

Theses of the doctoral dissertation

**Dynamics of bimolecular nucleophilic  
substitution and proton-transfer  
reactions on global *ab initio*  
potential energy surfaces**

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# 1 Introduction

Bimolecular nucleophilic substitution ( $S_N2$ )  $X^- + CH_3Y \rightarrow XCH_3 + Y^-$  occupies prominent position in organic chemistry. The  $S_N2$  mechanism includes the simultaneous formation and cleavage of bond between the central carbon atom and the nucleophile ( $X^-$ ) and the leaving group ( $Y$ ), respectively, while the configuration is inverted around the carbon center. This stereospecific process is called Walden inversion. Furthermore, at higher collision energies other reaction channels may open, such as the proton-abstraction  $X^- + CH_3Y \rightarrow CH_2Cl^- + HX$ , where proton-transfer occurs between the two reactants.

Theoretical investigation of the potential energy surface (PES) of the  $X^- + CH_3Y$  type reactions is extremely valuable to obtain detailed information about the transition-states and ion-dipole complexes, thereby overcoming the difficulties encountered in experimental studies. However, in many cases the reactions do not follow the minimum energy paths prescribed by the stationary points. Moreover, the majority of  $S_N2$  reactions violates the standard statistical theories such as the transition state theory. Thus, for accurate description of the atomic-level mechanism chemical dynamics simulations should be considered.

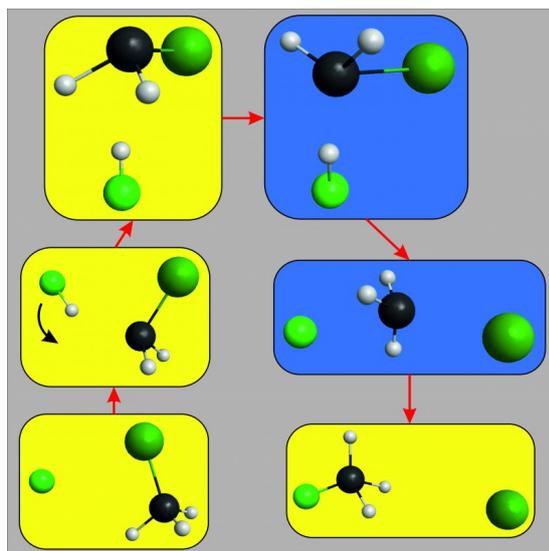
During my doctoral research I focused on two aspects: development of analytical potential energy surfaces for the  $F^- + CH_3F$  and  $F^- + CH_3Cl$  reactions, and unveiling how these reactions occur at atomic level via quasiclassical trajectory simulations employing the analytical PESs. The  $F^- + CH_3F$  reaction aroused our interest in many respects. On the one hand, the substitution channel is hardly to be probed experimentally, because there is only one stable fluorine isotope. On the other hand, dynamics simulations have not been applied before in order to describe the mechanism. Experimental data for the  $F^- + CH_3Cl$  reaction are more abundant; however, the previous dynamical results were based only on a single analytical PES and direct dynamics computations. Despite the reasonable agreement with experimental findings, the low-level electronic structure methods employed and the statistical uncertainty of the dynamical simulations may question the reliability of the theoretical results.

Toward the PES developments comprehensive tests were carried out in order to choose the most accurate *ab initio* method which is technically feasible at the same time for the computation of many energy points. The most important

characteristics of the fitted PESs are the following: (a) explicit invariant with respect to the permutation of like nuclei, (b) full-dimensional without any constraint on the coordinates, and (c) global in describing all the possible reaction pathways and product channels up to about 100 kcal mol<sup>-1</sup>.

With analytical PESs at hand I performed quasiclassical trajectory (QCT) computations, where the motion of the atomic nuclei is governed by classical mechanical laws, but quantum effects are also included. Specifically, the internal energy of the polyatomic reactants is prepared to be identical to a (ro)vibrational quantum state energy. Similarly, (ro)vibrational quantum states are assigned to the product molecules. The dynamical features of the reactions, such as product scattering angle, internal energy, and initial attack angle distributions may strongly depend on the collision energy, initial orientation, as well as initial vibrational and rotational state of the reactants. Furthermore, dynamical simulations may uncover novel mechanistic pathways. Our collaboration with the research group of Roland Wester (University of Innsbruck, Austria) facilitates comparisons with experimental results.

All in all, the agreement between PES properties, like relative energies, structural parameters, harmonic vibrational frequencies and long-range interactions, and the corresponding benchmark *ab initio* data, as well as the agreement between computed and measured dynamical properties will certainly stimulate further studies of similar reactions and continued development of the QCT method.



**Double-inversion mechanism of the S<sub>N</sub>2 reactions** - I. Szabó and G. Czako, *Nat. Commun.* 6, 5972 (2015)

## 2 Methods

During my PhD research the benchmark *ab initio* electronic structure computations and the computation of the PES energy points were performed using the MOLPRO program package. For post-CCSD(T) computations the MRCC program package interfaced to Molpro was employed. The sampling of the configuration space for potential energy surface construction, as well as the product analysis were done using my own computer codes developed using the FORTRAN 90 programming language. The fitting of the energy points and the quasiclassical trajectory simulations were performed with our in-house programs. For data analysis and visualization purposes the AWK scripting language and the MATHEMATICA and MACMOLPLT programs were used.

## 3 Results

1. I tested the performance of various standard electron-correlation [MP2, CCSD(T)], explicitly correlated [MP2-F12, CCSD(T)-F12], and composite *ab initio* methods with different correlation consistent basis sets for high-dimensional analytical potential energy surface developments. The accuracy of the relative potential energies computed for geometries covering the energy range of chemical importance for the  $F^- + CH_3F$ ,  $F^- + CH_3Cl$  and  $OH^- + CH_3F$  reactions was checked against highly accurate relative energies computed at the AE-CCSD(T)-F12b/cc-pCVQZ-F12 level of theory. I also investigated the effects of post-CCSD(T) electron correlation, core correlation, and scalar relativity. Our findings provide practical guidance for choosing the most efficient and accurate method at the same time for future PES developments.
2. I developed full-dimensional potential energy surfaces for the  $F^- + CH_3F$  and  $F^- + CH_3Cl$  reactions. The PESs are invariant with respect to the permutation of like atoms and describe the traditional back-side attack Walden inversion, the double-inversion and front-side attack retention pathways, as well as the proton-abstraction channel. The relative energies, structures, harmonic vibrational frequencies of the stationary points and the long-range

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ion-dipole interaction potentials all remarkably reproduce the corresponding *ab initio* values.

3. With potential energy surfaces at hand I have performed quasiclassical trajectory computations in order to get deep insight into the dynamics of the  $F^- + CH_3F$  and  $F^- + CH_3Cl$  reactions. For the  $F^- + CH_3Cl$   $S_N2$  reaction the integral cross sections substantially decrease with increasing collision energy, whereas in case of the  $F^- + CH_3F$   $S_N2$  reaction the excitation function is almost constant at higher collision energies. At low collision energy the slow indirect mechanism dominates, where complex formation in the pre- and post-reaction channels plays a major role. On the other hand, at higher collision energies the reaction follows mainly a fast direct rebound mechanism, whereas at large impact parameters the reactive events occur via direct stripping. The initial orientation of the reactants has no effect on the  $S_N2$  reactivity at low collision energy, while at high collision energy the probability of back-side attack is substantially enhanced. The integral cross sections of proton-abstraction increase as the collision energy increases for both systems. Furthermore, the CH stretching excitation has slight effect on the  $S_N2$  reactivity, but substantially enhances the proton-abstraction and lowers its threshold energy.
4. Trajectory animations of the  $F^- + CH_3Cl$   $S_N2$  reaction revealed a novel retention mechanism, called double inversion. The first step of double inversion is a proton-abstraction induced inversion via a  $FH \cdots CH_2Cl^-$  transition state, followed by the traditional Walden inversion. If the second inversion does not occur the reaction results in an inverted reactant. In contrast to the front-side attack pathway, which is a fast direct process, the double-inversion is a slow indirect process. Moreover, the double inversion opens well below the barrier height of the front-side attack. The CH stretching excitation significantly increases the probability of double inversion and induced inversion.
5. We identified the double inversion saddle point for all the  $X^- + CH_3Y$  [ $X, Y = F, Cl, Br, I$ ] type halogen exchange reactions and we generalized

## Publications covered in the thesis

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also the front-side attack mechanism. The energy levels of the abstraction asymptotes are always above the corresponding double-inversion barrier heights. In case of  $F^-$  nucleophile the double-inversion saddle points are below the front-side attack ones and the reverse holds for the other systems.

6. The effects of rotational "mode-specific" excitation on the  $S_N2$  reactions were investigated for the first time. For both  $F^- + CH_3Y(v = 0, JK)$  [ $Y = F, Cl$ ] reactions the excitation of the polyatomic reactant decreases the reactivity; however, in case of the  $F^- + CH_3Cl$  reaction the inhibiting effect of spinning rotation diminishes and even slight promotion is seen at higher collision energies.
7. The computed and measured angular and internal energy distributions, as well as the direct rebound fractions for the  $F^- + CH_3Cl$   $S_N2$  reaction show unprecedented agreement. Comparison of the  $F^- + CH_3Cl$  and  $F^- + CH_3I$   $S_N2$  reactions shed light on the influence of leaving group on  $S_N2$  reactions, which is attributed to the difference in potential energy landscapes, rather than to the difference in masses of the leaving groups.

## 4 Publications covered in the thesis

1. M. Stei, E. Carrascosa, M. A. Kainz, A. H. Kelkar, J. Meyer, **I. Szabó**, G. Czakó, and R. Wester, Influence of the leaving group on the dynamics of a gas-phase  $S_N2$  reaction, *Nature Chem.* 8, 151 (2016).
2. **I. Szabó** and G. Czakó, Rotational mode specificity in the  $F^- + CH_3Y$  [ $Y = F$  and  $Cl$ ]  $S_N2$  reactions, *J. Phys. Chem. A* 119, 12231 (2015).
3. **I. Szabó**, H. Telekes and G. Czakó, Accurate *ab initio* potential energy surface, thermochemistry, and dynamics of the  $F^- + CH_3F$   $S_N2$  and proton-abstraction reactions, *J. Chem. Phys.* 142, 244301 (2015).
4. **I. Szabó** and G. Czakó, Double-inversion mechanisms of the  $X^- + CH_3Y$  [ $X, Y = F, Cl, Br, I$ ]  $S_N2$  reactions, *J. Phys. Chem. A* 119, 3134 (2015).

5. **I. Szabó** and G. Czakó, Revealing a double-inversion mechanism for the  $F^- + CH_3Cl$   $S_N2$  reaction, *Nat. Commun.* 6, 5972 (2015).
6. G. Czakó, **I. Szabó** and H. Telekes, On the choice of the ab initio level of theory for potential energy surface developments, *J. Phys. Chem. A* 118, 646 (2014).
7. **I. Szabó**, A. G. Császár and G. Czakó, Dynamics of the  $F^- + CH_3Cl \rightarrow Cl^- + CH_3F$   $S_N2$  reaction on a chemically accurate potential energy surface, *Chem. Sci.* 4, 4362 (2013).

## 5 Additional publications

8. A. G. Császár, G. Czakó, T. Furtenbacher, E. Mátyus, C. Fábri, T. Szidarovszky, **I. Szabó**, and J. Sarka, Molecular structure and dynamics, *Magy. Kém. Foly.* 118, 181 (2012).
9. **I. Szabó**, C. Fábri, G. Czakó, E. Mátyus, and A. G. Császár, Temperature-dependent, effective structures of the  $^{14}NH_3$  and  $^{14}ND_3$  molecules, *J. Phys. Chem. A* 116(17), 4356 (2012).

## 6 Posters and talks

1. **I. Szabó**: Retention mechanisms for the  $F^- + CH_3Cl$   $S_N2$  reaction, AMMB Conference of the Hungarian Academy of Sciences, Mátrafüred, 2015
2. M. Stei, E. Carrascosa, M. A. Kainz, A. H. Kelkar, **I. Szabó**, G. Czakó, A. Dörfler, T. Michaelsen, J. Meyer, R. Wester: Imaging the influence of the leaving group and of vibrational excitation on  $S_N2$  reactions, XXV Dynamics of Molecular Collisions Meeting, Asilomar, USA, 2015
3. **I. Szabó**: Quasiclassical trajectory computations for  $S_N2$  reactions, ExoMol Short Talk, University College London, London, United Kingdom, 2014
4. **I. Szabó**, S. N. Yurchenko, J. Tennyson, A. G. Császár, T. W. Schmidt, G. B. Bacskay: Accurate (ro)vibronic energy levels of the  $C_2$  molecule, High

