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FACULTY OF SCIENCE AND INFORMATICS
DEPARTMENT OF PHYSICAL CHEMISTRY AND MATERIALS SCIENCE
CHEMISTRY DOCTORAL SCHOOL



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THESES OF THE DOCTORAL
DISSERTATION

Theoretical characterization of the mechanisms of
ion-molecule reactions

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1 Introduction

Many things in everyday life exist because of chemistry. The significance of basic research in the natural sciences often only becomes apparent a few years or decades later. Achieving the best possible control of chemical reactions and stereochemical selectivity in a more complex synthesis is very important for the chemical and pharmaceutical industries. However, in order to control reactions and to explore stereoselective mechanisms, we first need to understand the mechanisms of the simpler example reactions, for which reaction dynamics provides the opportunity to do.

In 1975, the work of Schatz and Kuppermann started the quantum mechanical description of small gas-phase reactions, and later the classical/quasi-classical trajectory (QCT) method was introduced for the dynamical study of larger systems that were still challenging for quantum dynamics. Today, QCT can be used to describe dynamics of systems larger than 10 atoms.

Bimolecular nucleophilic substitution (S_N2) is an important mechanism in organic chemistry and has been studied for a long time. Experimental studies in organic chemistry are basically on solution-phase reactions, but in the last few decades modern gas-phase crossed ion-molecular beam experimental methods have emerged thanks to the Wester group in Innsbruck, which have allowed the dynamic study of individual collisions.

These experiments can be easily compared with the results of QCT simulations, which are also used by our research group to gain a more accurate insight into the atomic-level mechanisms of gas-phase reactions. In the case of ion-molecule reactions, e.g. proton abstraction may occur in competition with S_N2 reactions, or bimolecular elimination may also be involved in the case of alkyl groups with more than one carbon atom. The Walden-inversion and front-side attack mechanisms of S_N2 reactions have been known for several decades, and in 2015 Szabó and Czako discovered the so-called double inversion mechanism. For a more complete picture of the mechanisms of S_N2 reactions, see the 2016 summary by Xie and Hase.

While the Hase group mostly uses direct dynamics simulations in their research, our research group specialises in the development of high-accuracy analytical potential energy surfaces (PES), in which we are among the world leaders.

2 Goals of the research

Our group has previously investigated the reaction $F^- + CH_3Cl$, which led to the discovery of double inversion. For this reason, the $F^- + CH_3CH_2Cl$ reaction has also been of great interest. In addition to the high accuracy mapping of the stationary points, we plan to pay special attention to the discovery of the so-called double-inversion transition state, which is the key to the existence of the assumed double-inversion pathway.

With the knowledge of the schematic potential energy surface (PES) of the system, we aimed to develop an analytical PES that would allow the execution of tens of thousands of trajectory simulations to understand the dynamics of the system. As the Wester group was in the process of studying the same system using gas-phase crossed ion-molecular beam experiments, there was the potential for a theoretical-experimental collaboration, which further justified the priority of this work.

In order to further understand the dynamics of the system, we considered performing vibration mode-specific dynamical simulations, the results of which may justify further experimental investigations.

The double inversion has been reported in the dynamics of several halide ion + methyl halide S_N2 reactions, but the identification based on the integration time proposed for the $F^- + CH_3Cl$ reaction could not be reliably applied to the $F^- + CH_3I$ system. Therefore, I decided to develop a trajectory-based method and to test a simpler vector-projection method instead of the Eckart-transformation used to distinguish inversion and retention on the two halide ion + methyl halide systems mentioned earlier.

Györi presented the ROBOSURFER package using the reaction $F^- + CH_3Br$, but the research focused only on the integral cross sections of the main product channels of the reaction to compare the potential energy surfaces. For this reason, a much more detailed analysis of the most promising PES III trajectories was our next goal to understand the dynamics of the system even more accurately.

3 Methods

During the mapping of the stationary points, I used the MolPro 2015 software package for the quantum chemical calculations (structure optimization, harmonic frequency calculation, etc.). The most accurate results are based on explicit-correlated coupled cluster and second-order Møller–Plesset perturbation calculations.

For the PES development, I used the monomial symmetrization approach (MSA) which is invariant for the permutations of identical atoms and the ROBOSURFER software package, which allowed automated PES development. The reactions were simulated using the quasi-classical trajectory (QCT) method, which describes the motion of the nuclei using classical physics, but adjusts the initial states according to quantum mechanical rotational-vibrational levels.

To analyse the trajectories I implemented my own program in FORTRAN90 and C++ languages. Based on the main characteristics of the simulations (attack and scattering angle, vibrational, rotational, translational and internal energy, etc.) I determined differential cross sections, from which I could infer the occurring mechanisms.

To distinguish between the inversion-retention S_N2 mechanisms, I used a simple vector-projection method. To distinguish between double inversion and front-side attack, I used a method based on the angle of attack of the transition state, for which I found the structure sought by backtracking the bond that dissociates during the reaction. A similar method was used to distinguish the mechanisms of bimolecular elimination. Eckart transformation and normal-mode analysis were used for vibrational mode-specific analysis of the products.

4 Results

T1. First in the world I mapped the schematic potential energy surface of the $F^- + CH_3CH_2Cl$ reaction using high accuracy *ab initio* methods. I have determined the structure of the previously unknown so-called double-inversion transition state [1].

Using explicit-correlated MP2-F12 and CCSD(T)-F12b methods, I optimized the structure of the stationary points with the aug-cc-pVDZ and aug-cc-pVTZ bases, respectively, and computed the *benchmark* results with the aug-cc-pVQZ basis sets and included a core correction using the cc-pCVTZ-F12 basis set. The zero-point energy correction was determined from the harmonic vibrational frequencies calculated with the aug-cc-pVDZ basis set. In addition to the mapped stationary points of the S_N2 and E2 reactions, I have put special emphasis on finding the so-called double-inversion saddle point, which has been used to prove the existence of the double-inversion reaction path. I compared the structures of some stationary points optimized by MP2 and coupled cluster methods.

T2. I developed a full-dimensional potential energy surface for the $F^- + CH_3CH_2Cl$ reaction and investigated the dynamics of the system using quasi-classical trajectory simulations. I have shown that instead of the thermodynamically more favorable S_N2 , the dominant mechanism of the reaction is the E2 [2].

A potential energy surface was developed for the $F^- + CH_3CH_2Cl$ reaction using an explicitly-correlated coupled cluster method with a double-zeta basis set (CCSD(T)-F12b/aug-cc-pVDZ), which was complemented with an additional triple-zeta basis-set correction using the explicitly correlated MP2 method. The potential energy surface describes the known major stationary points of the system within 1 kcal/mol error. The anti-E2 and Walden-inversion S_N2 product channels were found to be the most reactive in the dynamics study. Trajectories with a double-inversion mechanism have also been appeared in the development of PES, but they are less relevant for the present reaction because of their too low probability. The simulation results show good agreement with the scattering angle and kinetic energy distributions from the experimental work of the Wester group. In contrast to the thermodynamically more favourable S_N2 product, E2 is dominant, which can be explained by the wider reactive initial attack angle range.

T3. I have selected four vibrational normal-modes to study the dynamical effects arising from the excitation of reactants in the $F^- + CH_3CH_2Cl$ reaction. The S_N2 channel for C–Cl bond stretching, the proton abstraction for symmetric CH_2 bond stretching and the E2 and $FH\cdots Cl^- +$ ethylene channels for both symmetric C–H bond stretchings showed significant reactivity increase [3].

In addition to the ground state, I investigated the effects of excitation of 4 different vibrational normal-modes on the dynamics of the $F^- + CH_3CH_2Cl$ reaction using QCT simulations. The selected reactant vibrational normal-modes are C–Cl bond stretching, a CH_2 torsion and symmetric CH_2 and CH_3 bond stretching. The reactivities and internal energy distributions showed significant mode-specific effects. Substitution was most reactive with the C–Cl bond stretching, proton abstraction with the symmetric CH_2 bond stretching, and elimination mechanisms and the $FH\cdots Cl^- +$ ethylene product channel were more reactive with both symmetric C–H bond stretchings. Furthermore, the internal energy distributions of ethyl fluoride and ethylene also show significant mode-specificity. The internal energy, rotational and vibrational distributions of hydrogen fluoride did not show significant mode-specificity. Furthermore, the differential cross sections of the initial attack angle and scattering angle for each product channel were not dependent on vibrational excitation.

T4. I have proposed a vector-projection and a transition state attack angle based method to distinguish S_N2 mechanisms. I proved the correctness of the integration time-based retention mechanism assignment used in previous publications [4].

I have presented a vector-projection method that can be used to simply determine numerically the chirality of a three or four ligand molecule. I applied this method to distinguish between inversion and retention S_N2 mechanisms. Double inversion and front-side attack result in the same product, so to distinguish between them, I used the attack angle distribution of the last transition state of their trajectories before dissociation. Using this method, I demonstrated that the assignment based on integration time applied to the $F^- + CH_3Cl$ reaction worked correctly and that the retention S_N2 mechanisms of $F^- + CH_3I$ could be separated with sufficient reliability by this new method. The distribution of transition state attack angles is a single-peaked curve at collision energies below the front-side attack barrier and a double-peaked curve above it. Since the peaks do not overlap, we can define a boundary angle between them that separates the channels. This is chosen as 111° for practical reasons.

T5. I have analysed the dynamics of the $F^- + CH_3Br$ reaction in detail and also paid attention to the lower-probability product channels. I have showed the presence of low-probability retention S_N2 mechanisms [5].

In the study of the $F^- + CH_3Br$ reaction, in addition to the two main mechanisms already identified, S_N2 and proton abstraction, I have also discovered other less reactive reaction pathways. I have distinguished between the S_N2 mechanisms and identified additional possible product channels for induced inversion and $FH \cdots Br^- + CH_2$. I have also investigated differential cross sections for the two main reaction channels, showing that Walden inversion is achieved by the usual direct rebound mechanism, while proton abstraction proceeds by the direct stripping mechanism. The zero-point energy violation appears only for proton abstraction and is significant for both product species. Among the vibrational modes of methyl fluoride, the C–F bond stretching shows a more significant collision energy dependence, where the distributions shift towards lower energies with increasing collision energy, i.e., increasingly cold distribution curves are obtained. Increasing the collision energy also increases the rotational and vibrational excitability of the hydrogen fluoride produced during proton abstraction.

5 Publications

5.1 Publications directly related to the topic of the dissertation

- [1] Tajti, V. & Czakó, G. Benchmark *ab initio* characterization of the complex potential energy surface of the $F^- + CH_3CH_2Cl$ reaction. *The Journal of Physical Chemistry A* **121**, 2847–2854. <https://doi.org/10.1021/acs.jpca.7b01572> (Apr. 2017)
 $J_{IF,2017} = 2.836$
- [2] Meyer, J., Tajti, V., Carrascosa, E., Gyóri, T., Stei, M., Michaelsen, T., Bastian, B., Czakó, G. & Wester, R. Atomistic dynamics of elimination and nucleophilic substitution disentangled for the $F^- + CH_3CH_2Cl$ reaction. *Nature Chemistry* **13**, 977–981. <https://doi.org/10.1038/s41557-021-00753-8> (Aug. 2021)
 $J_{IF,2021} = 24.274$
(the first three authors are shared first authors)
- [3] Tajti, V. & Czakó, G. Vibrational mode-specific dynamics of the $F^- + CH_3CH_2Cl$ multi-channel reaction. *Physical Chemistry Chemical Physics* **24**, 8166–8181. <https://doi.org/10.1039/d2cp00685e> (Apr. 2022)
 $J_{IF,2021} = 3.945$
- [4] Papp, P., Tajti, V. & Czakó, G. Numerical separation of the front-side attack and double-inversion retention pathways of S_N2 reactions. *Chemical Physics Letters* **755**, 137780. <https://doi.org/10.1016/j.cplett.2020.137780> (Sept. 2020)
 $J_{IF,2020} = 2.328$
- [5] Tajti, V., Gyóri, T. & Czakó, G. Detailed quasiclassical dynamics of the $F^- + CH_3Br$ reaction on an *ab initio* analytical potential energy surface. *The Journal of Chemical Physics* **155**, 124301. <https://doi.org/10.1063/5.0065209> (Sept. 2021)
 $J_{IF,2021} = 4.304$

5.2 Publications not utilized but related to the dissertation

Czakó, G., Győri, T., Olasz, B., Papp, D., Szabó, I., Tajti, V. & Tasi, D. A. Benchmark *ab initio* and dynamical characterization of the stationary points of reactive atom + alkane and S_N2 potential energy surfaces. *Physical Chemistry Chemical Physics* **22**, 4298–4312. <https://doi.org/10.1039/c9cp04944d> (Feb. 2020)

$J_{\text{IF},2020} = 3.676$

Papp, D., Tajti, V., Győri, T. & Czakó, G. Theory finally agrees with experiment for the dynamics of the Cl + C₂H₆ reaction. *The Journal of Physical Chemistry Letters* **11**, 4762–4767. <https://doi.org/10.1021/acs.jpcllett.0c01263> (May 2020)

$J_{\text{IF},2020} = 6.475$

Czakó, G., Győri, T., Papp, D., Tajti, V. & Tasi, D. A. First-principles reaction dynamics beyond six-atom systems. *The Journal of Physical Chemistry A* **125**, 2385–2393. <https://doi.org/10.1021/acs.jpca.0c11531> (Feb. 2021)

$J_{\text{IF},2021} = 2.944$

Gruber, B., Tajti, V. & Czakó, G. Full-dimensional automated potential energy surface development and dynamics for the OH + C₂H₆ reaction. *The Journal of Chemical Physics* **157**, 074307. <https://doi.org/10.1063/5.0104889> (Aug. 2022)

$J_{\text{IF},2021} = 4.304$

Papp, D., Tajti, V., Avila, G., Mátyus, E. & Czakó, G. CH₄·F⁻ revisited: full-dimensional *ab initio* potential energy surface and variational vibrational states. *Molecular Physics*. <https://doi.org/10.1080/00268976.2022.2113565> (Aug. 2022)

$J_{\text{IF},2021} = 1.937$

Yin, C., Tajti, V. & Czakó, G. Full-dimensional potential energy surface development and dynamics for the HBr + C₂H₅ → Br(²P_{3/2}) + C₂H₆ reaction. *Physical Chemistry Chemical Physics* **24**, 24784–24792. <https://doi.org/10.1039/d2cp03580d> (Oct. 2022)

$J_{\text{IF},2021} = 3.945$

Nacsa, A. B., Tajti, V. & Czakó, G. Dynamics of the $\text{Cl}^- + \text{CH}_3\text{I}$ reaction on a high-level *ab initio* analytical potential energy surface. *The Journal of Chemical Physics* **158**, 194306. <https://doi.org/10.1063/5.0151259> (May 2023)

$J_{\text{IF},2021} = 4.304$

5.3 Statistics of publications

	Utilized publications	All
Number of publications	5	12
Cumulative impact factor	37.687	65.272

6 Conference participations

KeMoMo-QSAR symposium, Szeged, Hungary, May 24-25 2018

Tajti, V. A $\text{F}^- + \text{CH}_3\text{CH}_2\text{Cl}$ reakció komplex potenciálisenergia-felületének nagy pontosságú *ab initio* feltérképezése (lecture in Hungarian)

MTA Reaction Kinetics and Photochemistry Working Group Meeting, Veszprém, Hungary, November 8-9 2018

Tajti, V. and Czakó, G. A $\text{F}^- + \text{CH}_3\text{CH}_2\text{Cl}$ reakció komplex potenciálisenergia-felületének nagy pontosságú *ab initio* feltérképezése (lecture in Hungarian)

XXVIII International Symposium on Molecular Beams, Edinburgh, Scotland, June 23-28 2019

Tajti, V. and Czakó, G. Accurate *ab initio* thermochemistry, potential energy surface, and dynamics of the $\text{F}^- + \text{CH}_3\text{CH}_2\text{Cl}$ reaction (poster)

MTA Reaction Kinetics and Photochemistry Working Group Meeting, Online, November 6 2020

Tajti, V. and Czakó, G. Ion-molekula reakciók mechanizmusainak tanulmányozása (lecture in Hungarian)

KeMoMo-QSAR symposium, Szeged, Hungary, September 30 - October 1 2021

Tajti, V. and Czakó, G. Számítógéppel az ion-molekula reakciók mechanizmusainak nyomában (lecture in Hungarian)

MTA Reaction Kinetics and Photochemistry Working Group Meeting, Balatonvilágos (online), Hungary, May 19-20 2022

Tajti, V., Győri, T. and Czakó, G. Az elmélet és kísérlet együttműködése: a $F^- + CH_3CH_2Cl$ szubsztitúciós és eliminációs reakciók versengő dinamikája (lecture in Hungarian)

Gordon Research Conference on Molecular Interactions and Dynamics, Stonehill College, Easton, MA, USA, July 10-15 2022

Tajti, V., Győri, T., Papp, P. and Czakó, G. Theoretical investigation and numerical separation of competitive reaction pathways for ion-molecule reactions (poster)

Nacsa, A. B., Tajti, V. and Czakó, G. Toward the first-principles dynamics of the $Cl^- + CH_3I$ and $F^- + CF_3CH_2I$ reactions (poster)

Győri, T., Tasi, D. A., Tajti, V., Papp, D. and Czakó, G. Towards automated potential energy surface development with Robosurfer and ManyHF (lecture and poster)

XVI International Workshop on Quantum Reactive Scattering, Balatonföldvár, Hungary, September 4-9 2022

Győri, T., Tasi, D. A., Tajti, V., Papp, D. and Czakó, G. Tools for automated PES development: Robosurfer and ManyHF (lecture)

MTA Material and Molecular Structure Working Group Meeting, Mátrafüred, Hungary, October 21-22 2022

Győri, T., Tasi, D. A., Tajti, V., Papp, D. and Czakó, G. Towards automated potential energy surface development with Robosurfer and ManyHF (lecture in Hungarian)

MTA Reaction Kinetics and Photochemistry Working Group Meeting, Mátrafüred, Hungary, October 27-28 2022

Papp, D., Tajti, V., Avila, G., Mátyus, E. and Czakó, G. A $CH_4 \cdot Ar$ és a $CH_4 \cdot F^-$ komplexek rezgési dinamikája spektroszkópiai minőségű potenciálisenergia-felületeken (lecture in Hungarian)

Gruber, B., Tajti, V. and Czakó, G. Az $OH + C_2H_6$ reakció dinamikája egy automatikusan fejlesztett potenciálisenergia-felületen (lecture in Hungarian)