Final Report

PD-111900

Dynamics of polyatomic chemical reactions

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Introduction

The research supported by the present postdoctoral grant started in January of 2015 when I was a research associate at the Institute of Chemistry, Eötvös University. Then I was invited to join the faculty of the University of Szeged and from August of 2015 I continued the present project at the Department of Physical Chemistry and Materials Science of the University of Szeged. Using the support of a postdoctoral grant I established a new Computational Reaction Dynamics Research Group in Szeged. We published 15 papers including two *Nature Chemistry* articles and I gave several invited talks at international conferences with the support of the PD-111900 grant. Furthermore, at the end of 2015 I submitted my Doctor of the Hungarian Academy of Sciences dissertation, which was successfully defended in January, 2017. In 2017 I received a K NKFIH grant based partially on my achievements during the present PD-grant period.

The main goal of our research is to study the dynamics and mechanisms of polyatomic chemical reactions using ab initio potential energy surfaces (PESs) and the quasi-classical trajectory (QCT) method. We aim to reveal new reaction pathways as well as understand the energy efficiency and mode-specificity of chemical systems, which may help to control the outcome of chemical reactions. The summary of our research achievements is described below in chronological order.

Results

Double-inversion: A new reaction pathway for S_N2 reactions. In January 2015 we published a reaction dynamics study revealing a new retention mechanism, called double inversion, for the F^- + CH_3Cl S_N2 reaction [*Nat. Commun.* **6**, 5972 (2015)]. During double inversion a proton-abstraction-induced inversion is followed by a second inversion via the usual central transition state, thereby resulting in retention of configuration (Figure 1). Our finding received significant media attention; for example, the National Geographic Hungary, Index.hu, and the Hungarian Television highlighted the new reaction path. Even if the *Nature Communications* article on the new double-inversion mechanism appeared in 2015, this paper is not listed among the PD-111900-supported publications, because the work had been performed before the grant opened. Nevertheless, it is important to mention this

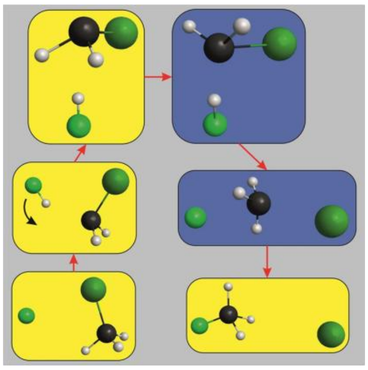

Figure 1. The double-inversion mechanism of S_N2 reactions.

double-inversion study, because the new reaction pathway provided motivation for other projects reviewed in this report. For example, in 2015 we investigated the generality of the new double-inversion mechanism [1] and found the so-called double-inversion transition state for all the 16 S_N2 reactions of $X^- + CH_3Y$ type, where X and Y = F, Cl, Br, I. We claimed that double inversion may be a general mechanism for S_N2 reactions.

Spin-orbit effects for a chemical reaction. Beside the above-discussed S_N2 reactions, I had collaboration with the group of Professor Schaefer (University of Georgia, GA, USA). We investigated the pathways for the $OH + Cl_2 \rightarrow HOCl + Cl$ and $HOCl + Cl \rightarrow HCl + ClO$ reactions [2]. Our benchmark study considering high-level ab initio computations including spin-orbit corrections provided the best theoretical estimates and predictions of the energetics of the $OH + Cl_2$ system.

A global PES and dynamics for $F^- + CH_3F$. We developed a global, full-dimensional, chemically accurate, ab initio PES for the $F^- + CH_3F$ system, which PES describes the Walden-inversion, front-side attack, and double-inversion S_N2 pathways as well as the proton-abstraction channel ($HF + CH_2F^-$) [3]. Quasi-classical trajectory simulations on the new PES showed that front-side attack is a significant mechanism at high collision energies. Double inversion can also occur in the $F^- + CH_3F$ reaction, though the double-inversion cross sections are small. Furthermore, the simulations found significant amount (around 20 %) of re-crossing trajectories showing that traditional transition-state-theory computations may overestimate the reactivity.

Rotational mode specificity in S_N2 reactions. We investigated, for the first time, the rotational mode specificity (*JK*-dependent reactivity) in S_N2 reactions [4]. For the $F^- + CH_3Y(v = 0,\ JK)$ [Y = F and Cl] S_N2 reactions we found that reactant rotational excitations usually decrease the reactivity, because the rotational motion counteracts the ion-dipole orientation effects. Further studies, inspired by ours, would be necessary to develop general qualitative rules for rotational mode specificity.

Unexpected leaving-group effect in S_N2 reactions. In 2016 we published a joint experimental–theoretical work in *Nature Chemistry* on the leaving-group effects on the dynamics of S_N2 reactions [5]. We found that the leaving group can have different influence on the dynamics of seemingly similar S_N2 reactions, e.g., $F^- + CH_3Cl$ and $F^- + CH_3I$. Furthermore, our theoretical results were in unprecedented agreement with the experimental data for a S_N2 reaction. These findings were highlighted by the national (delmagyar.hu) and international (phys.org) media.

The best quantum dynamics for a S_N2 reaction. Utilizing our full-dimensional analytical PES we studied the mode-specific dynamics of the $F^- + CH_3Cl$ S_N2 reaction using reduced-dimensional quantum as well as full-dimensional QCT methods. The present six-dimensional quantum simulations, carried out in collaboration with the group of Professor Minghui Yang, represent the highest-dimensional quantum dynamical study of a S_N2 reaction. Despite the fact that the above S_N2 reaction is barrierless (the Walden-inversion transition

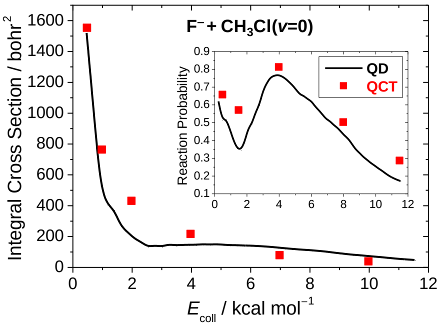

Figure 2. Quantum *vs.* classical dynamics of $F^- + CH_3Cl$.

state is energetically below the reactants), the quantum computations revealed significant mode-specificity, in good agreement with the QCT results. The quantum-mechanical and QCT excitation functions (integral cross sections as a function of collision energy) obtained for the ground-state $F^- + CH_3Cl(v = 0)$ S_N2 reaction were found to agree very well supporting the validity of the QCT method for S_N2 reactions (Figure 2). The results were published in the high-impact physical chemistry journal *J. Phys. Chem. Lett.* [6].

Mode-specific dynamics of $F^- + CHD_2Cl$. In 2016 we also investigated the multi-channel mode-specific dynamics of the $F^- + CHD_2Cl$ S_N2 and proton/deuteron-transfer reactions using our full-dimensional global ab initio PES [7]. QCT computations on the PES show that double inversion is promoted if we excite the CH or CD stretching mode of the reactant. Considering the proton/deuteron-transfer channels leading to either $HF + CD_2Cl^-$ or $DF + CHDCl^-$, the proton abstraction is found more likely than deuteron abstraction and the CH and CD stretching excitations enhance the HF and DF channels, respectively. Correlated scattering- and attack-angle distributions reveal that the direct abstraction processes usually go through back-side rebound, back-side stripping, and front-side stripping pathways. The CH and CD stretching modes do not behave as pure spectators in the abstraction reactions, since in all cases mainly vibrationally ground-state products are formed. The rotational distributions of the HF and DF products are also found to be cold, thus most of the available energy transfers into the relative translational energy of the products. In this study we have also tested the one-dimensional Gaussian binning (1GB) method, which was first proposed by us in 2009 [*J. Chem. Phys.* **131**, 244302 (2009)], for mode-specific polyatomic product analysis. The results show that the exact classical vibrational energy-based 1GB method provides physically correct final state distributions.

The first ab initio analytical PES for $F^- + CH_3I$. In 2017 we reported a global PES for the $F^- + CH_3I$ reaction which PES describes the S_N2 channel via the back-side attack inversion, front-side attack retention, and double-inversion pathways, as well as the proton-transfer channel [8]. The new PES is obtained by fitting high-level explicitly-correlated ab initio energy points using the permutationally invariant polynomial approach. This is the first full-dimensional ab initio analytical PES for the $F^- + CH_3I$ system, which opens the door for many dynamical simulations. We computed the cross sections and reaction probabilities of the S_N2 and proton-transfer channels as well as the scattering angle distributions and the product internal energy distributions for the S_N2 channel. The computed results were compared with available crossed-beam experiments showing remarkable agreement. Furthermore, additional experiments have recently been performed for this system in Professor Roland Wester's laboratory (University of Innsbruck), and we collaborate with the Wester group on the mode-specific dynamics of the $F^- + CH_3I$ S_N2 reaction. The joint experimental–theoretical results will be published soon.

S_N2 *vs.* E2 mechanisms. We performed a high-level ab initio benchmark study on the characterization of the stationary points of the PES of the $F^- + CH_3CH_2Cl$ reaction [9]. In the case of this system, besides the well-known S_N2 channel, an E2 elimination process can also occur. Furthermore, we have found a double-inversion transition state, for the first time for a reaction of an ethyl-halide. Following this ab initio study, we are currently working on developing a global PES for this system, which will open the door for collaboration with experimentalists.

Front-side complex formation in S_N2 reactions. As mentioned above in 2016 we found that the leaving group may have significant effect on the dynamics of S_N2 reactions. Since in 2017 we had PESs for both the $F^- + CH_3Cl$ and CH_3I reactions at hand, we could compare the dynamics of the two S_N2 reactions. The simulations revealed significant front-side complex formation for $F^- + CH_3I$, which steers the reactants away from the reactive orientations, thereby making the reaction more indirect, whereas the front-side complex formation is negligible for $F^- + CH_3Cl$, therefore this reaction is more direct [10]. Our study provides the first quantitative characterization of the front-side complex formation in the S_N2 process and highlights the role of these non-traditional minima in the dynamics of S_N2 reactions.

Benchmark ab initio study on $Cl^- + CH_3I$. Motivated by the novel stationary points recently revealed for S_N2 reactions, we performed a high-level ab initio characterization of the PES of the $Cl^- + CH_3I$ S_N2 and proton-transfer reactions [11]. On the qualitative side, we reported new minima and transition states for the $Cl^- + CH_3I$ system. On the quantitative side, we published definitive structures based on CCSD(T)-F12b/aug-cc-pVQZ computations as well as accurate relative energies obtained by considering electron correlation beyond the gold standard CCSD(T) level, extrapolation to the complete basis set limits, and core correlation contributions.

Mapping the angle-dependent barrier to reaction. The barrier of a chemical reaction plays a central role in chemistry, which has two major properties, the height and its dependence on geometry (Figure 3). The former has been widely studied, but the experimental determination of the latter has been impossible until now. In 2017 Kopin Liu's group developed a method to measure the angle-dependent barrier for the $Cl + CHD_3$ reaction. The experimental data were excellent agreement with my computed values. In order to perform this experiment the orientation of the reactants needs to be controlled. The resulting polarization-dependent differential cross sections were found to be in very good agreement with the aligned QCT results revealing different dynamics of end-on and side-on collisions. The experimental–theoretical results were published in a joint *Nature Chemistry* paper [12] in the issue of December, 2017.

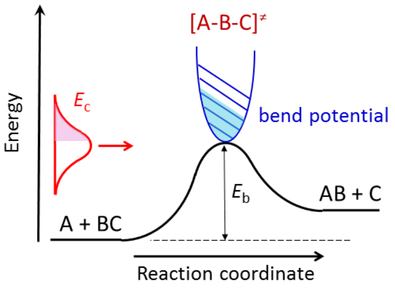

Figure 3. Transition-state bending potential of a chemical reaction.

Feature Article on S_N2 reactions. In 2017 we received an invitation to submit a Feature Article for *J. Phys. Chem. A* highlighting our recent research achievements. This article reviews our novel analytical PES-based approach to S_N2 reaction dynamics as well as many of the above described research findings including the double-inversion mechanism, leaving-group effect, front-side complex formation, the best quantum dynamics for S_N2 reactions, and the theoretical–experimental comparisons. The paper was featured on the front cover (Figure 4) of the journal [13].

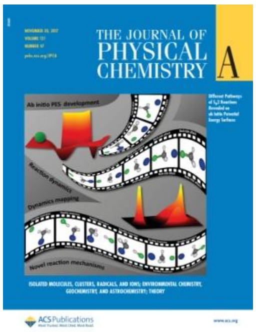

Figure 4. Cover.

Revealing novel reaction pathways for $Cl + CH_4 \rightarrow H + CH_3Cl$. QCT simulations for $Cl + CH_4$ on a new revised PES showed that significant fraction of the substitution channel does not proceed via Walden inversion, but results in retention of configuration. The trajectories revealed two different types of retention mechanisms, named edge- and vertex-attack. During edge-attack the Cl atom directly replaces a side H atom, whereas the vertex-attack proceeds via a H-abstraction-induced substitution. More details can be found in Ref. [14].

S_N2 reactions at nitrogen centers. Besides the above-discussed carbon-centered S_N2 reactions, we have studied S_N2 reactions at nitrogen (N) centrums. As a first step, we have characterized the $X^- + NH_2Y$ [X, Y = F, Cl, Br, I] reactions using explicitly-correlated ab initio methods providing benchmark stationary-point properties, which may guide future PES developments and dynamics studies [15].

Summary

We have studied the dynamics and mechanisms of fundamental chemical reactions based on an efficient analytical PES-based approach, introduced by us for S_N2 reactions. Our major achievements in the past 3 years can be summarized as follows:

(a) generalization of the double-inversion mechanism,
(b) uncovering unexpected leaving-group effects,
(c) high-level ab initio analytical PESs for the $F^- + CH_3F$ and $F^- + CH_3I$ systems,
(d) deciphering front-side complex formation in S_N2 reactions,
(e) the best quantum dynamics computation for a S_N2 reaction,
(f) benchmark ab initio data for several S_N2 reactions,
(g) vibrational and rotational mode specificity in S_N2 reactions,
(h) mapping the angle-dependent barrier to reaction,
(i) revealing novel retention pathways for the $Cl + CH_4$ substitution process.

The above work resulted in 15 research articles (cumulative impact factor: 108, corresponding-author papers: 14) including high-impact publications in *Nature Chemistry* (twice), *Chemical Science*, etc. and an invited Feature Article as well as several conference presentations including 6 invited talks and a Doctor of the Hungarian Academy of Sciences dissertation. Since this is a PD grant, it is worth emphasizing that none of the above-mentioned publications involved my PhD and postdoctoral advisers.

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J. Phys. Chem. A **121**, 2847 (2017)

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***J. Phys. Chem. Lett.* 8, 2917 (2017)**

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Direct mapping of the angle-dependent barrier to reaction for Cl + CHD_3 using polarized scattering data
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Dynamics and novel mechanisms of S_N2 reactions on ab initio analytical potential energy surfaces
J. Phys. Chem. A **121**, 9005 (2017) ***Feature Article***
This paper was featured on the front cover of JPCA

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Does the Cl + $CH_4 \rightarrow H + CH_3Cl$ reaction proceed via Walden inversion?
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[15] B. Hajdu and **G. Czakó***
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J. Phys. Chem. A DOI: 10.1021/acs.jpca.7b11927 (2018)

Conference presentations

G. Czakó
Kémiai reakciók dinamikája ab initio potenciális energia felületeken (in Hungarian)
Meeting of the Material and Molecular Structure Working Group of MTA
Mátrafüred, Hungary, February 27-28 2015 (**Talk**)

G. Czakó
Dynamics of hydrogen-abstraction and S_N2 reactions on ab initio analytical potential energy surfaces
XIII International Workshop on Quantum Reactive Scattering
Salamanca, Spain, July 6-10 2015 (**Invited talk**)

P. Szabó, G. Lendvay, and **G. Czakó**
Quasiclassical trajectory studies of the dynamics of a complex-forming bimolecular reaction: $CH_3 + HBr \rightarrow CH_4 + Br$
XIII International Workshop on Quantum Reactive Scattering
Salamanca, Spain, July 6-10 2015 (**Talk**)

G. Czakó
Dynamics of hydrogen-abstraction and S_N2 reactions on ab initio analytical potential energy surfaces
XXV Dynamics of Molecular Collisions Meeting
Asilomar, CA, USA, July 12-17 2015 (**Poster**)

M. Stei, E. Carrascosa, M. Kainz, A. Kelkar, I. Szabó, **G. Czakó**, A. Dörfler, T. Michaelsen, J. Meyer, and R. Wester
Imaging the influence of the leaving group and of vibrational excitation on S_N2 reactions
XXV Dynamics of Molecular Collisions Meeting
Asilomar, CA, USA, July 12-17 2015 (**Talk**)

G. Czakó
Dynamics of chemical reactions on ab initio potential energy surfaces
14th Central European Symposium on Theoretical Chemistry (CESTC)
Banská Bystrica, Slovakia, September 6-9 2015 (**Invited talk**)

M. Stei, E. Carrascosa, J. Meyer, T. Michaelsen, B. Bastian, M. A. Kainz, A. H. Kelkar, I. Szabó, **G. Czakó**, and R. Wester
Imaging the complex influence of the leaving group on nucleophilic substitution reactions
12th European Conference on Atoms Molecules and Photons (ECAMP12)
Frankfurt, Germany, September 5-9 2016 (**Poster**)

M. Stei, E. Carrascosa, J. Meyer, T. Michaelsen, B. Bastian, M. A. Kainz, A. H. Kelkar, I. Szabó, **G. Czakó**, and R. Wester
Imaging the complex influence of the leaving group on nucleophilic substitution reactions
21st European Conference on the Dynamics of Molecular Systems (MOLEC)
Toledo, Spain, September 11-16 2016 (**Poster**)

G. Czakó
Kémiai reakciók dinamikája ab initio potenciális energia felületeken (in Hungarian)

Meeting of the Reaction Kinetics and Photochemistry Working Group of MTA
Balatonalmádi, Hungary, May 29-30 2017 (**Talk**)

G. Czakó
Dynamics and novel mechanisms of S_N2 reactions on ab initio analytical potential energy surfaces
8th International Meeting on Atomic and Molecular Physics and Chemistry (IMAMPC)
Torun, Poland, June 19-22 2017 (**Invited talk**)

G. Czakó
Dynamics and novel mechanisms of S_N2 reactions on ab initio analytical potential energy surfaces
XIV International Workshop on Quantum Reactive Scattering
Trieste, Italy, July 3-6 2017 (**Invited talk**)

G. Czakó
Dynamics and novel mechanisms of S_N2 reactions on ab initio analytical potential energy surfaces
S_N2 Reaction Dynamics Symposium, ACS Southwest Regional Meeting
Lubbock, TX, USA, October 29 - November 1 2017 (**Invited talk**)

G. Czakó
Dynamics and novel mechanisms of reactions of atoms and ions with polyatomic molecules
WG1 Workshop, COST Action CM1401
Ciudad Real, Spain, December 11-12 2017 (**Invited talk**)