NKFI K-125317

FINAL REPORT

Understanding and controlling the atomic-level dynamics of chemical reactions: From fundamental processes to small biosystems

Gábor Czakó

We study the dynamics and mechanisms of chemical reactions on *ab initio* analytical potential energy surfaces. The project started on September 1, 2017 and was extended until November 30, 2023, because my Chinese postdoc could just join us in 2022 due to the pandemic situation. Below we summarize our research achievements supported by the present NKFI grant.

About our work in numbers (September 1, 2017 − November 30, 2023)

- 63 publications [1-63]
- 1 Nature Chemistry [30], 1 Science Advances [6], and 2 Chemical Science papers [26,34]
- 3 invited Feature/Perspective articles [1,15,25]
- 6 HOT PCCP [17,18,29,45,57,58] and 1 HOT Chemical Science [34] articles
- 3 papers selected for the Publication of the Month by the Hungarian Academy of Sciences [19,30,59]
- 8 journal covers (see Figure 1)
- 3 PhD dissertations
- 7 MSc theses
- 13 BSc theses
- 8 National Research Student Conference (OTDK) reports (two 2nd prizes and one 3rd prize)
- 8 invited talks at international conferences
- 45 talks at national meetings
- 16 posters at international conferences

Figure 1. Cover images of NKFIH-supported publications.

Methodological developments: ROBOSURFER and ManyHF

We finished a major method development in the first years of the present NKFI project, which was a key to the success of the proposed research. A program system, called ROBOSURFER, was developed, which allows automatic construction of *ab initio* analytical potential energy surfaces (PESs) for reactive chemical systems [16]. ROBOSURFER has received significant attention as our *JCTC* paper [16] was the most read article in the journal for several weeks and became a highly cited paper (as of May/June 2020) on *Web of Science*. Since the publication of ROBOSURFER in 2020, we already developed more than 20 PESs with the help of the program.

In order to make ROBOSURFER more efficient, we developed a practical automated method, called ManyHF, which can be used to find lower-energy Hartree–Fock (HF) solutions for PES development [38]. Test computations showed that ManyHF provides good solutions at almost every case where the default HF fails to converge or gives erratic solutions. Thus, ManyHF was proven to be a useful tool for automated PES developments and can treat systems which were previously thought to require the use of multi-reference methods. The ManyHF method was reported in *J. Chem. Phys.* as a Communication and the Editors highlighted our work on the Front Cover of the journal and the paper was selected as Featured.

Benchmark *ab initio* characterizations of reactive potential energy surfaces

We performed high-level *ab initio* computations for several reactive systems in order to determine benchmark structures and relative energies for the stationary points. The benchmark relative energies are obtained by composite methods usually considering post-(T), core correlation, scalar relativistic, and spin-orbit effects. These stationary-point characterizations are the first steps of the analytical PES developments and the reaction dynamics studies.

We studied the following systems:

- $X^- + NH_2Y$ [X,Y = F, Cl, Br, I] [3]
- $OH^- + CH_3Y$ [Y = F, Cl, Br, I] [7]
- $X + C_2H_6$ [X = F, Cl, Br, I] [9]
- $F^-(H_2O) + CH_3I$ [11]
- $X^- + CH_3Y$ [X = OH, SH, CN, NH_2, PH_2; Y = F, Cl, Br, I] [13]
- $OH + CH_4/C_2H_6$ [21]
- $F/Cl + CH_3NH_2$ [28,44]
- $OH^- + CH_3CH_2Y$ [Y = F, Cl, Br, I] [29]
- $X^- + SiH_3Y/CH_3Y$ [X,Y = F, Cl, Br, I] [35]
- $CN^- + CH_3Y$ [Y = F, Cl, Br, and I] [37]
- $Cl + CH_3CN$ [41]
- $OH + CH_3OH$ [51]
- OH + glycine [52]
- $F^- + CH_3CH_2I/CF_3CH_2I$ [57]
- $X^- + PH_2Y$ [X,Y = F, Cl, Br, I] [63]

Below we just highlight our most important results:

For $X + C_2H_6$ reactions besides the major hydrogen-abstraction channels, the H and CH_3 substitutions were revealed, for the first time, via Walden-inversion and front-side attack pathways [9].

We reported the first explicitly-correlated CCSD(T)-F12b investigation of the stationary points of the mono-hydrated $F^- + CH_3I$ system [11] revealing Walden-inversion, OH^- S_N2 inversion, front-side attack, double inversion, and water-induced double inversion pathways. The latter three retention mechanisms were proposed and characterized for the first time for micro-hydrated systems.

For $OH^- + CH_3CH_2Y$ besides the usual Walden-inversion S_N2 and *syn*- and *anti*-E2 pathways the double-inversion and front-side attack transition states were reported for the first time for the title reactions [29].

In the case of the $OH + CH_3OH$ system we carefully tested the effects of the choice of the basis sets, core correlation, post-(T) correlation, scalar relativity, and spin-orbit coupling on the relative energies [51]. Our findings may be utilized in future benchmark *ab initio* studies.

We characterized the three hydrogen-abstraction pathways of the OH + glycine reaction leading to H_2O and $H_2NCHCOOH$/$HNCH_2COOH$/H_2NCH_2COO [52]. This study was a first step toward full-dimensional PES development and dynamics for the OH + glycine reaction.

In collaboration with the Wester (Austria) and Viggiano (USA) groups, we investigated the influence of fluorination on the dynamics of the $F^- + CH_3CH_2I$ reaction in a joint experimental-theoretical study [57]. The computed relative energies of several competing product channels guided the analysis of the experimental results.

Potential energy surface developments and dynamics for the X + CH_4/C_2H_6/CH_3NH_2 [X = F, Cl, Br, I, OH] reactions

Reaction dynamics simulations on a new revised PES revealed novel mechanisms for the $Cl + CH_4$ reaction. Besides the hydrogen-abstraction channel, at high collision energies substitution pathways leading to $H + CH_3Cl$ open. Our major finding is that Walden inversion is not the only possible mechanism of this substitution process, but retention pathways also exist [2].

In collaboration with Lendvay and co-workers we investigated the kinetics of the $HBr + CH_3$ and $HBr + OH$ reactions. For the former system a new revised analytical *ab initio* PES was used. Our quasi-classical trajectory simulations provided excellent agreement with experiment on the temperature dependence of the rate coefficients [5].

We reported an accurate PES for the nine-atomic $Cl + C_2H_6$ reaction [19]. Dynamics simulations on this new PES finally provided excellent agreement between theory and experiment as Rakitzis wrote: "*theory explained the cold HCl rotational distributions from the nine-atom* $Cl + C_2H_6 \longrightarrow HCl + C_2H_5$ *reaction (8), resolving a nearly 25-year discrepancy with the experimental measurements*" [*Science*, **371**, 886 (2021)]. This publication was also selected as "Publication of the Month" by the Hungarian Academy of Sciences and the first author of this paper (Dóra Papp) was invited to give a talk about this study at the Stereodynamics 2022 conference in Crete. Later we also developed a PES for the $F + C_2H_6$ reaction [23] and investigated the mode-specific dynamics of the F/Cl + C_2H_6 systems [31,33]. In the case of $Cl + C_2H_6$ the rotational mode-specificity was also studied [40].

Moving beyond 9-atomic systems, in 2022 we developed a full-dimensional PES for the 10-atomic $OH + C_2H_6$ reaction [43]. Trajectory simulations show that hydrogen-abstraction leading to $H_2O + C_2H_5$ is the dominant channel of this reaction. At low collision energies the direct rebound mechanism dominates and as the collision energy increases the stripping pathway becomes favored. Using the new PES, we also performed vibrational mode-specific simulations for the $OH + C_2H_6$ reaction [60].

We developed the first full-dimensional PESs for the reactions of HBr [45] and HI [46] with C_2H_5. Quasi-classical trajectory (QCT) computations revealed the reactivity and angular/post-reaction energy distributions [45,46], as well as vibrational mode-specificity [49,54] for these reactions. Furthermore, we also studied the competition between the H-abstraction and the Br/I-abstraction pathways, showing the preference of the former at low collision energies and their co-dominance at high energies [58].

We developed a full-dimensional PES for the Cl + CH_3NH_2 reaction [61]. We showed how to handle Hartree−Fock convergence issues using our ManyHF method. Dynamics simulations on the new PES revealed that hydrogen abstraction from the methyl group is more likely than from the amino side.

Potential energy surface developments and dynamics for S_N2 reactions

Our group played a pioneering role in developing analytical PESs for bimolecular nucleophilic substitution (S_N2) reactions, thereby enabling efficient dynamics simulations.

Effects of the level of electronic structure theory are frequently tested for stationary-point properties, but little is known about the effects on the dynamics. We performed such a study revealing that some of the dynamical properties can significantly depend on the choice of the electronic structure theory [4].

In collaboration with the Wester and Guo groups, we studied the CH stretching excitation effects on the dynamics of the F^- + CH_3I reaction. Theory and experiment find in agreement that CH stretching excitation is spectator in the S_N2 reaction, whereas substantially enhances the proton-transfer process [6]. Our work was highlighted by ScienceDaily as “Breaking the bond: To take part or not?” Later we reported a QCT investigation on the mode-specific dynamics of the F^- + CH_3I reaction [8]. Unlike in the experimental work, theory considered the excitations of each of the six vibrational modes of the CH_3I molecule. We found that C-I excitation enhances the S_N2 inversion process, whereas CH excitation promotes proton abstraction.

We developed a numerical analysis method, which assigns every trajectory-geometry to a stationary-point structure using an exact Eckart-transformation approach [12]. Using this new analysis tool, stationary-point probability distributions and transition probability matrices were determined for the F^- + CH_3I reaction. We also developed a transition-state attack-angle-based method allowing numerical separation of the front-side attack and double-inversion retention pathways of S_N2 reactions [22]. The new method was tested for the F^- + CH_3Cl/CH_3I reactions, providing the first mechanism-specific retention cross sections for F^- + CH_3I. Furthermore, we also investigated the rotational mode specific dynamics of F^- + CH_3I [24] and reported a detailed QCT study of the F^- + CH_3Br reaction [32] as well as a new PES and dynamics for the Cl^- + CH_3I reaction [55].

Moving from 6-atomic S_N2 reactions to more complex 7-atom systems, we found that the gold-standard CCSD(T) method breaks down at certain geometries during the PES development for the OH^- + CH_3I reaction [18]. We showed how to solve this problem by employing a composite approach based on the CCSD-F12b and the Brueckner-type BCCD(T) methods. The new composite method made the future studies of similar challenging systems possible. Later in collaboration with the Wester group, we carried out trajectory simulations for the OH^- + CH_3I reaction using our previously-developed PES [50]. The computed scattering angle and product internal energy distributions are in good agreement with experiment.

In 2021 we started to study the dynamics of S_N2 reactions at nitrogen center. We developed an analytical PES for the F^- + NH_2Cl reaction, revealing a new hydrogen-bonded-complex-formation-induced multiple-inversion reaction pathway, which undermines the usual stereo-specificity of the S_N2 channel and produces a significant fraction of the products with retention of the initial configuration [26]. This work was featured on the front cover of *Chemical Science*.

In 2021 we also developed a high-level *ab initio* analytical PES for the nine-atomic $F^- + CH_3CH_2Cl$ reaction [30]. Our reaction dynamics simulations provided scattering angle and product internal energy distributions in excellent agreement with crossed-beam experiments of the Wester group. Moreover, unlike experiment, our simulations were able to separate the S_N2 ($Cl^- + CH_3CH_2F$) and E2 ($Cl^- + HF + CH_2CH_2$) channels, both leading to the same experimentally detectable anion (Cl^-). Our joint experimental-theoretical study was published in *Nature Chemistry* and received significant national and international media attention. Later we reported [39] a theoretical study on the vibrational mode-specific dynamics of $F^- + CH_3CH_2Cl$.

We also developed a full-dimensional PES for the $OH^- + CH_3F$ reaction in 2021 [34]. Dynamics simulations on the new PES revealed a novel product channel forming $HF + CH_3O^-$. We named this new pathway oxide ion substitution as the F^- ion is replaced by an O^{2-} ion. This result was published in *Chemical Science* [34] and our work was highlighted on the back cover.

In 2022 we developed a full-dimensional PES for the 8-atomic $NH_2^- + CH_3I$ polyatomic reaction [42]. The unique feature of this work is that this is the first analytical PES for an S_N2 reaction which involves a polyatomic nucleophile, besides the studies of the reactions of the $F^-(H_2O)$ complex. Trajectory simulations on the new PES revealed unconventional S_N2 retention pathways induced by complex formation, which turned out to be the most dominant retention pathways of the title reaction.

We reported the first analytical PES for a silicon (Si)-centered S_N2 reaction, $F^- + SiH_3Cl$ [56]. Unlike at carbon centers, here the retention pathway was found to be competitive with Walden inversion. We also investigated the dynamics of a P-centered S_N2 reaction, $F^- + PH_2Cl$, using a newly-developed PES [59]. Even if self-inversion of the reactant has a high barrier, the $F^- + PH_2Cl$ reaction is not stereospecific, because front-side attack retention pathways and pre-reaction complex-mediated multi-inversion mechanisms are open even at low collision energies. We also compared the dynamics of the $F^- + PH_2Cl$ reaction with its C- and N-centered analogues, showing significant dynamical central-atom effects.

Potential energy surface developments and vibrational dynamics for molecular complexes

In collaboration with the Mátyus group (Eötvös University), we developed the first full-dimensional PES for the $CH_4{\cdot}Ar$ system and investigated its vibrational quantum dynamics in full (12) dimensions [17]. This project demonstrates that our methodologies are capable to provide PESs of molecules and molecular complexes with spectroscopic accuracy (<1 cm^{-1}).

In 2022, also in collaboration with the Mátyus group, we developed a full-dimensional *ab initio* PES for the $CH_4{\cdot}F^-$ anion complex using the ROBOSURFER program package and computed the vibrational states of the CH_4 fragment and the $CH_4{\cdot}F^-$ complex using a variational method [48]. This is the first spectroscopic application of ROBOSURFER, which was proven to be very useful and capable to provide PESs with spectroscopic quality as the excellent agreement between the computed and measured vibrational energy levels of methane showed. The new PES opens the door for further spectroscopic/quantum dynamics studies for this challenging multi-well system.

Conformers of dehydrogenated and protonated amino acids

We are also working on studying the dynamics and reactions of small bio-systems. As a first step toward this direction, we reported benchmark structures and relative energies for the conformers of dehydrogenated glycine isomers, considering hydrogen abstraction from the methylene, amino, and carboxyl groups [20]. The dehydrogenated glycine isomers are the products of the OH + glycine reaction, which is under current investigation in our group.

We performed systematic conformational searches for protonated glycine [27], alanine [36], cysteine [47], and serine [53] and reported benchmark explicitly-correlated coupled-cluster structures and relative energies for the conformers of the amino acids and their protonated species. Benchmark proton affinities and gas-phase basicities of these amino acids were also obtained and found to be in excellent agreement with available experiments. Our work on glycine was featured on the front cover of *PCCP* [27].

Feature and Perspective articles

In 2017 our S_N2 studies were reviewed in an invited Feature Article in *J. Phys. Chem. A* [1]. In 2020 we received an invitation to write a Perspective article for *Phys. Chem. Chem. Phys.* highlighting the recent work of our group [15]. In 2021 we also published an invited Perspective article in *J. Phys. Chem. A*, which focuses on reaction dynamics simulations beyond six-atom systems, thereby defining a new age of the field [25]. All review articles were featured on the front cover of the journals and the photos and short bios of many group members appeared in the publications; thus, these were excellent opportunities to increase the international reputation of our group. Finally, our work was also highlighted in the Hungarian Chemical Journal [14], following a lecture at a "Quantum Chemistry in Hungary" seminar of the Academy.

Publications

[1] I. Szabó and **G. Czakó***
Dynamics and novel mechanisms of S_N2 reactions on *ab initio* analytical potential energy surfaces
J. Phys. Chem. A **121**, 9005 (2017) ***Feature Article on the front cover of JPCA***

[2] L. Krotos and **G. Czakó***
Does the $Cl + CH_4 \rightarrow H + CH_3Cl$ reaction proceed via Walden inversion?
J. Phys. Chem. A **121**, 9415 (2017)

[3] B. Hajdu and **G. Czakó***
Benchmark *ab initio* characterization of the complex potential energy surfaces of the $X^- + NH_2Y$ [X,Y = F, Cl, Br, I] reactions
J. Phys. Chem. A **122**, 1886 (2018)

[4] T. Győri, B. Olasz, G. Paragi, and **G. Czakó***
Effects of the level of electronic structure theory on the dynamics of the $F^- + CH_3I$ reaction
J. Phys. Chem. A **122**, 3353 (2018)

[5] S. Góger, P. Szabó, **G. Czakó**, and G. Lendvay*
Flame inhibition chemistry: rate coefficients of the reactions of HBr with CH_3 and OH radicals at high temperatures determined by quasiclassical trajectory calculations
Energy Fuels **32**, 10100 (2018)

[6] M. Stei, E. Carrascosa, A. Dörfler, J. Meyer, B. Olasz, **G. Czakó**, A. Li, H. Guo, and R. Wester*
Stretching vibration is spectator in nucleophilic substitution
Sci. Adv. **4**, eaas9544 (2018)

[7] D. A. Tasi, Z. Fábián, and **G. Czakó***
Benchmark *ab initio* characterization of the inversion and retention pathways of the $OH^- + CH_3Y$ [Y = F, Cl, Br, I] S_N2 reactions
J. Phys. Chem. A **122**, 5773 (2018)

[8] B. Olasz and **G. Czakó***
Mode-specific quasiclassical dynamics of the $F^- + CH_3I$ S_N2 and proton-transfer reactions
J. Phys. Chem. A **122**, 8143 (2018)

[9] D. Papp,* B. Gruber, and **G. Czakó***
Detailed benchmark *ab initio* mapping of the potential energy surfaces of the $X + C_2H_6$ [X = F, Cl, Br, I] reactions
Phys. Chem. Chem. Phys. **21**, 396 (2019)

[10] B. Bastian, E. Carrascosa, A. Kaiser, J. Meyer, T. Michaelsen, **G. Czakó**, W. L. Hase, and R. Wester*
Dynamics of proton transfer from ArH^+ to CO
Int. J. Mass Spectrom. **438**, 175 (2019)

[11] B. Olasz and **G. Czakó***
High-level-optimized stationary points for the $F^-(H_2O) + CH_3I$ system: Proposing a new water-induced double-inversion pathway
J. Phys. Chem. A **123**, 454 (2019)

[12] B. Olasz and **G. Czakó***
Uncovering the role of the stationary points in the dynamics of the $F^- + CH_3I$ reaction
Phys. Chem. Chem. Phys. **21**, 1578 (2019)

[13] D. A. Tasi, Z. Fábián, and **G. Czakó***
Rethinking the $X^- + CH_3Y$ [X = OH, SH, CN, NH_2, PH_2; Y = F, Cl, Br, I] S_N2 reactions
Phys. Chem. Chem. Phys. **21**, 7924 (2019)

[14] **G. Czakó***
Dynamics and mechanisms of fundamental chemical reactions
Magy. Kém. Foly. **125**, 100 (2019)

[15] **G. Czakó**,* T. Győri, B. Olasz, D. Papp, I. Szabó, V. Tajti, and D. A. Tasi
Benchmark *ab initio* and dynamical characterization of the stationary points of reactive atom + alkane and S_N2 potential energy surfaces
Phys. Chem. Chem. Phys. **22**, 4298 (2020) **Perspective – Front Cover**

[16] T. Győri* and **G. Czakó***
Automating the development of high-dimensional reactive potential energy surfaces with the ROBOSURFER program system
J. Chem. Theory Comput. **16**, 51 (2020) **Highly Cited Paper (as of May/June 2020)**

[17] G. Avila,* D. Papp,* **G. Czakó**,* and E. Mátyus*
Exact quantum dynamics background of dispersion interactions: case study for $CH_4.Ar$ in full (12) dimensions
Phys. Chem. Chem. Phys. **22**, 2792 (2020) **Selected as a 2020 HOT PCCP article**

[18] D. A. Tasi, T. Győri, and **G. Czakó***
On the development of a gold-standard potential energy surface for the $OH^- + CH_3I$ reaction
Phys. Chem. Chem. Phys. **22**, 3775 (2020) **Communication Selected as a 2020 HOT PCCP article**

[19] D. Papp, V. Tajti, T. Győri, and **G. Czakó***
Theory finally agrees with experiment for the dynamics of the $Cl + C_2H_6$ reaction
J. Phys. Chem. Lett. **11**, 4762 (2020) **Publication of the Month (MTA)**

[20] E. M. Orján, A. B. Nacsa, and **G. Czakó***
Conformers of dehydrogenated glycine isomers
J. Comput. Chem. **41**, 2001 (2020)

[21] B. Gruber and **G. Czakó***
Benchmark *ab initio* characterization of the abstraction and substitution pathways of the OH + CH_4/C_2H_6 reactions
Phys. Chem. Chem. Phys. **22**, 14560 (2020)

[22] P. Papp, V. Tajti, and **G. Czakó***
Numerical separation of the front-side attack and double-inversion retention pathways of S_N2 reactions
Chem. Phys. Lett. **755**, 137780 (2020)

[23] D. Papp* and **G. Czakó***
Full-dimensional MRCI-F12 potential energy surface and dynamics of the $F(^2P_{3/2}) + C_2H_6 \rightarrow HF + C_2H_5$ reaction
J. Chem. Phys. **153**, 064305 (2020)

[24] P. Papp and **G. Czakó***
Rotational mode specificity in the $F^- + CH_3I(v=0, JK)$ S_N2 and proton-transfer reactions
J. Phys. Chem. A **124**, 8943 (2020)

[25] **G. Czakó**,* T. Győri, D. Papp, V. Tajti, and D. A. Tasi
First-principles reaction dynamics beyond six-atom systems
J. Phys. Chem. A **125**, 2385 (2021) **Perspective − Front Cover**

[26] D. Papp* and **G. Czakó***
Facilitated inversion complicates the stereodynamics of an S_N2 reaction at nitrogen center
Chem. Sci. **12**, 5410 (2021) **Front Cover**

[27] A. B. Nacsa and **G. Czakó***
Benchmark *ab initio* proton affinity of glycine
Phys. Chem. Chem. Phys. **23**, 9663 (2021) **Front Cover**

[28] T. Szűcs and **G. Czakó***
Benchmark *ab initio* stationary-point characterization of the complex potential energy surface of the multi-channel Cl + CH_3NH_2 reaction
Phys. Chem. Chem. Phys. **23**, 10347 (2021)

[29] D. A. Tasi,* C. Tokaji, and **G. Czakó***
A benchmark *ab initio* study of the complex potential energy surfaces of the $OH^- + CH_3CH_2Y$ [Y = F, Cl, Br, I] reactions
Phys. Chem. Chem. Phys. **23**, 13526 (2021) **HOT PCCP article**

[30] J. Meyer, V. Tajti, E. Carrascosa, T. Győri, M. Stei, T. Michaelsen, B. Bastian, **G. Czakó**,* and R. Wester*
Atomistic dynamics of elimination and nucleophilic substitution disentangled for the $F^- + CH_3CH_2Cl$ reaction
Nat. Chem. **13**, 977 (2021) **Publication of the Month (MTA) and Publication of the Year (SZTE)**

[31] D. Papp,* J. Li, H. Guo, and **G. Czakó***
Vibrational mode-specificity in the dynamics of the $Cl + C_2H_6 \rightarrow HCl + C_2H_5$ reaction
J. Chem. Phys. **155**, 114303 (2021)

[32] V. Tajti, T. Győri, and **G. Czakó***
Detailed quasiclassical dynamics of the $F^- + CH_3Br$ reaction on an *ab initio* analytical potential energy surface
J. Chem. Phys. **155**, 124301 (2021)

[33] D. Papp* and **G. Czakó***
Vibrational mode-specific dynamics of the $F(^2P_{3/2}) + C_2H_6 \rightarrow HF + C_2H_5$ reaction
J. Chem. Phys. **155**, 154302 (2021)

[34] D. A. Tasi* and **G. Czakó***
Uncovering an oxide ion substitution for the $OH^- + CH_3F$ reaction
Chem. Sci. **12**, 14369 (2021) **Cover and 2021 Chemical Science HOT Article Collection**

[35] A. Á. Dékány, G. Z. Kovács, and **G. Czakó***
High-level systematic *ab initio* comparison of carbon- and silicon-centered S_N2 reactions
J. Phys. Chem. A **125**, 9645 (2021)

[36] A. Á. Dékány and **G. Czakó***
Benchmark *ab initio* proton affinity and gas-phase basicity of α-alanine based on coupled-cluster theory and statistical mechanics
J. Comput. Chem. **43**, 19 (2022)

[37] Z. Kerekes, D. A. Tasi, and **G. Czakó***
S_N2 reactions with an ambident nucleophile: A benchmark *ab initio* study of the $CN^- + CH_3Y$ [Y = F, Cl, Br, and I] systems
J. Phys. Chem. A **126**, 889 (2022)

[38] T. Győri* and **G. Czakó***
ManyHF: A pragmatic automated method of finding lower-energy Hartree−Fock solutions for potential energy surface development
J. Chem. Phys. **156**, 071101 (2022) **Front Cover and Featured**

[39] V. Tajti and **G. Czakó***
Vibrational mode-specific dynamics of the $F^- + CH_3CH_2Cl$ multi-channel reaction
Phys. Chem. Chem. Phys. **24**, 8166 (2022)

[40] D. Papp* and **G. Czakó***
Rotational mode-specificity in the $Cl + C_2H_6 \rightarrow HCl + C_2H_5$ reaction
J. Phys. Chem. A **126**, 2551 (2022)

[41] P. Tóth, T. Szűcs, and **G. Czakó***
Benchmark *ab initio* characterization of the abstraction and substitution pathways of the $Cl + CH_3CN$ reaction
J. Phys. Chem. A **126**, 2802 (2022)

[42] D. A. Tasi* and **G. Czakó***
Unconventional S_N2 retention pathways induced by complex formation: High-level dynamics investigation of the $NH_2^- + CH_3I$ polyatomic reaction
J. Chem. Phys. **156**, 184306 (2022)

[43] B. Gruber, V. Tajti, and **G. Czakó***
Full-dimensional automated potential energy surface development and dynamics for the $OH + C_2H_6$ reaction
J. Chem. Phys. **157**, 074307 (2022)

[44] T. Szűcs and **G. Czakó***
Benchmark *ab initio* potential energy surface mapping of the $F + CH_3NH_2$ reaction
Phys. Chem. Chem. Phys. **24**, 20249 (2022)

[45] C. Yin,* V. Tajti, and **G. Czakó***
Full-dimensional potential energy surface development and dynamics for the $HBr + C_2H_5 \rightarrow Br(^2P_{3/2}) + C_2H_6$ reaction
Phys. Chem. Chem. Phys. **24**, 24784 (2022) **2022 HOT PCCP article**

[46] C. Yin* and **G. Czakó***
Automated full-dimensional potential energy surface development and quasi-classical dynamics for the HI($X^1\Sigma^+$) + C_2H_5 → I($^2P_{3/2}$) + C_2H_6 reaction
Phys. Chem. Chem. Phys. **24**, 29084 (2022)

[47] A. B. Nacsa* and **G. Czakó***
Benchmark *ab initio* determination of the conformers, proton affinities, and gas-phase basicities of cysteine
J. Phys. Chem. A **126**, 9667 (2022)

[48] D. Papp,* V. Tajti, G. Avila,* E. Mátyus,* and **G. Czakó***
$CH_4 \cdot F^-$ revisited: full-dimensional *ab initio* potential energy surface and variational vibrational states
Mol. Phys. **121**, e2113565 (2023)

[49] C. Yin* and **G. Czakó***
Theoretical vibrational mode-specific dynamics studies for the HBr + C_2H_5 reaction
Phys. Chem. Chem. Phys. **25**, 3083 (2023)

[50] D. A. Tasi,* T. Michaelsen, R. Wester, and **G. Czakó***
Quasi-classical trajectory study of the OH^- + CH_3I reaction: Theory meets experiment
Phys. Chem. Chem. Phys. **25**, 4005 (2023)

[51] T. Győri* and **G. Czakó***
A comprehensive benchmark *ab initio* survey of the stationary points and products of the OH· + CH_3OH system
J. Chem. Phys. **158**, 034301 (2023)

[52] B. Gruber and **G. Czakó***
High-level *ab initio* mapping of the multiple H-abstraction pathways of the OH + glycine reaction
Phys. Chem. Chem. Phys. **25**, 5271 (2023)

[53] A. B. Nacsa,* M. Kígyósi, and **G. Czakó***
Protonation of serine: Conformers, proton affinities and gas-phase basicities at the “gold standard” and beyond
Phys. Chem. Chem. Phys. **25**, 8891 (2023)

[54] C. Yin* and **G. Czakó***
Vibrational mode-specific quasi-classical trajectory studies for the two-channel HI + C_2H_5 reaction
Phys. Chem. Chem. Phys. **25**, 9944 (2023)

[55] A. B. Nacsa, V. Tajti, and **G. Czakó***
Dynamics of the Cl^- + CH_3I reaction on a high-level *ab initio* analytical potential energy surface
J. Chem. Phys. **158**, 194306 (2023)

[56] A. Á. Dékány and **G. Czakó***
Exploring the versatile reactivity of the F^- + SiH_3Cl system on a full-dimensional coupled-cluster potential energy surface
J. Chem. Phys. **158**, 224303 (2023)

[57] T. Gstir, T. Michaelsen, B. A. Long, A. B. Nacsa, A. Ayasli, D. Swaraj, F. Zappa, F. Trummer, S. G. Ard, N. S. Shuman, **G. Czakó**, A. A. Viggiano, and R. Wester*
The influence of fluorination on the dynamics of the F^- + CH_3CH_2I reaction
Phys. Chem. Chem. Phys. **25**, 18711 (2023) **2023 HOT PCCP article**

[58] C. Yin* and **G. Czakó***
Competition between the H-abstraction and the X-abstraction pathways in the HX (X = Br, I) + C_2H_5 reactions
Phys. Chem. Chem. Phys. **25**, 20241 (2023) **2023 HOT PCCP article**

[59] A. Giricz, **G. Czakó**,* and D. Papp*
Alternating stereospecificity upon central-atom change: Dynamics of the F^- + PH_2Cl S_N2 reaction compared to its C- and N-centered analogues
Chem. Eur. J. **29**, e202302113 (2023) **Publication of the Month (MTA)**

[60] B. Gruber, V. Tajti, and **G. Czakó***
Vibrational mode-specific dynamics of the OH + C_2H_6 reaction
J. Phys. Chem. A **127**, 7364 (2023)

[61] T. Szűcs and **G. Czakó***
ManyHF-based full-dimensional potential energy surface development and quasi-classical dynamics for the Cl + CH_3NH_2 reaction
J. Chem. Phys. **159**, 134306 (2023)

[62] C. Yin* and **G. Czakó***
Full-dimensional automated potential energy surface development and detailed dynamics for the CH_2OO + NH_3 reaction
Phys. Chem. Chem. Phys. **25**, 26917 (2023)

[63] 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^- + PH_2Y [X, Y = F, Cl, Br, I] systems
Phys. Chem. Chem. Phys. **25**, 28925 (2023)