35} in 2017 Zhang and co-workers³⁰ reported seven-dimensional quantum dynamics computations for the hydrogen-exchange channel of the H + CH₄ and its

isotope-analogue reactions. In the case of the O(³P) + CH₄ reaction, the H + CH₃O channel was investigated by direct dynamics simulations and crossed-beam experiments.^{28,29} For Cl + CH₄ in 2011, we developed a global analytical PES which describes both the abstraction and substitution channels.³ Besides the many dynamical studies on this PES for the HCl + CH₃ channel,^{3,4,6,7,12,14} in 2012 we reported cross sections, reaction probabilities, and mode-specific product vibrational distributions for the H + CH₃Cl channel as well.^{4,17}

One may expect that the Cl + CH₄ \rightarrow H + CH₃Cl reaction proceeds with Walden inversion as described above. In a reaction dynamics simulation we can label the identical H atoms; thus, the configuration of the CH₃Cl product relative to that of CH₄ can be determined. A few years ago we developed a method which numerically analyzes the configuration of the product molecules.²⁰ This technique has been successfully applied to S_N2 reactions, leading to the discovery of the doubleinversion mechanism.^{20,23,24} Here we apply this method to the title reaction and find that a significant fraction of the CH₃Cl products is formed with retention of the initial configuration, indicating that Walden inversion is not the unique mechanism of the Cl + CH₄ substitution process. In section 2.1, we present the computational methods used to develop a modified version

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of the global PES of the $Cl(^{2}P_{3/2}) + CH_{4}$ reaction which accurately describes the new retention pathways besides the Walden-inversion and the hydrogen-abstraction processes. We perform quasiclassical trajectory (QCT) computations for the $Cl(^{2}P_{3/2}) + CH_{4}(v = 0)$ reaction at high collision energies using the new PES. In section 2.2, the QCT computational details are given, and the results are discussed in section 3. The paper ends with Summary and Conclusions in section 4.

2. COMPUTATIONAL DETAILS

2.1. Potential Energy Surface. The spin-orbit groundstate PES of the $Cl(^{2}P_{3/2}) + CH_{4}$ reaction reported in 2011,³ which accurately describes the hydrogen-abstraction and Walden-inversion substitution channels, was obtained by fitting 15875 ab initio energy points computed at the

composite level of theory. In order to improve the description of the new retention pathways, we selected 1353 additional configurations along many retention trajectories in an iterative QCT-fitting procedure and computed the ab initio energy points using the composite method of eq 1. The iterative QCTfitting procedure means that in each cycle (1) QCT computations are performed on the PES, (2) 100-500 configurations are selected along 5 or 10 retention trajectories, (3) the ab initio energies are computed at the selected geometries, (4) ab initio energy points with absolute deviations, from the PES values, larger than 1.0 kcal/mol are added to the database, and (5) the fit is done with the augmented database. We have done 12 iteration cycles until the retention pathways are accurately described with root-mean-square (RMS) errors comparable to the global RMS error in the respective energy range. We perform six-order weighted linear least-squares fits using permutationally invariant polynomials of $\exp(-r_{ii}/a)$ variables,^{38,39} where r_{ij} coordinates denote the interatomic distances and a is set to 2 bohr. The weight is $E_0/(E + E_0)$, where *E* is the energy relative to the global minimum and $E_0 =$ 31 kcal/mol. The final six-order fit of 17228 points results in 3262 coefficients and RMS errors of 0.28, 0.65, and 1.61 kcal/ mol in the energy intervals 0-31, 31-63, 63-157 kcal/mol, respectively. All the ab initio computations for the PES development and benchmark characterization of one of the saddle points are performed using the MOLPRO program package.40

2.2. Quasiclassical Trajectory Computations. QCT computations are performed for the $Cl({}^{2}P_{3/2}) + CH_4(\nu = 0)$ reaction using the new PES. The quasiclassical ground vibrational state of CH_4 is prepared using standard normal mode sampling.⁴¹ The initial distance of the reactants is $(x^2 + b^2)^{1/2}$, where *b* is the impact parameter and *x* is set to 10 bohr. The orientation of CH_4 is randomly sampled, and *b* is scanned from 0 to 7 bohr with a step size of 0.25 bohr. QCT computations are performed at collision energies (E_{coll}) of 40, 50, 60, 70, and 80 kcal/mol and 5000 trajectories are run at each *b*, resulting in 145000 trajectories at each E_{coll} . Cross sections are calculated using a *b*-weighted numerical integration of the reaction probabilities over impact parameters.

The configuration of the CH₃Cl product relative to that of CH₄ is determined using the following procedure: (1) let us label the H atoms of CH₄ as H(1)H(2)H(3)H(4). (2) The H atoms of the CH₃Cl product molecule are labeled as H(2 \rightarrow

1)H(3 \rightarrow 2)H(4 \rightarrow 3), H(1 \rightarrow 1)H(3 \rightarrow 2)H(4 \rightarrow 3), H(1 \rightarrow 1)H(2 \rightarrow 2)H(4 \rightarrow 3), or H(1 \rightarrow 1)H(2 \rightarrow 2)H(3 \rightarrow 3) if H(1), H(2), H(3), or H(4) atom of CH_4 , respectively, is substituted by Cl. (3) We define a reference structure, which is the equilibrium geometry of CH₃Cl, with labeled H atoms as H(1)H(2)H(3). (4) We transform the structure of the CH₃Cl product to the Eckart frame corresponding to the reference geometry using the methodology described in detail in refs 17, 20, and 42. The determinant of the transformation matrix, $det(\mathbf{C})$, can be either +1 or -1 corresponding to the same or inverted configuration of the CH₃Cl product relative to that of the CH₃Cl reference geometry. (5) To determine the CH₃Cl product configuration relative to that of the reactant CH₄, one has to consider which H atom of CH₄ is substituted by Cl. The value of $(-1)^n \det(\mathbf{C}) = +1/-1$, where *n* is the label of substituted H atom, means retention/inversion if H(1)H(2)-H(3)C atoms of CH_4 and the CH_3Cl reference have the same configuration and the reverse holds if the H(1)H(2)H(3)Cgroup of the CH₃Cl reference has an inverted configuration. The factor $(-1)^n$ accounts for the nonchemical configuration inversion (n = 1 and 3) and retention (n = 2 and 4) caused by odd and even number of H exchange(s), respectively, in the relabeling process of step (2).

3. RESULTS AND DISCUSSION

3.1. Properties of the Potential Energy Surface. The relative energies and structures of the stationary points on the global analytical PES of the $Cl(^{2}P_{3/2}) + CH_{4}$ reaction are shown in Figure 1. The HCl + CH₃ channel (5.8) is slightly endothermic with a late barrier (7.6), where the classical



Figure 1. Schematic of the global potential energy surface (PES) of the $Cl(^{2}P_{3/2}) + CH_{4}$ reaction showing the structures and classical relative energies of the stationary points. The distances (in Å) and energies obtained on the present analytical PES are compared to the accurate benchmark values taken from refs 3 and 4 for all the stationary points except for the highest-energy saddle point of $C_{4\nu}$ symmetry, where UCCSD(T)-F12b/aug-cc-pVTZ reference data with spin–orbit energy shift (this work) are shown. For more details see the Supporting Information. Note that the retention-substitution pathways may avoid the $C_{4\nu}$ saddle point as shown in Figure 5.

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energies, in kcal/mol, relative to the reactants are given in parentheses. There is a shallow van der Waals well (-0.4 or)-0.7 depending on the orientation of the reactants) in the entrance channel and a relatively deep minimum (2.5 kcal/mol relative to $HCl + CH_3$ in the product valley. The H + CH_3Cl substitution channel (25.8) is highly endothermic with a high Walden-inversion barrier (43.0) of $C_{3\nu}$ symmetry. As also shown in Figure 1, all the above-mentioned relative energies corresponding to the analytical PES agree within 1 kcal/mol (chemical accuracy) with relativistic all-electron CCSDT(Q)/complete-basis-set-quality benchmark values^{3,4} obtained from focal-point analysis. Furthermore, the PES values of the most important structural parameters are also in good agreement with high-level benchmark data. The above-described stationary-point properties on the new and old^{3,4} PESs are very similar; the main advantage of the new PES is that it describes the high-energy retention-substitution pathways more accurately.

Motivated by a previous study²⁸ on the $O(^{3}P) + CH_{4}$ system, which reported a $C_{2\nu}$ saddle point for the substitution channel, we have found a new first-order saddle point for the Cl + CH₄ reaction. Unlike for $O + CH_4$, the new $Cl + CH_4$ saddle point has $C_{4\nu}$ symmetry, where the Cl–C distance of 1.794 Å is very close to the corresponding bond length in CH₃Cl (1.791 Å), as seen in Figure 1. The CH distances are stretched by about 0.1 Å relative to CH bond length in CH_4 and CH_3Cl . The Cl-C-H angle of the new $C_{4\nu}$ saddle point is 103°, whereas one of the O–C–H angles is only 79° at the $C_{2\nu}$ saddle point of the O + CH₄ system,²⁸ showing the qualitative difference between the two reactions. The classical barrier height is 78.5 kcal/mol on the PES, which is significantly higher than that of the Waldeninversion pathway. We have performed benchmark UCCSD-(T)-F12b/aug-cc-pVTZ computations for the new $C_{4\nu}$ saddle point and found good agreement with the above-mentioned PES values as shown in Figure 1. This finding is remarkable because we did not know about this saddle point during the PES development.

A more detailed comparison between the stationary-point properties of the new PES and benchmark data are given in Tables S1-S7 for the geometries, relative energies, and harmonic vibrational frequencies.

3.2. Reaction Dynamics and Mechanisms. Excitation functions (integral cross sections vs E_{coll}) for the abstraction $(HCl + CH_3)$ and substitution $(H + CH_3Cl)$ channels of the $Cl(^{2}P_{3/2}) + CH_{4}(\nu = 0)$ reaction are shown in Figure 2. For the substitution reaction, the mechanism-specific inversion and retention cross sections are determined using the numerical technique described in section 2.2. As seen, the H + CH₃Cl channel opens around $E_{coll} = 40$ kcal/mol, in accord with the classical (adiabatic) Walden-inversion barrier height of 43.0 (40.4) kcal/mol. The substitution cross sections increase rapidly with increasing $E_{\rm coll}$ and approach the cross section of the HCl + CH₃ channel at $E_{coll} = 80$ kcal/mol. On the basis of Figure 2, at super high collision energies (e.g., $E_{coll} > 100$ kcal/ mol), H + CH₃Cl is likely to become the dominant product channel of the Cl + CH₄ reaction. In the E_{coll} range of 40–50 kcal/mol, the substitution reaction proceeds almost exclusively with Walden inversion. The retention pathway opens around $E_{\text{coll}} = 50 \text{ kcal/mol}$, and its cross sections increase rapidly. The inversion/retention fractions are 1.00/0.00, 0.99/0.01, 0.92/ 0.08, 0.79/0.21, and 0.63/0.37 at collision energies of 40, 50, 60, 70, and 80 kcal/mol, respectively; thus, the dominance of the inversion mechanism is suppressed as $E_{\rm coll}$ increases. The



Figure 2. Integral cross sections as a function of collision energy for the abstraction and substitution (via inversion and retention pathways) channels of the $Cl(^{2}P_{3/2}) + CH_{4}(\nu = 0)$ reaction.

above-mentioned threshold energy of the retention process is well below the classical (adiabatic) barrier height of 78.5 (69.7) kcal/mol, corresponding to the $C_{4\nu}$ saddle point indicating that the retention pathway may avoid this high-energy $C_{4\nu}$ transition state. More discussion on this finding will come below.

The opacity functions (reaction probabilities vs *b*) of the abstraction and substitution channels have drastically different shape as shown in Figure 3 at $E_{coll} = 80$ kcal/mol. At b = 0,



Figure 3. Reaction probabilities as a function of impact parameter for the abstraction and substitution (via inversion and retention pathways) channels of the $Cl(^{2}P_{3/2}) + CH_{4}(\nu = 0)$ reaction at a collision energy of 80 kcal/mol.

clearly the substitution channel dominates with a reaction probability of 69% (40% inversion and 29% retention), whereas the abstraction probability is only 2%. However, on the one hand, the substitution probability rapidly decreases with increasing *b*, and its maximum impact parameter is only 2–3 bohr (1–1.5 Å), which is comparable with a CH bond length. Significant difference between the shape of inversion and retention opacity functions is not seen. On the other hand, the abstraction probability shows a broad distribution over *b* from 0 to 6 bohr (3 Å), showing the highest reactivity of ~10% in the *b* range of 4–5 bohr. This high-*b* reactivity, which indicates significant stripping mechanism, causes the cross section obtained from a *b*-weighted integration to be slightly larger for the abstraction reaction than for the substitution process.

Product scattering angle distributions for the different reaction channels and mechanisms are shown in Figure 4 at



Figure 4. Scattering angle distributions for the abstraction and substitution (via inversion and retention pathways) channels of the $Cl(^{2}P_{3/2}) + CH_{4}(\nu = 0)$ reaction at a collision energy of 80 kcal/mol.

 E_{coll} = 80 kcal/mol. The HCl + CH₃ channel shows a clear dominance of forward scattering, whereas the H + CH₃Cl products are mainly backward scattered. The forward scattering of the former channel shows that the abstraction reaction proceeds via stripping mechanism at high collision energies. This finding is in agreement with experiments, which showed that the angular distributions shift from backward to forward scattering as E_{coll} increases in the Cl + CH₄ \rightarrow HCl + CH₃ reaction.⁴³ Examination of the mechanism-specific angular distributions for the substitution channel reveals qualitatively different distributions for the inversion and retention pathways. On the one hand, the inversion process is backward scattered peaking at 180° and showing virtually no scattering in the forward hemisphere $(0-90^\circ)$, indicating a direct rebound Walden-inversion mechanism. Walden inversion via stripping and indirect mechanisms is negligible because these pathways would result in scattering into sideways-forward and random directions, respectively. On the other hand, the retention pathway favors sideway scattering and significant distribution is seen in the forward directions as well. In the $0-120^{\circ}$ angular

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range, the retention cross sections are larger than the inversion ones.

Snapshots of three representative trajectories showing the face-attack, edge-attack, and vertex-attack substitution pathways are shown in Figure 5. The face-attack substitution, which corresponds to back-side attack in S_N2 reactions, proceeds via a classic direct rebound Walden inversion, where the Cl atom attacks the face of the tetrahedral CH4 molecule and the H atom leaves from the opposite side causing backward scattering, while an umbrella motion inverts the configuration around the carbon center. The trajectories have revealed two different novel retention pathways named as edge-attack and vertexattack mechanisms. In the case of the former, which is similar to front-side attack in $S_N 2$ reactions,²⁰ Cl attacks the edge of the CH_4 tetrahedron forming a $C_{2\nu}$ -like structure (at 40 fs), and then while a Cl-C bond forms one of the side, noncollinear C-H bonds breaks and the H atom leaves into sideway direction in accord with the scattering angle distributions. Vertex attack corresponds to an abstraction-induced substitution, where Cl abstracts an H atom and the ClH unit rotates away from the collinear configuration, and then the Cl-H bond breaks at the H-Cl-C angle of around 90°, while a Cl-C bond forms retaining the configuration of the CH₃ unit. Trajectory animations reveal that at b = 0, the edge attack is the dominant retention mechanism, whereas at b = 2, edge and vertex attacks have similar probability in accord with the increased abstraction probability, that may enhance the abstraction-induced vertex-attack substitution, at large *b* values. Along these retention pathways, a structure similar to the $C_{4\nu}$ transition state is not found. Furthermore, examination of many retention trajectories shows that even if some edge-attack collisions approach the C_{4v} geometry, the reaction may not go through this high-energy configuration, explaining the fact that the retention pathway opens well below the barrier corresponding to the $C_{4\nu}$ saddle point.



Figure 5. Snapshots of representative trajectories showing the inversion and retention mechanisms of the $Cl + CH_4 \rightarrow H + CH_3Cl$ reaction (b = 0 and $E_{coll} = 80$ kcal/mol).

4. SUMMARY AND CONCLUSIONS

We have improved the high-energy region of our previous analytical PES^{3,4} for the Cl(²P_{3/2}) + CH₄ reaction by adding 1353 energy points corresponding to the substitution channel via retention pathways. The new PES, obtained by a permutationally invariant fit to high-level composite ab initio data, accurately describes the high-energy substitution channel via inversion and retention mechanisms as well as the abstraction reaction. For the substitution channel, we have found a saddle point of $C_{4\nu}$ symmetry which, to the best of our knowledge, has never been reported before. The relative energies of all the stationary points agree with the high-level benchmark data within 1 kcal/mol showing that the PES has chemical accuracy.

Quasiclassical trajectory computations have been performed in the 40-80 kcal/mol collision energy range where both the abstraction and substitution channels are open. The inversion substitution channel opens around 40 kcal/mol in accord with its barrier height, whereas the threshold of the retention pathway is about 50 kcal/mol, well below the energy of the $C_{4\nu}$ saddle point. This behavior may be another example of the dynamics which do not follow the stationary points. In the collision energy range of the present study the abstraction process dominates, but at higher energies the substitution is significant and may supersede the abstraction as E_{coll} increases. At small impact parameters, the substitution process has much larger reaction probabilities than the abstraction. However, the substitution opacity functions decay rapidly and vanish around b = 1 Å, whereas the abstraction probability has a broad distribution favoring large impact parameters around 2-2.5 Å in accord with dominant forward scattering indicating direct stripping mechanism. The substitution reaction is clearly backward scattered via the inversion pathways indicating direct rebound mechanism, whereas the retention channel is mainly sideways scattered because the leaving H atom is at the side position relative to the forming Cl-C bond. A retention trajectory can proceed via either edge-attack or vertex-attack pathway, where the side-C-H bond breaks or the H atom is abstracted by Cl and the Cl-H bond breaks after rotation into side-position, respectively.

The present study shows that a seemingly simple reaction like Cl + CH₄ can be quite complex, especially at high collision energies. This is reminiscent of S_N2 reactions where many interesting reaction pathways and channels open at high collision energies.²⁴ In our work, two key factors made possible to reveal these novel reaction pathways. First, an accurate analytic PES is developed, which allows efficient trajectory computations. Second, a numerical technique is implemented to analyze the configuration of the product molecules, thereby distinguishing between inversion and retention pathways. This automatic stereospecific analysis led to the discovery of the double-inversion mechanism²⁰ for S_N2 reactions and the present retention pathways of the Cl + CH₄ system. Similar simulations could be performed for the H + CH₄ substitution reaction to resolve the long-standing debate about its inversion versus retention mechanism.³¹⁻³⁵ We hope that our work will motivate others in the field to focus on stereochemistry in reaction dynamics studies.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.7b10226.

Comparisons of the PES and benchmark structural parameters, relative energies, and harmonic vibrational frequencies for the stationary points of the $Cl + CH_4$ potential energy surface (PDF)

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Notes

The authors declare no competing financial interest.

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