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Theory of Gas Phase Scattering and Reactivity for Astrochemistry

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Report from the Workshop on Theory of Gas Phase Scattering and Reactivity for Astrochemistry Nov 23 – Dec 4, 2015

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Because of the very peculiar conditions of chemistry in many astrophysical gases (low densities, mostly low temperatures, kinetics-dominated chemical evolution), great efforts have been devoted to study molecular signatures and chemical evolution. While experiments are being performed in many laboratories, it appears that the efforts directed towards theoretical works are not as strong.

This report deals with the present status of chemical physics/physical chemistry theory, for the qualitative and quantitative understanding of kinetics of molecular scattering, being it reactive or inelastic. By gathering several types of expertise, from applied mathematics to physical chemistry, dialog is made possible, as a step towards new and more adapted theoretical frameworks, capable of meeting the theoretical, methodological and numerical challenges of kinetics-dominated gas phase chemistry in astrophysical environments.

A state of the art panorama is presented, alongside present-day strengths and shortcomings. However, coverage is not complete, being limited in this report to actual attendance of the workshop. Some paths towards relevant progress are proposed.

This workshop was organised at the initiative of the COST Action CM1401 "Our Astrochemical History"^a, with the generous support of the CAS@MPE laboratory^b, of the MIAPP^c, and the CNRS^d.

I. SYNTHETIC PRESENTATION

A. Gas phase chemistry in Astrophysics

We begin with a very broad presentation, and setting up the scene of chemistry. Next, we try and make an analytical description of the work in MIAPP/Garching. We finish with perspectives, and a table of the participants.

Chemistry in interstellar environments has many peculiarities, that makes it very different from chemistry in environments that are customary for the laboratory chemist. While the basic concepts of physical chemistry evidently remain, the physical conditions are such that many of the usual hypotheses do not hold. Being it interstellar gaseous matter (ISM), gases surrounding Solar System objects like comets and asteroids, the main constraints of the kind of chemistry we are dealing with are: (i) Very dilute conditions, number density $\rho \lesssim 10^{10} \text{ cm}^{-3}$ [1]; (ii) Large range of temperatures, with molecules observed at gas temperatures as low as 5-15 K; (iii) Overwhelming dominance of atomic and molecular hydrogen, which constitute more than 90% (in number) of the whole number density, all other elements but inert He being less than 1% in number. Main elements are O, C, Ne, Fe, N,

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Si, Ar, Mg, S, and all others present as traces, including alkaline elements, halogens and P.

As a consequence of the physical and chemical conditions, the main differences between laboratory chemistry and astrochemistry, which are relevant for this workshop could be described as follows:

1. Because of the low density and temperature in the ISM, the chemistry is never at thermodynamical equilibrium. Chemical processes are dominated by the kinetics and branching ratios of the reactions at hand, and are at steady state at best, even if astrophysical timescales are relatively long, characteristic times being of the order of $10^4 - 10^6$ years. Only in planetary atmospheres thermal equilibrium is reached.
2. In space, three-body collisions are absent (or extremely unlikely). This means that reactions like $A + B \rightarrow AB$ may only occur with photonic stabilisation, or else on the surface of a grain.
3. The often prevailing low temperatures of interstellar space prevent many reactions to take place, even with modest activation barriers. However, some reactions proceed through tunneling, especially so if involving atomic H (or D).
4. Ion chemistry plays a important role in space, mainly through cations (though anions are also present). Main ions are atomic species (in diffuse clouds) and protonated species (in molecular clouds).
5. In interstellar dilute environments, ionization of trace elements, such as C and S, may proceed by photon with $E < 13.6$ eV, photon of higher energy being absorbed by atomic H. However, cosmic rays (CR) are ubiquitous, even in the denser parts of the ISM and are the main primary source of energy that initiate chemical chains (by the reaction summarized by $H_2 + CR \rightarrow e^- + H_2^+$ followed by $H_2 + H_2^+ \rightarrow H_3^+ + H$).
6. For many environments of very low ionisation fraction, the neutral-neutral reactions are of importance, especially so those involving radicals tend to have higher rates at low temperatures [2]. However, ion/electron chemistry dominates the chemical evolution in many sectors of molecular complexification, like the successive hydrogenation of N^+ or CH^+ .

Great details may be found in many reviews (see e.g. [3–6]). Let us also underline that the chemistry of the ISM is relatively rich, with almost two hundred molecules detected, some of them quite unusual on the point of view of the laboratory: Long carbon chains, possibly charged – anions and cations –, and substituted (CH_3 , CN); some

cyclic molecules ($c-C_3H_2$), many radicals and protonated species, like the common HCO^+ , N_2H^+ , H_2O^+ and the all-important H_3^+ .

The precise identification of a chemical species (including all its isotopologues) is made possible from observed rotational/spectra from cm to FIR wavelengths and thanks to the fundamental spectroscopic experimental work which provide accurate frequencies to compare with. It makes use of large spectroscopic databases, still not precise enough especially so in the frequency region above 800–1000 GHz. Also, many isotopologues of the main molecules are detected, with D, ^{13}C , ^{15}N , ^{17}O , ^{18}O as main substitutes; even some multiply substituted isotopologues are detectable, like $^{13}C^{18}O$ or $D^{13}CO^+$. Complete spectroscopic databases for isotopologues, and for vibrational excited states are far from complete, and computation of rotational lines is still beyond possibilities, at the precision required ($\Delta\nu/\nu \leq 10^{-6}$). Present databases include the CDMS in Cologne [7] and the JPL in Pasadena [8] with other data bases found in links in the CDMS front page.

The quantitative description of the ISM necessitates a non equilibrium model of the radiative transfer of the most abundant molecular species. In order to achieve this, it has been known since a long time that the excitation/de-excitation of the various molecular lines is determined both by photon emission/absorption and by collisions with the main components of the molecular gas, or with electrons. In the ISM, the projectiles are mainly H_2 , H, e^- . For planetary atmospheres, dense regions of protoplanetary disks and atmospheres of Solar System objects, the main gas may be heavier, H_2O , CO_2 , N_2 , or CH_4 . In any case, the rates of energy exchange between the projectile and the target –the molecule being observed– determine the lines intensities for most rotational transitions, and also for some ro-vibrational transitions, if the FIR emission rate is low enough. This is especially true for electric-dipolar forbidden transitions, like magnetic (fine-structure) transitions in open shell atoms or radicals. Also, elastic/inelastic scattering computation open the way to ab initio computing of pressure broadening [9] and other collisional properties [10, 11].

Most of those statements have been known for years, and the importance of microscopic knowledge is fully recognized nowadays (see e.g. the special issue of Chemical Reviews, 2013, Volume 113, Issue 12). It has been a major endeavour, to try and model rates of reactions and incorporate them in the chemical reaction networks. Widely used networks may be comprehensive and even include surface reactions and adsorption/desorption [12–14]. Other networks are specialised for the chemical conditions of interest, like PDR’s or very cold pre-stellar core. Modern simulation tools include chemical models coupled to physical dynamics, in particular hydro- and magneto-hydro-dynamics. Change of thermal or transport properties because chemistry may occur and influence back hydrodynamics of the considered medium. Any of those networks necessitates the knowledge of $10^3 - 10^6$

reaction rates, at low pressure, and at variable temperatures and pressures.

It must not be forgotten that the characteristics of astrochemistry presented so far make it certainly peculiar, but it shares some of those peculiarities with a few other branches of physical chemistry. Let us mention here two representative cases:

- The diluted gas chemistry is prevalent in upper atmospheres, and ours too. Chemistry in our upper atmosphere, while quite distinct from the ISM (importance of the Solar wind and photons, massive presence of O, Cl, role of aerosols), presents some mechanisms and conditions that are quite similar.
- Also, for many years, combustion chemistry has been dealing with various radicals, built with the H, C, N, O elements principally. It is no chance that many of the chemical rates used in astrochemical databases originate in one way or another from rates used in combustion chemistry, even if physical conditions may be vastly different, see the massive database [15].

B. Aim of this workshop

Because of these very specific conditions, it has been recognized that much experience has to be gained, in order to understand model reliably the chemical evolution of matter in astrophysical environments. Several large agencies and several European and national initiatives tend to fund and favor research in the domain of *Laboratory Astrochemistry*, as it is presently called. While many experiments are running or are being set up in numerous laboratories, it has become clear lately that the chemical physics/physical chemistry theory that would adequately model astrochemistry is neither at the level of the astrophysics models, nor as sophisticated as the experiments which are now conceived and put into operations.

We feel it useful to describe where theory stands now in several European and international teams. We choose to focus on one specific subject, because of the width of possible themes: Gas phase molecular scattering, whether inelastic or reactive.

We have the aim to compute rates of energy exchange, rates and branching ratios of chemical reactions, in the temperature, pressure and abundance ranges relevant for astrophysical problems. We wish to have mathematical and physical theories, computer codes and models that are able to produce reliable, quantitative models of those astrophysics objects which are rich in molecules interacting with each other.

Two diagrams are presented below (Figures 1-1), which illustrate the goals and aims of this workshop. On both diagrams, the main themes of this workshop are the square boxes in red, and spectroscopy are the square blue boxes.

In the first one, one sees the usual way of describing the flow of information, back and forth from the observation on the sky to an understanding of the object, thanks to model presenting a spatial (or at least radial) structure in density, temperature, gas and grain content, degree of turbulence. The scheme underlines the necessity of the several levels of simulation that concur into finding a good model, validated by the conformity with observation, of lines shapes and intensities of the molecular species as well as the continuum maps or other maps of the object in the sky.

The second diagram shows the various inputs towards chemical physics/physical chemistry relevant properties, emphasizing both experimental and theoretical inputs.

Let us underline the importance of observation-induced molecular data (including species, like $c\text{-C}_3\text{H}_2$, or some anion whose spectroscopy used to be unknown, like C_6H^- , [16]). It is instructive to note that CH^+ , even if known in principle, was first detected in space by its optical transitions, then found in experimental plasmas by Douglas and Herzberg [17], in the very beginnings of molecular physics for astrophysics.

The goal of this workshop, on a synthetic/diagrammatic view, is to list (at least partially) the theoretical methods that are currently in use, for dealing with the *theoretical part* of the program, in the right hand side of figure 2. The theoretical goals split into two parts; the static part (or electronic part) of the program consists in determining the landscape in which the atoms (or nuclei) move (violet hexagons in figure 2, and also section II B). The dynamics part, in reddish in figure 2, deals with the much more complex problem of how do these atoms move in the landscape, including making and destroying chemical bounds and/or undergoing non adiabatic transitions (transfers of spin, electrons, protons).

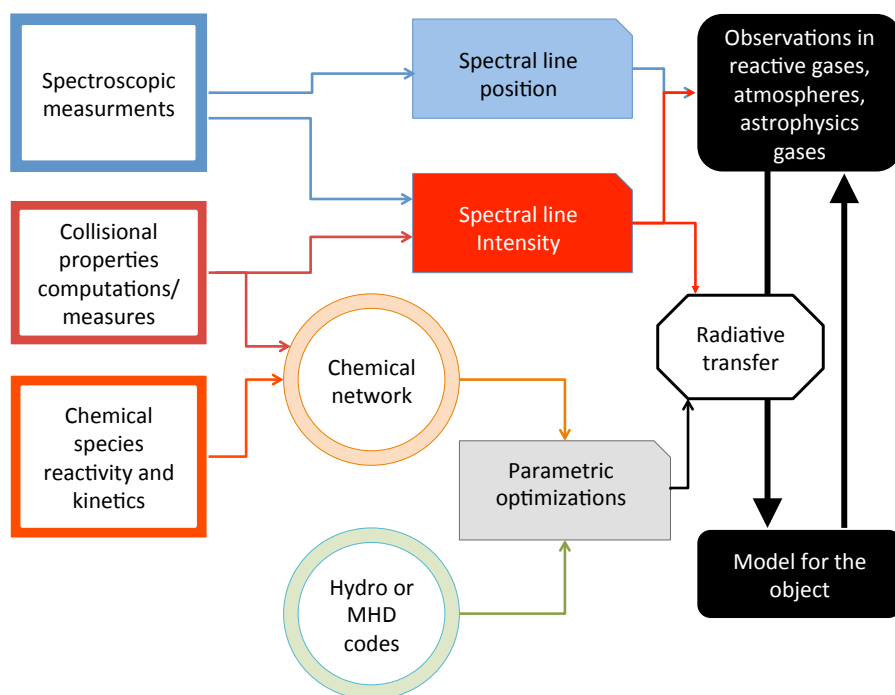


Figure 1. Schematic flow of information from the observation to the model of the objects, with inputs of molecular physics: spectroscopy, collisions, reactivity.

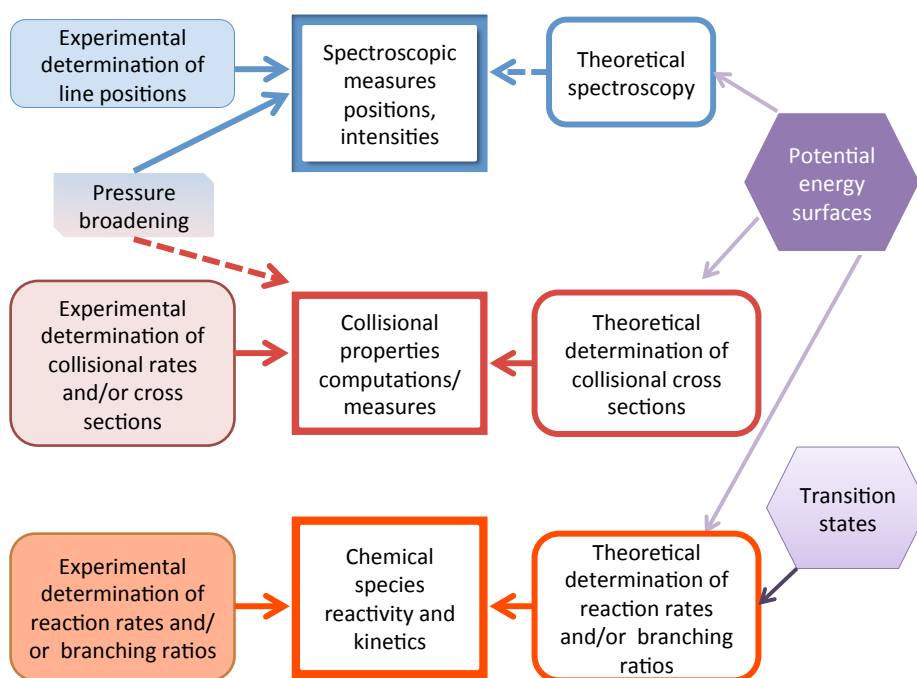


Figure 2. Schematic ways to determine the dynamical and spectroscopic data needed for figure 1. Experiments on the left, theory on the right. Note the 2 sources of dynamics, either the full PES surface or the stationary points of the Transition States.

II. ANALYTICAL PRESENTATION

In the present chapter II, sections are written by the author(s) explicitly stated. If none stated, section is written by the editors (see the footnotes in the list of authors).

A. Chemical Simulations of Interstellar Sources

Text by E. HERBST

The simulation of the chemistry that occurs in sources of the interstellar medium (ISM), in particular the dense interstellar medium, requires a large number of reactions, both in the gas phase and on the surfaces of dust particles [18]. Networks of chemical reactions now range in size from 10,000 to over 100,000 reactions depending upon the number of isotopomers included, especially those that include deuterium [19]. The newest networks are assumed to be useful at temperatures from 10 K to 800 K, but only a small fraction of the reactions have rate coefficients studied over such a wide range of temperature, often necessitating extrapolation or additional theoretical or experimental effort based on sensitivity analyses [20]. Most of the gas-phase reactions in the networks are ion-neutral processes, with the ions produced by bombardment of cosmic rays, mainly high-energy protons [21]. Reactions involving neutral species can also be important, despite the low temperatures in most of the ISM [22]. In addition, there are dissociative recombination reactions, in which molecular positive ions combine with electrons to form neutral fragments, neutral-neutral reactions that occur via tunneling [20] and radiative association reactions, in which a complex is formed, which then stabilizes by emission of a photon [13, 18]. These processes were designed initially to study cold dense clouds with typical temperatures of 10 K. For higher temperature sources, in which star formation has proceeded at least partially, neutral-neutral reactions with small barriers including endothermic processes assume more importance and have been subsequently included [23]. An example of network is presented in figure 3.

The reactions that occur on dust particle surfaces are assumed for the most part to occur via the Langmuir-Hinshelwood mechanism, which is based on diffusive motions of the surface reactants until they collide with one another and react [24]. This diffusive motion depends on molecular vibrational frequencies in potential wells coupled with tunneling or hopping of species from one well to another. Often, the barriers against hopping and tunneling are not known accurately for adsorbate-substrate pairs. The gas-phase and grain-surface chemistries are coupled by the processes of adsorption from the gas onto the grains, and desorption from the grain surfaces back to the gas. Adsorption is most efficient at the lowest temperatures, when the adsorbate sticks to the surface with only weak van der Waals-like binding, known as ph-

ysisorption. Thermal desorption, or sublimation, is inefficient at low interstellar temperatures (10 – 20 K) except for hydrogen and helium [25]. Non-thermal desorption at these temperatures occurs via a variety of mechanisms, mainly photodesorption and reactive desorption [26, 27]; the former has been studied in detail in recent years, while the latter has received much less study. The mechanism involves the transfer of a portion of the exothermicity of a surface reaction into kinetic energy able to eject the product from the surface.

To solve the kinetics so as to determine abundances, one can use rate equations for each species in the network, and integrate these coupled differential equations as a function of time [25]. The computer coding for this process is referred to as a 'chemical model' and the result a 'chemical simulation'. The steady-state condition is rarely reached before unphysically long times. Instead, large mantles of ices, mainly water, carbon dioxide, and carbon monoxide, grow in colder regions. Rate equations exist for both gas-phase and grain-surface species although the rate coefficients for the two phases are quite different, the former governed by trajectories involving both short-range and long-range forces, while the latter approximate a random, diffusive motion. The simplest treatment with rate equations is known as the two-phase approach, with the two phases referring to the gas and the surfaces of the dust particles. In other words, if an ice mantle of many monolayers exists, the chemistry occurring atop the highest monolayer is not differentiated from the chemistry underneath in the bulk ice. An extremely different approximation is known as the three-phase treatment [28, 29]; here, it is most often assumed that the bulk of the ice mantle undergoes no reactive chemistry at all. Both of these treatments are approximate for surface chemistry for a number of reasons. First, the chemistry occurring in the bulk is likely slower than that occurring on the surface, but is hardly occurring at a zero rate [30]. Secondly, the use of rate equations, while perfectly fine for gas-phase processes, is only approximate for surface reactions, based on the small number of reactive species per grain. More advanced treatments than the solution of rate equations are based on discrete but stochastic approaches. These approaches yield the number of species per grain, the uncertainty in this number, and the positions where the species lie in each monolayer. The most utilized stochastic approach today is a Monte Carlo realization of the stochastic nature of the physics and chemistry on a grain [31, 32]. Unfortunately, the use of a microscopic Monte Carlo method to solve the grain kinetics necessitates use of a similar, but macroscopic procedure for the gas-phase kinetics so that the clock for both chemistries is the same. Current computational methods for the Monte Carlo procedure are exceedingly 'expensive' and beset by some flaws. Not surprisingly, they can only be used for astronomically short periods of time at low temperature. Approximations for the Monte Carlo procedure can do somewhat better, but at the expense of limited accuracy [33].

Chemical simulations can be undertaken for a wide diversity of interstellar sources, many of which are evolutionary stages in the formation of stars and planets. If the physical conditions change during the existence of a particular stage, and if they are also heterogeneous, then the computer time and memory needed for full solution of the physics and the chemistry can be quite extensive, even if only rate equations are utilized for the chemistry. For example, the evolutionary stages of solar-type systems involve the gradual formation under the influence of gravity of so-called 'cold cores', which possess gas densities of 10^4 cm^{-3} , mainly H_2 , and gas and grain temperatures of 10 K [4]. The gas-phase molecules found in cold cores contain many exotic species by terrestrial standards; these include radicals, linear carbon chains, metastable isomers, isotopologues, cations, anions, and three-membered rings. Some cold cores collapse to dense objects known as pre-stellar cores, which possess higher densities in a central condensation where much of the gas phase heavier than H_2 is lost to mantles on grains. Eventually, the system becomes adiabatic and starts to heat up as material collapses onto the central condensation, now known as a protostar. As the collapsing gas and dust, now labelled a hot core, reach temperatures of 100 – 300 K, the molecular inventory changes to a terrestrial-type chemistry, with common organic molecules [34]. It is currently thought that at least some of these species are formed on warm dust particles and then sublime into the gas phase as the dust particles reach even higher temperatures [35]. In addition to the hot core, a nearly planar and dense disk forms around the protostar, and dust particles in the disk coagulate to form comets, meteors, asteroids, and even planets. The chemistries of all evolutionary stages of low-mass and high-mass star formation have been studied, with some stages better known than others. Protoplanetary disks are of great interest, but are small objects difficult to study observationally until recently, when a new generation of telescopes came into use. Most recently, the organic molecule methanol was detected in the gas phase of a protoplanetary disk, in partial agreement with a prior chemical simulation [36]. Advanced chemical simulations of protoplanetary disks should be combined with three-dimensional hydrodynamics to follow the collapse of a hot core into such a disk as the chemistry also occurs. At the present stage, such calculations do not quite reach the physical conditions observed for protoplanetary disks [37]. Nevertheless, the chemistry of planetary atmospheres surrounding exo-solar planets that are formed in older protoplanetary disks is a new field destined to achieve popularity.

B. At the root : Potential Energy Surface

Text by DENIS DUFLLOT AND JOÃO BRANDÃO

In order to compute dynamical effects, there are many ways to take care of the forces between the atoms and

molecules, depending mainly on the size of the problem at hand the precision desirable.

In all of the theoretical works described here, because of the reduced number of atoms, the concept of a complete Potential Energy Surface (PES) is valid and its usefulness is not challenged. Working on model surfaces was considered as non-relevant, except for some very mathematical works, or proofs of concept. This very strong statement stems from several concurring factors, which make the computation of PES the most reliable part of our program. It is absolutely obvious from all interventions that computing reactive or inelastic scattering dynamics necessitates a PES of 'high' quality, 'high' meaning here that the various approximations are carefully described and justified, see below. There seemed to be three reasons for that: (i) the constant development of more versatile and more precise formalisms in quantum chemistry; (ii) the existence of well-balanced suitable suites of gaussian atomic basis sets for the description of molecular wave functions; (iii) the rapid implementation of state-of-the-art equations in actual *ab initio* codes, widely available, either as free codes or as or commercial ones, both thoroughly maintained and supported. One of the best example is the MOLPRO code, particularly well adapted to our needs. Those codes incorporate many high precision methods: Coupled Clusters even at a higher level [39], the so-called golden standard CCSD(T) [40], explicitly correlated (F12) treatment of electronic cusps [41, 42], special methods for long range interactions, like SAPT [43, 44]. A description of the MOLPRO code is found in [45, 46]. Also, these codes are able to handle at different level of precision open and closed-shell problems, and even multi-configuration effects (several arrangements of the electrons among the available electronic levels), albeit in a less straightforward and less rapid way. Computation times are in general not negligible, and the quantum chemistry codes are not fully parallelized (generally limited to one node, to avoid inter-node communication). However, because the description of the PES necessitates computing usually a large number N of points, trivial parallelization is usually possible. It actually scales in a not straightforward way with the number of degrees of freedom, thanks to clever Monte-Carlo explorations or else to good fitting schemes (see below). This is feasible for small systems, but for larger systems strategies are needed to reduce the calculation to the chemical important region. As the computation of each point increases with the fourth power of number of basis set functions, stemming from the dimension of the matrices and the number configurations used in the calculation, the accurate energy estimation of each point became a crucial task. Besides, the main bottlenecks reside often, on the one hand, in the proper tests of the *ab initio* methods (choice of basis set, calibration), and on the other hand, in the fitting procedures.

In practice, experience is that 1 *ab initio* point/cpu is not the best choice. The number of integrals becomes very large necessitating huge RAM or disc storage. Dif-

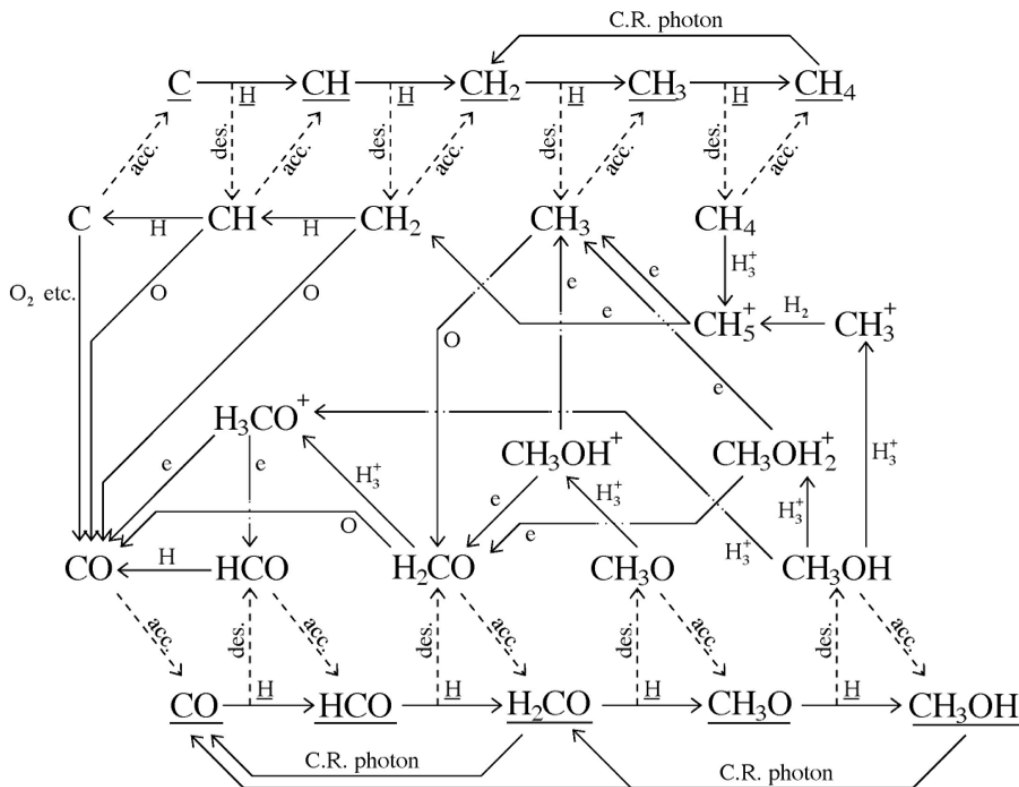


Figure 3. Low temperature chemical routes involving the conversion among solid and gaseous methanol, carbon dioxide, carbon monoxide, and methane. Grain-surface species are underlined. 'acc' and 'des' refer to adsorption onto grains and desorption from grains. Figure taken from [38]

ferent CPUs accessing the same memory or disc will be very time consuming. The best policy is to divide the calculation by regions and attribute each region to different nodes since each point can benefit from the wave function computed in an earlier calculation.

1. Methods for computing *ab initio* points

a. Non reactive scattering (elastic and inelastic)

Computing *ab initio* points for non-reactive scattering has not been extensively discussed during the course of the colloquium/workshop, since it was felt that the situation is quite favorable. Being it for interaction with H, H₂, or He, methods based on the CCSD(T) *ab initio* suites [40] are considered today to be of sufficient quality, especially so for non-asymptotic distances. The only problem remaining is the size of the atomic bases.

Computing inelastic S-matrix elements (and even more so for elastic S-matrix elements, required for pressure broadening or momentum transfer cross sections), necessitates having a PES precise of the order of a few percent, and a well-calibrated long-distance behaviour. It has been shown repeatedly that the CCSD(T) method must be used with care in order to achieve this level of precision: proper correction of the Basis-Set Superposi-

tion Errors (BSSE, [47, 48]), large and flexible enough atomic basis sets are needed. An example is the so called correlation consistent series of Dunning [49] (aug)-cc-pVNZ, with N running from D (double- ζ) to 7 (7- ζ) [50]. With such large sets of atomic basis sets, extrapolations towards infinite-basis sets are possible, even if quite heuristic (see e.g [51] and references cited therein).

There exist new perturbational schemes that take explicitly into account the wave-function cusp for vanishing inter-electronic distances between electrons. The newest versions (so-called F12 codes, [41, 42]) are now reliable. To summarize, employing a properly balanced basis set, and taking into account electronic correlations via a CCSD(T)-F12 method seems a satisfactory way to compute the non-binding interaction of He/H/H₂ with the molecule under study. It is not yet fully agreed upon, whether this method is sufficient at all distances, or whether a method especially suited for long distances (like SAPT, [43, 44], or else an *ab initio* computations of multipoles and polarizabilities, like in [52, 53]) is more economical and/or more precise.

Many examples of PES are now available, showing that the potential energy wells are well behaved and of modest depth (less than a few hundreds of cm⁻¹). Exceptions are some atom-H₂ interaction (for example the C(³P) + H₂, with the CH₂(³B₁) radical in the PES), or some ions-

molecule interactions, like $\text{HCO}^+ - \text{H}_2$, with a well depth of $\sim 1487 \text{ cm}^{-1}$, [54].

b. Reactive scattering When used to study reaction dynamics the Potential Energy Surfaces must fulfill certain requisites. They must cover all the accessible configurational space, from reactants to products; describe all the minima and saddle points with chemical accuracy. At room temperature $T \leq 1 \text{ kcal/mol} \approx 1 \text{ mE}_h$, but, for lower temperature studies, the precision should be higher; accurately describe the dissociation channels as well as the reactants and products; and preserve the permutational symmetry of identical atoms.

Additional care must be taken when studying low temperature interstellar chemistry. Interstellar chemistry often involves open-shell radicals as reactants and/or products. This implies special care in the description of the dissociation channels as the open-shell radicals usually present degenerate states, that produce quasi-degenerate PESs difficult to compute accurately due to convergence problems in the algorithms used. In addition, the energy differences between these PESs is of the order of the spin-orbit coupling which must be taken into account. These quasi-degenerate electronic states, often cross each other producing diabatic PESs and coupling terms that can be important to study the reaction dynamics. Often the reaction proceeds on the lower PES with small, submerge or non-existent barrier, being the reaction dynamics dependent of long-range part of the potential. This should have the correct R^{-n} behaviour, but the van der Waals coefficients involving open-shell systems are difficult to compute using the present available *ab initio* codes.

2. Methods for fitting *ab initio* points

Fitting the *ab initio* points onto one single functional used to be one bottleneck between the computing of isolated *ab initio* points and the subsequent dynamics. Indeed, full dynamics, as opposed to Transition State Theory or on-the-fly computing of potential energy [5] relies on a global functional expressing the whole PES noted as $\mathcal{F}(R, \Omega, r)$, R , intermolecular distance, Ω , angles that set the relative attitude of one molecule with respect to the other, r , the collective intramolecular coordinates. It is remarkable that this bottleneck has not been identified as such in the various interventions of the colloquium/workshop.

For inelastic scattering, MOLSCAT has all necessary subroutines for using the PES for each types of scattering (rotor/atom; rotor/rotor)[55]. For Hibridon, the different types of PES are entered in a more flexible way. Help and references to found in the Hibridon site <http://www2.chem.umd.edu/groups/alexander/hibridon/hib43/hibhelp.html>. Also, fitting codes exist that systematically fit the *ab initio* points onto the right functional forms for MOLSCAT, minimizing the errors and the number of needed parameters

Also, Szalewicz *et al.* devised an economical way to fit for non-reactive scattering, based on site-site expansions. This functional form has been treated for water-water potentials, and for large molecule (HCOOCH_3) colliding with helium [56]. Fully testing this economical way of describing the PES for inelastic scattering is desirable.

a. Fitting points for reactive scattering PES Another approach to build the PES is to smoothly join the *ab initio* point with cubic splines. The accuracy of this approach depends on the density of the data, but is unable to reproduce the long-range behaviour of the approaching species.

Despite all the improvements and experience of the last years, building a PES useful for reaction dynamical studies from *ab initio* data is still an art. No universal recipe is available for such desiderata. Different options can be used for problems like:

- Coordinates. Jacobi coordinates useful for scattering calculations are not suitable to describe bond breaking. Inter-atomic distances, hyperspherical coordinates, scaled coordinates, etc., are multiple choices available for fitting.
- Accurate description of the reaction fragments. One approach is the many-body expansion, where the total inter-atomic potential is defined as a sum of atomic, diatomic, triatomic, etc., terms. Each term should go to zero as one of its atoms departs from the others. This procedure warrants the correct dissociation of all the reaction channels but becomes infeasible for large systems.
- Permutation of identical atoms. The PES should be invariant to the exchange of identical atoms. This can be accomplished taking care of the coefficients of the polynomials or using symmetric coordinates to represent the potential.
- Treating different regions which have different energy behaviour. Chemical regions such as deep wells and transition states behave different from long-range interactions. The first ones depend on orbital superposition and decay exponentially with the inter-atomic distances while the second ones should approach zero with a R^{-n} dependence. How to join these regions? Using an energy switch approach or damping the R^{-n} at small R values.
- Curve crossing. Potential energy surfaces involving radicals frequently presents crossing of electronic states, Renner-Teller effects and Jan-Teller cusps. The treatment of those systems, building the adiabatic and diabatic crossing terms or fitting the adiabatic potentials are different ways to solve the problem.
- The functional form. This is a question where there are a lot of options. The use of Morse-like functions with varying parameters, the use of polyno-

mials damped for large R values, the use of localized polynomials, etc., are choices available for the fitting of the *ab initio* data.

C. Dynamics

Once the PES has been computed and the isolated points fitted onto a suitable functional form, the next step in our program is to perform dynamics on the PES. Several cases occur, that have been discussed in the course of the workshop. The case of elastic/inelastic scattering is usually the easiest case, even if some noticeable difficulties may arise (see IIC 1). Full dynamical solution of the reactive scattering problem remains extremely difficult, and is usually confined to either tri-atomic (possibly tetra-atomic) reaction, and/or to direct reactions, with sufficiently short reaction times in order for time-dependent solutions of the Schrödinger equation to remain practical.

1. Inelastic scattering and applications

Discussion lead by A. VAN DER AVOIRD, L. WIESENFELD

Quantum dynamics of elastic/inelastic scattering has been developed and perfected over the course of several decades, alloying today to treat large and sophisticated problems. It includes many elastic/inelastic scattering problems relevant for astrophysics: from hydrides of general formula XH_n (closed or open shell) to main molecules of interest to astrophysics, all in collision with He, H, H_2 , see Schöier *et al.* [57], Dubernet *et al.* [58], Roueff and Lique [59]. It must be underlined that a lot of effort has been devoted also to electronic collisions, which were not discussed during the course of this workshop [60].

All those systems are considered simple: Rigid target, sufficiently small number of rotational levels excited, low enough temperatures at which the rates $k(T)$ have to be computed. For those systems, it is considered that existing codes, either fully converged or with approximations that are known and under control, suffice for all practical purposes. It has been underlined that nowadays, elastic/inelastic scattering may be pushed towards very sophisticated problems, computed fully *ab initio*, as this workshop implies: heavy-heavy scattering (like CO-CO), pressure broadening, collision induced absorption, presence of external fields, very low T , down to the mK level. Recent progresses include inclusion of bending/stretching for small systems (like HCN, CO), some internal motion excitation (like CH_3OH).

However, the sophistication of present programs is such that the barriers towards more complex now are of computational nature. Those problems include, many more rotational levels (for heavier molecules, like $HCOOCH_3$,

$HNCO$, $HC(O)NH_2$), full quantum computation of doubly inelastic sections (both projectiles and targets undergo transition), bending modes of molecules like H_2O , converging elastic cross sections towards higher temperatures, in order to compute transport properties or pressure broadening [61][62]. Clearly efforts should be undertaken for being able to solve time independent Schrödinger equation with representative $N \times N$ matrices with $N \gtrsim 5000$.

2. Far from perfect: deep wells, bimolecular reactions

Computing of reaction states, branching ratios has been a major challenge for many years, even for three atoms reacting in a simple way. Many complications arise, that make these computations difficult:

1. *Definition of the coordinates* For inelastic scattering, one single system of coordinates suffices to describe the scattering for $-\infty < t < +\infty$, see figure 4, left panel. One single expansion of the potential, one single propagation at energy E of the Schrödinger wave function is enough to get the $S(E)$ -matrix, hence all imaginable observables. This is not at all true for reactive scattering as is exemplified in right panel of figure 4. One sees that at $-\infty < t < t_0$, the coordinate system is adapted in a different way (coordinate \mathbf{R} describes collision) then for $t_0 < t < +\infty$, where a different \mathbf{R}' is the scattering coordinate. It is possible to properly define so-called democratic coordinates that put all configurations on a same footing, for up to 4 centers, but at the expense of very cumbersome analytic wave function bases (see section IIE) and difficult description of the asymptotic channels.
2. *Multiple surfaces* While some reaction occur on one and single surface (some rearrangement reactions for singlet molecules, for example), in many cases of relevance in astrochemistry, ions and radical species are reactants. In those cases, a good description of the reaction event, including all channels and quantum numbers becomes a major task, very seldom put to fruition [63]. Several problems appear at the same time:
 - (a) Spin effects. When some of the species are open shell, all surfaces split according to the total electronic multiplicity. The degeneracies is usually different in the asymptotic channels and in the reactive part of the potential energy surfaces (PES), and the aspects of the various multiplets PES are vastly different. It means that branching ratios may be computed only by fully taking into account the spins. Furthermore, weak magnetic / spin-rotation terms allow for intersystem crossings, increasing further the complexities of the quantum treatment.

(b) Conical intersections and higher order singularities. Spin or charge result in several PES's describing the reaction. Generically (meaning, in a non-specific case, like identical particle effects) these surfaces intersect in several ways: avoided crossings, conical intersections, and for $n > 3$ atoms, higher order singularities, like intersection of conical lines. These lines/points make it difficult or impossible to propagate semi-classical trajectories, and make it necessary to resort to brutal approximations when propagating classical trajectories. It is very difficult to propagate wave-packets and even time-independent wave functions in such topologies. There also the need to properly define diabatic vs. adiabatic PES's, a problem with no unique solution.

3. *Indirect reactions* For $n = 3$ atoms, with a PES of one sheet, codes exist, capable of computing the S -matrix, like the ABC code. Some recent extension even allow some indirect reaction to take place [64], but at the expense of a great numerical effort. An interesting list is published by the CCCP6 group (<http://www.ccp6.ac.uk/downloads.htm>), even if partial.
4. *Tunneling* At low temperature, a few K, reactions may progress by tunneling, especially so if H or possibly D atoms are involved. This is a well-known characteristic of astrochemistry, and very low- T chemistry in general. Inclusion of tunneling has been described by various formalisms, the instanton being one of them [65]. Including those effects that go way beyond classical Transition State Theory is one of the goals of quantum TST, see below.

The situation seems thus very complex, and it appeared that we are far from being able to tackle the quantum reactivity in its full extent. We have neither a full algebraic/analytical picture, nor a set of algorithms capable of treating actual, interesting cases. The MCTDH (Multi-Configuration Time Dependent Hartree) formalism [63, 66] is very powerful for single surfaces –even multidimensional– and not too long interaction times. The ABC program does the same for three atoms in a time-independent case. Some formalisms keep on appearing, but except for very large brute force computations, it does not seem, in the editor's opinion, that a breakthrough has recently been reached, for a full quantum description of reactive scattering, even if some may argue that the so-called "polymer-ring" formalism is due to play a very interesting role [67, 68].

D. Transition states

Repeatedly in the course of the workshop, the concept of transition state theory (TST) appeared as one of the main tool able to be substituted to exact dynamics when it is obvious that numerics becomes impractical or unfeasible. TST is able to (i) conceptualise the outcome of a chemical reaction (ii) quantify the chemical rates, even if in an approximate way. While transition state theory is by no means a novel idea (it dates from 1913, see Fernandez-Ramos *et al.* [69]), its mathematical and chemical aspects have greatly been improved and extended. Both these aspects were of interest in the context of this workshop: The progress made in the mathematical community and the actual use in non trivial contexts, like radical-radical reactions.

The usual way to define a TS is to determine the minima of flux of probability density, from the reactant region to the product region. These minima of flux are considered as bottlenecks, and serve as supports for the rates to be introduced in the master equations for the overall chemical networks. Reactant and product regions are defined in a different way for mathematical aspects (regions of representative phase space) or for a quantum approximate view (quantum states of the reactants/products), figure 5. Note that a semi-classical TST is also part of the present program, based either on some Wigner picture of phase space, or, more simply, taking into account zero-point energies and elementary tunneling effects, possibly via instanton type of approximation.

There are several important features of TST, that make it the most attractive way to compute rate of chemical reactions, in many cases. In all common applications, the TST is based not on a full PES determination, long and painful, but rather simply on finding the stationary points of the PES. Many *ab initio* codes are very well suited for finding semi-automatically stationary points P_i . One proceeds then as follows, in a way compatible with a fully automated feature of the quantum chemistry code: (i) Form the Hessian $H(P_i)$ of the potential at the stationary point (symmetric matrix of second derivatives with respect to coordinates (We work here only in configuration space); (ii) Find its pairs of frequency eigenvalues, and concentrate on those P_i where all eigenvalues pairs are real, but for one which is imaginary; (iii) Let the imaginary pair be associated with eigenvectors ξ_i ; this ξ_i is the local reaction coordinate; (iv) all other coordinates are bath coordinates and serve to define the density of states at the TS; (v) this density of states, either at fixed energy or temperature, defines the flux from reactants to products. All details may be found in many references and textbooks (Mathematical context: [70]; physical chemistry context: [71]). This program is perfectly adapted for many reaction schemes, and has been used for decades.

Also, TST, being such an intuitive concept, and being defined both at fixed energy (micro canonical ensembles) and at fixed temperature (canonical ensembles), its do-

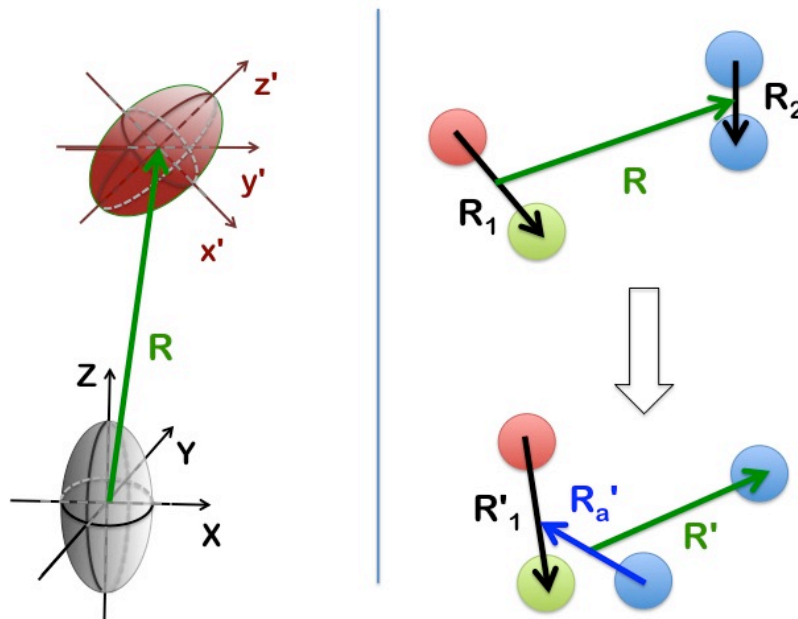


Figure 4. Figure schematizing the difference between elastic/inelastic scattering (Left) and reactive scattering (right). On the left (scattering), the two ellipsoid retain their character during the scattering process. One set of coordinate e.g. \mathbf{R} (R, θ, ϕ in the OXYZ frame) as well as the orientation of the $Ox'y'z'$ (e.g., three Euler angles α, β, γ). On the right hand side (reactivity), the asymptotic systems of coordinates change during the event, as exemplified by the figure.

main of definition has been extended to many abstract dynamical systems.

As a final point, it is obvious that TST is perfectly adapted for obtaining approximate (even with a very good approximation, see section IID3) reaction rate in the case where: the whole reaction is exoergic $-E(\text{products}) < E(\text{reactants})$ and where the energy of the TS is such that $E(P_i) > E(\text{reactants})$. Many of the rates proposed in databases for combustion [15] or astrochemistry (KIDA, <http://kida.obs.u-bordeaux1.fr/>) are based on TST at high temperature and finite pressure, even if these conditions are not fully relevant to many astrochemical environments. Many examples are vividly illustrated in chemical schemes showing the relative energies various asymptotic channels, reactants and products, TS and stable or meta-stable intermediates [72][73].

Astrochemistry relies on this definition of TS for many reaction schemes, even if it is not at all fully applicable. One of the way to salvage TST (or actually, it was one of the ways that led to its discovery) is to add the centrifugal barrier to the PES. For ion-neutral interactions, this leads to Langevin-like approximations, where the capture cross sections and rates depend on the multipole/polarizability of the neutral species. For neutral-neutral attractive PES (no barrier or low barrier at entrance), it leads to other formulations of capture theories,

like Faure, Wiesenfeld, and Valiron [74], Georgievskii and Klippenstein [75].

Clearly, astrochemistry, lacking thousands of reaction rates at temperature ranges from 10 to 1000 K, is in dire need of viable TST, which would be valid even if *no entrance barrier is present*, like for most ion-molecule, many radical-radical reactions and some radical-neutral reactions.

Note that in its usual forms TST predicts total reaction rates, while it often desirable to get branching ratios between the various products. Let us think of a very common model like: $A + BC \leftrightarrow ABC^* \leftrightarrow AB + C / AC + B$. The stable compound product ABC is produced from the excited form ABC^* by third body collision (pressure effects) or else photon emission, usually a slower process than decomposition. Hence, knowing the branching ratios is by no means a trivial task, experimentally or theoretically.

1. Mathematical grounding

Text by T. KOMATSUZAKI, H. TERAMOTO, M. TODA, AND L. WIESENFELD.

For most of the discussion, TST in mathematics is defined within the framework of *Hamiltonian classical dy-*

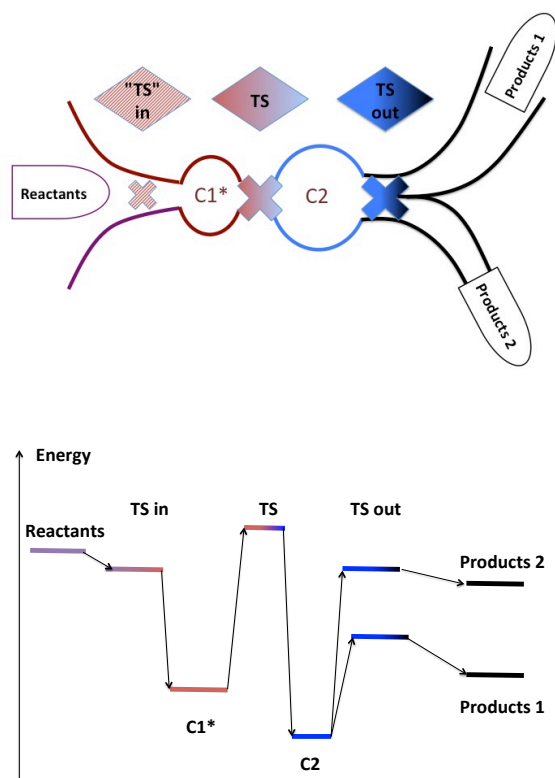


Figure 5. A scheme of the progression of a reaction similar to figure-1, from reactants, to two successive sets of complexes, an excited one C_1^* , a metastable one C_2 , and various exit routes. This type of scheme is very usual, and more on the simplified side here. Upper panel: A schematic view in some abstract phase space. Each step in this simplified model is separated from the next by a transition state -depicted by crosses. Lower panel: More usual picture with some reaction coordinate as horizontal axis and energy as a vertical axis. Same nomenclature for both panels. In some cases, several parallel routes exist.

namics. While for $n = 2$ degree of freedom (dof) systems (such as triatomic linear reaction), rigorous (classical) TST exists, for $n > 2$ degrees of freedom, the formalism is still under development. The energy domain at threshold or just above is now clearly understood (see below), but as soon as energy increases, all possible scenarios for the dynamics in the vicinity of the TS are not fully known, nor fully described. Let us state those points in more details.

A definition of TS at threshold for 2 dof was put forward some decades ago, based on periodic orbits [76]. For $n > 2$ the existence of suitable dividing manifolds in the Hamiltonian flows, while known for some years too [77, 78], has been fully appreciated only more recently [79–81]. The development of so-called "Normally Hyperbolic Invariant Manifolds" (NHIM), its application to

capture or unimolecular reactions steadily improved the understanding of Hamiltonian dynamics and its relation with TST.

The main property that classical dynamics fully clarified is the notion of 'no-return' TS. The NHIM's are defined as manifolds (hyper-surfaces) that act as "generalized saddle" in the phase space at which the system perpetually stays even with finite momenta and nonlinear couplings among the modes at threshold. The NHIM being an unstable equilibrium set, it has stable and unstable manifolds. The codimension of the stable and unstable manifolds is 1 at the energy. The property of codimension one is of crucial importance to define the state or domain of reactants and that of products. Codimension n means a dimension less than n from the dimension of the ambient space. For example, if the dimension of the ambient space is three, in order to divide the space one must have a space of two-dimension, i.e., a plane or surface. Likewise, if the dimension of the space is two, one must have a space of one-dimension, i.e., line. Otherwise, one cannot divide the space into two. It is known that the codimension one stable and unstable manifold emanating from the NHIM serve as the so-called reaction tube or conduit so that at the energy E , trajectories representing the shape of the molecules and originating on the reactant side move all the way necessarily through the reaction tube to the products side. Hence, measuring the flux of trajectories across a surface defined to intersect vertically the reaction tube in the phase space, i.e., serving as (rigorous) no-return TS amounts to measure the reaction flux at the energy E .

The dynamics at the threshold of the TS is fairly well characterised by now, including the integrability of the motion and various ways of introducing angular momentum [82], [83],[84].

Three avenues of progress are pursued now (let E^* be the threshold energy):

1. What is the fate of NHIM (that provides a natural definition of a no-return TS) at energies $E > E^*$? How does it survive, how does it bifurcate? Can we learn something from the well-known 2dof case?
2. Building on the preceding item, is there a way to go from a micro-canonical picture (flux at fixed E) to a canonical picture, yielding classical rates $k(T)$ directly, like it is doable numerically?
3. How is it possible to go from some kind of unimolecular/capture type of description towards a full description of a reaction, with multiple asymptotic channels and TS's.

The discussion in the workshop made it clear that, while the Hamiltonian dynamics pictures begin to emerge in a coherent way, applications towards actual reactions are still lacking, probably because of the widely different points of views, languages and knowledge bases of mathematical or molecular dynamicists.

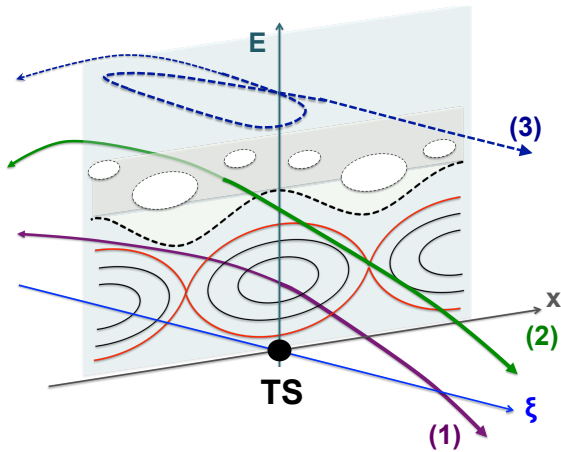


Figure 6. An abstract view of TS, beginning at threshold and extending up in total energy E . If we have n degrees of freedom, the ξ coordinate in the figure labels ξ, p_ξ , the canonical coordinates of the local reaction path. x labels the set (x_i, p_{xi}) , $i = 1, n - 1$, the bath coordinates. The trajectory (1) crosses the TS, when motion locally while crossing is fully regular, corresponding to the existence of approximate invariant of action variables, i.e., good quantum numbers). Trajectory (2) higher in E starts to experience chaos because of nonlinear couplings among the modes but yet free from recrossing because resonance is impossible between bath coordinates and reaction coordinate ξ whose frequencies are real and imaginary, respectively. For trajectory (3) much higher in E where chaos is developed so that one cannot deal with nonlinear couplings perturbatively. Reaction dynamics at such high energies are one of the central subjects in nonlinear dynamics theory of reactions. See for example, Ref. 85–88

2. Quantum Transition State Theory

Text by H. WAALKENS

Especially for reactions involving light atoms quantum effects might become important. Even with the computer power that we have today full-fledged ab initio quantum computations are often not feasible. In recent years it has been shown that the geometry underlying classical reaction dynamics and the algorithms to compute the geometric structures that govern reactions can be utilised and extended in such a way that quantum reaction rates can be computed very efficiently. The classical phase space structures which govern the reaction dynamics through a phase space bottleneck induced by a saddle equilibrium point can be computed in an algorithmic fashion from a Poincare-Birkhoff normal form expansion. The Poincare-Birkhoff normal form leads to a canonical transformation to new phase space coordinates in terms of which the classical dynamics locally decouples into a saddle (i.e. reaction) degree of freedom and centre (i.e. bath) degrees of freedom. The new normal form coordinates give explicit expressions for the various phase space

structures which control the classical transport across a saddle. This includes a recrossing free dividing surface and the directional flux through this surface is . The dividing surface is spanned by a normally hyperbolic invariant manifold (NHIM). The NHIM has stable and unstable manifolds which extend away from the saddle point into the reactants and products part of the phase space and channel reactive trajectories from reactants to products (and vice versa). The knowledge of which regions they sweep out in the reactants and products region is the key to understand state specific reactivities. The normal form expansion is of local validity and hence allows one to compute at first only the local pieces of the stable and unstable manifolds near the saddle. The local pieces can then however be grown into the reactants and products region by letting the flow of the original (untruncated) dynamical equations act on them.

In the semiclassical limit the classical phase space structures that govern reaction dynamics form the backbone also for the quantum mechanics of reactions. Similar to the classical case the quantum dynamics can also be locally decoupled to any desired order into saddle (reaction) and centre (bath) degrees of freedom. This can be achieved in terms of a quantum normal form expansion which yields a unitary transformation which 'locally' simplifies the Hamilton operator in the neighbourhood of the saddle to any desired order. The expansion can be cast into an algorithm using the Wigner-Weyl symbol calculus. The main difference to the classical case is then that the Poisson bracket being replaced by the Moyal bracket. What 'local' simplification means can be understood from the theory of micro local analysis. The quantum normal form allows one to compute quantum reaction rates with high precision (it takes full account of, e.g., tunnelling effects). It also allows one to compute very efficiently the complex energies of Gamov-Siegert resonance states which describe the decay of quantum wave packets initialised on the classical NHIM.

The quantum normal form can be considered to be a rigorous realisation of quantum transition state theory. Although the efficiency of the quantum normal form has been demonstrated for various systems that are also still many challenges and open question:

- Similar to the classical case the quantum normal form leads to an asymptotic series which has to be truncated at a suitable order. It is only valid in the neighbourhood of the saddle. In the absence of resonances between the centre degrees of freedom the normal form leads to integrable dynamics. Similarly the quantum dynamics resulting from the (truncated) quantum normal form results in as many commuting observables as classical degrees of freedom (i.e. all the centre degrees of freedoms have good quantum numbers). For high energies, it might no longer be reasonable to approximate the dynamics on the NHIM in terms of an integrable dynamics. This is similarly true in the quantum case. Especially it might happen that the NHIM

bifurcates or even get destroyed. Recently the case of Morse bifurcations of NHIMs has been studied classically. It highly desirable to also understand this in the quantum case.

- Recently it has been shown how the classical normal form expansion can be achieved in the presence of rotation- vibration coupling. The challenge here was that the symmetry reduced phase space of the N-body system given by the atoms that form a molecule is given as a quotient space for which it was unclear how to define canonical coordinates which form the starting point for a classical normal form expansion. It has been shown that such canonical coordinates can indeed be constructed and that the classical normal form expansion can then be carried out in the usual manner near a saddle. The difference in time scale between rotations and vibrations suggest however, that it is better to consider the saddles arising from rotation-vibration couplings from a nonlocal perspective. In fact the classical phase space structures that occur in this case should be considered again as Morse bifurcation of NHIMs. It is still an open question on how to do a quantum normal form for the case of rotation vibration coupling as such and in particular also taking into account the Morse bifurcations as already mentioned above.
- Another question that has not been tackled yet for the case of quantum reactions using the semiclassical approach mentioned above is how to deal with reactions across a succession of two or more saddle points. In [89] it has been argued that this situation can be approached using the technique of quantum Poincare maps introduced in [90]. This however has not been pursued yet.
- For the classical case, it has been shown how the coupling of a reacting system to a heat bath (described in terms a Langevin dynamics framework) can be taken into account for the classical normal form. For the quantum case, it is still an open question how to incorporate the coupling to a heat bath.
- Another problem that has intensely been discussed in the context of reaction dynamics in recent years is the occurrence of phase space bottlenecks not induced by saddles (in some context such bottlenecks are referred to as entropic barriers). Such bottlenecks appear to be in particular relevant for roaming dynamics. For two degrees of freedom, there are NHIMs formed by unstable periodic orbits associated with such bottlenecks. It is still an open problem how to treat such bottlenecks quantum mechanically.
- Finally it is worth mentioning that one important prerequisite for the quantum normal form machin-

ery to be applicable is the validity of the Born-Oppenheimer approximation. It would be highly desirable to also develop a quantum normal form to take into account non-adiabatic effects due to a conical intersection.

3. Practical implementation

Text by S. KLIPPENSTEIN.

For astrochemistry, much of the focus is on barrierless reactions since those with a significant barrier are too slow to be relevant at low temperatures. For barrierless reactions there is no saddle point on the PES (or if there is one it is submerged below the reactant energy), but a TS still exists as a dynamical bottleneck in the reactive flux. The location of the TS then arises from a balance between competing variations in the entropy and the enthalpy. This location varies dramatically with temperature, or equivalently, energy and angular momentum.

The variable reaction coordinate (VRC)-TST approach treats the intermolecular dynamics separately from the intramolecular dynamics, with the latter assumed to be vibrationally adiabatic. Meanwhile, the intermolecular dynamics is treated via variational TST employing phase space integration to accurately evaluate the TS partition functions for variably defined reaction coordinates. For a given PES, the VRC-TST method reproduces trajectory evaluations of the flux to within about 10%.

In general there are two distinct TS regimes. A long-range region, with a TS determined by long-range terms in the PES, determines the rate at low temperature. At higher temperatures, a short-range entropically driven bottleneck becomes important. Such a two TS picture is clearly seen for radical-molecule reactions, but also arises in many radical-radical and ion-molecule reactions.

The accurate prediction of rates with the VRC-TST method relies on the availability of an accurate description of the intermolecular PES. For radical-radical reactions, single reference methods are not applicable, and multi-reference methods such as CASPT2 or MRCI are generally used. Direct sampling of ab initio energies, with on the order of 10,000 evaluations required for reasonable convergence, provides an effective means for evaluating the requisite phase space integrals. For ion-molecule reactions, long-range expansions are appropriate for a fairly broad range of temperature. However, at high enough temperature, short-range effects become important and direct ab initio sampling is again effective.

For many reactions, the long-range portion of the potential energy surface is fairly complex, with multiple orientational minima correlating with a variety of final products. This complexity leads to what has come to be called roaming dynamics. The separation into conserved intramolecular and transitional intermolecular modes, which is at the heart of the VRC-TST approach, also

provides an effective approach for treating the dynamics and kinetics of roaming reactions [69][91, 92].

E. The specifics of H_n^+ and analogous cases

Text by O. RONCERO

Reactive collision rates are needed to properly account for the observed lines in different astrophysical environments and determine the physical conditions. Hydrogen is the most abundant element in space and low temperatures are typically found in molecular clouds. In this environments quantum effects are typically important. For this purpose the formation rates of simple hydrides like CH^+ and OH^+ , some of which were recently observed after the launch of the Herschel Space Telescope in 2010, can be obtained with quantum methods [93, 94]. Some of these molecules are very reactive and do not have time to thermalize, and therefore the state-to-state reactive rates determine the emission intensity of excited rotational states.

For reactive collisions the two main "exact" quantum methods nowadays available are the time-dependent wave packet method and the time-independent close coupling method. These last methods require the resolution of a set of coupled equations depending on a scattering coordinate. While feasible in inelastic collisions, provided that the number of coupled equation is not too large, for reactive scattering there is the additional problem of coordinates. For 3 atoms, the hyperspherical coordinates are well adapted and there are several codes nowadays available for reactive scattering. For larger systems the hyperspherical coordinates, as those defined for 4 [95] and 5 atoms [96] are difficult to implement, specially because the singularities of the Hamiltonian in those coordinates require the use of exact or approximate hyperspherical harmonics, which are difficult to obtain. In addition, the number of coupled channels increases enormously, making impractical their use even for 4 atoms systems.

Wave packet techniques seem to scale better for larger systems. For few 4 atom systems the groups of D. H. Zhang and more recently H. Guo [97] are now able to get state to state cross sections but typically considering only few reactive channels. Also, for larger systems they have been applied using reduced dimensionality models. For rather large systems the MCTDH approach [98] is a good alternative but the direct dynamics with this method is not well suited when long lived resonances are present. An alternative to use this method has been successfully applied by the group of U. Manthe for direct reactions with barrier using the full dimensional MCTDH propagations and the quantum transition-state concept [99]. However, for reactions involving long lived resonances and/or low temperatures (as 10K) all these methods fail.

The natural alternative is the use of classical methods. However, quantum effects are important at low temperatures and in the presence of light atoms like hydrogen.

Some "quantum" corrections need to be included, specifically to account for the zero-point energy and tunneling effects. For this there are a great number of semiclassical methods. A possible classification of some of these methods is as 'active', manipulating individual trajectories to overcome the problems, or "passive", in which trajectories non satisfying some criteria are neglected. Direct reactions are probably the best suited for being studied with classical methods. $H_2 + H_2^+ \rightarrow H_3^+ + H$ reaction is one of such reactions, highly exothermic, by approximately 1.2 eV. In this case two quantum effects, the Zero Point energy (ZPE) of the reagents and non adiabatic transitions, using the molecular dynamics with quantum transitions (MDQT) of Tully [100], were included in recent calculations using an accurate full dimensional PES with good descriptions of long range interactions [101]. The results obtained are in good agreement with experimental results [102], providing a good overall description of the process. However, this is not always the case because individual trajectories can not reproduce interference, and for that some ensembles of classical trajectories need to be account for, as done in many semiclassical methods. These methods are typically difficult to be applied to multidimensional problems. Recently, a whole collection of methods based on the path integral formalism have appear, as the ring polymer molecular dynamics [67], centroid dynamics [103], etc, and are receiving an increasing attention in the community, as observed by the fast grow in the number of papers.

At low temperatures and for systems presenting wells in the entrance channel, long lived complexes are formed. Under these conditions energy is redistributed among all degrees of freedom. The subsequent fragmentation can thus be described in many cases by purely statistical methods. The problem is to determine when direct mechanisms start having an important contribution, in detriment of the long-lived complex or statistical mechanisms. One example is $H_2 + H_3^+ \rightarrow H_3^+ + H_2$ exchange reaction, for which experimental results [104, 105] indicates that at low temperature (below 50 K) the results are consistent with statistical methods, accounting for nuclear spin permutation symmetry rules [106].

However, at higher temperatures (above 100 K) the experimental data indicates that the process is no longer statistical but direct. To describe the transition between these two mechanisms, a dynamically biased statistical method has been proposed, in which the statistical weight for the different rearrangement channels of products have been substituted by reaction probabilities obtained with a quasi-classical method [107]. In this system the ZPE is larger than the binding energy, and it was found that when the full ZPE of H_2 and H_3^+ reagents are considered, the ZPE is transferred to dissociating modes producing artificially too short lived complexes, the well known ZPE leakage, which gives non correct probabilities. To correct this ZPE problem, and considering that the ZPE of the H_5^+ complex is similar to that of the reagents, within 10-20 %, the ZPE of the reagents is reduced in order to

avoid its artificial flow. To do so, using RRKM theory, it is found that to get similar quantum and classical density of states at the H_5^+ well it is needed to reduce the ZPE of reagents to only 25 %. Doing so, the reaction probabilities did show a correct behavior, allowing to describe the transition between pure statistical mechanism at low temperatures and direct hop mechanism at high temperatures. Also, this simple model allows to determine the principal role played by ZPE in this kind of reactions. To get more precise results, the ZPE effect has to be accounted for, and for these purpose RPMD calculations [68] are performed now-a-days by Y. Sulemainov on this system.

1. Quantum/classical and quasi-classical dynamics

Text by A. FAURE

As explained above, semi-classical (or quantum-classical) and quasi-classical approximations provide interesting alternatives to quantum methods when the number of coupled-channels is exceedingly large. Semi-classical methods consists in solving the time dependent Schrödinger equation while in quasi-classical approximations the classical Hamilton equations of motion are integrated. Their common feature is that at least one degree of freedom (in general the relative motion) in the collision is treated classically.

The idea of a mixed quantum/classical theory is rather old (1950s) but difficulties in the application of semi-classical theories (e.g. classical S -matrix theory or WKB methods) have precluded them being routine computational tools. There is however a recent revival of interest for these theories and their application to inelastic scattering, in particular the mixed quantum/classical theory (MQCT) [108]. On the other hand, quasi-classical methods have been widely employed in reactive scattering and they have been also successful in inelastic scattering studies (e.g. Faure, Lique, and Wiesenfeld [109]). In the quasi-classical trajectory (QCT) approach, batches of trajectories are sampled with random (Monte Carlo) initial conditions are they are analyzed statistically. State-to-state observables (cross sections or rate coefficients) are extracted by use of the correspondence principle combined with the bin histogram method. We note that more elaborate binning approaches exist, in particular the Gaussian weighting method developed by Bonnet and Rayez [110]. A particular advantage of the QCT method is that the computational time decreases with increasing collision energy, in contrast to quantum close-coupling methods. QCT calculations however ignores interference and tunneling effects. In addition, the correspondence principle cannot be generalized to the case of asymmetric top molecules owing to assignment ambiguities [111]. This particular drawback makes the MQCT approach of Babikov & Semenov a very attractive and promising tool.

F. Spectroscopy: A short view

Text by L. BIZZOCCHI AND C. PUZZARINI.

High-resolution molecular spectroscopy is a powerful tool to investigate various molecular properties that are critical in the context of astrochemistry. To fully exploit the potentialities of rotational spectroscopy in this field, it is necessary to know accurately the spectroscopic parameters of the molecules of interest. These parameters are: the transition (rest) frequencies, their intensities, the corresponding pressure-broadening and shift coefficients and their temperature dependence. For the relevant species, the parameters obtained by laboratory studies are then collected in databases that are continuously updated and improved.

The first and more important application of laboratory measurements is thus the retrieval of accurate rotational rest frequencies, which opens the way to the detection of new molecules in space.

Highly precise determination of transition rest-frequencies (obtained when possible by sub-Doppler measurements [112]) are also important for common and widely-used molecular tracers. These data make sophisticated dynamical studies of star forming regions viable (see an example in figure 7). Laboratory measurements are not limited to the main isotopic species and to vibrational ground state because a sound spectral knowledge of rare isotopologues and of vibrationally excited states allows to extract from observations important chemical and physical insight on the interstellar gas, i.e., study isotopic fractionation mechanisms, estimate gas and dust temperature, and shed light on the complex, and presently poorly understood, gas-dust interactions.

In addition to the measurements accurate line positions and their analysis in order to provide accurate spectroscopic constants (that in turn can be used to accurately predict the rest frequencies of transitions not investigated in the lab), high-resolution spectroscopy can also efficiently support collisional dynamics studies. Indeed, in order to interpret observed interstellar spectra in terms of local physical conditions, one must consider the process of spectral line formation and this in turn requires a knowledge of rates for radiative and collisional excitation. Rotational state-to-state collisional rate coefficients are thus data of paramount importance for a proper modelling of line observations and represent another critical molecular physics' contribution to the astrochemistry. The calculation of the collisional cross-sections and rate constants can be carried out in the close-coupling theoretical framework proposed by [114] and implemented in the MOLSCAT code [115, 116]. These quantities are expressed in terms of the scattering matrix S which in turns, can be calculated by solving the time-independent Schrödinger equation involving the interaction potential V of the colliding system. One thus ends with the problem of computing a high-accuracy potential energy surface (PES) for the interaction between the tracer molecule and a perturber (He or H_2), a task that can

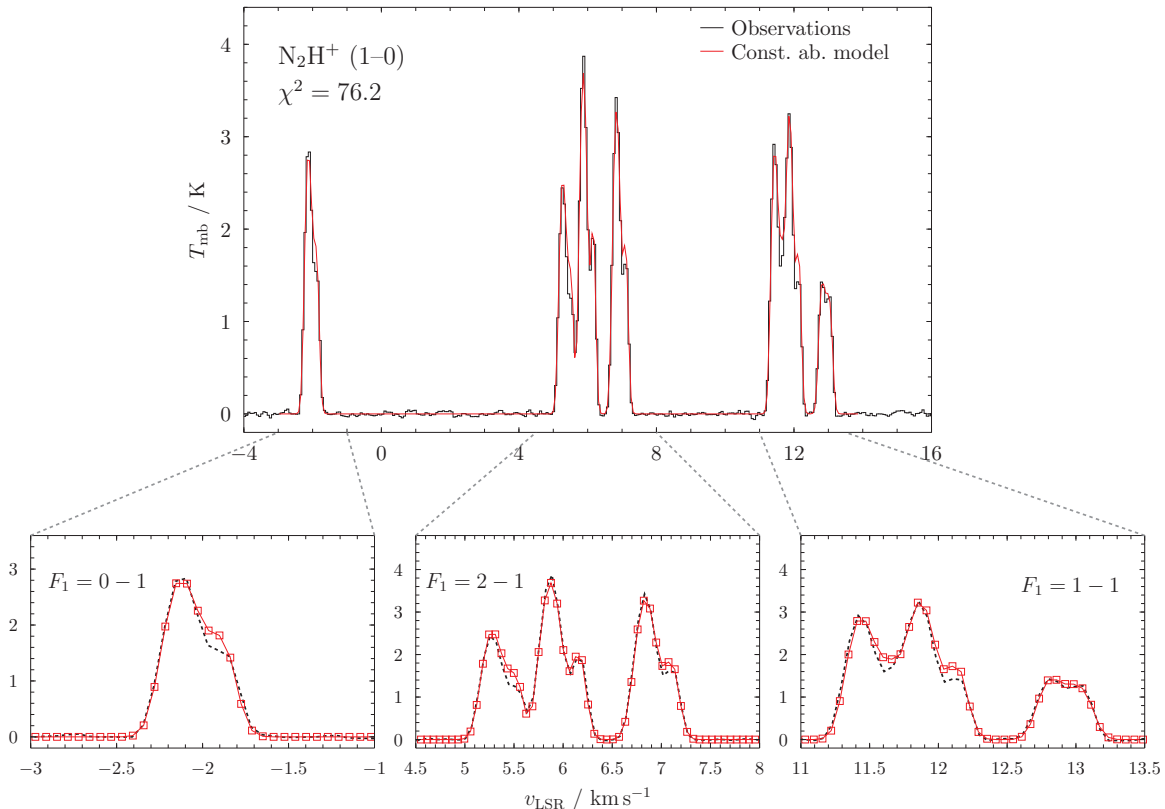


Figure 7. Non-LTE radiative transfer modelling of the N_2H^+ , $J=1-0$ transition observed towards the pre-stellar core L1544. The low turbulence of this cold and quiescent object allows accurate determination of the radial velocity infall profile. The histogram shows the observation data taken with the IRAM 30m telescope with 20 kHz frequency resolution. The red curve shows the model spectrum computed using a refined cold cloud model and constant molecular abundance throughout the core. The three zoom-in boxes allow to appreciate the almost perfect matching of relative intensity and line profile of all the seven hyperfine components that exhibit conspicuous excitation anomalies. The double-peak profile of each features is produced by the slow gravitational contraction motion. See [113] for full details of the analysis.

be efficiently tackled with ab initio theoretical chemistry methods.

This procedure has also a recognised and fruitful link to laboratory studies. Using MOLSCAT, one may also derive the parameters describing the collisional broadening of the rotational transitions: the line-broadening and line-shift coefficients are related to the real and imaginary parts of the cross-section and of the efficiency function, both derived via the S scattering matrix.

Experimental information on the line-widths can then be obtained in the molecular spectroscopy laboratory as a natural side-products of the rest-frequency measurements carried out in controlled pressure and temperature conditions (pressure broadening measurements). Although these studies can not directly estimate state-to-state rates, they provide an important experimental validation of the computational procedure. Parameters derived by line profile studies represent not only a stringent test of the accuracy of the PES used for the scattering calculations, but they also provide a mean to improve the theoretically computed potential by modifying it slightly

(morphing) to fit the experimental data [117].

III. PERSPECTIVE

A. The astronomical perspective

The interest for the astrochemical modelers would be to find new pathways forming efficiently molecules at low temperature via reactions that were though to be negligible based on high temperature measurements and assuming a purely Arrhenius behaviour at low-temperatures encounters in the ISM. The questions are how many of those kind of reactions exist and what would be their effects on gas-phase chemical models. Are ion-neutral reactions in the gas-phase and surface chemistry the only efficient ways to form molecules? Somehow we may have reach the limit of what ion-neutral reactions can synthesis. Surface chemistry seems to be capable of making up observed species but there are so many parameters that one can play to make it match. Neutral-neutral

pathways are still lacking experimental/theoretical rates that are validated for low temperature regimes, below some tens of Kelvin.

Also, there is a need for state-to-state reaction rates with vibrationally excited H_2 (one way to go over the barriers). In the low energy, the astrochemists are excited by the new experiments are very low temperatures where somehow the rates for neutral-neutral are not low or even higher than the rates at $\sim 1000\text{K}$. How theory is coping with those results: (i) low temperature rates for the $\text{OH} + \text{CH}_3\text{OH}$ reaction [118]; (ii) same, for the $\text{OH} + \text{H}_2$ reaction, [119].

Collisional data are central in any quantitative interpretation of feature-rich astronomical spectra together with the availability of open-source sophisticated radiative transfer tools (e.g. RADEX, van der Tak *et al.* [120], LIME, Brinch and Hogerheijde [121]). Astrochemical studies have focused in the past mostly on cold regions but recent (e.g., ALMA) and future instruments (like JWST) have/will have much improved sensitivities. Departures from local thermodynamical equilibrium (LTE) are dominant as lines from higher and higher levels are detected or when the interplay between the radiation from warm dust grains and that from the molecules is strong, the so-called infrared-pumped populations. The sub-millimeter array could observe vibrationally-excited rotational lines ($v = 1$) of CO lines toward the extreme carbon star IRC+10216. More recently the sub-millimeter ALMA telescope has the sensitivity to detect for asymptotic giant branch stars [122]. Dedicated searches for $v = 1$ lines not only of CO but also of large species like methanol will open an extra possibility to study warm molecular regions in addition to the $v = 1-0$ transitions seen in the near- and mid-infrared in the future with the MIRI spectrometer on board the JWST. Indeed line surveys of template objects such as toward the class 0 protostellar binary IRAS 16293-2422 [123] or towards the Orion (see e.g. Crockett *et al.* [124], for an example from the Herschel HEXOS program) show a large amount of unassigned lines that may be caused by rotational transitions within a vibrationally-excited level.

Extreme cases of departure from Local Thermodynamical Equilibrium are seen in astronomical masers for many species (OH, CH, H_2O , H_2CO , CH_3OH , SiO, HCN, NH_3 , SiS). The population inversion may occur when higher levels are populated by absorption of IR photons emitted by dust grains. Purely collisional masers are also observed and they are likely frequent in complex organic molecules, as demonstrated in the case of methyl formate. Such masing lines at radio wavelengths can be important for the identification of new complex species since definitive detection in the millimeter domain can prove challenging in line-rich sources. Masing lines are also found towards comets, planetary atmospheres, late-type star atmosphere, star-forming regions, and even extragalactic sources.

Therefore even for simple species such as CO, coverage of large number of rotational and vibrational levels in

theoretical works is needed. In addition to inelastic collisional data, reaction rates are needed for astrochemical modeling. Simultaneous modeling of the chemical composition and molecular excitation is becoming a routine endeavour.

This is numerically and computationally challenging and may require a re-thinking of the methods used so far in theoretical works.

B. The mathematical and numerical perspectives

In order to have a relevant impact on the reliability and precision on the chemical networks currently used (e.g. the UMIST, KIDA, or PDR networks), with their thousands of chemical rates, it has been shown during the workshop that full quantum computation of chemical reactions remains today out of reach, because of the huge size of the problems (the handling of huge matrices) and probably, the algorithms employed.

Two ways out have been delineated, that try and circumvent both the full PES computation and the full quantum computation: (i) large efforts have been devoted to the Transition state theory, which enables to compute at least rates for high enough temperatures, when quantum effects are not dominant. This remains today the best –if not only– choice for the many reactions that we have to deal with; (ii) for more precise large computations, time dependent methods, quantum or semi-classical have been evoked during the colloquium. While the former is used for systems comprising up to 4 or 5 atoms [125], the latter is not yet fully come of age [108, 126, 127]. Much more experience must be gained on this latter topic.

One method, not mentioned during the workshop, deserves a special mention, the ring polymer dynamics [65, 67, 68], that mimics the quantum dynamics in the vicinity of the TST. Here also, more experience must be gained in order to fully prove its ease of use, and range of precision.

It must be strongly underlined that the interaction between dynamical system theory in mathematics on the one hand, and TST or reaction rate theory remains unfortunately too tenuous. It is the editor's opinion that much is to be gained if reaction rate theory would have taken full advantage of the counter-intuitive properties of classical dynamics near threshold (the TST).

Most of the algorithms used in scattering insofar have been thought of and developed at a time when massively parallel computers were unheard of. While the actual ab initio point wise computations seem not to be a bottleneck, all subsequent stages in the quantum dynamics are very time-consuming. There is no consensus, let alone universal practical method to fit economically a PES functional form on a minimum number of ab initio points, especially for reactive scattering. No interactions with optimization techniques and mathematically oriented computational geometry have been described.

For most time-independent and time dependent quantum computations, most (up to 90–95%) of the computer time is spent in linear algebra, even when the code is fully optimized and makes use of present-day linear algebra specialized packages, like BLAS and LAPACK. Progressing further relies on novel approaches, like 'divide and conquer' strategies, or else on devising the problem with the parallelization in mind at the very beginning of the algorithms definitions and implementations.

In conclusion, **there is a real need for a large number of chemically oriented computations for astrophysics**, with the precision needed for relevant modeling. Many avenues remain open; they are ill-explored because there had been of lack of interest in low-T, low density, and non equilibrium chemistry. Now that new observations, new experiments keep on bringing results, theory, as a ways to model, understand, and predict observation and experiments must have the capabilities to answer these new challenges.

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AUTHORS AND INTERVENTIONS DURING COLLOQUIUM AND WORKSHOP

Speaker	Subject	Laboratory
Colloquium		
Paola Caselli	Introduction	MPE, Garching, Germany
Cecilia Ceccarelli	Molecular complexity in star forming regions: What we know and what we do not.	U. Grenoble, IPAG, France
Eric Herbst	Some Poorly Understood Classes of Interstellar Reactions	U. Virginia, USA
Wing-Fai Thi	Impact of collisional and chemical rates on astrochemistry modelling in protoplanetary disks	MPE, Garching, Germany
Nadia Balucani	Revisiting gas-phase chemistry in astrochemical models	U. Perugia, Italy
Liton Majumdar	KIDA (Kinetic database for Astrochemistry): Present and Future	U. Bordeaux, France
Denis Duflot	Ab initio study of small molecules PES: 2 case studies	U. Lille, France
João Brandão	Potential Energy Surfaces for reaction dynamics	U. Faro, Portugal
Alberto Rimola	Ab initio modeling of surface-induced reactions of astrochemical interest. Strategies and current limitations	U. Autònoma Barcelona, Spain
Cristina Puzzarini	Rotational spectroscopy as a tool to investigate molecules in space	U. Bologna, Italy
Ad van der Avoird	From scattering resonances to rate coefficients for astrophysical modelling	U. Nijmegen, The Netherlands
Stephen Klippenstein	A Priori Kinetics: Coupling Electronic Structure Theory with Statistics, Dynamics, and the Master Equation	Argonne Nat. Lab. (IL) USA
François Lique	Quantum scattering calculations: Closing the gap between observations and astrochemical models	U. Le Havre, France
Tijs Karman	Quantum mechanical calculation of the collision-induced absorption spectra of N ₂ and O ₂	U. Nijmegen, The Netherlands
Tamiki Komatsuzaki	Phase space geometry and chemical reaction dynamics: Past, present and future.	U. Sapporo, Japan

Mikito Toda	Dynamical reaction theory: Beyond the conventional statistical reaction theory	Nara Women U., Japan
Holger Waalkens	Quantum Transition State Theory	U. Groningen, The Netherlands
Alexandre Faure	Classical approach to energy transfer: Successes and limitations	U. Grenoble , France
Hiroshi Teramoto	Dynamical Reaction Theory: Beyond the conventional perturbation theory	U. Sapporo, Japan
Dmitry Babikov	Recent advances in the mixed quantum/classical theory of inelastic scattering	Marquette U., Milwaukee, USA
Fabien Gatti	MCTDH	U. Montpellier, France

Workshop

Tamiki Komatsuzaki	Status of the mathematical TST (1) Networks as dynamical systems	U. Sapporo, Japan
Eric Herbt	Current problems in Astrochemistry	U. Sapporo, Japan
João Brandão	Ab initio status, PES for open-shell systems	U. Algarve, Portugal
Holger Waalkens	Status of the mathematical TST, roaming, dynamical systems & Quantum TS	U. Groningen, The Netherlands
Stephen Klippenstein	Transition State Theory, radical-radical reactions	Argonne Nat. Lab. (IL), USA
Ad van der Avoird	Zeeman spectroscopy; inelastic collisions	U.Nijmegen, The Netherlands
Octavio Roncero	H_n^+ systems	CSIC, Madrid, Spain
Dmitris Skouteris	Time-dependant and time-independant reaction quantum dynamics	Scuole Normale Superiore, Pisa, Italy
Mikito Toda	Crises in chaotic scattering	Women U. Nara, Japan
Hiroshi Teramoto	Bifurcations in NHIMs	U. Sapporo, Japan