XIV International Workshop on Quantum Reactive Scattering

Trieste, Italy

3-6 July 2017
International Workshop On Quantum Reactive Scattering

Università degli Studi di Trieste
Trieste, Italy
3-6 July 2017
# Table of Contents

**Lectures:**

Tunnelling in water clusters from instanton and path-integral simulations  
Stuart C. Althorpe  
9

Elucidating the reaction mechanism through the $\Lambda$ doublet ratio  
F. J. Aoiz*, P. G. Jambrina**, A. Zanchet*, M. Menéndez*  
10

Mixed quantum/classical Theory for rotationally and vibrationally inelastic scattering  
D. Babikov  
11

Semiclassical treatment of polyatomic reaction dynamics  
L. Bonnet  
12

Computational approaches to molecular Science  
Joel M. Bowman (Keynote Talk)  
13

Deformed transition-state theory: deviation from Arrehenius behavior and application to chemical reactions within the moderate tunneling regime  
14

Quantum and semiclassical methods for molecular rate constants and vibrational spectra calculations  
M. Ceotto, C. Aieta, R. Conte, G. Di Liberto, F. Gabas  
15

Long range potential effects on the reactive and inelastic scattering in OH+H2 collisions: a quantum-classical study  
C. Martí*, L. Pacifici*, A. Laganà*, C. Coletti  
16

How to derive a physically meaningful analytic S matrix from numerical S matrix data  
J. N. L. Connor  
17

Calculation of tunneling splittings in polyatomic molecules and clusters using instanton theory  
M. T. Cvitaš  
18
Dynamics and novel mechanisms of SN2 reactions on ab initio analytical potential energy surfaces
G. Czakó

Benchmarking chemical reactivity in the deep tunneling regime: the ultra-cold behavior of the F+H2 reactive system and its isotopic variants
D. De Fazio*, V. Aquilanti*,**, S. Cavalli°

Efficient ways to build potential energy operators
Terry J. Frankcombe

Interferences between reaction mechanisms unravelled using a quantum analogue to the classical deflection function
P. García Jambrina*, M. Menéndez**, and F. J. Aoiz**

Quantum coherent control of the properties of a resonance state
A. García-Vela

Dynamics of reactive collisions in the interstellar medium
T. González-Lezana

Generation of accurate multi-dimensional potential energy surfaces of polyatomic molecular clusters and applications
M. Hochlaf

Isotope and symmetry effects in collisions involving ozone as intermediate
P. Honvault, G. Guillon

Quantum dynamics of H2 in a carbon nanotube: timescale separation and resonance enhanced tunneling

Investigation of non-adiabatic effects for a triatomic molecule: The use of a single potential energy surface with distance-dependent reduced masses for H3+
R. Jaquet, M. Khoma

Photodissociation reaction of SO2 and bound states on new ab initio potentials
Dynamics of the S(1D)+o-D2 →SD+D reaction at low collision energies: revisiting the sh2 system


Dynamics of complex-forming bimolecular reactions

P. Szabó*, S. Góger* and G. Lendvay*,**

Methanol dimer formation drastically enhances hydrogen abstraction from methanol by OH at low temperature

W. Siebrand*, Z. Smedarchina*, E. Martínez-Núñez, A Fernández-Ramos

Rmatreact: developing novel theoretical methodology to investigate ultra-cold atom-molecule collisions over deep potential wells

L. K. McKemmish*, T. Rivlin, J. Tennyson

The role of tunneling on the diffusion rate of H2 and D2 along a narrow swcn

M. Mondelo-Martell, F. Huarte-Larrañaga

State-to-state chemistry and quantum dynamics of the ultracold K +KBR reaction

J. F. E. Croft*, C. Makrides†, M. Li†, A. Petrov†, S. Kotochigova†, B. K. Kendrick‡, and B. Naduvalath*

Semiclassical quantization of rovibrational states of methane by adiabatic switching

T. Nagy and G. Lendvay

Nonadiabatic effects in quantum reactive collisions

P. Gamallo*, S. Akpinar**, P. Defazio°, and C. Petrongolo†

Reactive collisions at the cold temperatures of interstellar clouds: H2CO+OH example

O. Roncero

Full- and reduced-dimensionality semiclassical transition state theory: application to various chemical reactions

X. Shan (*) and David C. Clary

A diabatic electronic state system to describe the internal conversion of azulene

D. Skouteris
Regge poles as a practical tool: towards software for analysing resonance effects in reactive angular distribution
D. Sokolovski*,**, E. Akhmatskaya**,°, and D. De Fazio† 41

Non-statistical behaviors in gas phase uni- and bimolecular reactions. The role of chemical dynamics simulations
R. Spezia 42

Vibrational sympathetic cooling of BaCl+ by Ca atoms: theoretical study

Frequency-domain and time-domain transition state spectroscopy of cyclooctatetraene
T. Takayanagi 44

From a cost-effective wave function-based approach in electronic structure to accurate quantum dynamics
A. J. C. Varandas 45

Methyl cyanoformate decomposition: formation of HCN and HNC via concerted three-body dissociations
Saulo A. Vázquez 46

Ultra-fast electronic decoherence caused by nuclear motion and a possible path to attochemistry
R. Welsch*, C. Arnold*,**,° O. Vendrell1°,†, R. Santra1**,° 47

Posters
Rg–NO+ (X1Σ+) Van der Waals complexes: dynamics and bound state calculations
C. Orek*, J. Kłos**, F. Lique° and N. Bulut* 48

Quantum molecular dynamics for multidimensional systems by the basis expansion leaping multi-configuration gaussian (bel mcg)
T. Murakami*, T. J. Frankcombe 49

Programme 50
List of Participants: 51
TUNNELLING IN WATER CLUSTERS FROM INSTANTON AND PATH-INTEGRAL SIMULATIONS

Stuart C. Althorpe

The instanton [1] has played an important role in reaction rate-theory and in the closely related theory of tunnelling splitting. Here we present recent applications of instanton theory to analyse experimental measurements of tunnelling spectra in water clusters. [2] The talk will give a summary of instanton theory, explaining that instantons correspond to stationary points in the imaginary-time path-integral used to represent the quantum Boltzmann operator. We will show how instantons can be efficiently located using ring-polymer approaches to path-integration. We also present new methodology and results in which we attempt to correct for the approximations made by instanton theory in order to obtain numerically accurate quantum tunnelling splittings in water clusters.

ELUCIDATING THE REACTION MECHANISM THROUGH THE $\Lambda$ DOUBLET RATIO

F. J. Aoiz*, P. G. Jambrina**, A. Zanchet**, M. Menéndez*

*Dpto. Química Física, Universidad Complutense, Madrid, Spain
**Dpto. Química Física Aplicada, Universidad Autónoma de Madrid, Madrid, Spain
°Instituto de Física Fundamental CSIC, Madrid, Spain

In the last decade, the development of theoretical methods has allowed chemists to reproduce and explain almost all of the experimental data associated with elementary atom plus diatom collisions. However, there are still a few examples where theory cannot account yet for experimental results. This is the case for the preferential population of one of the $\Lambda$-doublet states produced by chemical reactions. It has been longer assumed that the ratio between the $\Lambda$-doublet levels $\Pi(A')$ and $\Pi(A'')$ should be directly related to the cross sections whenever there are two concurrent potential energy surfaces (PESs) of $A'$ and $A''$ symmetries. For the O($^3P$) + D$_2$ reaction, where both PESs have the same barrier and the $A''$ displays a broader “cone of acceptance”, it can be therefore expected that $\Pi(A'')$ levels would be more populated. However, recent experiments carried out by Minton and coworkers [1, 2] has challenged theoreticians by showing a strong propensity towards the $\Pi(A')$ regardless of the collision energy and final rovibrational states considered. Here, we will present a rigorous method to calculate the $\Lambda$-doublet populations from the cross sections on the $A'$ and $A''$ PES. The results obtained are in very good agreement with the experiment and show how the $\Lambda$-doublet populations are strongly influenced by the alignment of the product’s internuclear axis onto the recoil direction [3].

Our calculations have also been extended to other reactions and various collision energies. In particular, for the O($^3P$) + H$_2$ reaction it has been found interesting propensity in the tunnelling region where no classical reactivity takes place. The analysis of the purely quantum results via the lambda doublet populations allows one to elucidate the mechanisms at low collision energies for which QCT method cannot be used.

In addition, calculations for the O($^3P$) + HCl reaction in which also two PESs participate predict that the $\Lambda$-doublet ratio is close to 1 even though the $A''$ PES is far more reactive than the $A'$ PES, thus implying an important transfer of reactivity from the $A''$ PES to the $\Pi(A')$ level which can be traced back to the stereodynamics and hence of the reaction mechanism.

References
We developed a mixed quantum/classical theory (MQCT) for inelastic scattering where translational motion of collision partners is treated classically, while the internal degrees of freedom – rotational and/or vibrational motion – are treated quantum mechanically. Within this framework, we carried out calculations of rotationally inelastic cross sections in a broad range of collisional energies and compared results against the exact full quantum results for several real systems. For Na + N$_2$ and H$_2$ + N$_2$ the agreement is excellent through six orders of magnitude range of cross sections values and in a broad range of collision energies, even near excitation thresholds. Differential cross sections for Na + N$_2$ are also accurately reproduced, including quantum oscillations. For He + H$_2$, which is the lightest possible system and the most stringent test of our theory, we also observed very good agreement with exact quantum results in a broad range of collisional energies, $1 < E < 10000$ cm$^{-1}$, including the case of high rotational excitation, $j = 22$. Calculations of ro-vibrational quenching in CO(v=1) + He show similar features. For H$_2$O + He, one of the most important systems in astrochemistry, we found that at lower energies the typical errors for cross sections are on the order of 10%, which is acceptable. At higher collision energies our MQCT method always produces very accurate results (1-2%) and remains computationally affordable. We found that computational cost of the fully-coupled MQCT scales as $n^{2.3}$, where $n$ is the number of channels, which is more favorable than the full-quantum inelastic scattering calculations. This allows carrying out calculations on larger molecules and at higher collision energies, than was possible using the standard approach. For example, we carried out MQCT calculations for rotational excitation of methyl formate, HCOOCH$_3$ + He, a process important for interpretation of astrochemical observations. At energies near $E = 30$ cm$^{-1}$, where quantum calculations are affordable, the agreement is very good (5% difference). It is important that even for this heavy molecule MQCT remains computationally affordable at higher energies, up to $E = 1000$ cm$^{-1}$. Recently, using MQCT, we carried out the first ever calculations of rotational excitation in H$_2$O + H$_2$O (another process important in space, e.g., in cometary comas) collided with energies in the range $500 < E < 10,000$ cm$^{-1}$.

References

SEMICONDUCTIVE TREATMENT OF POLYATOMIC REACTION DYNAMICS

L. Bonnet

CNRS, Univ. Bordeaux, Institut des Sciences Moléculaires, UMR 5255, F-33400, Talence

It is shown that full dimensional classical trajectory calculations in a quantum spirit on a good quality potential energy surface allow the efficient simulation of experimental imaging results for polyatomic reactions. Two types of processes are considered: (i) the photofragmentation of the tetratomic molecule HNCO in the S1 state and (ii) the seven-atom reaction OH+CH4 and isotopic variants.

References


COMPUTATIONAL APPROACHES TO MOLECULAR SCIENCE
Joel M. Bowman (Keynote Talk)

Dept of Chemistry, Emory University, Atlanta, GA 30322 USA

The theoretical principles that govern the energetics and dynamics of molecules, molecular clusters, liquids, etc. are based in quantum mechanics, and so well-known. However, the computational implementation of these principles is highly demanding, owing to the “curse of dimensionality”. Nevertheless, much progress has been made, thanks to advances in computational hardware and software, and perhaps most importantly, the careful crafting of models. I will attempt to illustrate all of this in my talk, with a particular emphasis on chemical reaction dynamics and spectroscopy and the development of approaches to obtain precise representations of the Born-Oppenheimer potential energy surface that underlies the computational approach to Molecular Science.
DEFORMED TRANSITION-STATE THEORY: DEVIATION FROM ARRHENIUS BEHAVIOR AND APPLICATION TO CHEMICAL REACTIONS WITHIN THE MODERATE TUNNELING REGIME


*Grupo de Química Teórica e Estrutural de Anápolis. Unidade Campus de Ciências Exatas e Tecnológicas, Universidade Estadual de Goiás, 75001-970, Anápolis, Brazil. fatiolog@gmail.com.
**Dipartimento di Chimica, Biologia e Biotecnologie, Università di Perugia, Via Elce di Sotto 8, 06123, Perugia, Italy.
°Laboratório de Estrutura Eletrônica e Dinâmica Molecular. Instituto de Química, Universidade de Brasília, 70904-970, Brasília, Brazil.

In this talk, we formulate a phenomenological tool based on quantum chemistry and transition-state theory to cover cases where reaction kinetic rates deviate from Arrhenius law at low temperatures [1]. A parameter is introduced to describe the deviation for the systems from reaching the thermodynamic limit and is identified as the linearizing coefficient in the dependence of the inverse activation energy against the reciprocal temperature. Its physical meaning is given and is calculated explicitly when deviation comes from quantum tunneling. Here, a new derivation is given to previously established relationship of the parameter with features of the barrier in the potential energy surface. The application of deformed Transition-State Theory (-TST) to several hydrogen transfer reactions has showed promising results [2]. Among the widely investigated elementary reactions, ones that have been described successfully using the -TST, arc: F + H2 [3,4], F + HD [5], CH4 + OH [2], CH3Cl + OH [2], H2 + CN [2], CH3OH + H [6], abstraction and dissociation in the nitrogen trifluoride channels [7], proton rearrangement in curcumin [8], and methylhydroxycarbene [9]. Temperature range for the validity of the approach are assessed with respect to features of the potential energy barrier to reaction [1,2].

References

This presentation reports about a quantum approximation for thermal rate constant calculations. The approximate rate expression is obtained from a stationary phase approximation to the time integral of the flux-flux correlation function. The resulting expression is shown to barely depend on the position of the flux operators, i.e. of the dividing surfaces. This property opens the route to applications to complex systems. We show how the approximation works on one and two dimensional systems with predominant quantum effects over a wide range of temperatures and the results are within few percent of the exact values, for a reasonable range of dividing surface positions.[1]

In a second part of the presentation, we show an optimized approach for the calculation of the vibrational density of states and the thermal rate constants in high-dimensional systems. We introduce a new code, called ParAdensum, which is based on the implementation of the Wang–Landau Monte Carlo algorithm for parallel architectures and part of the MULTIWELL suite.[2] We test the accuracy of ParAdensum on several molecular systems and show a significant computational speed-up with respect to standard approaches. The new code can easily handle 150 degrees of freedom.[3]

In a third part, a new semiclassical “divide-and-conquer” approach is presented. Here, the goal is to demonstrate that semiclassical dynamics simulations of high dimensional real molecular systems are doable. We first show the calculation of the quantum vibrational power spectra of small molecules for which benchmark quantum results are available, and we calculate the spectrum of C_{60}, a system characterized by 174 vibrational degrees of freedom. The results show that quantum anharmonicities and purely quantum features like overtones are accurately accounted for, including when the molecular symmetry is broken and the degeneracy removed.[4]

References

LONG RANGE POTENTIAL EFFECTS ON THE REACTIVE AND INELASTIC SCATTERING IN OH+H₂ COLLISIONS: A QUANTUM-CLASSICAL STUDY

C. Martí*, L. Pacifici*, A. Laganà*, C. Coletti

Dipartimento di Farmacia, Università G. d'Annunzio Chieti-Pescara, via dei Vestini, 66100 Chieti, Italy
(*)Dipartimento di Chimica, Biologia e Biotecnologie, Università di Perugia, via Elce di Sotto, 06123 Perugia, Italy

We carried out a study of OH + H₂ scattering using a quantum-classical (QC) method, to obviate the heavy computational demand associated with full quantum calculations, treating vibrations according to quantum mechanics and both translations and rotations classically [1]. Furthermore, the largely decoupled nature of the classical mechanics component of the QC code and the compactness of the quantum one make the code highly distributable, so that a high speed gain was achieved through parallelization. The good agreement between the state specific quantum-classical reactive probabilities and the corresponding quantum ones prompted the extension of the study to state to state probabilities for non reactive vibrational energy exchange [2].

The study showed that H₂ reactive dynamics depends on the vibrational excitation, whereas the non reactive one is mainly vibrationally adiabatic. On the other hand, OH reactive dynamics is much less affected by its vibrational excitation.

Preliminary calculations on internal energy redistribution processes upon non reactive collisions showed that the QC code can be efficiently used to investigate quantum effects in inelastic scattering. However, in order to get reliable results in this respect, the potential energy surface has to take into account long range effects, which are essential to accurately evaluate the exchange of vibrational quanta. To this end, the potential energy surface [3] first employed in the study was modified by adding a long range tail, formulated according to an improved Lennard-Jones model [4], and its effect on reaction probabilities and rate constants as well as on vibrational energy exchange probabilities and rate constants has been evaluated and will be discussed.

References

HOW TO DERIVE A PHYSICALLY MEANINGFUL ANALYTIC S MATRIX FROM NUMERICAL S MATRIX DATA

J. N. L. Connor

School of Chemistry, The University of Manchester, Manchester M13 9PL, UK.

In recent years, much effort has been expended on the large-scale calculation of accurate, as well as approximate, quantum scattering (S) matrix elements for chemical reactions, allowing differential cross sections (DCSs) to be obtained by numerical summation of the partial wave series (PWS). A difficulty with this procedure is that different researchers are reaching opposite conclusions for the dynamics of a reaction, starting from the same, or similar, numerical S matrix data, e.g., the reactions: F + H$_2$ (resonances versus no-resonances), Mu + H$_2$ (tunnelling versus no-tunnelling).

A method has been developed [1, 2] which allows an analytic S matrix to be constructed from numerical S matrix data, in which all terms in the parametrized S matrix have a direct physical interpretation. The method exploits the QP decomposition of the S matrix, in which the positions and residues of Regge poles in the complex angular momentum (CAM) plane play a crucial role.[1, 2] We can then apply a uniform asymptotic/CAM theory to the PWS to interpret structure in the DCS. We apply the theory to the F + H$_2$ -> FH($v' = 3$) + H reaction and show that resonance Regge poles contribute to the small-angle scattering, with oscillations at larger angles arising from nearside-farside interference.[3]

References


CALCULATION OF TUNNELING SPLITTINGS IN POLYATOMIC MOLECULES AND CLUSTERS USING INSTANTON THEORY

M. T. Cvitaš
Rudjer Bošković Institute, Zagreb, Croatia

An exact treatment of tunnelling dynamics in molecular systems requires the potential energy surface (PES) that covers all geometries accessible to the nuclear wave function and scales exponentially with the number of degrees of freedom (DOF), so even for small gas-phase systems, it is a challenging computational task. The semiclassical instanton method [1] relies on the approximation in which only the dominant contribution to the quantum partition function is calculated, which comes from the stationary (Euclidean) action path for the motion of nuclear DOF on the PES, the instanton. The use of instantons to obtain tunnelling rates [2] and tunnelling splittings [3] in the polyatomic systems at a relatively low computational cost has recently gained in popularity. The instanton method for calculating tunnelling splittings between two symmetric wells consists of three time-consuming steps: (i) search of the instanton path, (ii) evaluation of hessians along the path and (iii) calculation of the fluctuation prefactor. In our numerical approach [4], we discretize the instanton trajectory using a set of equidistant system replicas. Instead of finding instantons at a particular temperature, one can search for instantons at a particular energy, whereby the stationary action path is converted into the minimum action path (MAP) [5]. We employ this idea and adapt the standard methods for finding minimum energy paths (MEP) [6], such as nudged elastic band and string/quadratic string method, for locating instantons with minimal number of system replicas (DOFs). The critical difference between the MEP and MAP finding is that the orientations of the system replicas with respect to each other are important in the MAP. We reorient the string ends towards the nearest neighbors using a quaternion algorithm and, optionally, we use an iterative process to reorient all replicas so as to minimize the action. The calculation of the fluctuation prefactor in the standard ring-polymer method relies on the diagonalization of a large banded matrix. Instead, we employ Mil’nikov-Nakamura formula in Cartesian coordinates and integrate a Ricatti equation using the interpolated potential/hessian along the instanton to obtain the prefactor in negligible time (in comparison with (i) and (ii)). The performance of the above methods is studied on benchmark systems, such as malonaldehyde, and water clusters (dimer, trimer, pentamer). The approach uses Cartesian coordinates, so it is general and easy to use, and has similar computational cost to the MEP finding, so it is widely applicable.

DYNAMICS AND NOVEL MECHANISMS OF S\textsubscript{N}2 REACTIONS ON AB INITIO ANALYTICAL POTENTIAL ENERGY SURFACES

G. Czakó

Department of Physical Chemistry and Materials Science, University of Szeged, Hungary

Simulations of bimolecular nucleophilic substitution (S\textsubscript{N}2) reactions have traditionally been performed using direct dynamics, in which the required forces are computed on-the-fly at relatively low-level of electronic structure theory. We have recently started to use a different approach based on analytical representation of the potential energy surfaces obtained at high-level of \textit{ab initio} theory, thereby allowing efficient quasi-classical trajectory computations and setting a new state-of-the-art for the dynamics simulations of S\textsubscript{N}2 reactions. Using this novel approach we have studied the F\textsuperscript{-} + CH\textsubscript{3}Y (Y = F, Cl, I) reactions \cite{1-6} and we are working on the more complex F\textsuperscript{-} + CH\textsubscript{3}CH\textsubscript{2}Cl system \cite{7} as well. The simulations revealed a new double-inversion reaction pathway \cite{2} and uncovered the impact of the leaving group \cite{4} on the dynamics of S\textsubscript{N}2 reactions.

References

BENCHMARKING CHEMICAL REACTIVITY IN THE DEEP TUNNELING REGIME: THE ULTRA-COLD BEHAVIOR OF THE F +H$_2$ REACTIVE SYSTEM AND ITS ISOTOPIC VARIANTS

D. De Fazio*, V. Aquilanti*,**, S. Cavalli°

*Istituto di Struttura della Materia, Consiglio Nazionale delle Ricerche, Rome, Italy
**Instituto de Fisica, Universidade Federal da Bahia, Salvador, Brazil
°Dipartimento di Chimica, Biologia e Biotecnologie dell’Università, 06123 Perugia, Italy

Recent attention to cold environments, either in the laboratory or under astrophysical and other conditions, is putting at the forefront the tunnel effect, a principal source of deviations from the Arrhenius rate law. Progress in theoretical chemical kinetics relies on accurate knowledge of potential energy surfaces, as provided by advanced quantum chemistry and tested against experiments [1]. To generate accurate rate data, quantum scattering calculations involve sophisticated algorithms to produce scattering matrix elements at given angular momenta (to be summed to yield cross sections) and as a function of collision velocities (to be integrated to give rate constants and temperature dependencies). Here illustrated are these passages, a milestone having been benchmark temperature dependent rate constants for the prototypical F + H$_2$ reaction [2], recently validated by experiments in the moderate tunnelling regime [3]. The F+ HD variant permits exploring tunnel as well as isotopic effects [4] and developing a phenomenology and interpretive ingredients down to the deep tunnelling regime [5,6] where the reactivity is strongly dominated by resonances and quantum effects.

In the conference we discuss and compare cold and ultra-cold reactive behaviours of the F +H$_2$ reaction and of its isotopic variants (F+HD and F+D$_2$) to deeply understand its dependence by the entrance channel behaviour of the potential energy surface [2]-[6].

Simplified dynamical treatments and ultra-cold theories will be employed to understand the various resonance features obtained by ‘exact’ quantum reactive scattering results and as they affect cross sections and kinetic behaviours.

EFFICIENT WAYS TO BUILD POTENTIAL ENERGY OPERATORS

Terry J. Frankcombe

University of New South Wales, Canberra, Australia

The accuracy of a quantum wave packet simulation is limited by the quality of the potential energy operator that is used to perform the calculation. This potential energy operator must be known for all regions of configuration space accessible to the wave packet, and in principle inaccuracies in the potential energy in any region of configuration space can degrade the accuracy of a simulation in often unpredictable ways. For molecular systems, ab initio electronic structure theory can calculate the value of the potential energy to high accuracy at any given point in configuration space, but these calculations can be expensive. A naive approach of calculating the potential energy everywhere it is needed presents an insurmountable practical barrier to undertaking wave packet simulations for more than a couple of atoms. Using Gaussian basis functions and local expansion approximations can help, but constructing potential energy operators from ab initio calculations remains expensive. In this presentation I will discuss some options for making the most use of the electronic structure theory calculations that are performed, contrasting and demonstrating several strategies that include continuous (semi-)global interpolation. I will particularly focus on the computational efficiency of potential energy operator construction strategies.
INTERFERENCES BETWEEN REACTION MECHANISMS UNRAVELLED USING A QUANTUM ANALOGUE TO THE CLASSICAL DEFLECTION FUNCTION

P. García Jambrina*, M. Menéndez**, and F. J. Aoiz**

*Departamento de Química Física Aplicada, Universidad Autónoma de Madrid, Madrid (Spain)
**Departamento de Química Física I, Universidad Complutense de Madrid, Madrid, Spain

The deflection function, the joint dependence of the reaction probability as a function of the orbital angular momentum and the scattering angle, provides a valuable insight on the reaction mechanism. For example, a strong correlation between the scattering angle and the orbital angular momentum should be expected for a direct reaction, while for reactions taking place through a long-lived complex no correlation should be found. Furthermore, the deflection function has been proved to be an invaluable tool to analyse interference patterns and to unravel the reaction mechanisms causing quantum interferences [1-2].

Using quasiclassical methods, the calculation of the deflection function is straightforward, and basically only requires labelling the trajectories according to their scattering angle and angular momentum. However, the deflection function cannot be easily defined in a pure quantum mechanical framework as, to calculate the products angular distribution, we need to include coherences between elements of the scattering matrix corresponding to different values of the angular momentum.

Here we define a quantum analogue of the classical deflection function. This analogue accounts for coherences between different values of the angular momentum and, where no interferences are observed, it renders similar results than the classical deflection function. Besides, it allows us to unravel the coherences between reaction mechanisms when one of them lacks of a classical analogue, such as that found when resonances are observed.

References

Resonance states are interesting objects that can behave as intermediate or doorway states from which some molecular processes can be activated. Thus, controlling the decay process of a given resonance implies to control the molecular process mediated by that resonance state. The two essential observable properties associated with the decay of a single resonance state are its lifetime and the final product fragment state distributions. Schemes to control the lifetime of a single resonance state have been developed for the cases of both overlapping [1,2] and isolated [3] resonances. Control strategies to modify the product fragment state distributions produced by the decay of a superposition of resonances [4-6], as well as of a single resonance [7], have also been proposed. A remarkably different behaviour is found depending upon whether the resonance state is completely isolated or overlapping with other resonances [7,8]. The different control schemes will be discussed.

Figure 1. Resonance lifetimes vs delay time for three different ratios of amplitudes between pulses (left panel) and transient Br2(B,vf=v'-1) fragment vibrational populations using different pulse chirps (right panel).

References

DYNAMICS OF REACTIVE COLLISIONS IN THE INTERSTELLAR MEDIUM

T. González-Lezana

IFF-CSIC, c/ Serrano 123, 28006 Madrid (Spain)

In recent investigations the dynamics of atom-diatom reactions with interest in the interstellar medium have been treated. Processes involving protonated mixed rare-gas dimers such as HeH$^+$ and NeH$^+$ with a proton transfer were studied by means of quantum mechanical, quasiclassical and statistical approaches in an attempt to characterize the intrinsic mechanics governing the reaction. Reaction probabilities, cross sections and rate constants have been calculated [1-4].

The H$^+$ + H$_2$ reaction has been the subject of an intense investigation since several years ago [5]. Its dynamics was found to vary as a function of the energy [6]. Theoretical rate constants [7] were employed in the development of chemical clocks to calculate the age of interstellar dark clouds in the first stages of stars formation [8,9]. In recent work, the temperature range for such rate constants has been extended [10].

References

Full understanding of the spectroscopy and the dynamical behaviour of molecular systems, either strongly or weakly bound, at different energy domains needs, at first glance, the full exploration of their global multidimensional potential energy surfaces (PESs). These species can be either in their electronic ground and / or electronically excited states. These PESs should cover the molecular regions where (meta)stable isomers can be located, the regions of the potential barriers (isomerization) and the asymptotic regions leading to fragmentation.

I will present a series of benchmarks where we closely compared PESs obtained using standard coupled cluster CCSD(T) and those generated using explicitly-correlated CCSD(T)-F12 methods. These works showed that the cost of a single point computation is strongly reduced using the CCSD(T)-F12 level (CPU time by ~240 and disk occupancy by ~35) for similar accuracy.[1] This procedure has been validated after comparison with experimental data including the rovibrational spectra of some clusters or some macroscopic properties of the corresponding monomers (e.g. pressure broadening coefficients, temperature dependence of the second virial coefficient, temperature variations of the first spectral moment of interaction-induced rototranslational). Hence, I will show that CCSD(T)-F12 multi-dimensional PESs, along both intra and intermonomer coordinates, can be generated “routinely” for accurate spectroscopic and dynamical calculations of medium-sized van der Waals and charge transfer molecular systems at low computational cost.

For illustration several examples will be shown: HCl-He,[2] C₃-H₂,[3] CO₂-CO₂,[4] CO₂-N₂,[5] ArNO⁺.[6,7]

References

ISOTOPE AND SYMMETRY EFFECTS IN COLLISIONS INVOLVING OZONE AS INTERMEDIATE

P. Honvault, G. Guillon

Laboratoire Interdisciplinaire Carnot de Bourgogne, UMR 6303 CNRS/Université de Bourgogne Franche-Comté, 21078 Dijon Cedex, France

Molecular oxygen O$_2$ is the most important molecule in Earth’s atmosphere and stratospheric ozone O$_3$ protects us from the UV radiation. The abundance in $^{16}$O being 99.8%, O$_2$ and O$_3$ exclusively formed from it are dominant, thereby giving a reference for any process involving oxygen. A strong enrichment (about 10%) of O$_3$ in both $^{18}$O and $^{17}$O (the so-called mass-independent fractionation MIF), has been observed decades ago [1] and reproduced in laboratory experiments [2]. Although this phenomenon remains globally unexplained, the three-body recombination O + O$_2$ + M $\rightarrow$ O$_3$ + M is believed to be the main process leading to this enrichment. At sufficiently low pressures, it can be partitioned into two steps: the formation of O$_3$ in a highly excited rovibrational state, from reaction O + O$_2$ $\rightarrow$ O$_3^*$ (step 1), and its subsequent stabilization by collision with an energy absorbing partner M (say N$_2$), O$_3^*$ + M $\rightarrow$ O$_3$ + M (step 2). Thus, the efficiency of the exchange reaction O + O$_2$ $\rightarrow$ O$_2^*$ + O, involving O$_3^*$ as an intermediate, is one of the key parameters to understand ozone formation. We have shown [3] that this reaction, initiated by step 1, is very fast with three identical $^{16}$O atoms involved, due to a quantum permutation symmetry effect. Consequently, it competes ferociously with step 2 described above, the latter becoming in this way much less effective.

We have reproduced experimentally observed negative temperature dependence for this reaction rate constant when $^{18}$O is involved, along with other groups [4]. We will sum up results of a computationally intensive full-quantum investigation of the dynamics of the $^{16}$O + $^{32}$O$_2$ [3], $^{16}$O + $^{32}$O$_2$ [5] and $^{17}$O + $^{32}$O$_2$ [6] processes supported by an accurate global potential energy surface for the O$_3$ ground state [7]. Our study based on a time independent approach incorporates explicitly, when necessary, the indistinguishability of the three atoms and yields quite accurate cross sections and rate constants for each process.

References

QUANTUM DYNAMICS OF H$_2$ IN A CARBON NANOTUBE: TIMESCALE SEPARATION AND RESONANCE ENHANCED TUNNELING


(**) Department of Material Science and Physical Chemistry & Institute for Theoretical and Computational Chemistry, University of Barcelona
(*) Theoretical Chemistry, University of Bielefeld.

The role of nanostructured materials in both fundamental and applied research is ever increasing due to their interesting and unique properties, from catalysis to electronics [1,2]. A specific field of interest is the understanding and development of storage devices for light gases, specially for energy applications (hydrogen) or environmental reasons (CO$_2$, H$_2$S).

Carbon nanotubes have been largely studied with the idea of designing possible storage devices for H$_2$ since the late 1990s [3]. However, a complete quantum dynamics description of the diffusion mechanism inside these structures is still lacking.

In this presentation, we will report on our quantum mechanical study of the diffusion of the H$_2$ molecule along a narrow (8,0) Single-walled Carbon Nanotube (SWCNT). The cylindrical shape of the potential energy surface, has prompted us to develop an exact diabatization formalism separating two sets of weakly coupled degrees of freedom: unbound and bound DOFs. By applying a complete separability assumption to the confined and unbound DOFs we have also developed an adiabatic approximation to the Hamiltonian, which increases the algorithm efficiency while maintaining the accuracy of the results. Both approaches have been employed to simulate Hydrogen diffusion along the SWCNT at temperatures in the 45-135 K range. The computational advantages provided by both method have enabled us to propagate the wave function beyond 15 picoseconds using the State Averaged - MCTDH [5] code, revealing a remarkable resonant structure as well as a noticeable tunnelling effect.

Financial support from the Spanish Ministerio de Economia y Competitividad (CTQ2013-41307-P) and Generalitat de Catalunya (2014- SGR-25) is acknowledged. M.M.-M. further thanks a pre-doctoral grant from the FPU program (FPU2013/02210) from the Spanish Ministerio de Educacion, Cultura y Deporte.

References
INVESTIGATION OF NON-ADIABATIC EFFECTS FOR A TRIATOMIC MOLECULE: THE USE OF A SINGLE POTENTIAL ENERGY SURFACE WITH DISTANCE-DEPENDENT REDUCED MASSES FOR H$_3^+$

R. Jaquet, M. Khoma

Theoretical chemistry, University Siegen, D-57068 Siegen, Germany

The influence of the BO potential energy surface and additional potential corrections (with different quality) on spectroscopic properties is well known. But how large is the influence of the quality of the potential surface on scattering probabilities of the H$_3^+$-system at very low collision energies? Is there experimental evidence that adiabatic, nonadiabatic and relativistic contributions are needed?

Before we perform quantum reactive scattering calculations at low collision energies we would like to investigate relatively small nonadiabatic effects on the rovibrational spectrum of H$_3^+$ and its isotopomers far away from the geometric region of the strong coupling/avoided crossing between H$_2$ + H$^+$ and H$_2^+$ + H arrangements.

Based on first principles, the influence of non-adiabatic effects on the vibrational bound states of H$_3^+$ has been investigated using distance-dependent reduced masses and only one single potential energy surface. For these new vibrational calculations potentials based on explicitly correlated wave functions are used where in addition, adiabatic corrections and relativistic contributions are taken into account. For the first time, several different fully distance-dependent reduced mass surfaces in three dimensions have been incorporated in the vibrational calculations.

Our aim is to perform in the near future quantum reactive scattering calculations using distance-dependent masses.
The SO\(_2\) molecule is an important species in atmospheric chemistry (acid rain), interstellar media (strong SO\(_2\) signals) and recently in the sulfur mass-isotope fractionation (S-MIF) effect as an indicator of Great Oxygenation Event in earth’s atmosphere 2.5 billion years ago. The geological record indicates that the disappearance of the S-MIF signal somewhere around 2.5 billion years ago points to the appearance of molecular oxygen in earth’s air caused by increased bioactivity. It is agreed that the interaction of sunlight with atmospheric SO\(_2\) is responsible for this S-MIF effect observed in rock record. Thus, to elucidate mechanisms behind it, it is important to characterize photochemistry of SO\(_2\) as precise as possible.

We present new developed potential energy surfaces\([1]\) calculated with explicitly correlated variants of CCSD(T) and MRCI methods which are important in the photodissociation process of the SO\(_2\)(X\(^1\)A\(^′\)) molecule leading to the SO(X\(^3\)Σ\(^−\))+O(\(^3\)P) products. This reaction is characterized by a complicated inter-system dynamics involving electronically excited singlet and triplet states, where several conical intersection appear. The low-energy wing of the C\(^1\)B\(^2\) ← X\(^1\)A\(^′\) absorption spectra in the UV-region is computed for several Sulphur isotopes. We show simulation of the photoabsorption spectra, the rovibrational bound states and the role of the excited triplet states in the photodissociation mechanism of SO\(_2\).

**Acknowledgments:** NASA Astrobiology Grant NNX13AJ49G-EXOR

References

DYNAMICS OF THE S(1D)+O-D2 \rightarrow SD+D REACTION AT LOW COLLISION ENERGIES: REVISITING THE SH2 SYSTEM


*Departamento de Química Física Aplicada, Facultad de Ciencias, Universidad Autónoma de Madrid, Madrid, Spain.
**Univ. Bordeaux, ISM, UMR 5255, F-33400 Talence, France. CNRS, ISM, UMR 5255, F-33400 Talence, France.
°Institut de Physique de Rennes, Université de Rennes I, Rennes, France.
†Departamento de Química Física Aplicada, Facultad de Química, Universidad Complutense, Madrid, Spain.

Reactive and elastic cross-sections, and rate coefficients, have been calculated for the S(1D) +D2(j=0) [1] reaction using a modified hyperspherical quantum reactive scattering method [2]. The considered collision energy ranges from the ultracold regime, where only one partial wave is open, up to the Langevin regime, where many of them contribute. Very recently, excitation functions for the system have been measured in the near cold regime using the angle-variable crossed molecular beam technique [1]. This experiment completes the set of measurements performed in Bordeaux on the isotopic variants of the SH2 reactive system. The study, which reached unprecedented low temperatures, began in 2010 [3]. Although less resolved than the isotopologue reactions with H2 or HD, some undulations are still visible in the medium energy domain of the title reaction. An overall good agreement is found between the experimental data and the theoretical calculations performed with different methods: quantum mechanics, semi-classical mean potential capture theory (sc-MPCT) and quasi-classical trajectory (QCT) methodology. We will show the results of extending the quantum calculations down to energies in the cold and ultracold domains. The complex scattering length will be discussed in terms of the recently published quantum defect theory by Idziaszek and coworkers [4, 5], providing some insight in the behavior of the system. Finally, the consideration of state-to-state reaction probabilities will allow the discussion of the statistical behavior of the system in the ultracold regime.

References
DYNAMICS OF COMPLEX-FORMING BIMOLECULAR REACTIONS
P. Szabó*, S. Góger* and G. Lendvay*,**

*Institute of Chemistry, University of Pannonia, P.O.B. 158, Veszprém, H-8201 Hungary
**Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences, Magyar tudósok krt. 2, H-1117 Budapest, Hungary

Reactions in which two reactants form a strongly or weakly bound complex are ubiquitous in atmospheric and combustion chemistry. Theoretical description of such reactions is generally based on some version of statistical rate theories. However, dynamical methods are essential in finding out what actually happens in the reacting system and can help us establish the connection between the shape of the potential energy surface and the dynamics of the reaction.

We present result on quasiclassical trajectory calculations on reactions

\[
\begin{align*}
H + ^3O_2 & \rightarrow OH + H \quad (R1a) \\
H + ^1O_2 & \rightarrow OH + H \quad (R1b) \\
CH_3 + HBr & \rightarrow CH_4 + Br \quad (R2) \\
OH + HBr & \rightarrow H_2O + Br \quad (R3)
\end{align*}
\]

In reactions R1a and R1b a strongly bound complex is formed. The trajectory calculations [1,2] showed numerous common dynamical features even though the topography of the potential surfaces is different except the presence of the deep potential well. This is found to occur partly because of the common features of the two potential surfaces, partly due to mechanical conservation rules, partly incomplete loss of memory in the complex. In reaction R1b a dominant fraction of trajectories tends to return to reactants after passing the barrier in the entrance channel and getting deeply immersed into the deep potential well of the HO2 complex.

In reactions R2 and R3 weakly bound complexes are formed by the reactants and in both cases the barrier separating the potential well corresponding to the complex from the products is sub-merged below the bimolecular reactant level. Not all complexes form immediately products. There is a large fraction of collisions in which the partners linger around one another for a long time without entering the potential well which turns out to be prevented by the centrifugal barrier arising because of angular momentum conservation. Excitation of reactant rotation and vibration reduces the rate. A significant fraction of trajectories return to reactants after passing the potential barrier and going halfway down on the slope of the potential surface on the product side of the potential surface. Reasons for these dynamical features will be discussed.

We acknowledge financial support by the OTKA Grant No. K108966.

References
METHANOL DIMER FORMATION DRASTICALLY ENHANCES HYDROGEN ABSTRACTION FROM METHANOL BY OH AT LOW TEMPERATURE

W. Siebrand*, Z. Smedarchina*, E. Martínez-Núñez, A Fernández-Ramos

Departamento de Química Física, Universidade de Santiago de Compostela, 15782, Spain
(*) National Research Council of Canada, Ottawa, Canada

The kinetics of the reaction of methanol with hydroxyl radicals is revisited in light of the reported new kinetic data, measured in cold expansion beams. The rate constants exhibit an approximately $10^2$-fold increase when the temperature decreases from 200 to 50 K, a result that cannot be fully explained by tunneling, as we confirm by new calculations [1].

These calculations also show that methanol dimers are much more reactive to hydroxyl than monomers and imply that a dimer concentration of about 30% of the equilibrium concentration can account quantitatively for the observed rates [1]. The assumed presence of dimers is supported by the observation of cluster formation in these and other cold beams of molecules subject to hydrogen bonding.

The calculations imply an important caveat with respect to the use of cold expansion beams for the study of interstellar chemistry.

References

RmatReact: Developing Novel Theoretical Methodology to Investigate Ultra-Cold Atom-Molecule Collisions over Deep Potential Wells

L. K. McKemmish*, T. Rivlin, J. Tennyson

Department of Physics and Astronomy, University College London
(*) laura.mckemmish@gmail.com

Cutting-edge experimental studies in the field of molecular science are pushing the limits of current theoretical frameworks, requiring the development of new quantum chemistry methodologies that are capable of describing systems in increased detail, particularly at high levels of internal energy up to and above dissociation.

One key area that would benefit from improved theoretical description is experimental ultracold chemistry studies, which aim to understand and ultimately control chemical processes at the quantum level, with reactants and products being fully specified in terms of quantum numbers. Adequately conceptualising such reactions presents the greatest challenge to chemical theory whilst accurate computation presents the greatest challenges to both electronic-structure theory and the quantum theory of nuclear motion, especially when the collisions occur over deep potential wells. We are working on developing a new methodology [1], RmatReact, to address these significant challenges by dividing a modelled molecular collision into two spatial regions: an inner-region solved once using an expensive, high accuracy calculation and a fast outer-region calculation performed for a fine grid of collision energies that provides process and reaction cross-sections. This technique has the potential to provide the theoretical framework to describe and motivate a whole generation of new experiments, addressing important and fundamental scientific problems associated with quasi-bound resonance states formed when two atomic or molecular systems collide at specific ultra-cold energies over deep wells.

References

THE ROLE OF TUNNELING ON THE DIFFUSION RATE OF H\textsubscript{2} AND D\textsubscript{2} ALONG A NARROW SWCN

M. Mondelo-Martell, F. Huarte-Larrañaga
Department of Material Science and Physical Chemistry & Institute for Theoretical and Computational Chemistry, C/ Martí i Franqués 1, 08028 Barcelona.

The rise of new materials presenting cavities and other structures with a characteristic dimension on the order of the nanometer has taken to the discovery of new physical phenomena. These quantum confinement effects play a major role on the electronic properties of the materials, and also on the behaviour of the molecules adsorbed therein [1]. The level fine control achievable nowadays during the synthesis of nanostructured materials allows for the design of new devices to tune the properties of the adsorbates -altering their electronic structure, their dynamics, and thus even their reactivity- in order to find new applications such as storage devices for light gases[2], molecular flasks[3], or quantum sieves[4,5,6]. The latter devices are able to separate isotopic mixtures of light molecules (such as H\textsubscript{2} from D\textsubscript{2}) due to the different zero point energy of the isotopologues.

Here we present a full quantum dynamics study of the diffusion of both hydrogen and deuterium along a narrow (8, 0) Single Walled Carbon Nanotube. Using the flux-correlation function method [7] and a time-scale separation approach to reduce the logical dimensions of the Hamiltonian from 6 to 2 without any loss of accuracy, we are able to achieve propagation times of 20~ps. This times are enough to converge the Cumulative Reaction Probability for the diffusion process, and obtain values of the Diffusion rate. Our results clearly show the existence of low-energy, first order shape resonances with a relevant contribution to the diffusion rate below 150 K. Due to the existence of this tunnelling effect, which is higher for H\textsubscript{2} than for D\textsubscript{2}, the Inverse Kinetic Isotope Effect (i.e. a higher diffusion rate for deuterium than for hydrogen) is not observed in this particular system. These observations may be helpful in the design of new quantum sieves.

References
STATE-TO-STATE CHEMISTRY AND QUANTUM DYNAMICS OF THE ULTRACOLD K+KBR REACTION

J. F. E. Croft, C. Makrides, M. Li, A. Petrov, S. Kotochigova, B. K. Kendrick, and B. Naduvalath

Department of Chemistry, University of Nevada, Las Vegas, NV 89154, USA
Department of Physics, Temple University, Philadelphia, Pennsylvania 19122, USA
Theoretical Division (T-1, MS B221), Los Alamos National Laboratory, Los Alamos, NM 87545, USA

An ultimate goal in chemistry is the absolute control of quantum states of both reactants and products. This is not achievable at normal temperatures due to a thermal population of internal quantum states. The ultracold regime offers such a possibility where a precise control over initial states including, nuclear spin orientation is possible. In a landmark experiment, research groups at JILA were able to produce an ultracold gas of $^{40}$K$^{87}$Rb molecules at nano Kelvin temperatures where even the nuclear spins were oriented [1]. Rate coefficients for exothermic reactions between KRb+KRb and KRb+K were also reported at a temperature of about 250 nK. It was shown that by merely flipping a nuclear spin of the KRb molecule, the KRb+KRb reaction could be turned on and off. However, an explicit quantum dynamics study of these reactions has not been reported so far. Here, we report results of full quantum dynamics study of the K+KRb reaction with rovibrational quantum state resolution of the product K$_2$ molecule [2]. Comparisons are made with experimental data and predictions of a universal model based on the quantum defect theory. A statistical analysis of the product rotational population reveals a Poissonian distribution which is attributed to the high density of states of the intermediate K$_2$Rb complex and strong coupling between different reaction channels. We also investigate the reverse reaction that leads to the formation of KRb molecules in collisions of vibrationally excited K$_2$ with an Rb atom.

SEMICLASSICAL QUANTIZATION OF ROVIBRATIONAL STATES OF METHANE BY ADIABATIC SWITCHING

T. Nagy and G. Lendvay
IMEC, RCNS, Hungarian Academy of Sciences,
H-1117, Magyar tudósok körútja 2, Budapest, Hungary

The quasiclassical trajectory (QCT) method is widely used in the state-resolved theoretical investigations of elementary reactions in gas phase. In the QCT method, the motion of atoms is simulated classically, and the only quantum effect considered is that the initial rovibrational states of reactant molecules are semiclassically quantized. Initial states are usually prepared using normal mode sampling, a method based on the rigid rotor (RR) and harmonic oscillator (HO) approximation, which reduces the problem of quantization to that of independent vibrational and rotational normal modes.

A sensible expectation is that the ensemble of classical molecular states generated by normal mode sampling should all have the same total angular momentum and energy, which are equal or close to the exact quantum mechanical (QM) expectation values of the represented quantum state. However, the energy distribution of the ensemble obtained within the RR/HO approximation usually, because of anharmonicities, has a significant spread and even its mean energy is not close to the corresponding QM value.

Primitive semiclassical theory and Ehrenfest’s adiabaticity theorem provides a physically established means, called adiabatic switching (AS), to prepare initial states with semiclassical quantization of the fully coupled anharmonic Hamiltonian [1][2]. A previous application of AS to CH$_4$ was unsuccessful [3]. We revisited the problem and reported on successful convergence of semiclassical zero-point energy in the previous QRS meeting [4] by using a general, approximation-free procedure. Bowman and coworkers also successfully applied adiabatic switching to methane [5], though with the approximation of Eckart embedding.

Now we present our approximation-free AS procedure in detail. In addition, we generalize the AS procedure to the quantization of rotationally excited states [6]. The methods will be demonstrated on the quantization of excited vibrational and rotational states of the CH$_4$ molecule. Highly monoenergetic ensembles can be obtained with mean energies close to the exact QM value, and it is shown that the converged results are insensitive to the choice of coordinates used in the definition of the zeroth-order Hamiltonian.

References
[1] Ehrenfest, Philos. Mag. Ser. 6 33, 500 (1917)
NONADIABATIC EFFECTS IN QUANTUM REACTIVE COLLISIONS

P. Gamallo*, S. Akpinar**, P. Defazio°, and C. Petrongolo†

*Departament de Ciència de Materials i Química Física & Institut de Química Teòrica i Computacional, Universitat de Barcelona, C/ Martí i Franquès 1, 08028 Barcelona, Spain
**Department of Physics, Firat University, 23169 Elazig, Turkey
°Dipartimento di Biotecnologie, Chimica, e Farmacia, Università di Siena, Via A. Moro 2, 53100 Siena, Italy
†Istituto per i Processi Chimico Fisici, CNR, Via G. Moruzzi 1, 56124 Pisa, Italy

It is well known that the chemical dynamics is mainly ruled by the Born-Oppenheimer approximation on the ground electronic state and by nonadiabatic couplings on the excited electronic species. Nonadiabatic effects are important whenever two or more electronic states are degenerate in some regions of the configurational space, as in Conical Intersections, Renner-Teller interactions, and Spin-Orbit couplings. We here present three example of nonadiabatic reactive collisions: the Conical Intersection in the OH($\Sigma^+\Sigma^+$)+H($\Sigma^+$) reactions, the Renner-Teller dynamics of the OH($\Pi\Pi$)+H+ collisions, and the Renner-Teller and Spin-Orbit effects in N$_2$($\Sigma^+_g$)+O($\Pi^+_d$)[1], considering up to four product channels from the initial to the same or to lower-lying PESs. Employing MRCI PESs and couplings and the coupled-channel real wave packet method, we discuss initial-state-resolved reaction probabilities, real-time mechanisms, integral cross sections, and rate constants, resolved on the product electronic states. As an example, Fig. 1 and 2 present the OH$^+$ correlation diagram of the first two electronic states and the integral cross sections of the investigated product channels [1]. We clearly see that Renner-Teller couplings open both quenching channels from the excited to the ground PES, and that these nonadiabatic channels are much more reactive than the adiabatic proton exchange.

A complex chemistry takes place in cold molecular clouds in the interstellar medium. The gas phase reaction for the formation of many organic molecules present a barrier and for this reason their formation are typically modelled at surfaces of ices. However, recently it has been found a non-Arrhenius behavior at low temperatures, below 100 K, with a fast increase of the rate with decreasing temperature [1-3] for the reaction of methanol with OH, which is known to have a barrier of about 0.3 eV. The reaction of formaldehyde with OH also shows this behavior [4]. This behavior is simulated with Quasi-Classical trajectory calculations on a full-dimension potential energy surface recently developed [4].

References

FULL- AND REDUCED-DIMENSIONALITY SEMICLASSICAL TRANSITION STATE THEORY: APPLICATION TO VARIOUS CHEMICAL REACTIONS

X. Shan (*) and David C. Clary

Physical and Theoretical Chemistry Laboratory, Department of Chemistry, University of Oxford, South Parks Road, Oxford, OX1 3QZ, UK
(*) xiao.shan@chem.ox.ac.uk

In a semiclassical transition state theory (SCTST), the reaction probabilities are directly calculated from the harmonic frequencies and anharmonic constants of the transition state [1-7]. The results can then be used to compute the reaction rate constants. We investigate the performance of SCTST in various chemical reactions. The following topics will be discussed in the talk:

1. **Comparing SCTST to quantum reactive scattering (QRS).** We apply SCTST to analytical potential energy surfaces (PESs) and compare results for the rate constants using SCTST and the QRS [5,6].

2. **Comparing reduced-dimensional (RD) to full-dimensional (FD) SCTST.** We compute vibrational frequencies and anharmonic constants using quantum chemistry software packages [8,9] and apply the RD method to SCTST [7]. In particular, a one-dimensional (1D) SCTST is investigated for various bimolecular hydrogen-abstraction reactions.

3. **Application to unimolecular reaction.** We apply the 1D SCTST to a unimolecular reaction that involves pericyclic hydrogen-atom transfer in a phosphorus-containing organic compound. The resulting rate constants are compared with new experimental data.

References

A DIABATIC ELECTRONIC STATE SYSTEM TO DESCRIBE THE INTERNAL CONVERSION OF AZULENE

D. Skouteris

Scuola Normale Superiore, Piazza dei Cavalieri 7, Pisa, Italy

A diabatic system of two electronic potential energy surfaces as well as the coupling between them is presented. The system is to be used to study the dynamics of the S1 to S0 internal conversion of azulene and is based on single point calculations of the minima of the two surfaces and a dipole-quadrupole (DQ) diabatization. Based on this, a couple of harmonic diabatic surfaces together with a linear coupling surface have been devised. Some dynamics results pertaining to surface populations and vibrational selectivity are shown obtained with our G-MCTDH code.

"The most significant activities mentioned herein are performed in the framework of the ERC Advanced Grant Project DREAMS "Development of a Research Environment for Advanced Modelling of Soft Matter", GA N. 320951."
In a chemical reaction, reactants may form long-lived (or not so long-lived) intermediate states. Such quantum mechanical resonances usually leave signatures in the integral (ICS) and differential (DCS) cross sections. Resonance contributions may take different forms. Recently, we made available the first user-friendly computer code ICS_Regge [1,2], which uses numerical scattering data to extract the information about the Regge poles, and accurately evaluates the contribution from each resonance. Here we report a prototype of a similar code (which we call DCS_Regge) whose purpose is to analyse the resonance effects in a state-to-state reactive DCS. In particular, we will look at such effects in the small- and large-angle scattering [3], and perform a detailed nearside-farside analysis [4,5] in both the angular and the energy domains. We apply the code to a simple potential scattering model, and to the benchmark F+HD→HF+D reaction in the resonance-rich region of collision energies from 58.54 to 197.54 meV.

References

NON-STATISTICAL BEHAVIORS IN GAS PHASE UNI- AND BIMOLECULAR REACTIONS. THE ROLE OF CHEMICAL DYNAMICS SIMULATIONS

R. Spezia

Laboratoire Analyse et Modélisation pour la Biologie et l'Environnement, UMR 8587 CNRS, CEA, Université d'Evry-Val-d'Essonne, Université Paris Saclay, Bd F.Mitterrand, 91025 Evry, France
riccardo.spezia@univ-evry.fr

Studying reaction dynamics is crucial to understand from a microscopic point of view how chemical reactions proceed. In many cases, statistical theories, like transition state theory, RRKM or phase space theory, can be successfully used. However, dynamical effects, like non-equilibrium reactivity or reaction dynamics not following the minimum energy path (MEP) on the potential energy surface (PES) are possible (see Ref. [1] and reference therein). Using chemical dynamics simulations is a typical way of identifying such important phenomena. We have recently investigated these aspects in different gas phase reactions, in which it is more likely that the actual reactive trajectories do not follow the MEP since there is not solvent to dissipate the excess energy. Here we will give an overview on the most important results in particular for: (i) unimolecular dissociation of molecular ions related to collision-induced dissociation in mass spectrometry; (ii) ion-molecule reactive collisions.

We will give two examples taken from our recent studies: (i) collision induced dissociation of Ca$^{2+}$/formamide complex and (ii) synthesis of formamide by ion-molecule collision.

In the first case we have found that non-statistical mechanism, the so-called shattering, is important to obtain high-energy structures observed experimentally [2]. Furthermore, by performing dynamical simulations starting from the transition states previously located on the reactive PES we were able to point out that the following dissociations involve trajectories not following the MEP [3]. Consequences on mass spectra will be discussed.

In the case of formamide synthesis, reaction dynamics show that products are obtained without following the MEP [4]. This is particularly intriguing since it can suggest a mechanism to obtain high-energy structures even under low internal energy (temperature) conditions in which one could expect that the most stable isomer is mainly populated. Applications to understanding mechanisms for the formation of observed complex molecules in space will be discussed.

References

VIBRATIONAL SYMPATHETIC COOLING OF BA.CL+ BY CA
ATOMS: THEORETICAL STUDY

T. Stoecklin*, P. Halvick*, A. Gannouni**, M. hochlaf**, Svetlana Kotochigova° and Eric R. Hudson†

*UMR 5255-CNRS, Institut des Sciences Moléculaire, Université de Bordeaux, 351 cours de la Libération, 33405 Talence Cedex, France; e-mail: thierry.stoecklin@u-bordeaux.fr
**Université Paris-Est, Laboratoire Modélisation et Simulation Multi Echelle, MSME UMR 8208 CNRS, 5 bd Descartes, 77454 Marne-la-Vallée, France
°Department of Physics, Temple University, Philadelphia, Pennsylvania 19122, USA 2. Department of Chemistry, National Taiwan University, Taipei 10617, Taiwan
†Department of Physics and Astronomy, University of California, Los Angeles, California 90095, USA

The internal structure of molecules offers a host of scientific and technological opportunities, including the manipulation of quantum information, critical insight into quantum chemistry, and improved tests of the Standard Model. To utilize this potential of molecules typically requires the preparation of molecular samples at very low temperatures, where only a single quantum state is occupied. Unfortunately, experiments attempting to reach these temperatures by buffer gas cooling have found that though the molecular motion and rotation are quickly cooled to the cryogenic temperature [1,2], the molecular vibration relaxes at impractically long timescales [3]. Here, we theoretically explain the recently observed exception to this rule: efficient vibrational cooling of BaCl+ by a laser-cooled Ca buffer gas [4]. We perform intense close-coupling calculations that agree with the experimental result, and use both quantum defect theory and a statistical capture model to provide an intuitive understanding of the system. This result establishes that, in contrast to the commonly held opinion, there exists a large class of systems that exhibit efficient vibrational cooling and therefore supports a new route to realize the long-sought opportunities offered by molecular structure [5].

References

FREQUENCY-DOMAIN AND TIME-DOMAIN TRANSITION STATE SPECTROSCOPY OF CYCLOOCTATETRAENE

T. Takayanagi

Department of Chemistry, Saitama University
Shimo-Okubo 255, Sakura-ku, Saitama City 338-8570, JAPAN

The concept of transition state has been playing an essential role for understanding of detailed mechanisms and dynamics of chemical reactions. The transition state is defined as a specific region (around the saddle point) of the potential energy surface that governs the reaction as a dynamical bottleneck within the Born-Oppenheimer framework. If the geometry of a stable negative ion is similar to the transitions state structure of the neutral reaction, photodetachment of the negative ion can be used to selectively and directly produce the transition state structure due to good Franck-Condon overlap. This photodetachment scheme has been frequently employed in the so-called “transition state spectroscopy” techniques.

In the workshop, I would like to address the transition-state spectroscopy experiments of the cyclooctatetraene unimolecular reaction [1, 2] from the theoretical side. The equilibrium structure of the COT anion has $D_{4h}$ symmetry, which is similar to the ring-inversion transition state connecting two equivalent $D_{2d}$ tub-shaped COT minima on the neutral potential energy surface. The $D_{4d}$ transition state structure is located along the bond-alternation reaction pathway, where the transition state structure with $D_{4h}$ symmetry is also connecting the two equivalent $D_{4d}$ transition states with the adjacent CC double/single bonds being interchanged. The frequency-domain transition state spectroscopy experiment was performed by measuring the photodetachment spectrum of COT by Lineberger’s group [1]. They showed well-resolved transition peaks, which have been qualitatively assigned as the vibrational states of the transient structure associated with the bond-alternation pathway. On the other hand, the time-domain transition state spectroscopy experiment was carried out by Zewail’s group [2]. They created a nuclear wave packet starting from the COT $D_{4h}$ structure by detaching an excess electron from COT with a femtosecond laser pulse. The time-evolution of the wave packet was monitored in real-time using a two-photon ionization pulse. They have observed a broad oscillatory feature as a function of the delay time between the detachment pulse and ionization pulse. The observed time-dependent feature was tentatively assigned to the ring-inversion dynamics.

We have recently performed detailed theoretical calculations to address the above-mentioned two types of transition state spectroscopy experiments using both reduced-dimensionality quantum reactive scattering method and classical trajectory method [3, 4]. In the workshop, I will present the results of our recent calculations.

References
The talk begins with the celebrated Born-Oppenheimer approximation. The electronic problem is then addressed, and progress surveyed on extrapolation of calculated raw *ab initio* energies to the complete basis set (CBS) limit. A cost-effective wavefunction-based Möller-Plesset perturbation-theoretic (MP2) method combined with CBS extrapolation from the first steps, \((d,t)\) or just \(d\) or \(t\), of the hierarchical staircase is then shown to rival with Kohn-Sham density functional theory both accuracy- and time-wise [1]. The energies so obtained may then be given the quality of couple-cluster type via a variable-scaling opposite spin method [2]. Due to known limitations of single-reference methods, multi-reference configuration interaction calculations are ultimately demanded, with the case illustrated for small, yet challenging, carbon clusters [3]. The talk concludes with an overview of ongoing quantum dynamics studies [4], and prospective remarks.

References

The UV photodissociation of cyano containing hydrocarbons has been postulated as a possible source of hydrogen cyanide (HCN) and hydrogen isocyanide (HNC) molecules observed in a variety of astrophysical environments [1]. To investigate this possibility, we have performed calculations to simulate the decomposition of methyl cyanoformate (MCF) that takes place upon photoexcitation at 193 nm. Multi-configuration self-consistent field calculations were used to compute potential energy curves for the ground and four lowest energy singlet excited states of MCF. At 193 nm, dissociation is predicted to occur predominantly on the repulsive S2 state, resulting in formation of NCCO+CH3O. Nevertheless, minor pathways leading to the production of highly excited ground state MCF may be available via cascading internal conversion from nascent S2 population. An automated transition-state search algorithm [2,3] was employed to identify the corresponding ground state dissociation channels, and RRKM and kinetic Monte Carlo simulations were used to calculate the associated branching ratios. Although channels leading to formation of HCN and HNC are not the most important reaction pathways, it is interesting to notice that these species are formed via concerted three-body dissociations, a type of processes that has attracted great interest in recent years [4,5]. Quasi-classical trajectories were run to calculate internal energy distributions for the nascent HCN and HNC species. The results were compared with experimental data, showing good agreement.

References

ULTRA-FAST ELECTRONIC DECOHERENCE CAUSED BY NUCLEAR MOTION AND A POSSIBLE PATH TO ATTOCHEMISTRY

R. Welsch*, C. Arnold**,°, O. Vendrell¹,†, R. Santra¹

*Center for Free-Electron Laser Science, DESY, 22607 Hamburg, Germany
**Department of Physics, Universität Hamburg, 20355 Hamburg, Germany
°The Hamburg Centre for Ultrafast Imaging, 22761 Hamburg, Germany
†Department of Physics and Astronomy, Aarhus University, Denmark

Ultrafast, coherent broad-band pulses can be used to create coherent superpositions of electronic states of a molecular ion. Photoionization triggers not only electronic dynamics observed as charge migration [1], but also nuclear motion, leading to electronic decoherence. Long-lived coherences are predicted by theories that focus on the evolution of the electronic subsystem [1].

In this talk, the effect of nuclear motion on electronic coherence is discussed. First, the case of an adiabatic, fully quantum-dynamical framework including all nuclear degrees of freedom will be considered [2]. We find that electronic coherence is lost within few femtoseconds, leading to a mixed state. In application to paraxylene and phenylalanine, it is seen that the rapid decoherence is not caused by the fast C-H vibrations, but rather by the interplay of a large number of low-frequency modes.

Second, we discuss the effect of non-adiabatic nuclear dynamics on the decoherence in a two-dimensional two-state linear vibronic coupling model system. In addition, we investigate a possible path towards achieving attochemistry. The ability to control molecular pathways by manipulating the electronic degrees of freedom is a prerequisite for attochemistry [3]. In particular, we discuss the possibility of steering a nuclear wavepacket by imprinting a relative phase between the two electronic states in the presence of non-adiabatic couplings [4].

Novel three dimensional (3D) ab-initio potential energy surfaces are calculated for all rare gases from He to Xe atoms in collision with the ionic molecule NO$^+$($X^1\Sigma^+$) using the explicitly correlated variant of the coupled cluster method with single, double, and noniterative triple excitations [CCSD(T)-F12] using the correlation-consistent, triple-zeta (cc-pVTZ-F12) atomic basis sets augmented with mid-bond functions and auxiliary basis for the explicitly correlated part. Estimated dissociation energy from harmonic zero point energies and anharmonic bound states calculations are presented [1]. The calculated ro-vibrational energies are compared with previous theoretical and experimental results. Close-coupling calculations of the collisional rotational excitation integral cross sections of NO$^+$ by He, Ne, and Ar are calculated for total energies up to 1000 cm$^{-1}$ using the new Rg-NO$^+$ potential energy surfaces. The calculated rate coefficients are compared with available theoretical data and a good arrangement is found between literature and the present theoretical data. The new sets of state-to-state rate coefficients may be used for improvements in astrophysical and atmospheric modeling.

Acknowledgments: This work has received financial support from the Scientific Research Projects Coordination Unit of Firat University (FÜBAP) through project no. FF.15.03.

We also would like to thank to Octavio Roncero for useful discussions.

References:
Quantum molecular dynamics simulations of chemical reactions are needed to fully understand the dynamical processes of molecules. Accurate wave-packet propagation is an attractive means of attaining accurate quantum molecular dynamics simulations. The variational multi-configuration Gaussian (vMCG) method uses localized Gaussian functions as a basis set to perform wave packet calculations. vMCG has shown some success in carrying out wave-packet propagation. In vMCG time evolution, the equations of motion for the expansion coefficients and the parameters of Gaussian basis functions have to be solved. vMCG, however, requires a large number of Gaussian basis sets for tunnelling cases, which are often the most important aspect of chemical reaction simulations, and becomes numerically stagnant. The computational cost for solving the equations of motion becomes prohibitive. Here, the new method we call the basis expansion leaping multi-configuration Gaussian (BEL MCG) method [1] has been developed. In the BEL MCG, the wave-packet propagation is performed for short times without changing the basis of Gaussian functions and then re-expression of the propagated wave function is carried out to yield a new basis set adapted to the time-evolved wave function. The BEL MCG can be used the propagation of the multidimensional systems because the rapid increase in the number of the basis functions for tunnelling scenario can be inhibited and the difficult propagation of basis function parameters is avoided. This talk will describe recent developments in the formulation and application of BEL MCG to a several representative reaction profiles and setups.

Fig. 1 A tunnelling case

References
<table>
<thead>
<tr>
<th>QRS 2017</th>
<th>Monday July 3rd</th>
<th>Tuesday July 4th</th>
<th>Wednesday July 5th</th>
<th>Thursday July 6th</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Registration</td>
<td>9:00 - 10:00</td>
<td>J. Bowman: Keynote Talk</td>
<td>ICCSA Keynote Talk</td>
</tr>
<tr>
<td></td>
<td>IC CSA 2017 Official Opening</td>
<td>10:00 - 10:20</td>
<td>Coffee break</td>
<td>10:00 - 10:20</td>
</tr>
<tr>
<td></td>
<td>QRS1. Chair V. Aquilanti</td>
<td>11:00 - 11:30</td>
<td>14. L. Bonnet</td>
<td>10:30 - 11:20</td>
</tr>
<tr>
<td></td>
<td>QRS opening</td>
<td>11:30 - 12:00</td>
<td>15. C. Coletti</td>
<td>11:20 - 11:50</td>
</tr>
<tr>
<td></td>
<td>2. G. Czakó</td>
<td>13:30 - 14:00</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3. T. J. Frankcombe</td>
<td>14:00 - 14:30</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Lunch</td>
<td>14:30 - 15:00</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>QRS2. Chair A. Laganà</td>
<td>15:00 - 15:30</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4. F. J. Aoiz</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5. J. N. L. Connor</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>6. D. Sokolovski</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>7. D. De Fazio</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Coffee break</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>12:30 - 13:30</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Lunch</td>
<td>13:30 - 14:00</td>
<td>D. Babikov</td>
<td>13:30 - 14:00</td>
</tr>
<tr>
<td></td>
<td>QRS3. Chair A. Varandas</td>
<td>14:00 - 14:30</td>
<td>S. C. Althorpe</td>
<td>14:30 - 15:00</td>
</tr>
<tr>
<td></td>
<td>8. C. Petrongolo</td>
<td>14:30 - 15:00</td>
<td>M. T. Cvita</td>
<td>15:00 - 15:20</td>
</tr>
<tr>
<td></td>
<td>9. A. Garcia-Vela</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>10. P. Horváth</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>11. M. Hochlab</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>12. T. Nagy</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Poster session</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>15:00 - 15:50</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>QRS6. Chair A. Lombardi</td>
<td>15:50 - 16:20</td>
<td>M. Ceotto</td>
<td>15:00 - 15:50</td>
</tr>
<tr>
<td></td>
<td>20. R. Spezia</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>21. M. Ceotto</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>QRS9. Chair F. Palazzetti</td>
<td>16:20 - 16:50</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>34. R. Welich</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>35. J. Klos</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>36. S. A. Vázquez</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>37. D. Skouteris</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>38. M. Mondelo Martelli</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Excursion (6:00 pm)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>18:20 - 19:00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>ICCSA 2017 Welcome reception</td>
<td>19:00 - 23:00</td>
<td></td>
<td>Gaia Dinner</td>
</tr>
</tbody>
</table>
List of Participants:

Stuart C. Althorpe, University of Cambridge, sca10@cam.ac.uk
F. Javier Aoiz, University Complutense Madrid, aoiz@quim.ucm.es
Vincenzo Aquilanti, University of Perugia, vincenzoaquilanti@yahoo.it
Dmitri Babikov, Marquette University, dmitri.babikov@marquette.edu
Laurent Bonnet, Bordeaux University, claude-laurent.bonnet@u-bordeaux.fr
Joel M. Bowman, Emory University, jmbowma@emory.edu
Niyazi Bulut, Firat University, bulut_niyazi@yahoo.com
Valter Henrique Carvalho-Silva, Universidade Estadual de Goiás, fatioleg@gmail.com
Michele Ceotto, Università degli Studi di Milano, michele.ceotto@unimi.it
Cecilia Coletti, Università G. d’Annunzio, ccoletti@unich.it
Jonathan N. L. Connor, University of Manchester, j.n.l.connor@manchester.ac.uk
Marko T. Cvitas, Institute Rudjer Boskovic, marko.cvitas@gmail.com
Gabor Czakó, Secretariat of the Hungarian Academy of Sciences, czako.gabor@chem.u-szeged.hu
Noelia Faginas-Lago, University of Perugia, noelia.faginaslago@unipg.it
Dario De Fazio, Istituto di Struttura della Materia, CNR, defazio.dario@yahoo.it
Terry J. Frankcombe, UNSW Canberra, T.Frankcombe@adfa.edu.au
Pablo García-Jambrina, Universidad Autonoma de Madrid, pablojambrina@gmail.com
Alberto García-Vela, Consejo Superior de Investigaciones Científicas (CSIC), garciavela@iff.csic.es
Tomás González-Lezana, IFF-CSIC, t.gonzalez.lezana@csic.es
Majdi Hochlab, UPEM, majdi.hochlab@u-pem.fr
Pascal Honvault, Labo ICB, UBFC, pascal.honvault@univ-fcomte.fr
Fermin Huarte-Larrañaga, Universitat de Barcelona, fermin.huarte@ub.edu
Ralph Jaquet, University Siegen, ralph.jaquet@uni-siegen.de
Jacek A. Kłos, University of Maryland, jklos@umd.edu
Manuel Lara Garrido, Universidad Autónoma de Madrid, mlaragar@gmail.com
Gyorgy Lendvay, Research Centre for Natural Sciences, lendvay.gyorgy@ttk.mta.hu
Andrea Lombardi, University of Perugia, andrea.lombardi@unipg.it
Emilio Martínez-Núñez, Universidad Santiago de Compostela, emilio.nunez@usc.es
Laura K. McKemmish, University College London, laura.mckemmish@gmail.com
Manel Mondelo Martell, Universitat de Barcelona, manel.mondelo@ub.edu
Tatsuhiko Murakami, UNSW Canberra, t.murakami@adfa.edu.au
Balakrishnan Nauduvath, University of Nevada, naduvala@unlv.nevada.edu
Tibor Nagy, Research Centre for Natural Sciences, nagy.tibor@ttk.mta.hu
Federico Palazzetti, University of Perugia, federico.palazzetti@unipg.it
Carlo Petrongolo, IP CF-CN R, petrongolo@ipcf.cnrt.it
Octavio Roncero, Inst. Física Fundamental (CSIC), octavio.roncero@csic.es
Xiao Shan, University of Oxford, xiao.shan@chem.ox.ac.uk
Dimitrios Skouteris, Scuola Normale Superiore, dimitrios.skouteris@sns.it
Dmitri Sokoloski, University of the Basque Country, dgsokol15@gmail.com
Riccardo Spezia, CNRS - Université d'Evry, riccardo.spezia@gmail.com
Thierry Stoecklin, Université de Bordeaux, thierry.stoecklin@u-bordeaux.fr
Toshiyuki Takayanagi, Saitama University, tako@mail.saitama-u.ac.jp
António Varandas, University of Coimbra, varandas@uc.pt
Paulo A. Vázquez, University of Santiago de Compostela, saulo.vazquez@usc.es
Ralph Welsch, Center for Free-Electron Laser Science, ralph.welsch@desy.de