

MQCT – A PROGRAM FOR CALCULATIONS OF INELASTIC SCATTERING OF TWO MOLECULES

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We develop theoretical methodology and write a user-ready computer program to carry out the calculations of rotational-vibrational-translational energy transfer in a collision of two molecules, within a framework of the mixed quantum/classical theory (MQCT). In this approach the translational motion of scattering partners is treated classically, while the internal motion of each molecule (rotation, vibration) is described by quantum mechanics [1]. Time-dependent framework is adopted, which includes the propagation of mean-field trajectories for the translational motion (the Ehrenfest approach), and the time-evolution of probability amplitudes for the internal quantum states of the molecules, driven by their collision process. Energy is exchanged between the translational, rotational, and vibrational degrees of freedom but the total energy is conserved (on average).

The most demanding component of the full-coupled MQCT calculations is calculations of the potential gradient averaged over all quantum states of collision partners (the mean-field potential) at each time step. But recently we proposed a simplified version of MQCT, in which the classical and quantum degrees of freedom can be partially decoupled. This method, named *adiabatic trajectory*, or AT-MQCT, happens to be both efficient and accurate [2,3], see Fig. 1.

In MQCT program there are ten system types, from the simplest rigid-diatom + atom, to the most general case of two asymmetric-top rotor molecules. For each system, MQCT calculations can be initiated by indicating the rotational and vibrational constants of collision partners. Those are used by the code to set up and diagonalize Hamiltonian matrix for rotational motion (using the basis set of symmetric-top functions) in order to determine the rotational states of the system (energies and wavefunctions). Potential energy surface expressed in the Euler angles of the fragments is also required. State-to-state transition matrix is computed in the body-fixed reference frame. In this version of MQCT the vibrational motion is supported for the diatomic molecules only, but the goal is to introduce vibration for other system types in the future. A detailed user manual and an example of input file for each system type will be provided with the code.

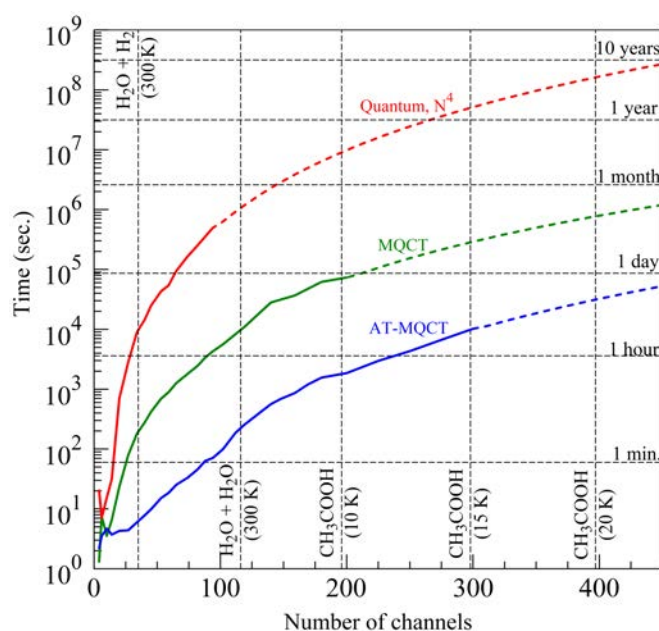


Figure 1: Numerical cost of two versions of MQCT vs full-quantum calculations (MOLSCAT), for molecular systems of increasing complexity (number of channels).

References

- [1] A. Semenov, B. Mandal and D. Babikov, *Comp. Phys. Com.* 252, 107155 (2020)
- [2] B. Mandal, A. Semenov and D. Babikov, *J. Phys. Chem. A* 124, 9877-9888 (2020)
- [3] B. Mandal, C. Joy, A. Semenov, D. Babikov, *ACS Earth Space Chem.* 6, 521-529 (2022)

HOW TO UNDERSTAND STRUCTURE IN THE ANGULAR SCATTERING OF THE STATE-TO-STATE $\text{H} + \text{HD} \rightarrow \text{H}_2 + \text{D}$ REACTION

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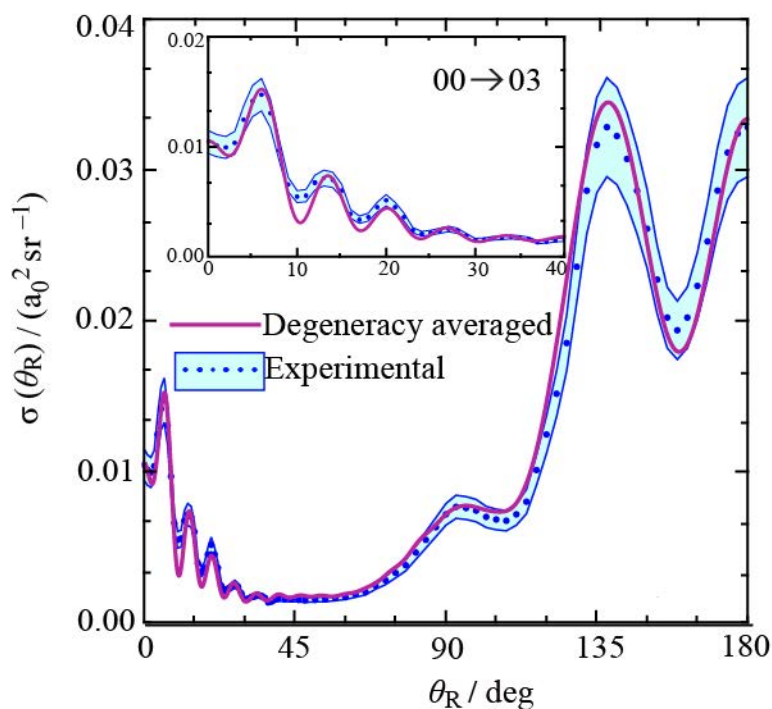
Yuan *et al.* [1] have reported state-of-the-art measurements of degeneracy-averaged differential cross sections (daDCSs) for the $\text{H} + \text{HD} \rightarrow \text{H}_2 + \text{D}$ reaction, measuring for the first-time fast oscillations in the small-angle forward region of the daDCSs. We theoretically analyse the angular scattering dynamics in order to quantitatively understand the physical content of structure in the DCSs. We study the $\text{H} + \text{HD}(v_i = 0, j_i = 0, m_i = 0) \rightarrow \text{H}_2(v_f = 0, j_f = 0, 1, 2, 3, m_f = 0, 1, 2, \dots, j_f) + \text{D}$ reaction for the whole range of scattering angles from $\theta_R = 0^\circ$ to $\theta_R = 180^\circ$, where v, j, m are the vibrational, rotational and helicity quantum numbers respectively for the initial and final states. We use accurate quantum scattering matrix elements computed by Yuan *et al.* at a translational energy of 1.35 eV for the BKMP2 potential energy surface.[1]

We firstly consider states with $m_f = 0$. [2] The following theoretical techniques are employed to analyse the DCSs: (a) Full and Nearside-Farside (NF) partial wave series (PWS) and local angular momentum (LAM) theory, including resummations of the full PWS up to third order. We also use window representations of the scattering matrix, which give rise to truncated PWS, (b) Six asymptotic (semiclassical) small-angle glory theories and four N rainbow theories, (c) We introduce ‘‘CoroGlo’’ tests, which let us distinguish between glory and corona scattering at small angles for Legendre PWS, (d) The semiclassical optical model (SOM) of Herschbach is employed to understand structure in the DCSs at intermediate and large angles. Our conclusions are: (a) The small-angle peaks in the DCSs arise mainly from glory scattering. For the $000 \rightarrow 020$ transition, there is also a contribution from a broad, or hidden, N rainbow, (b) At larger angles, the fast oscillations in the DCSs arise from NF interference, (c) The N scattering in the fast oscillation region also contains a hidden rainbow for the $000, 020, 030$ cases, (d) At intermediate and backward angles, the slowly varying DCSs, which merge into slow oscillations, are explained by the SOM. Physically it shows this structure in a DCS arises from direct scattering and is a distorted mirror image of the corresponding probability versus total angular momentum quantum number plot.

Secondly, we consider states with $m_f > 0$. [3] These states have DCSs that are identically zero in the forward ($\theta_R = 0^\circ$) and backward ($\theta_R = 180^\circ$) directions. We start with the PWS for the scattering amplitude expanded in a basis set of reduced rotation matrix elements. Our main theoretical tools are two variants of NF theory applied to six transitions: (1) We apply unrestricted, restricted, and restricted Δ NF decompositions to the PWS including resummations. The restricted and restricted Δ NF DCSs correctly go to zero in the forward and backward directions when $m_f > 0$, unlike the unrestricted NF DCSs which incorrectly go to infinity. We also exploit LAM theory to provide additional insights into the reaction dynamics. Properties of reduced rotation matrix elements of the second kind play an important role in the NF analysis, together with their caustics. (2) We also apply the approximate N SOM theory at intermediate and large angles. We show there are two different reaction mechanisms. The fast oscillations at small angles (sometimes called Fraunhofer diffraction/oscillations) are a NF interference effect. In contrast, the slow oscillations at intermediate and large angles are a N effect, which arise from direct scattering, in a ‘‘distorted mirror image’’ mechanism. We also compare with the experimental data.

References

- [1] D. Yuan, S. Yu, W. Chen, J. Sang, C. Luo, T. Wang, X. Xu, P. Casavecchia, X. Wang, Z. Sun, D. H. Zhang and X. Yang, Direct observation of forward-scattering oscillations in the $\text{H} + \text{HD} \rightarrow \text{H}_2 + \text{D}$ reaction. *Nat. Chem.* 10, 653 (2018).
- [2] C Xiahou and J. N. L. Connor, Glories, hidden rainbows and nearside-farside interference effects in the angular scattering of the state-to-state $\text{H} + \text{HD} \rightarrow \text{H}_2 + \text{D}$ reaction, *Phys. Chem. Chem. Phys.* 23, 13349 (2021).
- [3] C. Xiahou and J. N. L. Connor, Nearside-farside analysis of the angular scattering for the state-to-state $\text{H} + \text{HD} \rightarrow \text{H}_2 + \text{D}$ Reaction: Nonzero helicities. *J. Phys. Chem. A*, 125, 8734 (2021).



Plot of quantum daDCS (purple curve), together with experimental results (dots) and their estimated errors (blue) for the $v_i = 0, j_i = 0 \rightarrow v_f = 0, j_f = 3$ transition.

ROTATIONAL-VIBRATIONAL RESONANCE STATES

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Resonance (quasibound) states are characterized by an energy that is above the lowest dissociation threshold of the potential energy hypersurface of the system; thus, resonances have finite lifetimes. All molecules possess a large number of long- and short-lived resonance states. A considerable number of rotational–vibrational resonance states are accessible not only via quantum-chemical computations but also by spectroscopic and scattering experiments. In a number of chemical applications, most prominently in spectroscopy and reaction dynamics, consideration of rotational–vibrational resonance states is becoming more and more common. There are different first-principles techniques to compute and rationalize rotational–vibrational resonance states: one can perform scattering calculations or one can arrive at rovibrational resonances using variational or variational-like techniques based on methods developed for determining bound eigenstates [1]. The latter approaches can be based either on the Hermitian (L^2 , square integrable) or non-Hermitian (non- L^2) formalisms of quantum mechanics. This talk reviews the basic concepts related to and the relevance of shape and Feshbach-type rotational–vibrational resonance states, discusses theoretical methods and computational tools allowing their efficient determination, and shows numerical examples on the identification and characterization of rotational–vibrational resonances of polyatomic molecular systems, based on published [2,3,4] and unpublished results.

References

- [1] A. G. Császár, I. Simkó, T. Szidarovszky, G. C. Groenenboom, T. Karman, and A. van der Avoird, Rotational-Vibrational Resonance States, *Phys. Chem. Chem. Phys.* 22, 15081-15104 (2020)
- [2] I. Simkó, T. Szidarovszky, and A. G. Császár, Toward Automated Variational Computation of Rovibrational Resonances, Including a Case Study of the H₂ Dimer, *J. Chem. Theory Comput.* 15, 4156 (2019)
- [3] D. Papp, T. Szidarovszky, and A. G. Császár, A General Variational Approach for Computing Rovibrational Resonances of Polyatomic Molecules. Application to the Weakly Bound H₂He⁺ and H₂CO Systems, *J. Chem. Phys.* 147, 094106 (2017)
- [4] D. Papp, J. Sarka, T. Szidarovszky, A. G. Császár, E. Mátyus, M. Hochlaf, and T. Stoecklin, Complex Rovibrational Dynamics of the Ar·NO⁺ Complex, *Phys. Chem. Chem. Phys.* 19, 8152-8160 (2017)

USES OF INSTANTONS IN THE CALCULATIONS OF VIBRATIONAL TUNNELING SPECTRA

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In molecular systems with multiple energetically stable minima, vibrational states localized in the wells interact via tunneling. The interaction manifests itself in the energy shifts in the spectra. For symmetry-related minima, it results in the splittings of the otherwise degenerate states. The size of the matrix elements that connect the states localized in different wells is highly sensitive to the height and shape of the potential energy barriers that separate them and can vary over many orders of magnitude even in a single system. The calculation of the energy shifts and splittings using exact variational methods is therefore very demanding and limited to systems of only few atoms.

Instanton theory provides a way to calculate the shifts at a much reduced computational cost in full dimensionality. It is based on determining the minimum action paths (MAPs) that connect pairs of minima and evaluating the corresponding matrix elements semiclassically using a harmonic expansion of the potential around the MAPs. We generalized the approach by Mil'nikov and Nakamura [1,2] to treat the systems with many minima, which regularly feature asymmetric tunneling paths. We accomplish this using three different approaches: the instanton evaluation via Jacobi fields [3], a modified WKB method [4] and the propagation of Heller's wavepackets in imaginary time, all of which give identical results.

We apply the method to calculate the tunneling splitting patterns of some partially deuterated water trimers [5], with the asymmetry of potential along the tunneling path and the energy asymmetry of the localized states. The splitting patterns were interpreted in terms of cluster rearrangements and compared to experiment. We also apply the method in combination with VCI energies of localized states to obtain the energies of low-lying states in malonaldehyde (homoisotopic and partially deuterated) [6]. For this purpose, we devised an N -state model ($N > 2$) and evaluated the matrix elements between inequivalent states of different minima to obtain a good agreement with the accurate MCTDH results [7].

References

- [1] G. V. Mil'nikov and H. Nakamura, Practical implementation of the instanton theory for the ground-state tunneling splitting, *J. Chem. Phys.* 115, 6881-6897 (2001)
- [2] G. V. Mil'nikov and H. Nakamura, Instanton theory for the tunneling splitting of low vibrationally excited states, *J. Chem. Phys.* 122, 124311 (2005)
- [3] M. Eraković, C. L. Vaillant and M. T. Cvitaš, Instanton theory of ground-state tunnelling splittings with general paths, *J. Chem. Phys.* 152, 084111 (2020)
- [4] M. Eraković and M. T. Cvitaš, Tunnelling splittings of vibrationally excited states using general instanton paths, *J. Chem. Phys.* 153, 134106 (2020)
- [5] M. Eraković and M. T. Cvitaš, Tunnelling splitting patterns in some partially deuterated water trimers, *Phys. Chem. Chem. Phys.* 22, 25396-25407 (2021)
- [6] M. Eraković and M. T. Cvitaš, Vibrational tunneling spectra of molecules with asymmetric wells: a combined vibrational configuration interaction and instanton approach, *J. Chem. Theory Comput.* 18, 2785-2802 (2022)
- [7] T. Hammer and U. Manthe, Iterative diagonalization in the state-averaged multi-configurational time-dependent Hartree approach: excited state tunneling splittings in malonaldehyde, *J. Chem. Phys.* 136, 054105 (2012)

FIRST-PRINCIPLES REACTIVE SCATTERING BEYOND SIX-ATOM SYSTEMS

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In the past two decades first-principles theory was able to describe the dynamics of six-atomic chemical reactions with high accuracy using analytical *ab initio* potential energy surfaces (PESs) and quasi-classical and/or time-dependent quantum methods. For example, we studied the F/Cl/O/Br + CH₄ [1–4] and F⁻ + CH₃F/CH₃Cl/CH₃Br/CH₃I [5–8] reactions using the above methods. One of our current research directions is to move beyond these six-atom reactions and construct full-dimensional PESs for larger systems, allowing efficient dynamics simulations. To achieve this goal, we developed the ROBOSURFER program system [7] for automatic PES generation and the ManyHF method [9] for solving electronic structure issues frequently occurring in certain regions of the configuration space. With the help of ROBOSURFER, we have already developed full-dimensional high-level *ab initio* PESs for the F/Cl/OH + C₂H₆ [10–12], HBr/HI + C₂H₅ [13], OH⁻ + CH₃F/CH₃I [14,15], NH₂⁻ + CH₃I [16], and F⁻ + CH₃CH₂Cl [17] reactions involving 7–10 atoms. Reaction dynamics simulations on these PESs reveal unexpected reaction pathways like the oxide-ion substitution in OH⁻ + CH₃F [14], the competition between the different reaction channels and mechanisms, vibrational and rotational mode-specificity, post-reaction energy distributions as well as excellent agreement with experiments [10,11,17]. In the present talk I will focus on the F⁻ + CH₃CH₂Cl reaction, where theory played an essential role in disentangling the substitution and elimination pathways in collaboration with experiment [17].

References

- [1] G. Czakó, B. C. Shepler, B. J. Braams and J. M. Bowman, Accurate *ab initio* potential energy surface, dynamics, and thermochemistry of the F + CH₄ → HF + CH₃ reaction, *J. Chem. Phys.* 130, 084301 (2009)
- [2] G. Czakó and J. M. Bowman, Dynamics of the reaction of methane with chlorine atom on an accurate potential energy surface, *Science* 334, 343 (2011)
- [3] G. Czakó and J. M. Bowman, Dynamics of the O(³P) + CHD₃(*v*_{CH} = 0, 1) reactions on an accurate *ab initio* potential energy surface, *Proc. Natl. Acad. Sci. U.S.A.* 109, 7997 (2012)
- [4] G. Czakó, Accurate *ab initio* potential energy surface, thermochemistry, and dynamics of the Br(²P, ²P_{3/2}) + CH₄ → HBr + CH₃ reaction, *J. Chem. Phys.* 138, 134301 (2013)
- [5] I. Szabó, H. Telekes and G. Czakó, Accurate *ab initio* potential energy surface, thermochemistry, and dynamics of the F⁻ + CH₃F S_N2 and proton-abstraction reactions, *J. Chem. Phys.* 142, 244301 (2015)
- [6] I. Szabó and G. Czakó, Revealing a double-inversion mechanism for the F⁻ + CH₃Cl S_N2 reaction, *Nat. Commun.* 6, 5972 (2015)
- [7] 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)
- [8] B. Olasz, I. Szabó and G. Czakó, High-level *ab initio* potential energy surface and dynamics of the F⁻ + CH₃I S_N2 and proton-transfer reactions, *Chem. Sci.* 8, 3164 (2017)
- [9] 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)
- [10] D. Papp and G. Czakó, Full-dimensional MRCI-F12 potential energy surface and dynamics of the F(²P_{3/2}) + C₂H₆ → HF + C₂H₅ reaction, *J. Chem. Phys.* 153, 064305 (2020)
- [11] D. Papp, V. Tajti, T. Győri and G. Czakó, Theory finally agrees with experiment for the dynamics of the Cl + C₂H₆ reaction, *J. Phys. Chem. Lett.* 11, 4762 (2020)
- [12] B. Gruber, V. Tajti and G. Czakó, Full-dimensional automated potential energy surface development and dynamics for the OH + C₂H₆ reaction, *J. Chem. Phys.* 10.1063/5.0104889 (2022)

- [13] C. Yin, V. Tajti and G. Czako, Full-dimensional potential energy surface development and dynamics for the $\text{HBr} + \text{C}_2\text{H}_5 \rightarrow \text{Br}({}^2\text{P}_{3/2}) + \text{C}_2\text{H}_6$ reaction, submitted for publication (2022)
- [14] D. A. Tasi and G. Czako, Uncovering an oxide ion substitution for the $\text{OH}^- + \text{CH}_3\text{F}$ reaction, *Chem. Sci.* 12, 14369 (2021)
- [15] D. A. Tasi, T. Györi and G. Czako, On the development of a gold-standard potential energy surface for the $\text{OH}^- + \text{CH}_3\text{I}$ reaction, *Phys. Chem. Chem. Phys.* 22, 3775 (2020)
- [16] D. A. Tasi and G. Czako, Unconventional $\text{S}_{\text{N}}2$ retention pathways induced by complex formation: High-level dynamics investigation of the $\text{NH}_2^- + \text{CH}_3\text{I}$ polyatomic reaction, *J. Chem. Phys.* 156, 184306 (2022)
- [17] J. Meyer, V. Tajti, E. Carrascosa, T. Györi, M. Stei, T. Michaelsen, B. Bastian, G. Czako and R. Wester, Atomistic dynamics of elimination and nucleophilic substitution disentangled for the $\text{F}^- + \text{CH}_3\text{CH}_2\text{Cl}$ reaction, *Nat. Chem.* 13, 977 (2021)

THE HITCHIKER'S GUIDE TO THE WAVEFUNCTION

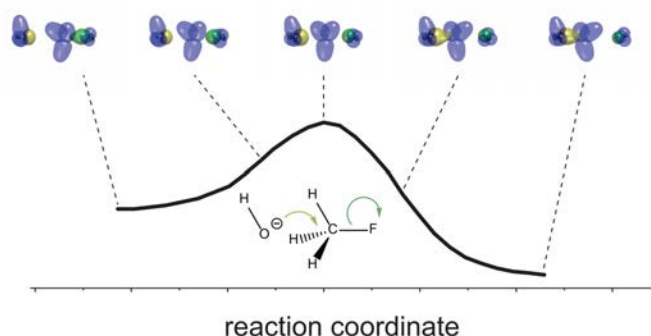
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Schrödinger's wave mechanics is a very successful formulation of quantum mechanics. The Schrödinger picture is the dominant paradigm used within essentially all computational chemistry and much of fundamental physics at everyday energies. A significant fraction of modern scientific computation is spent performing calculations that are formulated within the wave mechanics picture.

The wave function can be viewed as the central object within wave mechanics. Wave functions are functions that inherently inhabit high dimensional spaces. Whether these wave functions represent time independent stationary states or time dependent wave packets, the multi-particle wave function that describes N quantum mechanical particles in real space is a function of $3N$ degrees of freedom, with each degree of freedom describing "motion" of one of the particles and directions independently of the others.

The wave function is usually single valued, but contains all of the information about a quantum system that is possible to know. Understanding the structure of the wave function for any particular system could then be seen to be fundamental to understanding the nature of the physical system that the wave function describes. Yet residing in a mere three spatial dimensions, humans struggle to visualise and comprehend the full structure of these high dimensional functions. One may then argue that although we have the capability to calculate wave functions to a high level of accuracy, we rarely have solid justification in claiming that we understand what the detailed results of these calculations may be. We cannot visualise the results of our calculations as a pan-dimensional being living in a higher dimensional space would.

Over a number of years, we have been developing a method of interrogating high dimensional wave functions in order to reveal their high dimensional structure [1-7]. Our approach relies on the indistinguishability of fundamental particles, which implies that the entire information content of the wave function that in principle fills $3N$ dimensional space can be reduced to the value of the wave function on a slice of this space. The entire wave function can be reproduced by replicating the wave function from this slice onto other slices of the space by relabelling the coordinates, possibly with a sign change. In other words, the high dimensional wave function is inherently a tiling of $3N$ space. The structure of a self-consistent tiling gives insight into the structure of the full dimensional wave function. We call this method the Dynamic Voronoi Metropolis Sampling (DVMS) method, as it relies on a weighted random walk of a population of Monte Carlo points, constrained in part by a Voronoi decomposition of the $3N$ space.



Isosurfaces of projections of the DVMS tile onto 3D space for the electronic wave function of an S_N2 reaction at various points along the reaction path.

In this talk I will give an overview of our work to date. So far this has focussed on time independent electronic wave functions that can be calculated in great detail with advanced quantum chemistry methods. Unlike the native molecular orbital theory representations of these wave functions, analysis of the wave function tilings reveals the intuitive chemical motifs that have been developed by chemists prior to the widespread application of quantum theory to chemistry: core and valence structures, well-defined single, double or triple bonds, lone pairs, “curly arrow” electron motion over the course of a reaction, resonance, etc. The method also allows us to clearly articulate the effect of post-Hartree Fock correlation on the wave function in a way that is completely equivalent to our analysis of uncorrelated Hartree Fock wave functions.

References

- [1] Y. Liu, T. J. Frankcombe and T. W. Schmidt, Chemical bonding motifs from a tiling of the many-electron wavefunction, *Phys. Chem. Chem. Phys.* 18, 13385 (2016)
- [2] Y. Liu, P. Kilby, T. J. Frankcombe and T. W. Schmidt, Calculating curly arrows from ab initio Wavefunctions, *Nature Comm.* 9, 1436 (2018)
- [3] Y. Liu, P. Kilby, T. J. Frankcombe and T. W. Schmidt, Electronic transitions of molecules: vibrating Lewis structures, *Chem. Sci.* 10, 6809 (2019)
- [4] Y. Liu, T. J. Frankcombe and T. W. Schmidt, Visualizing the 30-Dimensional Antisymmetrized Electronic Structure of Water: The Emergence of Lone Pairs, *J. Phys. Chem. Lett.* 11, 735 (2020)
- [5] Y. Liu, P. Kilby, T. J. Frankcombe and T. W. Schmidt, The electronic structure of benzene from a tiling of the correlated 126-dimensional wavefunction, *Nature Comm.* 11, 1210 (2020)
- [6] Y. Liu, T. J. Frankcombe and T. W. Schmidt, Electronic Wavefunction Tiles, *Aust. J. Chem.* 73, 757 (2020)
- [7] Y. Liu, T. J. Frankcombe and T. W. Schmidt, The Hitchhiker’s Guide to the Wave Function, *J. Phys. Chem. A* 126, 979 (2022)

INFLUENCE OF CONICAL INTERSECTIONS IN THE PHOTODISSOCIATION MECHANISMS OF ALKYL RADICALS

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Alkyl radicals are known to play an important role as intermediates in photoinduced reactions in atmospheric, interstellar, and combustion chemistry. Among the alkyl radicals, methyl and ethyl are the simplest ones, and they are involved in several crucial processes of atmospheric and astrophysical interest. In this presentation recent experimental and theoretical results on the photoexcitation of both methyl [1-4] and ethyl [5-8] to the 3s and 3p Rydberg states, and their further photodissociation dynamics, will be reviewed. The experimental findings are rationalized and explained with the aid of high-level *ab initio* calculations for the two radicals, and also by means of quantum dynamical simulations in the case of methyl [4]. One of the main focus is to analyze the role played by the nonadiabatic couplings between the excited states involved, and in particular by the conical intersections identified. Interestingly, it is found that even for these small and relatively simple radical molecules, the presence of different nonadiabatic couplings causes a rich variety of fragmentation mechanisms.

References

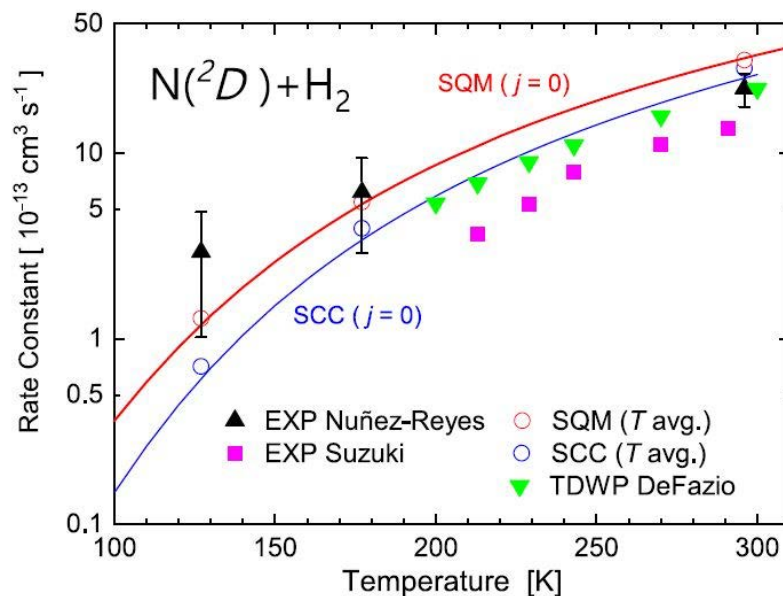
- [1] G. Balerdi, J. Woodhouse, A. Zanchet, R. De Nalda, M. L. Senent, A. García-Vela, and L. Bañares, Femtosecond predissociation dynamics of the methyl radical from the 3p_z Rydberg state, *Phys. Chem. Chem. Phys.* 18, 110 (2016)
- [2] S. Marggi Poullain, D. V. Chicharro, A. Zanchet, M. G. González, L. Rubio-Lago, M. L. Senent, A. García-Vela, and L. Bañares, Imaging the photodissociation dynamics of the methyl radical from the 3s and 3p_z Rydberg states, *Phys. Chem. Chem. Phys.* 18, 17054 (2016)
- [3] A. Zanchet, L. Bañares, M. L. Senent, and A. García-Vela, An *ab initio* study of the ground and excited electronic states of the methyl radical, *Phys. Chem. Chem. Phys.* 18, 33195 (2016)
- [4] A. García-Vela, Photodissociation of the methyl radical: the role of nonadiabatic couplings in enhancing the variety of dissociation mechanisms, *Phys. Chem. Chem. Phys.* 23, 25911 (2021)
- [5] D. V. Chicharro, S. Marggi Poullain, A. Zanchet, A. Bouallagui, A. García-Vela, M. L. Senent, L. Rubio-Lago, and L. Bañares, Site-specific hydrogen-atom elimination in photoexcited ethyl radical, *Chem. Sci.* 10, 6494 (2019)
- [6] S. Marggi Poullain, D. V. Chicharro, A. Zanchet, L. Rubio-Lago, A. García-Vela, and L. Bañares, The 3s versus 3p Rydberg state photodissociation dynamics of the ethyl radical, *Phys. Chem. Chem. Phys.* 21, 23017 (2019)
- [7] D. V. Chicharro, A. Zanchet, A. Bouallagui, L. Rubio-Lago, A. García-Vela, L. Bañares, and S. Marggi Poullain, Site-specific hydrogen-atom elimination in photoexcited alkyl radicals, *Phys. Chem. Chem. Phys.* 23, 2458 (2021)
- [8] S. Marggi Poullain, L. Rubio-Lago, D. V. Chicharro, A. Bouallagui, A. Zanchet, O. Yazidi, A. García-Vela, and L. Bañares, Imaging the elusive C-C bond dissociation channel of photoexcited ethyl radical, *Mol. Phys.* 120:1-2 e1984598 (2022)

REACTIVE SCATTERING OF ATOM-DIATOM PROCESSES OF ASTROPHYSICAL INTEREST

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In this communication we report results of combined experimental and theoretical investigations on the kinetics of reactive atom-diatom collisions between molecular hydrogen and electronically excited atoms C(¹D) [1], N(²D) [2], O(¹D) [3,4] or S(¹D) [5]. Values of the rate constant over a temperature range between 50 and 300 K have been calculated by means of a statistical quantum method [6] and compared with measurements obtained with the CRESU method [7]. Similar theoretical methods were employed in an exhaustive study of the H⁺ + H₂ and H⁺ + HD [8,9] reactions to calculate rate constants between 10 and 3000 K which constitute useful inputs for astrophysical models [10].



- [1] T. González-Lezana *et al.* *J. Chem. Phys.* **148**, 234305 (2018).
 [2] D. Nuñez-Reyes *et al.* *Phys. Chem. Chem. Phys.* **22**, 23609 (2020).
 [3] D. Nuñez-Reyes *et al.* *Phys. Chem. Chem. Phys.* **20**, 4404 (2018).
 [4] D. Nuñez-Reyes *et al.* *J. Phys. Chem. A* **123**, 8089 (2019).
 [5] T. González-Lezana *et al.* *Chem. Phys. Lett.* **763**, 138228 (2021).
 [6] T. González-Lezana *Int. Rev. Phys. Chem.* **26**, 29 (2007).
 [7] K. M. Hickson *et al.* *Int. Rev. Phys. Chem.* **40**, 457 (2021).
 [8] P. Honvault *et al.* *Phys. Rev. Lett.* **107**, 023201 (2011).
 [9] T. González-Lezana and P. Honvault, *Int. Rev. Phys. Chem.* **33**, 371 (2014).
 [10] D. R. Flower *et al.* *MNRAS* **507**, 3564 (2021); L. Pagani *et al.* *A&A* **551**, A38 (2013)..

ULTRACOLD CHEMISTRY AND COLLISION COMPLEXES

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Ultracold molecular gases are being studied because they are promising platforms for quantum simulation and quantum computation, and they may be used in high precision measurements of fundamental physical constants. Ultracold gases can be stored in a magnetic or optical dipole traps and achieving a long trap life time is important in applications. In this talk I will focus on collisional complexes since they play a key role in trap loss.

In the 2010 experiment at JILA creating an ultracold gas of KRb it was found that the trap loss rate could be explained by the formation of collisional complexes, which were lost by a barrierless exothermic chemical reaction: $\text{KRb} + \text{KRb} \rightarrow \text{K}_2 + \text{Rb}_2$ [1]. Surprisingly, similar loss rates were found in subsequent experiments on RbCs and other molecules for which only endothermic reaction pathways are available. An early attempt to explain this involved the idea of "sticky collisions" [2,3]. The estimated life times of the collisional complexes were sufficiently long to assume they may be lost by collisions with a third molecule. Our later, more accurate estimates gave much shorter life times, ruling out this mechanism for most systems [4,5]. Still, we found that the collision complexes could still be lost by absorption of photons from the trap laser [6]. This idea was confirmed for $^{87}\text{Rb}^{133}\text{Cs}$ [7] and for KRb [8] in experiments with modulated trap intensities. In other experiments on $^{23}\text{Na}^{39}\text{K}$ and $^{23}\text{Na}^{87}\text{Rb}$, however, trap intensity modulation did not suppress trap loss.

If the dynamics of the collision complex is chaotic, its life time can be calculated with Rice-Ramsperger-Kassel-Marcus (RRKM) theory, *i.e.*, from the ratio of the density-of-states (DOS) and the number of channels that allow for the breakup of the complex, while assuming the total angular momentum is conserved. When an external electric field is present, only the projection of the total angular momentum is conserved, so many partial waves contribute to the DOS, and within the model, the lifetime increases. Whether this actually occurs depends on whether the entire energetically allowed phase space is actually sampled ergodically during a collision. We developed a quantitative theory to predict at which external field strength this symmetry breaking occurs [9]. Classical trajectories are used to model the collision complex in an electric field, which we expect to be accurate since typically the DOS is huge. The breakup of the complex though, occurs through a few, or only one, channel, which requires a quantum treatment. We show how to combine a classical trajectory calculation with a proper quantum treatment of the breakup channels in order to compute the life time of a collision complex. The method is suitable for treating rare events, *i.e.*, the trajectories have to be run for only a fraction of the life time of the complex. We find that surprisingly small electric fields may increase the life time substantially. It is often assumed that nuclear spin is conserved in collisions. By using the hyperfine coupling as the symmetry breaking coupling we confirm this assumption quantitatively by direct calculation for RbCs. Finally, we use this method to compute trap loss as a result of spontaneous emission and absorption of black-body radiation, and we find that these processes are slow.

Experimental loss rates have been reported for several systems. Comparing these loss rates with theoretical values may provide information on the loss mechanism. Converged quantum scattering calculations using *ab initio* potentials are prohibitively expensive for all but the simplest systems. However, quantum defect theory (QDT), which describes the scattering process with only a few parameters related to long-range and short-range effects, provides insightful approximations. In particular, analytic expressions for the loss rate in the ultracold regime have been derived as a function of the "quantum defect" parameter $0 \leq \gamma \leq 1$, where $\gamma=1$ corresponds to complete absorption of the flux in the short range [10]. The loss rate for $\gamma=1$ is called *universal* since it only depends on the long-range potential and not on the short range phase shift. It has been assumed that reactions proceeding through a collision

complex will result in universal rates if the dynamics of the complex is chaotic and the probability of the complex breaking up through the reactant channel is negligible. I will present a “lossy QDT” model (LQDT) in which the collision complex is described by short-range resonances which depend on two parameters: the elastic partial width describing the breakup of the complex through the entrance channel, and the inelastic partial width describing the loss of the complex through chemical reaction or otherwise [11]. Surprisingly, we find that the rates are in general not universal. When the inelastic partial width is large, resonances may overlap, and the rate is nonuniversal with $\nu=1/4$, which is consistent with the experimentally observed value of $\nu=0.26(3)$ for RbCs [12].

To find an expression for the thermally averaged rate in LQDT, an assumption must be made for the product of the density of states (ρ) and the elastic partial widths (γ) of the resonances. The above results were obtained from the Weisskopf estimate $\rho\gamma=1/2\pi$. A rate close to universal may be obtained by assuming a value for $\rho\gamma$ that is exactly four times larger. Another way to find the universal result is by assuming a specific background scattering length. Both scenarios require fine-tuning, and suggesting that an observed universal rate may actually indicate nonchaotic short-range dynamics.

References

- [1] S. Ospelkaus, K. K. Ni *et al.*, *Quantum-state controlled chemical reactions of ultracold potassium-rubidium molecules*, *Science* **327**, 853 (2010)
- [2] M. Mayle, B. P. Ruzic, and J. L. Bohn, *Statistical aspects of ultracold resonant scattering*, *Phys. Rev. A* **85**, 062712 (2012)
- [3] M. Mayle, G. Quémener, B. P. Ruzic, and J. L. Bohn, *Scattering of ultracold molecules in the highly resonant regime*, *Phys. Rev. A* **87**, 012709 (2013)
- [4] A. Christianen, T. Karman, and G. C. Groenenboom, *Quasiclassical method for calculating the density of states of ultracold collision complexes*, *Phys. Rev. A* **100**, 032708 (2019)
- [5] A. Christianen, T. Karman, R. A. Vargas-Hernández, G. C. Groenenboom, and R. V. Krems, *Six-dimensional potential energy surface for NaK-NaK collisions: Gaussian Process representation with correct asymptotic form*, *J. Chem. Phys.* **150**, 064106 (2019)
- [6] A. Christianen, M. W. Zwierlein, G. C. Groenenboom, and T. Karman, *Photoinduced two-body loss of ultracold molecules*, *Phys. Rev. Lett.* **123**, 123402 (2019)
- [7] P. D. Gregory, J. A. Blackmore, S. L. Bromley, and S. L. Cornish, *Loss of ultracold RbCs molecules via optical excitation of long-live two-body collision complexes*, *Phys. Rev. Lett.* **124**, 163402 (2020)
- [8] Y. Liu, M.-G. Hu, M. A. Nichols, D. D. Grimes, T. Karman, H. Guo, and K.-K. Ni, *Photoexcitation of long-lived transient intermediates in ultracold atoms*, *Nat. Phys.* **16**, 1132 (2020)
- [9] M. P. Man, G. C. Groenenboom, and T. Karman, *Symmetry breaking in sticky collisions between ultracold molecules*, arXiv:2203.13598 (2022)
- [10] Z. Idziaszek and P. S. Julienne, *Universal rate constants for reactive collisions of ultracold molecules*, *Phys. Rev. Lett.* **104**, 113202 (2010)
- [11] A. Christianen, G. C. Groenenboom, and T. Karman, *Lossy quantum defect theory of ultracold molecular collisions*, *Phys. Rev. A* **104**, 043327 (2021)
- [12] P. D. Gregory, M. D. Frye, *et al.*, *Sticky collisions of ultracold RbCs molecules*, *Nature Commun.* **10**, 3104 (2019)

QUANTUM DYNAMICS OF ISOTOPE EXCHANGE REACTIONS : THE OZONE EXAMPLE

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Statement of the problem: Molecular oxygen is the most important molecule in Earth's atmosphere, not only the origin of extra marine life forms, but also the precursor of stratospheric ozone which protects them from 98% of the sun UV radiations. Isotopic analysis allows one to trace back the origin of elements constituting certain primitive materials. O₂ and O₃ formed from ¹⁶O isotope are dominant, thereby giving a reference for any process involving oxygen. Against all odds, a strong enrichment, about 10% greater than one would expect statistically, of O₃ in both ¹⁸O and ¹⁷O, the so-called mass-independent fractionation (MIF), has first been observed decades ago [1]. This phenomenon has since been reproduced many times in laboratory experiments [2]. However, its proper quantum first principles explanation has never been attained. Ozone is formed from termolecular recombination reaction $O + O_2 + M \rightarrow O_3 + M$ (M=N₂, O₂ or Ar) [3], part of famous Chapman cycle. One of its two proposed mechanisms (Lindemann) is initiated by oxygen exchange reaction $O + O_2 \rightarrow O_3^* \rightarrow O_2 + O$. The study of the latter, as well as that of intermediate complex O₃^{*}, is thus important for a full understanding of stable O₃ formation.

Methodology: We have used a high quality *ab initio* potential energy surface [4] to perform computationally intensive full quantum investigation of the dynamics of this scattering process.

Results: We shall present cross sections and rate constants [5] for the O + O₂ reaction, together with lifetimes [6] of intermediate species O₃^{*}. We will discuss observed isotope effects, and the importance of symmetry in relation to nuclear spins [7].

References

- [1] K. Mauersberger, Measurement of heavy ozone in the stratosphere, *Geophys. Res. Lett.* 8, 935-937 (1981)
- [2] M. H. Thiemens, J. E. Heidenreich, III, The mass-independent fractionation of oxygen: a novel isotope effect and its possible cosmochemical implications, *Science* 219, 1073-1075 (1983)
- [3] M. V. Ivanov, D. Babikov, On molecular origin of mass-independent fractionation of oxygen isotopes in the ozone forming recombination reaction, *PNAS* 110, 17708-17713 (2013)
- [4] V. Tyuterev, R. Kochanov, A. Campargue, S. Kassi, D. Mondelain, A. Barbe, E. Starikova, M. R. DeBacker, P. G. Szalay, S. Tashkun, Does the reef structure at the ozone transition state toward the dissociation exist? New insight from calculations and ultrasensitive spectroscopy experiments, *Phys. Rev. Lett.* 113, 143002-1-4 (2014)
- [5] G. Guillon, P. Honvault, R. Kochanov, V. Tyuterev, First principles computed rate constant for the O + O₂ isotopic exchange reaction now matches experiment, *J. Phys. Chem. Lett.* 9, 1931-1936 (2018)
- [6] E. Privat, G. Guillon, P. Honvault, Direct time-delay computation applied to the O + O₂ reaction at low energy: lifetime spectrum of the O₃^{*} species, *J. Chem. Phys.* 154, 104303-1-9 (2021)
- [7] G. Guillon, M. Lepers, P. Honvault, Quantum dynamics of ¹⁷O in collision with ortho- and para-¹⁷O¹⁷O, *Phys. Rev. A* 102, 012810 (2020)

**TOOLS FOR AUTOMATED PES DEVELOPMENT: ROBOSURFER
AND MANYHF**

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Developing high accuracy reactive potential energy surfaces is a formidable task. Even if ab-initio data can be fitted accurately, one is still left with the twin difficulties of selecting the geometries included in the fitting set, as well as assuring the quality of the ab-initio data. Without automated PES development tools neither the quality of the surfaces obtained nor the amount of human labour required remains tenable as the size and complexity of systems under study increases.

For this reason, the Robosurfer program system [1] was developed, which automates the development of surfaces through an iterative approach. This procedure enabled the development of PESs for systems as complicated [2] as $\text{CH}_3\text{CH}_2\text{Cl} + \text{F}^-$. Unfortunately, running ab-initio calculations at a diverse set of far-from-equilibrium geometries is fraught with difficulty, chiefly SCF convergence failures and the breakdown of the triples approximation in CCSD(T) can occur.

In three doublet systems we have found many cases where landing on the wrong Hartree–Fock (HF) solution leads to >100 kcal/mol errors in CCSD(T) energies. To combat this, we developed [3] the ManyHF method, which can locate multiple HF solutions, and use the best one for any given geometry.

The (T) failures we have encountered in $\text{CH}_3\text{I} + \text{OH}^-$ are resolved [4] with the use of Brueckner coupled-cluster theory, which yields more robust (T) contributions than traditional CCSD(T).

References

- [1] 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), [10.1021/acs.jctc.9b01006](https://doi.org/10.1021/acs.jctc.9b01006)
- [2] J. Meyer, V. Tajti, E. Carrascosa, T. Győri, M. Stei, T. Michaelson, B. Bastian, G. Czakó and R. Wester, Atomistic Dynamics of Elimination and Nucleophilic Substitution Disentangled for the $\text{F}^- + \text{CH}_3\text{CH}_2\text{Cl}$ Reaction, *Nat. Chem.* 13, 977 (2021), [10.1038/s41557-021-00753-8](https://doi.org/10.1038/s41557-021-00753-8)
- [3] 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), [10.1063/5.0080817](https://doi.org/10.1063/5.0080817)
- [4] D. A. Tasi, T. Győri and G. Czakó, On the Development of a Gold-Standard Potential Energy Surface for the $\text{OH}^- + \text{CH}_3\text{I}$ Reaction, *Phys. Chem. Chem. Phys.* 22, 3775 (2020), [10.1039/C9CP07007A](https://doi.org/10.1039/C9CP07007A)

**A COMPLETE CONSIDERATION OF NON-ADIABATIC EFFECTS
(UP TO ORDER $O(\mu^{-2})$, μ = REDUCED NUCLEAR MASS) IN A
TRIATOMIC MOLECULE:
INFLUENCE ON THE ROVIBRATIONAL ENERGIES OF H_3^+**

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It is generally accepted that radiative association of ions with molecules plays an important role in the molecular synthesis in the super-cold, low-density environment of the interstellar medium. One of the crucial steps in the investigation of cross-sections for radiative association (and the infrared predissociation spectrum¹ of H_3^+ , with ca. 100 transitions per wavenumber) is the calculation of the ro-vibrational bound states and resonances near the dissociation limit. Because H_3^+ has a binding energy of ca. 35000 cm^{-1} , the accurate determination of the highest bound energy levels can be demanding. For the description of radiative association of a strongly bound molecule, we need a good potential energy and dipole surface, an efficient reactive scattering implementation and an efficient way of calculating high-lying bound states and resonances. But, it is already problematic to calculate with spectroscopy accuracy all rovibrational transitions $< 16000 cm^{-1}$.

The main focus of this talk is the investigation of the influence of non-adiabaticity on the rovibrational bound states of H_3^+ . For this purpose a full configuration interaction (FCI) treatment using Gaussian basis functions is applied to calculate the energies of the electronic states as well as all couplings between them caused by the nuclear motion.

These 'derivative couplings' were evaluated up to second order by means of a perturbation treatment using the 'some-over-states'-strategy. While this has been possible already for H_2^+ and H_2 , nothing equivalent has been available for H_3^+ . The present work² is an extension of the investigation of earlier non-adiabatic investigations based on first derivative couplings of electronic states that led to the concept of geometry-dependent effective nuclear masses³ needed for only one single potential energy surface⁴. Our new implementation allows to include for the first time also for H_3^+ all non-adiabatic effects (coupling of second-derivatives, and second-derivatives with first-derivatives) up to the order of $O(\mu^{-2})$, μ being the reduced nuclear mass.

These new inclusions of all nonadiabatic effects could reduce also for H_3^+ the deviations to experimental data for most rovibrational levels ($< 16000 cm^{-1}$) to less than 0.1 cm^{-1} without any empirically adjustable parameters. For H_3^+ , the accuracy is slightly improved when also relativistic and QED effects are taken into account⁵. For some questionable assignments of observed transitions in H_3^+ we propose a new labeling. In future investigations we are going to use linear response theory to analyse non-adiabaticity for triatomics with more than 2 electrons.

¹A. Carrington, R. A. Kennedy, J. Chem. Phys., **81**, 91 (1984)

²R. Jaquet, J. Mol. Spectr., **384**, 111585 (2022)

³R.M. Herman, A. Ashgarian, J. Mol. Spectr. **19**, 305 (1966)

⁴R. Jaquet, M. Khoma, J. Phys. Chem. A, **121**, 7016 (2017); J. Chem. Phys., **147**, 114106 (2018); Mol. Phys., **116**, 3507 (2018); J. Math. Chem., **57**, 701 (2019)

⁵R. Jaquet, M. Lesiuk, J. Chem. Phys., **152**, 104109 (2020)

DYNAMICAL IMPLICATIONS OF HILLTOPS AND CALDERAS

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Features on multidimensional potential energy surfaces (PESs) such as higher index saddles, nearly flat regions (calderas), and multiple and bifurcated transition states have important dynamical implications for rates and mechanisms in several classes of reactions [1]. There is now ample experimental and computational evidence [2,3,4] for such reactions being inherently non-statistical, even in the condensed phase [5]. Two crucial questions arise in this context. What is the appropriate generalization [6], if any, of the phase space transition state theory in such cases? To what extent is the quantum dynamics sensitive to the aforementioned features?

In this talk I will present two short stories to highlight the essential dynamical aspects. The first one [7] has to do with the phenomenon of dynamic matching. Utilizing a model Hamiltonian I will argue that dynamic matching persists even for PESs with rather deep wells. The classical dynamical origins of non statistical branching ratios and the correspondence with quantum dynamics will be shown. Our study is complimentary to the recently proposed [8] rigorous phase space based criterion for the manifestation of dynamic matching. The second story [9] pertains to a model for double proton transfer reaction. Here, at high energies, the crucial role of index-2 saddle point in deciding whether the mechanism is concerted or stepwise will be illustrated. The results indicate that the mechanism inferred from low dimensional model studies can switch upon coupling low frequency transverse modes to the proton transfer coordinates. Moreover, a phase space understanding of the notion of a “dynamically concerted” [2] reaction will be provided.

References

- [1] D. J. Tantillo, Dynamic effects on organic reactivity - Pathways to (and from) discomfort, *J. Phys. Org. Chem.* 34: e4202 (2021)
- [2] Z. Yang and K. N. Houk, The dynamics of chemical reactions: Atomistic visualisations of organic reactions, and homage to van't Hoff, *Chem. Eur. J.* 24, 3916 (2018)
- [3] J. Rehbein and B. Wulff, Chemistry in motion - off the MEP, *Tet. Lett.* 56, 6931 (2015)
- [4] Z. Wang, J. S. Hirschi and D. A. Singleton, Recrossing and dynamic matching effects on selectivity in a Diels-Alder reaction, *Angew. Chem. Int. Ed.* 48, 9156 (2009)
- [5] B. K. Carpenter, J. N. Harvey and A. J. Orr-Ewing, The study of reactive intermediates in condensed phases, *J. Am. Chem. Soc.* 138, 4695 (2016)
- [6] P. Collins, G. S. Ezra and S. Wiggins, Index k saddles and dividing surfaces in phase space with applications to isomerization dynamics, *J. Chem. Phys.* 134, 244105 (2011)
- [7] P. Pandey and S. Keshavamurthy, Dynamic matching - Revisiting the Carpenter model, *J. Phys. Org. Chem.* e4404 (2022)
- [8] M. Katsanikas, V. J. García-Garrido and S. Wiggins, The dynamical matching mechanism in phase space for caldera-type potential energy surfaces, *Chem. Phys. Lett.* 743, 137199 (2020)
- [9] P. Pandey, S. Naik and S. Keshavamurthy, Influence of low frequency modes on dynamical concertedness in double proton transfer dynamics, *Commun. Nonlinear Sci. Numer. Simul.* 109, 106326 (2022)

RRKM THEORY FOR REACTIVE INTERMEDIATES

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In recent years, the Lester group has developed a novel and very effective methodology for examining the *E,J*-resolved dissociation of highly unstable reactive intermediates including hydroperoxyalkyl radicals ($\bullet\text{QOOH}$) and Criegee intermediates [1,2,3]. Their approach involves an in situ generation of the intermediate coupled with stabilization in a pulsed jet expansion followed by time-resolved IR pump-UV probe action spectroscopy. Variation of the IR pump wavelength yields *E*-resolved dissociation rate constants for a variety of energies. The UV probe is used to observe laser-induced fluorescence of OH radicals. These observations from the Lester group provide important new challenges and tests for theoretical models.

We will directly compare a priori implementations of RRKM theory with these groundbreaking experimental measurements of the dissociation rate. These comparisons highlight (i) our ability to obtain high accuracy predictions for the reaction energies, (ii) the importance of including multidimensional hindered rotor treatments, (iii) deep tunneling in the Criegee intermediates, and (iv) the role of heavy atom tunneling in the $\bullet\text{QOOH}$'s. For the Criegee intermediates we have explored a variety of systems, which highlight the effects of stereochemistry, resonance stabilization, and 1,6 as opposed to 1,4 H-transfers on the kinetics, as well as the possibility for multistage roaming dynamics.

Part of our theoretical analysis includes a novel treatment of tunneling [4], which we review in detail. A new closed-form rate expression is obtained for the non-separable tunneling rate constant at low temperatures. It introduces a novel "entanglement factor" that modulates the reaction rate. Furthermore, we extend this expression to properly account for the conservation of angular momentum. In contrast, previous calculations have considered only vibrational transverse modes and so effectively employed a decoupled rotational partition function for the orientational modes. Notably, this analysis also yields a simple theoretical model for describing the tunneling effects in the vicinity of the crossover temperature (the temperature where tunneling becomes the dominating mechanism). This model allows one to naturally classify, interpret, and predict experimental data. Among other things, it quantitatively explains in simple terms the so-called "quantum bobsled" effect, also known as the negative centrifugal effect, which is related to curvature of the reaction path. Taken together, the expressions obtained allow one to predict the thermal and *E* resolved rate constants over broad ranges of temperatures and energies.

References

- [1] Y. Fang, F. Liu, V. P. Barber, S. J. Klippenstein, A. B. McCoy, M. I. Lester, Communication: Real Time Observation of Unimolecular Decay of Criegee Intermediates to OH Radical Products, *J. Chem. Phys.* 144, 061102 (2016).
- [2] M. I. Lester, S. J. Klippenstein, Unimolecular Decay of Criegee Intermediates to OH Radical Products: Prompt and Thermal Decay Processes, *Acc. Chem. Res.* 51, 978–985 (2018).
- [3] A. S. Hansen, T. Bhagde, K. B. Moore III, D. R. Moberg, A. W. Jasper, Y. Georgievskii, M. F. Vansco, S. J. Klippenstein, M. I. Lester, Watching a Hydroperoxyalkyl Radical ($\bullet\text{QOOH}$) Dissociate, *Science*, 373, 679-682 (2021).
- [4] Y. Georgievskii, S. J. Klippenstein, Entanglement Effect and Angular Momentum Conservation in a Nonseparable Tunneling Treatment, *J. Chem. Theo. Comp.* 17, 3863-3885 (2021).

MOLECULAR NETWORKS BY INVARIANT SHAPE COORDINATES AND DEFORMATION INDEXES

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The classification of large molecules according to structural similarities is a relevant issue in biochemistry [1], even more in the upcoming big data era. The proper choice of parameters, containing invariant structural information, is a convenient way to induce mapping and grouping of structures, depending on predominant structural motifs, individual amino acid geometries or connectivity properties. Few-body hyperspherical coordinates provide the appropriate framework from which shape parameters and deformation indexes [2-4] may be inferred and applied to characterize complex structures, represented as a network of vertices and links.

References

- [1] S. Konno, T. Namiki and K. Ishimori, *Sci. Rep.* 16654 (2019)
- [2] A. Lombardi, *AIP Conference Proceedings*, 2343 (1), 020004 (2021)
- [3] L. Andrea, N. Faginas-Lago, N. and L. Pacifici, *Protein Networks by Invariant Shape Coordinates and Deformation Indexes*. In: Gervasi, O., Murgante, B., Misra, S., Rocha, A.M.A.C., Garau, C. (eds) *Computational Science and Its Applications – ICCSA 2022 Workshops*. ICCSA 2022. *Lecture Notes in Computer Science*, vol 13382, 348-359 (2022).
- [4] V. Aquilanti, A. Lombardi, E. Yurtsever, *Phys.Chem. Chem. Phys.* 4 (20), 5040 (2000)

PHOTODISSOCIATION AND NONADIABATIC DYNAMICS OF SMALL ORGANIC MOLECULES

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The photodissociation dynamics of small saturated and unsaturated hydrocarbons have been studied using Direct Dynamics Trajectory Surface-Hopping (DDTSH) method in conjunction with Tully's fewest switches algorithm.¹ After excitation of the molecule into the Franck-Condon region of the excited singlet state, the molecule in most cases hops to ground singlet state through nonradiative decay via conical intersection. Our calculations show the evidence of roaming mediated nonadiabatic pathways for the elimination of molecular hydrogen from propane at 157 nm.² Approximately one-third of the trajectories those resulted in a triple dissociation channel, $\text{CH}_3 + \text{C}_2\text{H}_4 + \text{H}$ completed in the ground singlet state following a nonadiabatic path via the C–C and C–H dissociation coordinate conical intersection S_1/S_0 .³ Photofragmentation of propyne at 193 nm on the other hand follows predominantly adiabatic pathway resulting products in the excited singlet state.

In the photodissociation of methyl hydroperoxide $(\text{CH}_3\text{OOH})^4$ at 193 nm, H atom elimination due to O–H bond scission partially occurs through the S_1/S_0 conical intersection leading to the ground state products.

Our recent photodissociation dynamics study of 1-pyrazoline ($\text{C}_3\text{N}_2\text{H}_6$) at 334 nm indicates that two types of S_1/S_0 conical intersections drive its decay fully to the ground state nonradiatively forming trimethylene diradical in the ground singlet state followed by formation of different hydrocarbons, such as, cyclopropane, propene, ethylene and methylene.

References

1. Tully, J. C., Molecular dynamics with electronic transitions. *J. Chem. Phys.* **1990**, *93* (2), 1061-1071.
2. Rauta, A. K.; Maiti, B., Roaming mediated nonadiabatic dynamics in molecular hydrogen elimination from propane at 157 nm. *Chemical Physics Letters* **2016**, *661* 83–88.
3. Rauta, A. K.; Maiti, B., Trajectory surface hopping study of propane photodissociation dynamics at 157 nm. *J. Chem. Phys.* **2018**, *149*, 044308-11.
4. Mahata, P.; Maiti, B., Photodissociation Dynamics of Methyl Hydroperoxide at 193 nm: A Trajectory Surface-Hopping Study. *The Journal of Physical Chemistry A* **2021**, *125* (48), 10321-10329.

PRODUCT STATE CONTROL AND FAST BARRIER PASSAGE IN POLYATOMIC REACTIONS

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Reactions of atoms with methane are prototypical examples of polyatomic reaction processes which are intensively studied by experiment and theory. Combining the quantum transition state concept and the numerically efficient (multi-layer) multi-configurational time-dependent Hartree (MCTDH) approach, rigorous full-dimensional quantum dynamics calculations can study these six atom reactions. First principles-based theory can predict various observables ranging from thermal rate constants to fully quantum state resolved reaction probabilities. The talk provides an introduction into the underlying theory and discusses recent results [1,2].

The state-to-state reaction dynamics of $\text{H}+\text{CHD}_3\rightarrow\text{H}_2+\text{CD}_3$ shows an apparently counter-intuitive correlation between the quantum states of reactants and products: increasing the energy in the reactant's CD_3 umbrella vibration reduces the energy in the corresponding product vibration. An in-depth analysis extends the "loss of vibrational memory"-principle and reveals the crucial role of the effective dynamical transition state: its geometry is controlled by the vibrational states of the reactants and subsequently controls the quantum state distribution of the products. This finding enables generalizing the concept of transition state control of chemical reactions to the quantum state-specific level.

Accurate quantum dynamics simulations of the $\text{Cl}+\text{CH}_4\rightarrow\text{HCl}+\text{CH}_3$ reaction demonstrate that the passage of the reaction barrier occurs within only a few ten femtoseconds despite the presence of heavy atoms in both reactants. This surprisingly short time scale results from correlated motion of the transferring hydrogen atom and the hydrogen atoms in the methyl fragment which facilitates irreversible barrier passage without relevant participation of heavy atoms. Resonance effects resulting from the heavy-light-heavy characteristics of the reaction system, which were observed in reactive scattering studies, do not affect the thermal rate constant. The calculated thermal rate constants are in perfect agreement with experiment. Evaluating the accuracy of approximate approaches, ring polymer molecular dynamics calculations are surprisingly found to significantly underestimate the accurate rate constant.

References

- [1] R. Ellerbrock, B. Zhao, and U. Manthe, *Sci. Adv.* 8, eabm9820 (2022)
- [2] H. Hoppe and U. Manthe, *J. Phys. Chem. Lett.* 13, 2563 (2022)

ELECTRON INDUCED REACTIVITY IN MOLECULAR CATIONS

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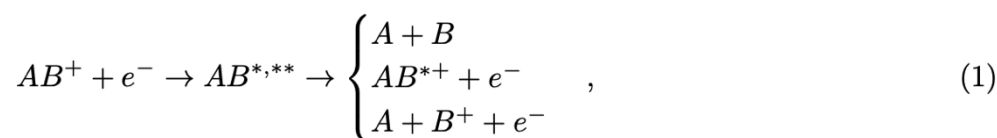
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Electron-impact dissociative recombination, ro-vibrational (de)excitation and dissociative excitation of hydride cations



are in the heart of the molecular reactivity in the cold ionized media [1], being major charged particles destruction reactions and producing often atomic species in metastable states, inaccessible through optical excitations. They involve super-excited molecular states undergoing predissociation and autoionization, having thus strong resonant character.

Consequently, they are subject to beyond-Born-Oppenheimer theoretical approximations, and often require rather quasi-diabatic than adiabatic representations of the molecular states. In addition, they involve particularly sophisticated methods for modelling the collisional dynamics, able to manage the superposition of many continua and infinite series of Rydberg states.

We use the Multichannel Quantum Defect Theory [2], capable to account the strong mixing between ionization and dissociative channels, open - direct mechanism - and closed - indirect mechanism, via capture into prominent Rydberg resonances [3, 4] correlating to the ground and excited ionic states, and the rotational effects. These features will be illustrated for several cations of high astrophysical, planetary atmosphere and cold plasma physical relevance such as SH⁺ [5], N₂⁺[6] and CH⁺ [4, 7], comparisons with other existing theoretical and experimental results being performed.

Advancement in the theoretical treatment - as the effect of the energy-dependence of the quantum defect on vibronic interactions for the benchmark cation H₂⁺, the isotopic effects for diatomic and polyatomic systems like H₂⁺ [8] and N₂H⁺, etc. - will be presented.

Research supported by the Normandy region, CNRS-PCMI, ANR Labex EMC3 and NKFIH-OTKA.

References

- [1] I. F. Schneider, O. Dulieu and J. Roberts (eds.), Eur. Phys. J. Web of Conf. 84 (2015)
- [2] Ch. Jungen (ed.), Molecular Applications of Quantum Defect Theory, IOP, Bristol, (1996)
- [3] I. F. Schneider et al, J. Phys. B 24, L289 (1991).
- [4] J. Zs. Mezei et al, ACS Earth and Space Chem. ,3 2376 (2019).
- [5] D. O. Kashinski et al, J. Chem. Phys. 146, 204109 (2017).
- [6] A. Abdoulanziz et al, J. Appl. Phys. 129, 053303 (2021).
- [7] A. Faure et al, MNRAS 469, 612 (2017).
- [8] M. D. Epée Epée et al, MNRAS 512, 424 (2022).

TWO-STATE REACTIVITY IN Fe-CATALYZED β -HYDROGEN ELIMINATION OF ETHYL CATION

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The efficiency of a spin-crossover reaction in β -hydrogen transfer between $\text{Fe}(\text{C}_2\text{H}_5)^+$ and $\text{HFe}(\text{C}_2\text{H}_4)^+$ has been studied [1].

The chemical reaction systems included transition metals have multiple low-lying electronic states with different spin multiplicities in general due to the nearly degenerate d -orbitals of the transition metals. The two-state reactivity with the relatively large spin-orbit couplings could induce the reduction of the reaction barrier along the lower potential energy surface (PES) between the nonrelativistic PESs with different spin multiplicities [2].

The triplet-quintet spin-crossover between $\text{Fe}(\text{C}_2\text{H}_5)^+$ and $\text{HFe}(\text{C}_2\text{H}_4)^+$ has been described by the intrinsic reaction coordinate (IRC) using the spin-coupled effective Hamiltonian model [3]. As shown in Fig. 1, the barrier height of the triplet state is much lower than that of the quintet state while the stable states of $\text{Fe}(\text{C}_2\text{H}_5)^+$ and $\text{HFe}(\text{C}_2\text{H}_4)^+$ are quintet state. The description indeed presents a phenomenon of the two-state reactivity.

The cumulative reaction probability for triplet and quintet states of the three-dimensional model has been obtained by nonadiabatic transition state wavepacket (TSWP) dynamics [4] in order to clarify the spin-transition mechanisms. Nonadiabatic transition occurs via ${}^5\text{FeC}_2\text{H}_5^+ \rightarrow {}^3\text{TS} \rightarrow {}^5\text{HFeC}_2\text{H}_4^+$ from the results of the cumulative reaction probability at an energy region which correspond to the one of lower triplet spin state around the TS. It has also been clarified that the one-dimensional cumulative reaction probability obtained by TSWP is significantly larger than the probability estimated by the single-passage Landau-Zener formula. This indicates the reaction probability is determined owing to the multiple spin-crossover repeatedly.

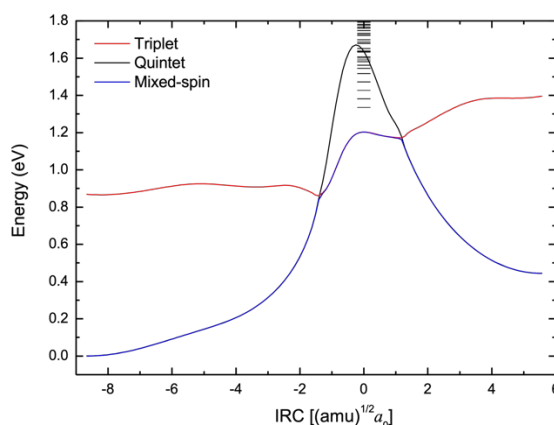


Fig. 1 The PESs along the IRC.

References

- [1] T. Murakami, T. Takayanagi, Triplet-quintet spin-crossover efficiency in β -hydrogen transfer between $\text{Fe}(\text{C}_2\text{H}_5)^+$ and $\text{HFe}(\text{C}_2\text{H}_4)^+$, *Comput. Theor. Chem.*, submitted.
- [2] V. D. Dergachev, *et al.*, NAST: Nonadiabatic Statistical Theory Package for Predicting Kinetics of Spin-Dependent Processes, *Topics Current Chem.*, **380**, 15 (2022)
- [3] T. Takayanagi, T. Nakatomi, Automated reaction path searches for spin-forbidden reactions, *J. Comput. Chem.*, **39**, 1319 (2018)
- [4] D.H. Zhang, J.C. Light, The cumulative reaction probability for the $\text{H}_2 + \text{OH}$ Reaction, *J. Chem. Phys.*, **106**, 551 (1997)

NON-ADIABATIC AND STEREODYNAMIC EFFECTS IN COLD COLLISIONS

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The prospect of probing chemical reactions in the extreme quantum limit has become a reality in recent years thanks to the rapid advancement in molecule cooling, trapping, and imaging technologies for quantum state-resolved product detection [1,2]. Ultracold molecules also offer exciting opportunities to explore electronically non-adiabatic effects in chemical reactions that are resolved at the single partial-wave level [3]. Stereodynamic control of inelastic rotational quenching in bimolecular collisions has also been demonstrated recently using the Stark-induced Adiabatic Raman Passage (SARP) technique where isolated resonances control the product angular distribution [4]. I will discuss recent progress in the theoretical treatment of the $\text{Li}+\text{CaF}\rightarrow\text{LiF}+\text{Ca}$ chemical reaction in the cold regime as well as non-adiabatic dynamics in the ultracold $\text{Li}+\text{LiNa}\rightarrow\text{Li}_2+\text{Na}$ reaction [3]. I will also discuss stereodynamic control of bimolecular collisions involving HD and D₂ prepared by the SARP techniques [4,5].

References

- [1] M.-G. Hu, Y. Liu, D. D. Grimes, Y.-W. Lin, A. H. Gheorghe, R. Vexiau, N. Bouloufa-Maafa, O. Dulieu, and K.-K. Ni, *Science* 366, 1111 (2019)
- [2] Y. Liu, M.-G. Hu, M. A. Nichols, D. Yang, D. Xie, H. Guo, and K.-K. Ni, *Nature* 593, 379 (2021)
- [3] B. K. Kendrick, H. Li, M. Li, S. Kotochigova, J. F. E. Croft, and N. Balakrishnan, *PCCP* 25, 5096 (2021)
- [4] H. Zhou, W. E. Perreault, N. Mukherjee, and R. N. Zare. *Science* 374, 960 (2021)
- [5] P. G. Jambrina, M. Morita, J. F. E. Croft, J. Avoiz, and N. Balakrishnan, *J. Phys. Chem. Lett.* 13, 4064 (2022)

BEYOND THE NORMAL MODE PICTURE: THE IMPORTANCE OF THE REACTANT'S INTRAMOLECULAR MODE COUPLING IN QUASICLASSICAL TRAJECTORY SIMULATIONS

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In quasiclassical trajectory simulations of bimolecular reactions of polyatomic molecules, the sets of initial coordinates and momenta of the colliding molecules generated by the widely used normal mode sampling (NMS) are generally nonstationary and evolve during the initial free flight of the reactants. In several isotopologues of the $\text{CH}_4 + \text{H}$ abstraction reaction, the calculated cross sections were found to oscillate as a function of the initial separation of reactants [1]. Adiabatic switching produces stationary ensembles of initial states, which was shown to yield unambiguous reaction probabilities and cross sections regardless of the choice of coordinate system used in the zeroth-order harmonic Hamiltonian [2]. Utilizing this method, we tested the importance of the temporal evolution of the initial states generated by NMS. The excitation functions calculated for four isotopologue reactions with the stationary initial conditions were well reproduced when the calculated oscillatory cross sections were averaged over an entire period of the oscillation (one-period averaging), but in extreme cases the cross sections were overestimated by up to 70 %. The largest deviation was observed for the DCH_3 on the Corchado–Bravo–Espinoza–García (CBE) [3] and for the HCD_3 isotopologue on the Zhang–Braams–Bowman No. 3 (ZBB3) [4] potential surface, respectively. Overall, one-period averaging provides a reasonably good correction to the non-stationarity of the initial states generated by normal-mode sampling, but its accuracy seems to vary currently unpredictably, and it is often sensitive to the choice of coordinates used for normal mode sampling. Therefore, it seems advisable to use the adiabatic switching method for the preparation of initial states in quasiclassical trajectory simulations.

References

- [1] T. Nagy, A. Vikár, and G. Lendvay, *J. Chem. Phys.* 144, 14104 (2016)
- [2] T. Nagy and G. Lendvay, *J. Phys. Chem. Letters* 8, 4621 (2017)
- [3] J. C. Corchado, J. L. Bravo, and J. Espinosa-García, *J. Chem. Phys.* 130, 184314 (2009)
- [4] X. Zhang, B.J. Braams, and J.M. Bowman, *J. Chem. Phys.* 124, 021104 (2006).

FORMATION OF SMALL MOLECULES IN INTERSTELLAR SPACE

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It is essential to know the roles of gas-phase and gas-grain processes for understanding the chemical evolution of the interstellar medium (ISM). In this work we investigate the formation of small molecules through radiative association. In radiative association two species collide and during the collision a photon is emitted, which carries away enough energy that the fragments become bound to each other. The emission of the photon is an improbable event giving small cross sections for molecule formation through radiative association. However, since the ISM is so dilute, energy loss by three-body collisions are even less likely. Thus, radiative association can still be an important process for forming new molecules, particularly in dust poor regions.

Successful experimental measurements of radiative association rate constants for small molecules are few due to the small cross sections. It is thus of interest to perform theoretical calculations to estimate these rate constants. Here we perform quantum dynamical calculations of cross sections and rate constants for the formation of CO [1,2], HCO [3], $(\text{NaH}_2)^+$ [4] and $(\text{AlH}_2)^+$ [5] through radiative association.

CO and HCO may be important species in the formation of complex organic molecules in space. It has for instance been proposed that a possible route for methanol formation could be to successively add H to CO [6]:



The formation of CO by radiative association was calculated both for forming ^{12}CO and ^{13}CO . Surprisingly large isotope effects were obtained, which will be mentioned and discussed.

The thermal rate constants that we calculate for the H + CO radiative association are so small that in a cold interstellar medium this cannot be the process in the first step of the sequence shown above leading to the formation of methanol.

I may also bring up radiative association between H_2 (D_2) and Na^+ or Al^+ to form $(\text{NaH}_2)^+$ or $(\text{AlH}_2)^+$ and the deuterated versions. For $(\text{AlH}_2)^+$ formation we find the rate constant to be 3-4 orders of magnitude larger than the previous calculation by Petrie & Dunbar, but still too small to matter in astrochemistry. The $(\text{NaH}_2)^+$ formation on the other hand is fast enough that it should be included in chemistry models of dense molecular clouds.

References

- [1] S. Antipov, M. Gustafsson and G. Nyman, MNRAS 430, 946 (2013).
- [2] M. Gustafsson and G. Nyman, MNRAS 448, 2562 (2015).
- [3] T. Stoecklin, P. Halvick, H-G. Yu, G. Nyman and Y. Ellinger, MNRAS 475, 2545 (2018).
- [4] D. Burdakova, G. Nyman and T. Stoecklin, MNRAS 485, 5874 (2019).
- [5] D. Burdakova, G. Nyman and T. Stoecklin, MNRAS 503, 3089 (2021).
- [6] A. Tielens and W. Hagen A&A 114, 245 (1982).
- [7] M. Zámečníková, P. Soldán, M. Gustafsson and G. Nyman, MNRAS 489, 2954 (2019).
- [8] M. Zámečníková, M. Gustafsson, G. Nyman and P. Soldán, MNRAS 492, 3794 (2020).

REACTION DYNAMICS ON AB INITIO POTENTIAL ENERGY SURFACES: F/Cl + C₂H₆ AND F⁻ + NH₂Cl/PH₂Cl REACTIONSDóra Papp and Gábor Czakó

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We develop full-dimensional analytical potential energy surfaces using the ROBOSURFER program package [1], which surfaces allow the accurate quasi-classical dynamical investigations of polyatomic reactive systems. We study the dynamics of the F/Cl + C₂H₆ → HF/HCl + C₂H₅ reactions [2,3] and obtain excellent agreement with experiments, this way solving a 25-year-old contradiction for the latter reaction regarding the rotational-state distribution of the HCl product [3]. Vibrational and rotational mode-specificity is also investigated for atom + ethane reactions [4,5,6]. We also study N- and P-centered ion + molecule reactions, namely the F⁻ + NH₂Cl/PH₂Cl systems, resulting in Cl⁻ + NH₂F/PH₂F (S_N2 path) and HF + NHCl⁻/PHCl⁻ (proton-transfer) products. We find that stereospecificity, taken for granted at C-centered S_N2-reactions, is undermined in the N-centered case due to the newly-discovered multi-inversion mechanism [7], whereas at P center it is somewhat restored [8].

References

- [1] T. Gyóri 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)
- [2] D. Papp, V. Tajti, T. Gyóri and G. Czakó, Theory finally agrees with experiment for the dynamics of the Cl + C₂H₆ reaction, *J. Phys. Chem. Lett.* 11, 4762 (2020)
- [3] D. Papp and G. Czakó, Full-dimensional MRCI-F12 potential energy surface and dynamics of the F(²P_{3/2}) + C₂H₆ → HF + C₂H₅ reaction, *J. Chem. Phys.* 153, 064305 (2020)
- [4] D. Papp, J. Li, H. Guo and G. Czakó, Vibrational mode-specificity in the dynamics of the Cl + C₂H₆ → HCl + C₂H₅ reaction, *J. Chem. Phys.* 155, 114303 (2021)
- [5] D. Papp and G. Czakó, Vibrational mode-specific dynamics of the F(²P_{3/2}) + C₂H₆ → HF + C₂H₅ reaction, *J. Chem. Phys.* 155, 154302 (2021)
- [6] D. Papp and G. Czakó, Rotational mode-specificity in the Cl + C₂H₆ → HCl + C₂H₅ reaction, *J. Phys. Chem. A* 126, 2551 (2022)
- [7] D. Papp and G. Czakó, Facilitated inversion complicates the stereodynamics of an S_N2 reaction at nitrogen center, *Chem. Sci.* 12, 5410 (2021)
- [8] A. Giricz, G. Czakó and D. Papp, manuscript in preparation (2022)

OPTIMISING MASTER EQUATION PARAMETERS WITH TRACE FITTING

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Although advances in theoretical chemical kinetics and the increase in computational power has made it possible to accurately predict rate coefficients in a truly ab initio fashion, most master equation calculations of gas-phase reactions contain parameters whose values are either estimated or fitted against experimental data. In particular, the value used for the collisional energy transfer parameter $\langle \Delta E \rangle_{\text{down}}$ is rarely based on ab initio calculations. To optimise master equation parameters against experimental data, what one has traditionally done is to adjust their values so as to minimise the difference between modelled and measured rate coefficients. This approach often works, but runs into trouble in at least two scenarios: a) when the kinetic behaviour of a system is complicated it may be difficult to extract rate coefficients from experimental traces and/or b) when the Bartis-Widom analysis that is used to extract rate coefficients from master equation simulations fails. To avoid these complications, Medeiros et al. [1] have introduced a procedure in which experimental traces are directly compared to those produced by a master equation model and the adjustable parameters are varied to minimise the difference between the two. This comparison is valid even when a traditional rate coefficient description of a system does not exist.

In the presentation we will illustrate how we have used experiments, computations, and trace fitting to investigate the reactions between allylic and propargylic radicals with oxygen molecules. A feature of these reactions is that the traditional "rate coefficient fit" is not applicable at higher temperatures ($T > 400$ K) and trace fitting is needed to perform a global fit that covers the studied temperature range. The results of the fits will be discussed. Specifically, we will show how the value of $\langle \Delta E \rangle_{\text{down}}$ changes when the structure of the radical is slightly changed or when the bath gas is changed from helium to nitrogen.

References

[1] D. J. Medeiros, S. H. Robertson, M. A. Blitz, P. W. Seakins, Direct Trace Fitting of Experimental Data Using the Master Equation: Testing Theory and Experiments on the OH + C₂H₄ Reaction, *J. Chem. Phys. A* 124, 20 (2020)

NON-ADIABATIC QUANTUM DYNAMICS OF THE ELECTRONIC QUENCHING $\text{OH}(\text{A}^2\Sigma^+) + \text{Kr}$

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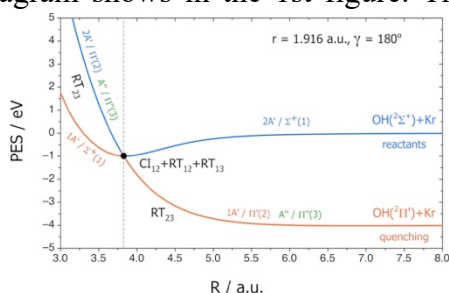
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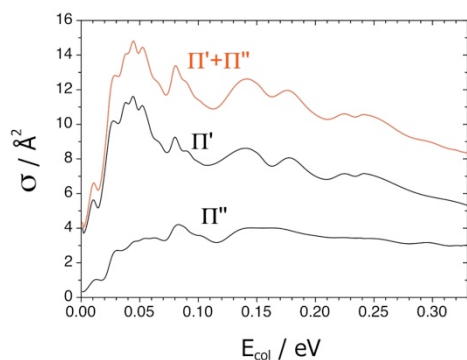
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We present the quantum dynamics of the title collision with OH^* in the ground rovibrational state, using three diabatic electronic states $\Sigma^+(1)$, $\Pi'(2)$, and $\Pi''(3)$, coupled by one Conical-Intersection (CI) and eight Renner-Teller (RT) matrix elements, as the correlation diagram shows in the 1st figure. The time-dependent mechanism and initial-state-resolved



quenching probabilities, integral cross sections, thermal rate constants, and thermally-averaged cross sections are calculated extending the real wave-packet (WP) method [1] to the rotation and to three coupled electronic states.

The global minimum of the $\Sigma^+(1)$ PES favours a Kr--OH collision towards the CI_{12} seam that opens the quenching. Also the smaller RT couplings are now effective and the ordering of the non-adiabatic interactions is $\text{CI}_{12} \gg \text{RT}_{23} > \text{RT}_{13} > \text{RT}_{12}$. Conical-Intersection and Renner-Teller



effects are non-addictive but in competition, as for other collisions and spectroscopy. This is due to the different geometries where these couplings are large and to the WP's motion through them. We find that CI couples and rules the dynamics, whereas RT's modulate & tune. As the cross sections show in the 2nd figure, the OH product is preferably formed in the $\Pi'(2)$ state but also $\Pi''(3)$ is well populated, in agreement with the experimental findings [2]. Because CI cannot open the $\Pi''(3)$ channel, which are only

open by RT, these latter couplings are absolutely necessary for reproducing the observed electronic distribution of the products. Finally, the quantum cross section and rate constant agree with those measured [2].

References

- [1] S. K. Gray and G. G. Balint-Kurti, *J. Chem. Phys.* 108, 950 (1988).
 [2] J. H. Lehman et al, *J. Phys. Chem. A* 117, 13481 (2013).

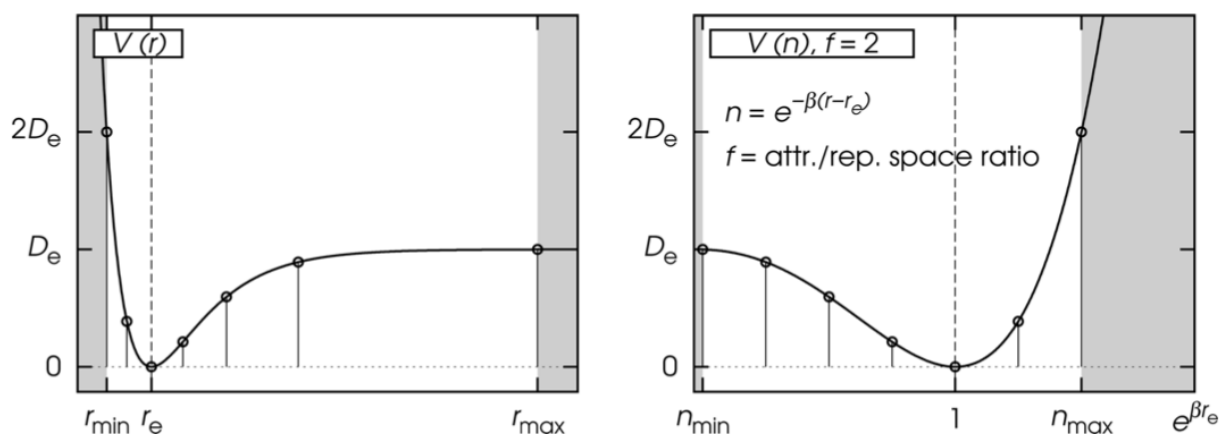
CONFIGURATION-SPACE SAMPLING IN POTENTIAL ENERGY SURFACE FITTING: A SPACE-REDUCED BOND-ORDER GRID APPROACH

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Potential energy surfaces (PESs) for use in dynamics calculations of few-atom reactive systems are commonly modeled as functional forms fitting or interpolating a set of electronic energies computed at many nuclear configurations. The very first step in quantum reactive scattering calculations is thus the choice of an appropriate set of nuclear configurations, i.e. molecular geometries, for which electronic energies are to be computed. In this contribution, an automated procedure for optimal configuration-space sampling in generating this set of energies will be described. The scheme is based on a space-reduced formulation of the so-called bond-order variables allowing for a balanced representation of the attractive and repulsive regions of a diatom configuration space [1,2]. Uniform grids based on space-reduced bond-order variables are proven to outperform those defined on the more conventional bond-length variables in converging the fitted/interpolated PES to the computed one with increasing number of grid points. Benchmark calculations are discussed for the prototype reaction $\text{H} + \text{H}_2$, using both a local-interpolation (modified Shepard) and a global-fitting (Aguado-Paniagua) scheme. Finally, the modeling of the dynamics of the astrochemical reaction $\text{C} + \text{CH}^+ \rightarrow \text{C}_2^+ + \text{H}$ all the way down from configuration-space sampling to the calculation of the thermal rate constant will be illustrated [3,4].



References

- [1] S. Rampino, *Chemistry at the Frontier with Physics and Computer Science: Theory and Computation*, Elsevier, Amsterdam, (2022)
- [2] S. Rampino, Configuration-space sampling in potential energy surface fitting: a space-reduced bond-order grid approach, *The Journal of Physical Chemistry A* 120, 4683-4692 (2016), DOI: [10.1021/acs.jpca.5b10018](https://doi.org/10.1021/acs.jpca.5b10018)
- [3] L. Pacifici, M. Pastore, E. Garcia, A. Laganà, S. Rampino, A dynamics investigation of the $\text{C} + \text{CH}^+ \rightarrow \text{C}_2^+ + \text{H}$ reaction on an ab initio bond-order like potential, *The Journal of Physical Chemistry A* 120, 5125-5135 (2016), DOI: [10.1021/acs.jpca.6b00564](https://doi.org/10.1021/acs.jpca.6b00564)
- [4] S. Rampino, M. Pastore, E. Garcia, L. Pacifici, A. Laganà, On the temperature dependence of the rate coefficient of formation of C_2^+ from $\text{C} + \text{CH}^+$, *Monthly Notices of the Royal Astronomical Society* 460, 2368-2375 (2016), DOI: [10.1093/mnras/stw1116](https://doi.org/10.1093/mnras/stw1116)

HITTING THE TRIFECTA: HOW TO SIMULTANEOUSLY PUSH THE LIMITS OF SCHRÖDINGER SOLUTION WITH RESPECT TO SYSTEM SIZE, CONVERGENCE ACCURACY, AND NUMBER OF COMPUTED STATES

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Methods for solving the Schrödinger equation have seen an explosive growth in recent years, as the importance of incorporating quantum effects in numerical simulations in order to obtain experimentally accurate data becomes increasingly recognized. In practical terms, there are just three primary factors that currently limit what can be achieved. These are: (a) SYSTEM SIZE, i.e., the number of degrees of freedom that can be treated explicitly quantum mechanically; (b) NUMERICAL ACCURACY, measured in terms of convergence with respect to ALL POSSIBLE computational parameters such as basis sizes; (c) ENERGY EXCITATION or the total number of accurately computed states. Broadly speaking, current methods can deliver on any two of these goals, but achieving all three at once remains an enormous challenge.

In this presentation, we shall describe just such a method, and demonstrate how it can be used to “hit the trifecta” in the context of molecular vibrational spectroscopy calculations [1]. In particular, we compute thousands of vibrational states for the 12D acetonitrile molecule (CH₃CN), to a target numerical convergence of a few 10⁻² cm⁻¹ or better. In other words, we compute ALL vibrational states for this six-atom system in full quantum dimensionality, and throughout the entire dynamically relevant spectral range, to near spectroscopic accuracy. To our knowledge, no such vibrational spectroscopy calculation has ever previously been performed—although given the generality of the method, we anticipate there will be many more such calculations to follow.

References

[1] J. Sarka and B. Poirier, “Hitting the Trifecta: How to Simultaneously Push the Limits of Schrödinger Solution with Respect to System Size, Convergence Accuracy, and Number of Computed States”, *J. Chem. Theory Comput.* **17**, 7732-7744 (2021).

GETTING CO₂ TO REACT ISN'T EASY: HITTING IT HARD WITH ATOMIC OXYGEN OR WITH HOT ELECTRONS

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Getting CO₂ to react isn't easy. In this work we discuss two approaches to doing this that involve high energy processes, and we use computational chemistry methods to reveal what are the possible mechanisms.

In our first study we consider CO₂ in the gas phase, and we collide the molecule with either atomic oxygen or argon. Here the calculations are done using "direct dynamics" in which trajectories are propagated on the ground state Born-Oppenheimer potential energy surface, with CO₂ initially in its zero point state (quasiclassical method) with zero temperature rotations. What we see is consistent with a modest barrier for oxygen exchange (about 0.86 eV) leading to a relatively large cross section (several atomic units). In addition, we have calculated cross sections for oxygen abstraction and insertion-elimination in which O' + CO₂ gives CO + OO', and O₂ + CO', respectively. These reactions have a higher barrier (2.48 eV and 3.52 eV, respectively) and the cross sections are down by a factor of 10 from the exchange cross section even at energies well above the barrier.

The BOMD calculations used to generate these cross sections for O + CO₂ are concerned with dynamics on the lowest triplet potential surface (the ground state of the reactants) and therefore do not account for intersystem crossing (ISC). In an effort to investigate the effect of nonadiabatic processes involving the singlet and quintet surfaces, we performed QCT calculations that include trajectory surface-hopping (TSH) at collision energies of 7.5 and 9.5 eV. These show that the overall exchange cross section is small, however hopping in combination with abstraction or dissociation has a high enough probability such that the total cross sections for abstraction change (decrease) by as much as 20% compared to the BOMD results, and the cross sections for dissociation, which are very small, change (increase) by factors of four or more.

Another way to make CO₂ react is by adding or subtracting electrons, as a result of photoexcitation when the CO₂ is in contact with a gold nanocluster (or nanoparticle). This process is especially efficient when the gold cluster is excited at a wavelength where plasmon excitation can occur, leading to what is called plasmon-driven chemistry. Recently a new opportunity has arisen for describing this that is described based on the DFTB+ electronic structure model. We have used this method to describe both spectra and reactions involving tetrahedral clusters with 20, 56 and 120 atoms. The spectra show results that are in excellent agreement with results obtained long ago using a conventional TDDFT calculations, but the present calculations are done in minutes rather than days. RT-TDDFT calculations with this method show that dissociation is induced by transfer of charge to the CO₂ while the pulse is on. This temporarily excites the CO₂ to repulsive states, providing a detailed model for the plasmon-driven process that we plan to use more generally to study many plasmon-driven chemical reactions in future studies.

PADÉ_II, ICS_REGGE, AND DCS_REGGE: COMPUTER PROGRAMS WHICH MAY HELP TO LEARN MORE ABOUT WHAT HAPPENS IN A CHEMICAL REACTION

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Theoretical study of a chemical reaction involves three necessary steps. First, one constructs a good potential surface, then he or she solves the Schrödinger equation and, last but not least, intends to interpret and understand the numerical results thus obtained. The interpretation can be done in many ways. There are various semiclassical methods [1]. Time delay techniques could help one identify capture into long-lived intermediate states [2]. Perhaps, the most general, and in any case complimentary to the above, is the complex angular momentum (CAM) approach [3]-[5]. The theory seeks to relate the observable effects to the (Regge) poles of the scattering matrix in the CAM plane. Although less well known than their complex energy counterparts, Regge poles often prove to be the most useful ones. Both integral (ICS) and differential (DCS) cross sections involve summations over partial waves at a fixed energy. They are, therefore, amenable to an analysis in terms of the singularities of the summand, i.e., in terms of the poles in the complex plane of the total angular momentum.

Over the last ten years we have prepared a suite of computer codes for CAM analysis of numerical scattering data, [6]-[8], which are the main topic of our presentation. The first of the three codes, **PADÉ_II** [6], finds the Regge poles of a numerical S-matrix element, evaluated at the physical (integer) values of the total angular momentum. The second code, **ICS_REGGE** [7], uses this information for the analysis of a state-to-state reactive ICS. The third, and the most recent, program, **DCS_REGGE** [8] applies the analysis to reactive angular distributions. We will discuss the purpose of these programs, and illustrate their use on several examples.

References:

- [1] C Xiahou and J. N. L. Connor, Glories, hidden rainbows and nearside-farside interference effects in the angular scattering of the state-to-state $H + HD \rightarrow H_2 + D$ reaction, *Phys. Chem. Chem. Phys.* 23, 13349 (2021)
- [2] S. Cavalli and D. De Fazio, The time-delay route to reactive scattering resonances: The case of the $F+H_2 \rightarrow HF + H$ reaction, *Phys. Scripta* 76, C21 (2007)
- [3] J.N.L. Connor, New theoretical methods for molecular collisions: The complex angular momentum approach, *J. Chem. Soc. Faraday Trans.* 86, 1627 (1990)
- [4] D. Sokolovski, and A. Msezane, Semiclassical complex angular momentum theory and Padé reconstruction for resonances, rainbows, and reaction thresholds, *Phys.Rev.A* 70, 032710 (2004)
- [5] J.N.L. Connor, Resonance Regge poles and the state-to-state $F + H_2$ reaction: QP

- decomposition, parametrized S matrix, and semiclassical complex angular momentum analysis of the angular scattering, *J.Chem.Phys.* 138, 124310 (2013)
- [6] D. Sokolovski, E. Akhmatskaya and S.K. Sen, Extracting *S*-matrix poles for resonances from numerical scattering data: Type-II Padé reconstruction, *Comp. Phys. Comp.* 182, 448 (2011)
- [7] E. Akhmatskaya and D. Sokolovski, Numerical Regge pole analysis of resonance structures in elastic, inelastic and reactive state-to-state integral cross sections, *Comp. Phys. Comm.* 185, 2127 (2014)
- [8] E. Akhmatskaya and D. Sokolovski, Numerical Regge pole analysis of resonance structures in state-to-state reactive differential cross sections, *Comp. Phys. Comm.* 277, 108370 (2022)

POLYATOMIC RADIATIVE ASSOCIATION BY QUASICLASSICAL TRAJECTORY CALCULATIONS

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Radiative association (RA) is one of many important processes that contribute to molecule production in dust-poor regions of interstellar space. The description of the scattering process in the presence of a radiation field is challenging. Owing to the elaborate quantum mechanical treatment, most of the previous dynamical calculations have focused either merely on diatomic molecule formation or on a few triatomic systems. Since the quantum dynamics methods are not feasible for larger polyatomic molecules, we have developed two trajectory-based methods in order to characterize the dynamics and kinetics of polyatomic molecule formation through radiative association. One is for RA in absence of electronic transitions based on the classical Larmor theory of radiation, and another for the calculation of RA through electronic transitions based on the semiclassical surface-hopping formalism. Both methods can provide a practical but still efficient solution to obtain quantum state resolved RA cross sections or rate constants for arbitrary polyatomic systems. Furthermore, our methods are not only applicable for the description of RA but they can be used for the semiclassical characterization of any molecular process where either spontaneous or stimulated emission occurs.

**SIMULATING THE ROVIBRATIONAL POLARITONS OF H₂O IN
INFRARED MICROCAVITIES**

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The confinement of molecules into microscale optical or plasmonic cavities can lead to the formation of hybrid light-matter states, called polaritons, which offer a unique way to design and control chemical processes at the molecular level [1]. Recent experiments show that the formation of vibrational polaritons in microfluidic infrared (IR) cavities can modify the kinetics and thermodynamics of thermally activated chemical reactions [2], however, the theoretical understanding of such processes is lacking so far. Most simulation methods are either far from having predictive power [3,4], or are limited in terms of available molecular models [5,6]. In my presentation I will talk about some recent theoretical progress in combining the efficient theoretical tools available in high-resolution theoretical molecular spectroscopy and quantum chemistry with those in quantum optics to obtain efficient and accurate numerical protocols to simulate the (ro)vibrational polaritons of molecules in IR microcavities [7]. Numerical results are presented for H₂O.

References

- [1] T. W. Ebbesen, *Acc. Chem. Res.* 49, 2403 (2016).
- [2] K. Hirai, J. A. Hutchison, and H. Uji-I, *ChemPlusChem* 85, 1981 (2020).
- [3] J. A. Campos-Gonzalez-Angulo, and J. Yuen-Zhou *J. Chem. Phys.* 152, 161101 (2020).
- [4] X. Li, A. Mandal, P. Huo, *Nat. Commun.* 12, 1315 (2021).
- [5] F. J. Hernández and F. Herrera, *J. Chem. Phys.* 151, 144116 (2019).
- [6] F. Pavošević, S. Hammes-Schiffer, A. Rubio, and J. Flick, *arXiv:2112.02138* (2021).
- [7] T. Szidarovszky, P. Badankó, G. J. Halász and Á. Vibók *J. Chem. Phys.* 154, 064305 (2021).

DYNAMICS OF THE $\text{OH}^- + \text{CH}_3\text{F}$ REACTION: THE OXIDE ION SUBSTITUTION

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In chemistry one of the well-known reactions is the bimolecular nucleophilic substitution ($\text{S}_{\text{N}}2$). Moving beyond the prototypical $\text{X}^- + \text{CH}_3\text{Y} \rightarrow \text{Y}^- + \text{CH}_3\text{X}$ ($\text{Y}, \text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$) $\text{S}_{\text{N}}2$ reactions, the most studied seven-atomic reactions are the $\text{OH}^- + \text{CH}_3\text{Y} \rightarrow \text{Y}^- + \text{CH}_3\text{OH}$. [1] In 2002, Hase and co-workers examined the $\text{OH}^- + \text{CH}_3\text{F}$ reaction using direct dynamics simulations. [2] The 64 trajectories initiating from the $[\text{HO}\cdots\text{CH}_3\cdots\text{F}]^-$ barrier revealed that the H-bonded $\text{CH}_3\text{OH}\cdots\text{F}^-$ global minimum of the potential energy surface is avoided, and instead the F^- leaves directly along the $\text{O}-\text{C}\cdots\text{F}^-$ axis.

After nearly 20 years, we investigated the rule of the deep minimum on the $\text{OH}^- + \text{CH}_3\text{F}$ reaction by considering almost 1 million full-length quasi-classical trajectories at several collision energies. [3] To implement this high-level dynamical characterization, a global full-dimensional *ab initio* potential energy surface is developed [3] utilizing the in-house ROBOSURFER [4] program package. Our simulations uncovered a novel exothermic reaction pathway leading to the $\text{HF} + \text{CH}_3\text{O}^-$ products. In the presentation, it will be discussed that how this so-called oxide ion substitution takes place and how competitive it is with the other reaction channels.

References

- [1] R. Wester, Fifty years of nucleophilic substitution in the gas phase, *Mass Spec Rev.* 41, 627–644 (2022)
- [2] L. Sun, K. Song and W. L. Hase, A $\text{S}_{\text{N}}2$ reaction that avoids its deep potential energy minimum, *Science* 296, 875–878 (2002)
- [3] D. A. Tasi and G. Czakó, Uncovering an oxide ion substitution for the $\text{OH}^- + \text{CH}_3\text{F}$ reaction, *Chem. Sci.* 12, 14369–14375 (2021)
- [4] T. Györi and G. Czakó, Automating the development of high-dimensional reactive potential energy surfaces with the ROBOSURFER program system, *J. Chem. Theory Comput.* 16, 51–66 (2020)

ELECTRON INITIATED CHEMISTRY

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Electron collisions are a major initiator of chemical processes. In natural environments this can be found at the top of the atmosphere, in radiation damage to living species or in the interstellar medium. In technology, spark plugs and many lasers rely on electron collision as do the plasma chemistries which are increasingly driving many modern industrial processes. Electrons initiate chemistries by breaking up species via dissociative attachment / recombination or electron impact dissociation as well via creating excited (metastable) and hence reactive states of a molecule. There is therefore great demand for reliable electron – molecule collision cross sections. For a variety of reasons this demand has to largely met by theory [1].

The R-matrix method provides a robust method of calculating electron collision cross sections for a whole range of species including molecular ions and radicals [2]. The latest version of the code, UKRmol+ [3], allows for the treatment both large targets and diffuse electronic states. UKRmol+ has been made generally accessible via the Quantemol electron collisions (QEC) expert system [4].

Examples of such calculations will be presented at the meeting.

References

- [1] K. Bartschat, M.J. Kushner, Electron collisions with atoms, ions, molecules, and surfaces: Fundamental science empowering advances in technology, *Proc. Nat. Acad. Sci.*, **113**, 7026 (2016)
- [2] J. Tennyson, Electron - molecule collision calculations using the R-matrix method, *Phys. Rep.*, **491**, 29-76 (2010)
- [3] Z. Masin, J. Benda, J.D. Gorfinkiel, A.G. Harvey, J. Tennyson, UKRmol+: a suite for modelling of electronic processes in molecules interacting with electrons, positrons and photons using the R-matrix method, *Computer Phys. Comms.*, **249**, 107092 (2020).
- [4] B. Cooper et al., Quantemol Electron Collision: an expert system for performing UKRmol+ electron molecule collision calculations, *Atoms*, **74**, 97 (2019).

ENERGY TRANSFER AND ROTATIONAL RAINBOW OF FORMALDEHYDE SCATTERED FROM SURFACES

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Inelastic scattering between gas molecules and surface is a fundamental process that has been investigated extensively. During this process, energy exchange between the gas and the surface happens, resulting in changes in the internal and translational degrees of freedom of the gas molecules. The energy transfer between the gas and surface is closely linked to residence time of the gas molecules on the surface. However, the mechanism of energy transfer between the molecule and surface is quite complicated and still not well understood. In recent gas-surface scattering experiments,¹ axis-specific rotational excitation of formaldehyde upon scattering on the gold surface was observed. Their results indicate a high propensity to excite *a*-axis rotation (twirling motion about C-O bond axis), rather than the *b*-axis (C-O tumbling motion) or *c*-axis (cartwheeling motion) rotations, for the scattered formaldehyde molecules.

In the work presented here, we used classical dynamics simulation to understand energy transfer in formaldehyde-surface collisions, to probe the mechanism of interconversion of translational energy to rotational energy. We investigated two systems, formaldehyde scattering from Au(111) surface^{1,2,3} and formaldehyde scattering from graphene surface⁴. Our simulations capture the trend of the experiments for the formaldehyde-Au scattering, both in terms of rotational energy distribution, as well as trapping probabilities. However, for the formaldehyde-graphene inelastic scattering, the preferential axis-excitation was found to depend on the collision energies.

References

- [1] G. Barratt Park et al. *An axis-specific rotational rainbow in the direct scatter of formaldehyde from Au(111) and its influence on trapping probability*, Phys. Chem. Chem. Phys. 19, 19904 (2017).
- [2] X. Zhang et al. *A Global ab Initio Potential Energy Surface for Formaldehyde*, J. Phys. Chem. A. 108, 8980 (2004).
- [3] A P Sutton and J Chen. *Long-range finnis–sinclair potentials*, Philos. Mag. 61, 139 (1990).
- [4] L. S. Dodda and Upakarasamy Lourderaj. *Modeling the formaldehyde–graphene interaction using a formaldehyde–pyrene system*, Phys. Chem. Chem. Phys. 15, 17479 (2013).

FROM MOLECULAR SHAPES TO REACTION DYNAMICS

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No problem has an exact solution in Physics and Chemistry. The most notable approximation is due to Born and Oppenheimer (BO). Despite significant work to go beyond, the BO approximation lies at the heart of the molecular shape concept, and is the main route for studying reaction dynamics. After recalling briefly the BO approximation, we show how to explain molecular linearity and planarity without calculations on the molecules themselves. We then turn to global potential energy surfaces and their use in spectroscopy and reaction dynamics, in all cases addressing recent or ongoing work.

POTENTIAL ENERGY SURFACE DEVELOPMENTS AND DYNAMICS FOR THE REACTIONS OF C₂H₅ WITH HBR AND HI

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How chemical reactions proceed step by step at the atomic level is one of the central questions in chemistry. Following our previous work on the $F + C_2H_6 \rightarrow HF + C_2H_5$ [1] and $Cl + C_2H_6 \rightarrow HCl + C_2H_5$ [2] systems, here we report accurate dynamics simulations for the reactions of $HBr + C_2H_5 \rightarrow Br + C_2H_6$ and $HI + C_2H_5 \rightarrow I + C_2H_6$ using full-dimensional spin-orbit-corrected analytical potential energy surfaces (PESs). Using ROBOSURFER [3] with the ManyHF-based [4] UCCSD(T)-F12a/cc-pVDZ-F12(-PP) *ab initio* method, we fitted the energy points through the permutationally-invariant monomial symmetrization approach [5]. The spin-orbit coupling at the level of MRCI-F12+Q(5,3)/cc-pVDZ-F12(-PP) is taken into account. The energies on the PES are compared to the relativistic all-electron CCSDT(Q)/complete-basis-set-quality benchmark relative energies [6] of the stationary points. Our simulations show very alike behavior for these two reactions. No significant collision energy dependence of the reaction probabilities and cross sections is found in the range of 5-40 kcal/mol in both reactions. When the collision is 1 kcal/mol, however, the reaction probability is much lower, unlike a similar but smaller case: $HBr + CH_3$ [7]. Our simulations also revealed that these two reactions preferred H-side attack, side-on CH_3CH_2 attack, and forward scattering. The post-reaction distributions of energy are also analyzed.

References

- [1] 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)
- [2] 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)
- [3] 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)
- [4] 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)
- [5] Z. Xie and J. M. Bowman, Permutationally invariant polynomial basis for molecular energy surface fitting via monomial symmetrization, *J. Chem. Theory Comput.* 6, 26 (2010)
- [6] 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)
- [7] D. Gao, X. Xin, D. Wang, P. Szabó, and G. Lendvay, Theoretical dynamics studies of the $CH_3 + HBr \rightarrow CH_4 + Br$ reaction: integral cross sections, rate constants and microscopic mechanism, *Phys. Chem. Chem. Phys.* 24, 10548 (2022)

UNRAVELING THE CRUCIAL ROLE OF SPIN-ORBIT COUPLINGS IN THE REACTIVE COLLISION $S^+ + H_2$

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SH^+ is a widespread molecular ion in diffuse interstellar clouds, and has also been detected in emission toward the Orion Bar photodissociation region (PDR). In warm and dense PDRs, SH^+ is thought to form by exothermic reactions of S^+ with vibrationally excited H_2 ($v>1$). The viability of this hypothesis have been confirmed by theoretical simulations reaction which demonstrate that for vibrational level $v=2$ or higher of H_2 , the reaction exhibit high rate constants.

From an experimental point of view, scarce data are available. As the reaction of the ground state ion is endothermic by almost 1 eV, the SH^+ product is observed only at high collision energies where translational energy brings the needed energy to reach products, as predicted by the theoretical simulations. Interestingly, it appears from this experimental study that spin-orbit couplings may play a significant role on the reaction, motivating a new theoretical study of the reaction, now including the spin-orbit interactions.

Calculations show that spin-orbit interaction does indeed play an important role in this reaction, and that for energies below the threshold of formation of SH^+ , long lived H_2S^+ complex may form, opening the possibility of a radiative association. To check this hypothesis, a new series of experiments were performed using the CERISE setup at synchrotron SOLEIL.