

THESES OF DOCTORAL (Ph.D.) DISSERTATION

**Thermochemical and dynamical investigation of the  
Cl/F + CH<sub>3</sub>NH<sub>2</sub> reactions using theoretical methods**

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## 1. Introduction

Within theoretical chemistry, the properties of the examined systems are determined using mathematical methods and fundamental physical laws. By performing computations, chemical processes can be explored at the molecular level, enabling the design of targeted experiments. Consequently, the number of the expensive measurements and experimental risks can be reduced. Using the most modern electronic structure methods, the geometries, harmonic vibrational frequencies, and relative energies of stationary points, *etc.*, associated with reactive chemical systems, can be determined with high accuracy. The thermochemical parameters obtained from these calculations facilitate the planning of further experimental and theoretical work. Additionally, the structures identified in the most important regions of chemical systems can be pivots in fitting sets needed for potential energy surface (PES) developments. Using PES, reaction dynamics investigations can be conducted. Simulations can uncover individual reaction pathways and mechanisms, and even predict reaction outcomes. The reaction dynamics method based on the so-called quasi-classical trajectory (QCT) approach is a widely used and well-established technique. The term “classical” refers to the description of the motion of atomic nuclei using the laws of classical physics. However, since the initial state is set according to quantum mechanical vibrational-rotational levels, the use of prefix “quasi” is justified. This method allows for highly accurate modeling of chemical reactions, enabling the step-by-step tracking of their progress at the atomic level.

For decades, there has been significant scientific interest in studying reactions between atoms and molecules. In the literature, numerous experimental and theoretical studies can be found on the extensive examination of the F/Cl + H<sub>2</sub>/H<sub>2</sub>O/NH<sub>3</sub>/CH<sub>4</sub>/C<sub>2</sub>H<sub>6</sub> systems. However, moving beyond these systems – which contain only equivalent H atoms – many diverse and competing pathways can open in reactions between atoms and molecules with at least two functional groups. This reaction family includes the reaction of methylamine (CH<sub>3</sub>NH<sub>2</sub>), which consists of an amino group (–NH<sub>2</sub>) and a methyl group (–CH<sub>3</sub>), with chlorine or fluorine atom. In these cases, experimental and theoretical studies in the literature investigated the hydrogen-abstraction pathways involving the two functional groups leading to HCl/HF + CH<sub>2</sub>NH<sub>2</sub>/CH<sub>3</sub>NH. For instance, in 2003 a study determined the rotational distribution of HCl molecules formed during the Cl + CH<sub>3</sub>NH<sub>2</sub> hydrogen-abstraction reactions from experimental measurements. Additionally, theoretical mapping of the stationary points associated with these two reaction channels was conducted at the G2//MP2/6-311G(d,p) theoretical level, and some

trajectories were calculated using on-the-fly method. A combined theoretical-experimental investigation was also carried out by Nielsen and co-workers in 2015 for this system. They determined the rate constants for the two hydrogen abstractions (HAs) both theoretically and experimentally. Their calculations revealed the stationary points associated with these two HAs, where the energies of structures optimized at the MP2/cc-pVTZ theoretical level were determined at the CCSD(T)-F12a/aug-cc-pVTZ level. For the F + CH<sub>3</sub>NH<sub>2</sub> system, beyond early experimental studies (around the 1980s) that determined the rotational distributions of HF/DF from selective deuterium substitution reactions of the methyl and amino groups, Schaefer and co-workers studied this system theoretically in 2013. In their calculations, they used the CCSD(T) method and the aug-cc-pVnZ [*n* = 2(D), 3(T), 4(Q)] basis sets to determine the stationary points of the hydrogen-abstraction pathway.

My thesis focuses on the thermodynamic and reaction dynamics investigation of Cl/F + CH<sub>3</sub>NH<sub>2</sub> systems, as a continuation of the scientific pathway of the aforementioned research studies.

## 2. Objective

During the doctoral work, our goal was to provide deeper insights into the mechanisms of the Cl/F + CH<sub>3</sub>NH<sub>2</sub> reactions beyond the previously studied hydrogen-abstraction channels. Our plans included exploring the following reaction pathways by mapping the stationary points: substitution of one hydrogen atom of the methyl and amino groups, as well as the entire methyl and amino groups, with a chlorine or fluorine atom. Since these reactions can proceed via Walden-inversion and front-side-attack mechanisms, we aimed to identify the corresponding transition states and minimum complexes for these pathways. Additionally, we sought to improve the accuracy of the results obtained from previous studies. We intended to achieve this by applying the explicitly-correlated CCSD(T)-F12b method and calculating the following corrections: basis set effects up to aug-cc-pVQZ (for Cl + CH<sub>3</sub>NH<sub>2</sub>) and cc-pV5Z-F12 (for F + CH<sub>3</sub>NH<sub>2</sub>), post-(T) electron correlation effects up to CCSDT(Q), core-electron correlation energy contributions, scalar relativistic effects, zero-point energy (ZPE) corrections, and geometry-dependent spin-orbit coupling effects.

In addition to the thermodynamic investigations of the Cl/F + CH<sub>3</sub>NH<sub>2</sub> systems, the main motivation for the reaction dynamics research was the lack of full-dimensional, analytical potential energy surfaces (PES) in the literature. Moreover, while there have been experimental studies examining the methyl (CH<sub>3</sub> HA) and amino hydrogen abstraction (NH<sub>2</sub> HA) pathways, theoretical reaction dynamics analyses are notably scarce. Our aim was to develop full-dimensional, high-accuracy PESs for both systems, enabling efficient QCT simulations. Additionally, our work plan included comparing the data extracted from these simulations with experimental results. Through detailed analyses, we can provide deeper insight into the dynamics of systems belonging to the family of reactions between Cl/F atoms and organic molecules.

### 3. Methods

To determine the energies, structures, and harmonic vibrational frequencies of the stationary points, we applied the second-order Møller–Plesset perturbation (MP2) and unrestricted explicitly-correlated coupled-cluster [UCCSD(T)-F12b] methods as implemented in the 2015 version of the MOLPRO program package. The most accurate geometries and frequencies were determined at the UCCSD(T)-F12b/aug-cc-pVTZ theoretical level, while the potential energies at these structures were calculated using the UCCSD(T)-F12b method with aug-cc-pVQZ (for Cl + CH<sub>3</sub>NH<sub>2</sub>) and cc-pV5Z-F12 (for F + CH<sub>3</sub>NH<sub>2</sub>) basis sets. To achieve even more accurate results, we also performed the following energy correction calculations for each stationary point: post-CCSD(T) correlation, core-electron correlation, scalar relativistic effects, spin–orbit coupling correction, and ZPE correction. The energy contributions beyond (T) were calculated using the MRCC program interfaced with MOLPRO.

We obtained the potential energy surfaces by fitting a permutation-invariant polynomial to the fitting set which describes the most important energy regions of the chemical systems that form the basis of the doctoral work. During the calculations of the energy points, we used the ManyHF method to eliminate Hartree–Fock convergence problems occurring in the entrance channels. The quality of the PES was improved by the ROBOSURFER program package, which automatically expands the fitting set with geometries derived from quasi-classical trajectory simulations. The QCT simulations, conducted both during the development and for the final reaction dynamics investigation, were performed using custom programs available in our research group. I implemented FORTRAN90 programs for the analysis of the final trajectories. The visualization of the trajectories was done using the MacMolPlt program. Additionally, solving several smaller tasks (such as file handling, program executions, and data processing) required writing AWK and Shell scripts.

## 4. Results

**T1. By mapping the potential energy surfaces of the Cl/F + CH<sub>3</sub>NH<sub>2</sub> systems at a high level of theory, we not only explored the previously studied abstraction reaction pathways but also, for the first time, identified the stationary points belonging to the substitution pathways. The relative energies of these structures were determined with energy corrections taken into account, providing the most accurate insights into the thermodynamic properties of the reactions to date.**

During the mapping of the potential energy surfaces of both the Cl + CH<sub>3</sub>NH<sub>2</sub> and F + CH<sub>3</sub>NH<sub>2</sub> systems, we identified the stationary points associated with the following six reaction channels:

1. Methyl hydrogen-abstraction (CH<sub>3</sub> HA)
2. Amino hydrogen-abstraction (NH<sub>2</sub> HA)
3. Methyl hydrogen-substitution (CH<sub>3</sub> HS)
4. Amino hydrogen-substitution (NH<sub>2</sub> HS)
5. Methyl-substitution (MS)
6. Amino-substitution (AS)

For the chlorine + methylamine system we identified the configurations corresponding to Walden-inversion and front-side-attack mechanisms for the third and sixth reaction channels. For the fluorine + methylamine system we identified these configurations for the sixth reaction channel. By accurate determination of the reaction enthalpies, we demonstrated that, while both hydrogen-abstraction (HA) reactions and amino- and methyl-hydrogen substitution reactions are exothermic for the fluorine + methylamine system, only the two HA reactions are exothermic for the chlorine + methylamine system, with all substitution pathways being endothermic. In addition to mapping the structures of the transition states and product-like minimum complexes along each reaction pathway, we discovered a deep minimum (PREMIN) in the entrance channel for both the fluorine and chlorine systems. On the Cl + CH<sub>3</sub>NH<sub>2</sub> surface, this structure represents the classical global minimum, while the structure at the lowest relative energy point on the vibrationally adiabatic surface is the complex in the methyl-hydrogen abstraction product channel (CH<sub>3</sub> HA MIN''). We also identified this latter structure for the F + CH<sub>3</sub>NH<sub>2</sub> system, where it represents the global minimum on both the classical and adiabatic PES.

**T2. By analyzing the computed energy corrections, we confirmed that their inclusion is essential for achieving chemical accuracy. We demonstrate that the theoretical level applied in mapping the F + CH<sub>3</sub>NH<sub>2</sub> reaction exhibits basis set convergence within 0.1 kcal mol<sup>-1</sup>, making it an excellent choice for our high-level calculations.**

To calculate the most accurate potential energies of the stationary points, we used the CCSD(T)-F12b method, which accounts for triple excitations perturbatively. However, the impact of higher excitations is quite significant, as our post-(T) correction calculations demonstrated that the sum of the absolute values of the  $\delta[T]$  and  $\delta[(Q)]$  contributions is around 1 kcal mol<sup>-1</sup>. Given that correlation methods by default only consider the correlation of valence shell electrons, our core-electron correlation ( $\Delta_{\text{core}}$ ) calculations also accounted for the contribution of electron correlation of the core shells. We included the relativistic effects by calculating the scalar relativistic effect ( $\Delta_{\text{rel}}$ ) and the energy shift due to the spin-orbit coupling (SO). Although both the  $\Delta_{\text{core}}$  and  $\Delta_{\text{rel}}$  effects are on the order of a few tenths of a kcal mol<sup>-1</sup>, they are crucial for achieving highly accurate results. Our calculations successfully reproduced the spin-orbit shift of 0.84 kcal mol<sup>-1</sup> for the chlorine atom and 0.37 kcal mol<sup>-1</sup> for the fluorine atom at the reactant asymptote. To achieve accuracy within 1 kcal mol<sup>-1</sup>, these contributions cannot be neglected.

In our study of the F + CH<sub>3</sub>NH<sub>2</sub> system, we also extended our research to examine the basis set dependence of our results determined using the UCCSD(T)-F12b method. We investigated how the relative energies calculated with the UCCSD(T)-F12b/aug-cc-pVnZ ( $n = D, T, Q$ ) and cc-pVnZ-F12 ( $n = D, T, Q, 5$ ) methods compare to those obtained with the UCCSD(T)-F12b/cc-pV5Z-F12 method, which is used for determining *benchmark* values. As expected, the deviations decrease with increasing basis set size. The most important conclusion was that the calculations are highly reliable based on the root mean square deviation of 0.07 kcal mol<sup>-1</sup> obtained for the differences between the cc-pVQZ-F12 and cc-pV5Z energies, as the basis set convergence is within 0.1 kcal mol<sup>-1</sup>.

**T3. We demonstrated that by applying the ManyHF method, we can successfully solve the Hartree-Fock convergence issues in the entrance channel of the Cl/F + CH<sub>3</sub>NH<sub>2</sub> systems. Subsequently, we developed full-dimensional, accurate analytical potential energy surfaces for the two reactions.**

As the first step in creating the fitting set required for PES development, we generated additional points by random displacement of the geometries of optimized stationary points

obtained from the mappings. However, during quantum chemical calculations on these points, the default HF method implemented in MOLPRO typically converged to an unrealistically high-energy electronic state in the reactant region. The solution for this issue was provided by the ManyHF method developed in our group, which selects the reference for correlation calculations from multiple Hartree–Fock solutions, specifically the one yielding the lowest energy. Thus, PES development was conducted at a ManyHF-based composite theoretical level. This was based on calculations performed using the explicitly-correlated coupled-cluster method with a double-zeta basis set (ManyHF-UCCSD(T)-F12a/cc-pVDZ-F12), supplemented with triple-zeta basis corrections using the RMP2-F12 method (ManyHF-RMP2-F12/cc-pVTZ-F12 – ManyHF-RMP2-F12/cc-pVDZ-F12). The resulting surfaces accurately describe the most important stationary points of the Cl/F + CH<sub>3</sub>NH<sub>2</sub> complex systems, so they can be used for conducting reaction dynamics simulations.

**T4. Through the execution and analysis of reaction dynamics simulations, we demonstrated that although substitution pathways open at high collision energies, the two hydrogen-abstraction pathways remain the dominant channels of the Cl/F + CH<sub>3</sub>NH<sub>2</sub> reactions. For these abstraction reactions, we also showed that with increasing collision energy, the reactions become more direct and typically occur at the functional group where from the halogen atom attacks the methylamine.**

Utilizing the developed surfaces, we simulated and analyzed approximately 800 000 trajectories for both systems across various collision energies ( $E_{\text{coll}}$ ) and impact parameters. Based on the probabilities and integral cross sections determined for the six reaction channels presented in the first thesis point, we demonstrated that the methyl and amino hydrogen-abstraction channels, which occur at all collision energies, are far more significant than the substitution reactions that open at higher collision energies. Consequently, detailed dynamical characterizations were performed for these two reactions in both the chlorine and fluorine systems. The attack angle distributions obtained from our calculations revealed that during abstractions, the H atom originates from the functional group of methylamine that the attacking halogen atom approaches. By determining the scattering angle distributions of the products, we inferred the mechanisms of the reactions. For both CH<sub>3</sub> HA and NH<sub>2</sub> HA, increasing the collision energy resulted in a dominance of forward-scattered products, suggesting a direct stripping mechanism. On the other hand, at lower collision energies, more isotropic distributions indicate that the mechanisms are indirect.



**T5. By calculating the energy distributions of the products for the  $\text{Cl/F} + \text{CH}_3\text{NH}_2$  reactions, we revealed that a significant portion of the collision energy is transferred into the translational energy of the products. Additionally, among the diatomic products, HF is formed in a vibrationally excited state. The rotational quantum number distributions of the HF molecule obtained from our calculations show good agreement with the results of experimental methods conducted under conditions similar to our simulations.**

During the reaction dynamics studies, we established from the strong collision-energy dependence of the translational energy distributions of the products that a significant portion of the  $E_{\text{coll}}$  used in the simulations is transferred into the translational energy of the products. The fact that the peaks of the distributions shift toward higher energies with increasing  $E_{\text{coll}}$  confirms the mechanism shift determined in the previous thesis point, as products from direct reactions have higher translational energies than those from indirect reactions. The internal energies of diatomic molecules and radical products formed during reactive trajectories were also calculated and divided into vibrational and rotational energy components. By characterizing these, we highlighted that the HF formed during the hydrogen-abstraction reactions of  $\text{F} + \text{CH}_3\text{NH}_2$  is vibrationally excited. This can be well explained considering the energies determined during our thermodynamic analysis, as we demonstrated that these reactions are exothermic. Additionally, our results from geometry optimizations support this, as the H–F bond in the transition state is significantly elongated compared to the equilibrium bond length of the HF molecule. Consequently, after the hydrogen is stripped away, the diatomic molecule forms in a vibrationally excited state.

Finally, we had the opportunity to compare the rotational quantum number distributions determined for hydrogen chloride and hydrogen fluoride with experimental results found in the literature. The results of our simulations show good agreement with the so-called arrested relaxation data, as this method aims to prevent the relaxation of the formed HF and the occurrence of secondary reactions during the experiments.

## 5. Publications

### List of publications forming the basis of the thesis

1. T. Szűcs and G. Czakó, Benchmark *ab initio* stationary-point characterization of the complex potential energy surface of the multi-channel Cl + CH<sub>3</sub>NH<sub>2</sub> reaction, *Physical Chemistry Chemical Physics* 23(17), 10347–10356 (2021), IF<sub>2021</sub> : 3.945
2. T. Szűcs and G. Czakó, Benchmark *ab initio* potential energy surface mapping of the F + CH<sub>3</sub>NH<sub>2</sub> reaction, *Physical Chemistry Chemical Physics* 24(34), 20249–20257 (2022), IF<sub>2022</sub> : 3.3
3. T. Szűcs and G. Czakó, ManyHF-based full-dimensional potential energy surface development and quasi-classical dynamics for the Cl + CH<sub>3</sub>NH<sub>2</sub> reaction, *Journal of Chemical Physics* 159(13), 134306 (2023), IF<sub>2023</sub> : 3.1
4. T. Szűcs and G. Czakó, Automated potential energy surface development and comprehensive dynamics for the F + CH<sub>3</sub>NH<sub>2</sub> reaction, *Journal of Chemical Physics* 160(6), 064304 (2024), IF<sub>2023</sub> : 3.1

$$\sum \text{IF} = 13.445$$

### List of publications related to the thesis

1. P. Tóth, T. Szűcs, and G. Czakó, Benchmark *ab initio* characterization of the abstraction and substitution pathways of the Cl + CH<sub>3</sub>CN reaction, *Journal of Physical Chemistry A* 126(18), 2802–2810 (2022), IF<sub>2022</sub> : 2.9
2. B. Ballay, T. Szűcs, D. Papp, and G. Czakó, Phosphorus-centered ion-molecule reactions: benchmark *ab initio* characterization of the potential energy surfaces of the X<sup>-</sup> + PH<sub>2</sub>Y [X, Y = F, Cl, Br, I] systems, *Physical Chemistry Chemical Physics* 25(42), 28925–28940 (2023), IF<sub>2023</sub> : 2.9
3. P. Tóth, T. Szűcs, T. Győri, and G. Czakó, Dynamics of the Cl + CH<sub>3</sub>CN reaction on an automatically-developed full-dimensional *ab initio* potential energy surface, *Journal of Chemical Physics*, in press (2024), IF<sub>2023</sub> : 3.1

$$\frac{\sum \text{IF} = 8.9}{\sum \sum \text{IF} = 22.345}$$

## Additional publications

1. R. Ambrus, P. Szabó-Révész, T. Kiss, E. Nagy, T. Szűcs, T. Smausz, and B. Hopp, Application of a suitable particle engineering technique by pulsed laser ablation in liquid (PLAL) to modify the physicochemical properties of poorly soluble drugs, *Journal of Drug Delivery Science and Technology* 57, 101727 (2020), IF<sub>2020</sub> : 3.981
2. I.Z. Papp, A. Szerlauth, T. Szűcs, P. Béltéky, J.F.G. Perez, Z. Kónya, and Á. Kukovecz, Fabrication and characterization of a bifunctional zinc oxide/multiwalled carbon nanotube/poly(3,4-ethylenedioxythiophene): Polystyrene sulfonate composite thin film, *Thin Solid Films* 778, 139908 (2023), IF<sub>2023</sub> : 2.0

$$\frac{\sum \text{IF} = 5.981}{\sum \sum \sum \text{IF} = 28.326}$$

## 6. Talks and posters

October 21-22, 2021: MTA Reaction Kinetics and Photochemistry Working Group Meeting, Mátrafüred, Tímea Szűcs and Gábor Czakó, A Cl + CH<sub>3</sub>NH<sub>2</sub> reakció potenciálisenergia-felületének nagy pontosságú *ab initio* feltérképezése (talk)

July 10-15, 2022: Gordon Research Conference on Molecular Interactions and Dynamics, Stonehill College, Easton, MA, USA, Tímea Szűcs and Gábor Czakó, High-level *ab initio* stationary-point characterizations of atom + molecule multi-channel reactions (poster)

June 8-9, 2023: MTA Reaction Kinetics and Photochemistry Working Group Meeting, Balatonvilágos, Tímea Szűcs and Gábor Czakó, A Cl + CH<sub>3</sub>NH<sub>2</sub> reakció dinamikájának elméleti modellezése (talk)

November 12-17, 2023: International Conference on Molecular Energy Transfer in Complex Systems, Jaipur, India, Tímea Szűcs and Gábor Czakó, Spin-orbit-corrected full-dimensional *ab initio* potential energy surface development and dynamics for the Cl/F + CH<sub>3</sub>NH<sub>2</sub> reactions (poster)

November 24-25, 2023: MTA Material and Molecular Structure Working Group Meeting, Mátrafüred, Tímea Szűcs and Gábor Czakó, Automated potential energy surface developments and dynamics simulations for the Cl/F + CH<sub>3</sub>NH<sub>2</sub> reactions (talk)

May 30-31, 2024: MTA Reaction Kinetics and Photochemistry Working Group Meeting, Balatonvilágos, Tímea Szűcs and Gábor Czakó, S<sub>N</sub>2 reakció két reaktív centrummal: A CN<sup>-</sup> + CH<sub>3</sub>I rendszer dinamikája egy globális potenciálisenergia-felületen (talk)