

**European Network on
REACTION DYNAMICS:
Experimental and Theoretical Studies on the Dynamics of Reactions of
Atoms and Radicals of Fundamental and Practical Importance**

THIRD YEAR PROGRESS REPORT

from 01/03/2002 to 28/02/2003

RESEARCH RESULTS

The Joint Programme of work set out the proposed research under several distinct, but overlapping tasks which fall under two main headings: Experimental Studies of Reaction Dynamics, and Theoretical Studies of Reaction Dynamics. The various teams have fulfilled most of the commitments set out in the Joint Programme of work for the third year. In particular, strong, synergistic collaborations between the various teams, which had led already to several joint publications during the first two years, have continued fruitfully during the third year and have led to several other (16) joint publications (2 printed, 5 in press, 1 submitted, and 8 in preparation). In addition, the various teams have published several other papers reporting work related to the network and containing acknowledgment to it. The results have been presented at various International Conferences in form of Invited Lectures, Oral Communications, and Poster Contributions by several team members, including Young Researchers.

We describe now the scientific highlights obtained during the third year period of the Network.

The principal targets of the Perugia group (**P1**) during the third year of the Network were to measure differential cross sections (DCSs) for the prototype 3-atom *insertion* $C(^1D)+H_2$ reaction, in order to compare them with the results of theoretical calculations carried out in other laboratories of the Network. A characterization, by spectroscopic techniques, of OH radical beams was also foreseen, in order to carry out measurements of DCS for the prototype 4-atom reaction $OH + CO$ using OH radicals well characterized in their internal quantum states. These objectives have been largely achieved.

The DCS measured in Perugia (**P1**) for the prototype *insertion* reaction $C(^1D)+H_2$ have been compared with the results of accurate quantum scattering calculations (carried out by Launay's group in France) as well as with QCT calculations performed in Madrid (**P5**) on a very recent *ab initio* PES. A joint (**P1** and **P5**) publication, involving also the French group, is currently in preparation for *J. Chem. Phys.* Measurements have also been extended to the isotopic variant $C(^1D)+D_2$, for which the Madrid team has performed QCT calculations on the *ab initio* PES for comparison with experiments. This will lead to another joint (**P1**, **P4** and **P5**) publication, where the YR Rolf Bobbenkamp is involved in, as well as the YR Andrea Russo, who has participated in the work during his secondment period from Bielefeld to Perugia.

Work on *insertion* reactions has continued to also encompass the reaction $N(^2D)+H_2$. After having published in *Phys. Rev. Letters* (2002) a first report on a combined experimental/theoretical study of the prototype *insertion* reaction $N(^2D)+H_2$, in which DCS measured in Perugia (**P1**) were compared with accurate quantum scattering calculations (carried by the group of Launay in France) and with QCT calculations performed by the Madrid group (**P5**) on an *ab initio* PES, a full joint (**P1** and **P5**) paper for *J. Chem. Phys.* is now in preparation.

The set-up of a new experiment aimed at the spectroscopic characterization, by LIF (laser-induced-fluorescence), of supersonic beams of OH radicals (as well as of other radicals, such as CN and also atomic species as $O(^3P)$ and $C(^3P)$) has been successfully completed and the first measurements on OH obtained. The OH radicals were found to be rotationally significantly hot, because the high j levels populated in the radio-frequency discharge beam source at about 1200 K do not relax completely following the supersonic expansion. This should be taken into account

when comparing the experimental results on the reactive scattering of OH + CO with theoretical calculations. A close collaboration with the highly experienced Nijmegen team (**P3**) through a secondment of the YR Raluca Cireasa from Nijmegen to Perugia has been particularly useful. Another YR, pre-doc Andrea Russo from Bielefeld (**P4**), has also been collaborating to the LIF project during a secondment period from Bielefeld to Perugia, where he has brought his past experience with YAG lasers contributing critically to the advancement of the experiment. A joint contribution (**P1**, **P3**, and **P4**) on the characterization of OH beams by LIF has been accepted for presentation at the XX International Symposium on Molecular Beams (Lisbon, June 2003). A joint publication is in preparation. The OH beams will be used to study, during the next few months, the dynamics of the prototypical four-atom reactions OH + CO, of interest also to other teams in the Network. For these experiments, an improved set-up of the crossed beam apparatus, implemented during the third year, will be used which should allow higher sensitivity and velocity resolution.

Work has continued also on the prototype *abstraction* reaction $\text{Cl}(^2\text{P})+\text{H}_2$. DCS measured in Perugia at three collision energies have been compared for the first time with exact quantum scattering calculations on coupled potential energy surfaces computed *ab initio* by the Stuttgart team (**P7**), in collaboration with Prof. M. H. Alexander (University of Maryland, USA). A joint publication which explores spin-orbit effects in this fundamental reaction has just been submitted to *Phys. Rev. Letters*. Also this joint publication involves YRs from different teams (D. Skouteris from Perugia (**P1**) and G. Capecchi, ex-postdoc from Stuttgart (**P7**)). In addition, YR D. Skouteris in Perugia has developed a time-dependent wavepacket program to study the dynamics of three-atom reactions. This program has the unique feature that it can handle the presence of more than one electronic potential energy surface at a time with diabatic coupling between them, going thus beyond the Born-Oppenheimer approximation. First applications have been made on the reaction $\text{Cl}+\text{H}_2$, in collaboration with the Stuttgart team, leading already to three joint publications between **P1** and **P7** (two in press, and a third in preparation).

DCSs for $\text{O}(^1\text{D})+\text{D}_2$ at high E_c obtained in Perugia (**P1**) have been analyzed together with complementary results from Oxford (Expt) (**P2**) and compared with the results of QCT calculations on *ab initio* PESs (both ground and excited state) in collaboration with Madrid (**P5**): the role of the first excited H_2O PES is analyzed. A joint publication is in preparation. New measurements of DCS at low E_c have been carried out for $\text{O}(^1\text{D})+\text{H}_2$ stimulated by the fact that accurate quantum scattering calculations are available for this isotopic variant (carried out by Launay's group in France); detailed comparisons experiment/theory (quantum and QCT) have been nearly completed and a joint publication with the Madrid team (**P5**) is in preparation

In Oxford (Expt) (**P2**), the principal highlights of the third year have concerned studies of the hydrogen abstraction reactions between fast H atoms and H_2O or D_2O . Two joint papers have now been completed (see below). The first paper describes measurements of OH (OD) quantum state populations, differential cross-sections and kinetic energy release distributions for both reactions at a collision energy of 2.5 eV. The new results are compared with quasi-classical trajectory (QCT) calculations (performed by the Madrid team (**P5**)) on the most recently developed potential energy surface (PES), known as the YZCL2 PES (developed by M.A. Collins and D.H. Zhang). The Oxford work suggests that the YZCL2 PES is the most reliable of those currently available, and, even at the very high energy of the study, provides a good qualitative (but not yet a quantitative) description of the dynamics of the reaction.

The Oxford team have completed an experimental determination of the absolute cross-section of the $\text{H} + \text{H}_2\text{O}$ abstraction reaction at a collision energy of 2.5 eV. There has been a long-standing controversy about the magnitude of the abstraction reaction cross-section, with theory yielding a value as much as a factor of ten smaller than previous experimental determinations. At the high energies of the experiments, the absolute cross-section provides a particularly demanding test of theory. The Oxford team (**P2**) have been fortunate enough to collaborate with the groups of M.A. Collins (who has extended his PES for use up to 2.5 eV), D.H. Zhang (who has performed very impressive QM scattering calculations), and with the Madrid group (**P5**) (who have performed a

QCT study of the reaction). In a paper recently submitted to *Physical Review Letters* (and now in press), it is shown that the new experimental estimate for the cross-section is about a factor of two smaller than the theoretical value provided by these workers. While this is an improvement on the previous state of affairs, and gives an indication of the current level of agreement between experiment and current *ab initio* theory, it also suggests that further work is required before a quantitative understanding of the reaction is achieved.

The Oxford team have made very significant improvements to the sensitivity of their ion-imaging machine, which allows them to apply this method to study of bimolecular (as opposed to photochemical) reactions. At the same time they have been developing the methods they will use to analyse the data (see publications below), and very recently applied this to some experimental results on the Cl plus ethane and butane reactions, acquired using the PHOTOLOC technique coupled with ion-imaging detection. The experiments were performed at the IELS (Forth) institute in Crete, in collaboration with Professor T.N. Kitsopoulos. The analysis of these data suggests rather more forward scattering than previously thought on the basis of other PHOTOLOC experiments by the group of Zare at Stanford University, but appear to be in better qualitative agreement with recent crossed molecular beam studies by Suits and coworkers.

At Nijmegen (**P3**), the main scientific highlight of this period was the determination of the steric effects in OH-HCl collisions. Despite of big experimental problems with both the laser equipment and the pulsed beam sources the team finally succeeded in measuring clear and reproducible differences between "O" and "H" side collisions. The results for both the relative state-to-state cross sections and the steric factors deviate from general propensities which have been observed in previous experiments on OH scattering by Ar and other species. A possible cause for these deviations might be the occurrence of a reaction between OH and HCl. In collaboration with the group of Van der Avoird it became possible to compare the experimental results with the first theoretical values available as obtained in quantum scattering calculations using a new *ab-initio* potential developed by Klos, in which the rotation of the HCl molecule is neglected. YR R. Cireasa has been presenting the results as oral communications at several international conferences, and also as seminars in various universities. A publication for *J. Chem. Phys.* is in preparation.

In addition, the molecular beam machine has been modified to enable REMPI measurements on reaction products of four atom collision systems. Hereto also the laser equipment has been replaced by a more powerful system. A VUV generating gas cell has been constructed and mounted in front of the collision area. The first VUV REMPI experiments on Cl atoms produced in a discharge have been successfully performed. In a collaboration with the group of Parker preparations are made for velocity map imaging of the reaction products. Related to this research a new experiment has been started up in which the photodissociation of OH radicals by UV radiation is studied using velocity map imaging techniques. First results on REMPI spectra of OH have been obtained. New vibrational states in the $D^2\Sigma^-$ and $3^2\Sigma^-$ states have been observed.

At Bielefeld (**P4**), work has been concentrated on the reactive scattering of the prototype A+BC reaction $\text{Li}+\text{HF}\rightarrow\text{LiF}+\text{H}$. Due to the initial delay caused by the change of leadership and research objectives the project started on April 9, 2002 when we could fill in the position for a long time. The first part of the work was devoted to the reconstruction and modification of the molecular beam machine we use for this project. Pre-doc A. Russo, and later on also post-doc A. Paladini, have been working actively on this project. So far the following technical work has been completed: (i) the differentially pumped oven chambers have been modified to shorten the distance between nozzle and scattering volume (ii) detector and detector chamber have been re-assembled and tested (iii) all time-of-flight devices used to characterize the beams and products have been completed and are now operational. (iv) The novel rotatable HF source chamber that allows to vary the intersection angle of the beams between 35° and 90° is under construction and will be available within a few weeks. This chamber is crucial for our main research objective, namely to lower the collision energy of the Li+HF system to 20 meV. (v) Presently, a Stern-

Gerlach magnet is being designed which allows to separate the elastically scattered Li atoms from the LiF products both being detected with the same efficiency by our surface ionisation detector. Presently, the apparatus is being used to measure differential reaction cross sections for Li+HF at a 90^0 intersection angle at various HF nozzle temperatures. The data contain information about the dependence of the differential cross sections on the initial rotational states of HF and will help to decide on partially contradictory predictions on this subject.

The Madrid group (**P5**) has fulfilled most of the commitments within the Network for the third year. Presently, a great effort is devoted to the understanding of the dynamics of prototype insertion reactions, $O(^1D)+H_2$, $S(^1D)+H_2$, $N(^2D)+H_2$ and $C(^1D)+H_2$ and isotopic variants, in a combined theoretical and experimental research in collaboration with the groups of Perugia (**P1**), Oxford-Exp (**P2**), as well as with the group of J.-M. Launay (Rennes, France). In this research, new experiments carried out in Perugia are compared with quantum mechanical (QM) and quasi-classical trajectory (QCT) calculations on the most recent potential energy surfaces (PES) existing for these reactive systems. In particular, the study of the $N(^2D)+H_2$ reaction has led to the publication of a joint (**P5** and **P1**) article in *Physical Review Letters*. Some other works on the dynamics of the $O(^1D)+H_2$ and $C(^1D)+H_2$ reactions are in progress. In addition, a new QCT code has been developed to treat the four-atom $H+H_2O$ and $H+N_2O$ reactions, and the results obtained have been compared with the experimental results mainly obtained by the Oxford-Expt (**P2**) group and with QM calculations carried out by D.H. Zhang and co-workers in Singapore. Recently, there has been several publications on these systems by our group. In particular, a joint collaboration between the Oxford-Experimental (**P2**) and Madrid (**P5**) groups with the collaboration of the group of D.H. Zhang in Singapore has been accepted for publication in *Physical Review Letters*. Another joint effort is being directed towards the understanding of the Li+HF reaction dynamics. In this sense, a completely new *ab initio* potential energy surface based on state-of-the-art Quantum Chemistry calculations has been developed by the group of Werner (Stuttgart) (**P7**) and a thorough time-dependent and time-independent QM as well as QCT study has been undertaken. This work will yield in a near future the publication of several papers. All these developments have permitted the publication of three papers in which four groups within the Network have participated (Madrid (**P5**), Oxford Experimental (**P2**), Stuttgart (**P7**) and Perugia (**P1**)), and some other papers are in preparation. From the experimental side, the REMPI apparatus is completely operative and extensive experiments on the dynamics and stereodynamics of the photodissociation of CH_3SCH_3 have been performed. The velocity map ion imaging technique has been implemented and it is permitting the performance of photon initiated experiments with imaging detection of products. The results have been presented at many international conferences as several invited lectures and many poster contributions.

During this period the Oxford theory group (**P6**) have continued with their work on insertion reactions, as was planned at the end of the second year. However, rather than develop the ABC program to study these reactions, a completely new time-dependent wave packet program has been written instead. This program uses the novel transmission-free absorbing potential that we discovered last year (and recently published in *J. Chem. Phys.*) and discussed at the mid-term review meeting of the network. The main advantage of this potential is that it is completely determined by specifying the width of the absorbing region, and the results are guaranteed to improve as the absorbing region is widened. It is therefore straightforward to get converged results with the new potential without any fine-tuning of parameters. Writing a completely new time-dependent wave packet program has also been a major project that has provided excellent training for the RTN postdoc T. Gonzales-Lezana. The present version of the program calculates exact initial state-selected reaction probabilities for all values of the total angular momentum quantum number, without invoking any angular momentum decoupling approximation. It gives results that are identical to those of the ABC program for those reactions (such as $H+D_2$, $F+HD$ and $Cl+HD$) to which that program can be applied. However, it is potentially much more powerful

than the ABC program, and we have already used it to obtain preliminary results for a variety of insertion reactions including H+O₂ and Li+HF. Note that the latter of these reactions is an agreed target of the network; an accurate *ab initio* potential energy surface for the reaction has been calculated by Werner (Stuttgart) (**P7**) and intriguing experimental results are available from the group of Loesch (Bielefeld) (**P4**).

D. Manolopoulos has recently written an authoritative *News and Views* article for *Nature* that references a paper by the Madrid group (see: *Nature* **419**, 266 (2002)). He has also given an Invited lecture at the American Chemical Society National Meeting in the spring 2002.

At Stuttgart (**P7**), using coupled potential energy surfaces (PES) for the Cl(²P_{3/2}, ²P_{1/2}) + H₂ reaction, non-adiabatic and spin-orbit effects in the entrance channel have been studied. In the current period the analytic fits of the potentials were improved and finished, and a publication involving the YR G. Capecchi is in preparation.

The fits have been used in exact quantum scattering calculations of integral and differential cross sections for Cl(²P_{3/2}, ²P_{1/2})+H₂. It was found that the reaction of excited Cl has a lower energy threshold than that of ground state Cl, and therefore at low collision energies the excited state is more reactive than the ground state. However, at energies above the threshold for the Cl(²P_{3/2})+H₂ reaction the cross sections for ground-state chlorine atoms become much larger. These theoretical results are in strong contrast to recent experimental results of K. Liu et al., who predict that the spin-orbit excited Cl(²P_{1/2}) state is more reactive than the ground state. A first report on this important studies, with YR G. Capecchi, has been published in the prestigious journal *SCIENCE*. Recently, calculations of differential cross sections on the coupled PES have been carried out for the first time and the results have been compared with the experimental results obtained in Perugia, leading to a joint publication, just submitted to *Phys. Rev. Letters*, between the **P1** and **P7** teams. This study corroborate the theoretical prediction of a lower reactivity of excited Cl atoms with respect to ground state Cl atoms. A joint publication on the calculations of quantum rate constants for this reaction in collaboration with the Muenchen team (**P8**) is also in preparation.

Finally, a detailed *ab initio* study of a new potential energy surface for the prototypical A+BC reaction Li+HF, studied experimentally in Bielefeld (**P4**), has been completed and a joint publication with the Madrid team (**P5**), where also dynamic calculations are under way, is currently in preparation.

At Munich (**P8**), thermal rate constants have been calculated for the HCl+OH reaction which is being studied in Nijmegen (**P3**). Accurate quantum calculations accounting rigorously for the overall rotation (all J CC-calculations) have been performed using the MCTDH method. Previously, similar rigorous descriptions of four-atom systems have been limited to the H₂+OH reaction. An article describing this work and involving the YR Firmin Huarte-Larranaga has been accepted for publication in the *J. Chem. Phys.*. Another paper involving the YR F. Huarte-Larranaga on the calculations of accurate quantum rate constants for the reaction O+CH₄ has been published in the *J. Chem. Phys.* A joint publication with the Stuttgart team (**P6**) on the quantum calculations of rate constants for the Cl+H₂ reaction including spin-orbit effects is in preparation. The results were presented by the YR in several poster contributions at international conferences and in an Invited Seminar at the University of Salamanca. U. Manthe has presented the results in several Invited Lectures.