

Research Training Network (RTN) on REACTION DYNAMICS

(Contract Number: HPRN-CT-1999-00007)

Report for Mid-Term Review on 21-6-2002

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Information Summary

IHP Research Training Network title : REACTION DYNAMICS: Experimental and Theoretical Studies on the Dynamics of Reactions of Atoms and Radicals of Fundamental and Practical Importance

Network short title : REACTION DYNAMICS

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Name of co-ordinator : Prof. Piergiorgio Casavecchia

Organisation : Università degli Studi di Perugia,
Dipartimento di Chimica

Address : Via Elce di Sotto, 8
06123 Perugia, IT

Telephone : +39 075 585 5514

Telefax : +39 075 585 5606

E-mail : piero@dyn.unipg.it

Network home page: http://www.chm.unipg.it/chimgen/Reaction_Dynamics.html

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PART A - RESEARCH RESULTS

A.1 Scientific Highlights

Background

Over the past 40 years there have been tremendous efforts worldwide to understand the dynamics of chemical reactions. Undoubtedly, advances in the field have resulted from concurrent and collaborative advances in theory and experiment. In particular, over the last 20 years the focus of physical chemists has been on prototype systems; and the driving force has been that what is learnt on prototype reactions would illuminate the entire field. Workhorses have been two benchmark reactions: $H+H_2$ and $F+H_2$, for which detailed comparison between state-of-the-art experiments and state-of-the-art theory - exact quantum mechanical scattering calculations and extensive classical simulations on accurate *ab initio* potential energy surfaces - were reported. Despite this success, however, until quite recently studies of reaction dynamics were confined to systems selected, in general, not for their chemical interest, but because of their suitability for experimental study. Moreover, all theoretical treatments of reaction dynamics were confined to the adiabatic ground state potential energy surface, while the role of excited surfaces and of non-adiabatic effects may be quite important. Recent exciting advances in experiment and theory show that reaction dynamics is a field capable of yielding much detailed and fundamental information also about processes that are basic to a wide range of more complex scientific and technological processes. The extension of combined experimental and theoretical investigations at the state-of-the-art level beyond the reactions $H+H_2$ and $F+H_2$ to encompass elementary reactions that play a central role in areas of practical interest, as combustion and atmospheric chemistry, and also astrochemistry, i.e., reactions involving hydrogen, chlorine, oxygen, nitrogen, and carbon atoms, and hydroxyl (OH) and imidogen (NH) radicals, and the study of the role of excited state surfaces and non adiabatic effects, are a major scientific challenge. This can only be pursued if strong groups involved in experiments and in theoretical calculations of reaction dynamics get together in a joint project. A major scientific goal of the proposed Network aims at realizing this project.

The proposed joint research programme has two main aims.

- Use state-of-the-art powerful complementary experimental techniques to study the detailed dynamics of important reactions of great relevance from both fundamental and practical points of view.
- Use state-of-the-art quantum chemical methods for calculating *ab initio* the potential energy surfaces (PESs) which describe the reactions studied experimentally, and on these surfaces carry out scattering calculations using state-of-the-art quantum mechanical as well as classical methods, in order to predict the quantities which are experimentally measured. Furthermore, the plan envisaged to develop new theoretical approaches to treat chemical reactions occurring on multiple PESs with inclusion of non-adiabatic couplings, and to implement new methods to overcome the dimensionality problem in the theoretical treatment of reactions involving more than 3 atoms.

From this combination of experimental and theoretical approaches, the Network's overriding aim is to improve substantially our level of understanding of molecular reactive collisions and then of the forces that drive chemical reactivity, a central theme of chemistry.

The Network officially commenced on 1 March 2000, and an inaugural meeting was held in Perugia in May 2000. Since that time, significant progress has been made towards meeting the objectives originally laid out in the Work Plan under two main headings. The first one - **Experimental Studies of Reaction Dynamics** - comprising two sub-headings: **3-Atom Reactions**, and **4-Atom Reactions**; the second one - **Theoretical Studies of Reaction Dynamics** - comprising four sub-headings: **Ab Initio Calculations of Potential Energy Surfaces**, **Quantum Scattering Calculations**, **Quasiclassical Trajectory Calculations**, and **Rate Constant Calculations**. In particular, strong, synergistic collaboration between the various teams has led to a considerably large number (**19**) of joint publications (8 printed, 1 in press, 1 submitted, and 9 in preparation; see list in **Section A.2 and Annex A-Abstracts of joint publications**). In addition, the various teams have produced **25** papers reporting work related to the Network and containing Acknowledgment to it (some printed, some in press, and some in preparation, several of them involving YRs financed by the Network - see **List** at the end of Section A.2). Finally, many team members, including YRs (post-docs funded by the Network or other sources) have presented their results at many International Conferences, in form of Invited Talks (30), Oral Contributions (4), and Posters (see **Annex A - Invitations 1** for the specific Invited Talks and Oral Contributions). Several team members have already received invitations (6) for Invited Lectures (on topics subject of the Network) at International Conferences to be held from the Summer 2002 onward (see **Annex A - Invitations 2**). We will now give some of the main highlights of the work of the Network to date, under these same six sub-headings.

Experimental Studies of Reaction Dynamics: 3-Atom Reactions

The main task of the groups in *Perugia*, *Oxford (Expt)*, and *Bielefeld*.

In *Perugia*, using a sophisticated Crossed Molecular Beam apparatus with rotating mass spectrometer detector and TOF analysis, differential cross sections (DCSs) have been measured for the prototype *abstraction* reaction $Cl(^2P_{3/2,1/2}) + H_2$ and D_2 at different collision energies, including values very near to the threshold. The role of rotational excitation and spin-orbit excitation was explored. The results have been compared with those of exact QM calculations (carried

out in *Stuttgart* and in some part *Madrid*) and QCT calculations (carried out in *Madrid*) on the newly developed *ab initio* ground state PES and the newly developed multiple PESs including non-adiabatic and spin-orbit effects, calculated in *Stuttgart*: this has led to four joint publications (2 printed, 1 submitted, and 1 in preparation).¹⁻⁴ This combined experimental/theoretical work represents one of the most detailed to date for a 3-atom reaction, and in particular the experiments have stimulated the accurate dynamical treatment which involves multiple PESs and the inclusion of non-adiabatic and spin-orbit effects. From the comparison experiment/theory it is concluded that the new *ab initio* ClH₂ surface is the most accurate to date. The YR fellow D. Skouteris has implemented, in a collaboration *Perugia-Stuttgart*, time-dependent programs for the calculation of cross sections and a first application to the reaction Cl(²P)+H₂ has been made, leading to a joint publication involving two YRs from different teams.³

The *Perugia* team has also measured, for the first time, DCSs for the two prototypical *insertion* reactions N(²D)+H₂(D₂) and C(¹D)+H₂. These experiments have extended, along the Periodic Table, studies of insertion reaction beyond the most known O(¹D)+H₂ reaction, and have stimulated in other laboratories (in USA and in France, respectively) the calculation of an accurate *ab initio* PES and also, for the first time for insertion reactions, of accurate (i.e., converged) QM scattering calculations (in the group of Launay, in Rennes, FR). Simultaneously, QCT calculations have been carried out in *Madrid* using the same PESs, and this has already led to two joint publications (one just accepted in *Physical Review Letters*,⁵ and another in preparation⁶) and to two related publications.^{1a,2a} Quantum effects have been evidenced in the N(²D)+H₂ reaction and attributed to tunneling through the centrifugal and potential barrier.⁵ While the agreement between experiment and QM results is very good for N(²D)+H₂, this is less good for C(¹D)+H₂, which indicates that the *ab initio* PES is more reliable for NH₂ than for CH₂. More joint papers will follow.

Finally, in *Perugia* new measurements have also been performed on the insertion reaction O(¹D)+H₂(D₂) which has also been studied using different techniques in *Oxford(Expt)* and theoretically in *Madrid*. The role of the first excited PES was pointed out and rationalized theoretically. Two joint publications are in preparation.^{7,8}

The reaction O(¹D)+H₂ has also been investigated in *Oxford(Expt)* using the photon-initiated technique with LIF detection. The principal concern has been of elucidating the role of excited electronic states and to assess the reliability of state-of-the-art QM scattering calculations, which just have become available for this system. A collaborative work with the *Madrid* team and also other teams outside the Network has led to a joint publication in *Phys. Rev. Letters*⁹; a more detailed collaborative paper is in preparation.¹⁰ A joint paper has also been published on the isotopic variant O(¹D)+HD for which a multisurface QCT study was performed.¹¹ Many of the recent activities of the group have been highlighted in an invited Feature Article in the *Journal of Physical Chemistry*.^{7a} The team has also completed and published^{6a} a study of the light-atom transfer reaction O(³P)+HBr→OH+Br, in which the aim was to determine the relative reactivity of channels leading to production of ground state and excited state Br atoms. This work is strictly related to theoretical work carried out in the other *Oxford(Theory)* team, since light-atom transfer reactions tend to display rich quantum behaviour.^{17a} The Oxford group has also completed the building of an ion-imaging experiment (initially not envisaged in the contract), in which they plan to study photon-initiated reactions. A paper concerning data analysis methods has been submitted to *J. Chem. Phys.*^{8a} The apparatus is already producing useful photodissociation data which has led to a joint publication¹² with *Madrid* where ion-imaging is also being set-up. It is hoped that these new experiments will enable them to study a much wider range of bimolecular reactions that they currently have access to.

In *Bielefeld* crossed beam experiments have been set-up to explore the low-energy behavior of the integral cross section, as well as differential cross sections, for the prototypical, asymmetric *A+BC* reaction Li+HF→LiF+H. The results will be compared with both QM and QCT calculations carried out on a new, state-of-the-art *ab initio* PES for Li+HF calculated in *Stuttgart* and fitted in collaboration with *Madrid*.¹³

Experimental Studies of Reaction Dynamics: 4-Atom Reactions

The teams at *Perugia*, *Oxford(Expt)*, *Nijmegen* and *Madrid* have all started to make important experimental contributions to the Network (with *Madrid* having contributed mostly theoretically so far), although this was a main topic of investigation during the second part of the Work Plan.

At *Perugia*, efforts have concentrated on improving the sensitivity of the crossed beam apparatus and on setting up a LIF system to characterize spectroscopically the OH beams to be used in the reactive scattering studies of the benchmark OH+CO and OH+D₂ reactions. The LIF machine has been assembled and is about ready to become operative. Soon, measurements of DCSs for OH+CO will start (this was envisaged indeed for the 3rd year). In *Oxford(Expt)*, significant progress has been made in the study of the stereodynamics of the reaction H+H₂O, the prototypical 4-atom reaction, of great importance also from a theoretical point of view. DCSs and kinetic energy release distributions at the quantum state-resolved level have been measured and the results interpreted in collaboration with *Madrid* and the groups of Collins in Australia (which has recently developed the most accurate PES) and Zhang in Singapore, which should resolve a major inconsistency between theory and experiment for this important abstraction process. A paper has already been published^{5a} and joint publications are in preparation.¹⁴ Work on the stereodynamics of the reactions H+CO₂ and H+N₂O was completed early, in the initial stages of the Network, and it was published neglecting to add the acknowledgment to the Network («*The H + N₂O → OH(v',N') + N₂ reaction: OH rotational angular momentum polarization*», M. Brouard, S. Gatenby, D.M. Joseph, and C. Vallance; *J. Chem. Phys.* **113** 3162 (2000); «*The H + CO₂ → OH(v',N') + CO reaction: OH rotational angular momentum polarization*.» M Brouard, I.Burak, D.W. Hughes, K.S. Kalogerakis, and J.P. Simons; *J. Chem. Phys.* **113** 3172 (2000)).

In *Nijmegen* the research was aimed at the study of orientation effects in inelastic scattering of OH radicals. Simultaneously, preparations were made for reactive scattering experiments. An intense, unique, pulsed electrical discharge source for OH radical beams was developed. The experiments on non-reactive scattering culminated in the following highlights: (1) Measurement of molecular reorientation in rotationally elastic scattering of OH by Ar. Determination of differential and integral cross sections for reorientation of the molecular axis of OH as a function of the initial orientation, published in *Phys. Rev. Lett.*^{9a} (2) Determination of inelastic cross sections for rotationally inelastic scattering of OH by N₂ and CO and the measurement of the effects of OH orientation on these inelastic collisions.^{10a} (3) Characterization of an intense pulsed molecular beam source of cold OH radicals.^{11a} More recently, non-reactive scattering of OH radicals with HCl were studied and preparations were made for (1+1) REMPI detection in reactive scattering experiments. Inelastic cross sections for rotationally inelastic scattering of OH by HCl were determined and measurements of the effects of OH orientation on the inelastic collisions were made. A publication involving YR R. Cireasa is in preparation.^{12a}

In *Bielefeld* the reactive scattering of OH+H₂ will not be pursued, as discussed in the 1st and 2nd year reports and in Section B.2, as a consequence of the change in the team leader and in the subject of investigation, the focus being changed to the reaction Li+HF. The experimental apparatus was optimized to measure integral cross sections for Li+HF down to very low collision energies, where peculiar quantum effects are theoretically predicted; these measurements are about to start. The experimental work has stimulated intense theoretical work in other teams (see below).

In *Madrid* a new pump-probe apparatus with REMPI detection has been completed and tested successfully with photodissociation work on CH₃SCH₃, studied jointly with Nijmegen, where velocity map ion-imaging was used, and this has led to a joint publication.¹⁵ Velocity map ion-imaging is under advanced construction also in *Madrid*, and soon the apparatus will be ready to study the 4-atom reaction H+N₂O.

Theoretical Studies of Reaction Dynamics: Calculations of Potential Energy Surfaces

The calculation of accurate potential energy surfaces (PESs) is a central theme in this Network, since the PESs are needed to carry out dynamics calculations for comparison with experimental data and can therefore substantially improve our understanding of reaction dynamics. The group in *Stuttgart* has contributed greatly to this theme.

Initially, a ground state adiabatic PES for ClH₂ was calculated without including spin-orbit interaction; dynamics calculations using this ground state PES have been carried out for the reaction Cl(²P)+H₂ and D₂ and compared with experimental results obtained in *Perugia* and QCT results obtained in *Madrid*. This has resulted in three joint publications.^{1,2,16} This new PES has the correct long-range behavior and was able to rationalize recent experimental findings in the Cl+HD reaction (D. Skouteris, D.E. Manolopoulos, W. Bian, H.-J. Werner, L.-H. Lai and K. Liu, *Science* **286**, 1713 (1999)). Later on, coupled PESs were for the first time calculated by YR Gabriella Capecchi for Cl(²P_{3/2},²P_{1/2}) + H₂ including spin-orbit interaction.^{20a} Recently, using the coupled PESs non-adiabatic and spin-orbit effects in the entrance channel for the Cl(²P_{3/2},²P_{1/2}) + H₂ reaction have been studied. The analytic fits have been used in exact QM scattering calculations of integral and differential cross sections for Cl(²P_{3/2},²P_{1/2})+H₂; a publication involving two YRs is in preparation.^{21a} It was found that the reaction of excited Cl has a lower energy threshold than 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. The reactivity of the ground-state potential (correlating with Cl(²P_{3/2})+H₂) is reduced as compared to single state calculations, which is due to additional inelastic scattering caused by non-adiabatic transitions to the non-reactive spin-orbit states. 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. Further experimental and theoretical work will be necessary to resolve this discrepancy. A first report on these important studies have been recently published in the prestigious journal *SCIENCE*.^{19a} Several other publications, some joint with other Network teams, are in preparation.^{4,17}

In addition, in *Stuttgart* high-level MRCI wavefunctions with a very large basis set were used for calculating a new state-of-the-art PES for the reaction Li+HF, which has become a new important project within the Network with experiments being carried out in *Bielefeld*. The *ab initio* points have been fitted using the functional form proposed by Aguado and Paniagua, in collaboration with the *Madrid* team, and this has led to a joint publication.¹³ It will be very interesting to perform dynamics calculations on this new PES and compare the results with those obtained on earlier, more approximate PESs. This will be done during the 3rd year of the contract. Finally, in *Stuttgart* significant progress has been made towards direct dynamics studies of 4-atom reactions (OH+H₂).

Theoretical Studies of Reaction Dynamics: QM Scattering Calculations

The *Oxford(Theory)* group has been invaluable to the Network in developing efficient codes for performing QM scattering calculations, which are the rigorous link between the potential energy surface and the experiments. Significant contributions to this theme has also come from *Stuttgart*, and also *Madrid* and *Perugia*.

At *Oxford*, early on in the first year of the network the first version of the hyperspherical coordinate reactive scattering program ABC was finalized and made available for general use (D. Skouteris, J. Castillo and D.E. Manolopoulos, *Comput. Phys. Commun.* **133**, 128 (2000)). This is the program that is used by several of the other groups in the network to perform their QM reactive scattering calculations. D. Skouteris has done post-doc work in *Stuttgart* (though

not on EC funds), and currently he is post-doc within the Network in *Perugia*. J. Castillo has done this past year post-doc work (again not on EC funds) with the *Madrid* team and has recently taken an academic position in Madrid. At around the same time, the ABC program was used to study a very interesting transition state resonance in the low energy threshold region of the $F+HD \rightarrow HF+D$ reaction in collaboration with groups in the USA and Taiwan. This study was particularly important because it provided the first conclusive evidence for the observation of a reactive scattering resonance in a molecular beam experiment.^{16a} More recently, collaboration with M. H. Alexander (USA) and H-J. Werner (*Stuttgart*) resulted in a highly detailed *ab initio* study of spin-orbit effects in the $F(^2P)+H_2$ reaction, using a modified version of the ABC program. This study of electronically non-adiabatic effects in chemical reactivity was one of the original objectives of the network and it has already led to a joint publication with the *Stuttgart* group,¹⁸ moreover, it is complementary to the study of similar effects on the $Cl(^2P)+H_2$ reaction, which were very recently carried out in *Stuttgart* by YR G. Capecchi.^{19a, 21a}

At *Oxford(Theory)*, early on in the second year of the network a coupled-channel statistical theory of atom-diatom insertion reactions was developed by combining the early statistical ideas of Pechukas and Light with the coupled-channel capture theory of Clary and Henshaw. The resulting theory was applied to the $N(^2D)+H_2$ and $O(^1D)+H_2$ insertion reactions, which have been studied experimentally by the *Oxford (Expt)* and *Perugia* teams, and was found to give results in excellent agreement with the exact QM calculations of Honvault and Launay. This work was done in collaboration with the YR fellow Fermin Huarte-Larranaga from the *Munich* group during his research training visit (secondment) to Oxford, and it has led to a Network joint publication.¹⁹ Since then, the Oxford YR fellow Thomas Gonzalez-Lezana and PhD student Edward Rackham have been applying the same statistical theory to the $H+O_2$ combustion reaction, with rather interesting results; a publication is in preparation.^{18a} The *Oxford* team are now continuing with their adaptation of the ABC program to treat insertion reactions, so that they can calculate "exact" results for comparison with the statistical theory.

Finally, in a collaboration with Professor Bowman from Emory University, the *Oxford* group have applied the ABC program to a detailed study of the $O(^3P)+HCl$ reaction and shown that the low-energy resonances that are seen in this reaction on the latest *ab initio* PES are due to quasi-bound quantum states in the reactant and product van der Waals wells.^{17a} This study is relevant to the network because the same methodology can be applied to the $O(^3P)+HBr$ reaction which has been studied experimentally by the *Oxford(Expt)* group.^{6a}

QM scattering calculations have been performed extensively on the reactions $Cl+H_2(D_2)$,^{2-4,16,19a,21a} in *Stuttgart* and in part also in *Madrid*,² the latter team have also done QM calculations on the excited PES of $O(^1D)+H_2$.^{7,9,10,13a}

YR D. Skouteris in *Perugia* has developed, in collaboration with *Stuttgart*, a time-dependent wavepacket program to calculate cross sections and a first application has been made on the reaction $Cl+H_2$, leading to a joint publication.³ In *Perugia*, time-dependent QM calculations have been performed also on the $Li+HF$ reaction, which is being studied experimentally in *Bielefeld*. A publication has just been submitted.^{4a}

Theoretical Studies of Reaction Dynamics: QCT Scattering Calculations

The theoretical group in *Madrid* has been invaluable to the Network in performing detailed QCT calculations on *ab initio* PESs, comparing them with QM calculations and simulating experimental results obtained by other teams. The simulation of experimental results has contributed greatly in keeping the other Network partners in touch. The team has extended the QCT code to study non-adiabatic processes using the surface hopping methodology and the new code has been applied to study non-adiabatic effects in the $O(^1D)+H_2, HD, D_2$ reactions.^{7-11,13a} Comparisons with QM results have been performed.^{15a} The $Cl(^2P)+D_2$ reaction has been studied by using the QCT and QM methods on a new PES developed by the *Stuttgart* group and the results have been compared with the experiments of the *Perugia* group.¹ In addition, a new QCT code has been developed to treat four-atom reactions and first results concerning the $H+H_2O$ and $H+N_2O$ reactions have been obtained. In particular, QCT calculations have been performed for $H+H_2O$ on a new *ab initio* PES.^{14a} All these developments have permitted the publication of five joint papers in which four groups within the Network have participated (*Madrid, Oxford(Expt), Stuttgart* and *Perugia*)^{1,2,9,11,16} and three more are in preparation.^{7,8,10} More recently, QCT calculations have also been performed for the insertion reactions $N(^2D)+H_2$ and $C(^1D)+H_2$, in which comparison have been made with exact QM results on an *ab initio* PES and with the experimental DCS measured in *Perugia*. A joint paper is currently in press in *Phys. Rev. Letters*⁵ and another is in preparation.⁶ From the experimental side in *Madrid* the REMPI apparatus is completely operative and first experiments on the photodissociation of CH_3SCH_3 have been performed. A joint work on the photodissociation of this molecule between the *Madrid* and *Nijmegen* groups has been already published.¹⁵

Theoretical Studies of Reaction Dynamics: Rate Constant Calculations

At *Muenchen* the accurate full-dimensional calculation of the $H+CH_4 \rightarrow H_2+CH_3$ reaction rate has been carried out and published^{20a} and this can be considered as a major step forward in the accurate quantum treatment of reaction processes. Previously only reactions with up to four-atoms had been treated accurately in their full dimensionality. In the above mentioned calculations a six-atom reaction could be described in an accurate full-dimensional calculation for the first time. This progress was made possible by the combined use of direct rate constant computation based on flux correlation functions and multi-configurational time-dependent Hartree wave packet propagation. The results of these calculations provide new insight into the multi-dimensional character of polyatomic reaction systems and provide an important benchmark for the development of approximate dynamical methods and accurate potential energy surfaces.

More recently, accurate full-dimensional (12D) quantum calculations investigated the reaction dynamics of H+CH₄ in an increased energy and temperature range. These calculations required additional computational techniques: a rigorous statistical sampling scheme was employed to study thermal rate constants at temperatures above 500 Kelvin and to compute the reactant partition function. This has led to the publication of several papers^{22a-25a} always involving the YR Fermin Huarte-Larranaga. Collaborations with *Stuttgart* on rate constant calculations for the Cl+H₂ reaction including spin-orbit effects have been done. The results confirm the accuracy of an approximate treatment of the spin-orbit coupling used in previous collaborative work (U. Manthe, W. Bian and H.-J. Werner, *Chem. Phys. Lett.* 313, 647 (1999)). The calculations are now complete and a joint article is in preparation.¹⁷

In conclusion, the Network has been highly successful in addressing a whole range of fundamental issues in Reaction Dynamics, especially in relation to prototypical 3-atom reactions, which were the main topic during the first part of the Work Programme. The advancement with respect to the current state-of-the-art can be identified in the following points:

- (1) Calculation of a new, fully *ab initio*, improved PES for the Cl+H₂ reaction; QM and QCT scattering calculations on this PES and comparison with DCS measurements: improved agreement between experiment and theory (*numerous joint publications*).
- (2) Calculation, for the first time, of "coupled" potential energy surfaces for the Cl(²P_{3/2}, ²P_{1/2}) + H₂ reaction, and study of non-adiabatic and spin-orbit effects in the entrance channel. Exact QM scattering calculations of integral and differential cross sections for Cl(²P_{3/2}, ²P_{1/2})+H₂ on the *ab initio* coupled surfaces, including non-adiabatic and spin-orbit coupling (a first publication in *Science*, 2002; more in preparation). This work was anticipated by similar, novel joint work on the related F(²P_{3/2}, ²P_{1/2})+H₂ reaction (*JCP*, 2000).
- (3) Experimental investigation of the dynamics of the insertion reactions N(²D)+H₂ and C(¹D)+H₂, for the first time via measurements of differential cross sections, and comparison with accurate, state-of-the-art QM scattering calculations, which were stimulated by the present experiments and represented the first ever performed for an insertion reaction (*Phys. Rev. Letters*, 2002, and *JCP*, in preparation). From comparisons with both QM and QCT results, characterization of quantum effects in N(²D)+H₂ (*Phys. Rev. Letters*, 2002).
- (4) Investigation, both experimentally and theoretically, of the role of excited surfaces in the O(¹D)+H₂ reaction (*Phys. Rev. Letters*, 2001; *JCP*, in preparation).
- (5) Development of a coupled-channel statistical theory for insertion reactions (*CPL*, 2001).
- (6) New, improved *ab initio* potential energy surface for the prototypical A+BC reaction Li+HF (*JCP*, in preparation).
- (7) Experimental investigation of the stereodynamics of the 4-atom reaction H+H₂O(D₂O) at the quantum state resolved level (*JCP*, 2001).
- (8) Development of an intense, unique, pulsed electrical discharge source of OH radicals, fully state selected (*CPL*, 2001). Inelastic scattering of OH radical with Ar, CO, and N₂ using with oriented beams of OH (*Phys. Rev. Letters*, 2001 and *JCP*, 2001).
- (9) Accurate rate constant calculations for Cl+H₂ on *ab initio* coupled PESs including spin-orbit interaction (in preparation) and for polyatomic reactions (H+CH₄) (*JCP*, 2000-2001-2002)

The great relevance of the work carried out in this Network is also witnessed by the invitations received by many team members to present a large number of Invited Talks at numerous International Conferences and Workshops (see **Annex A - Invitations 1 and 2**).

Much work remains to be done, and an exciting period of challenging new experiments and theoretical calculations lies ahead.

A.2 Joint Publications and Patents

These appear in order of citation in section A.1, *not* in order of importance (YRs are indicated in bold).

1. N. Balucani, L. Cartechini, P. Casavecchia, G. G. Volpi, F. J. Aoiz, L. Bañares, M. Menéndez, W. Bian and H.-J. Werner
Dynamics of the Cl+D₂ reaction: a comparison of crossed molecular beam experiments with quasi-classical trajectory calculations on a new ab initio potential energy surface
Chem. Phys. Lett., **328**, 500-508 (2000).
Teams involved: PERUGIA - MADRID – STUTTGART
2. D. Skouteris, H.-J. Werner, F. J. Aoiz, L. Bañares, J. F. Castillo, M. Menéndez, N. Balucani, L. Cartechini, P. Casavecchia, G. G. Volpi
Experimental and theoretical differential cross sections for the reactions Cl+H₂/D₂
J. Chem. Phys. **114**, 10662-10672 (2001).
Teams involved: PERUGIA - MADRID – STUTTGART
3. **D. Skouteris**, A. Lagana', **G. Capecchi**, H.-J. Werner
Wavepacket calculation for the Cl+H₂ reaction
Journal of Computational Methods in Sciences and Engineering (submitted 15 April 2002).
Teams involved: PERUGIA - STUTTGART
4. **G. Capecchi**, **D. Skouteris**, H.-J. Werner, N. Balucani, P. Casavecchia
Theoretical simulations of molecular beam experiments for the Cl(²P_{3/2,1/2) + H₂ reaction based on quantum reactive scattering calculations on coupled potential energy surfaces}
J. Chem. Phys. or Chem. Phys. Lett. (in preparation)
Teams involved: STUTTGART - PERUGIA
5. N. Balucani, L. Cartechini, G. Capozza, E. Segoloni, P. Casavecchia, G. G. Volpi, F. J. Aoiz, L. Banares, P. Honvault, J.-M. Launay
Quantum effects in the differential cross sections for the insertion reaction N(²D)+H₂
Phys. Rev. Letters (2002, in press).
Teams involved: PERUGIA - MADRID
6. N. Balucani, L. Cartechini, G. Capozza, P. Casavecchia, G. G. Volpi, F. J. Aoiz, L. Banares, P. Honvault, J.-M. Launay
Experimental differential cross sections for the reaction C(¹D)+H₂ versus accurate quantum and quasiclassical trajectory scattering calculations on an ab initio potential energy surface
J. Chem. Phys. (in preparation).
Teams involved: PERUGIA - MADRID
7. N. Balucani, L. Cartechini, G. Capozza, E. Segoloni, P. Casavecchia, G. G. Volpi, F. J. Aoiz, L. Banares, P. Honvault, J.-M. Launay
Experimental differential cross sections for the reaction O(¹D)+H₂ versus accurate quantum and quasiclassical trajectory scattering calculations on an ab initio potential energy surface
J. Chem. Phys. (in preparation).
Teams involved: PERUGIA - MADRID
8. N. Balucani, P. Casavecchia, F. J. Aoiz, L. Banares, J. F. Castillo, M. Brouard, W. Denzer, C. Vallance
Differential cross sections and rotational distributions for the reaction O(¹D)+D₂ compared to quasiclassical trajectory scattering calculations on an ab initio potential energy surface
Phys. Chem. Chem. Phys. (in preparation)
Teams involved: PERUGIA - MADRID - OXFORD(expt)
9. F. J. Aoiz, L. Bañares, J. F. Castillo, M. Brouard, W. Denzer, C. Vallance, P. Honvault, J.-M. Launay, A. J. Dobbyn and P. J. Knowles

Insertion and Abstraction Pathways in the Reaction $O(^1D)+H_2\rightarrow OH+H$ **Phys. Rev. Lett.**, **86**, 1729-1732 (2001).Teams involved: MADRID – OXFORD (Expt)

10. P. Honvault, J.-M. Launay, M. Brouard, W. Denzer, C. Vallance, F. J. Aoiz, L. Bañares, J. F. Castillo
The role of the A'' excited state in the $O(^1D)+H_2$ reaction: experiment versus theory
J. Chem. Phys. (in preparation)
Teams involved: MADRID – OXFORD (Expt)
11. F. J. Aoiz, L. Bañares, M. Brouard, J. F. Castillo and V. J. Herrero
The dynamics of the $O(^1D)+HD$ reaction: a quasiclassical trajectory multisurface study
J. Chem. Phys., **113**, 5339-5353 (2000).
Teams involved: MADRID – OXFORD (Expt)
12. M. Bass, M. Brouard, A.P. Clark, B. Martinez-Haya and C Vallance
Angular momentum alignment in the 308nm photolysis of Cl_2 using Fourier moment velocity-map imaging
J. Chem. Phys. or **Chem. Phys. Lett.** (in preparation).
Teams involved: OXFORD(Expt) – MADRID
13. M. Paniagua, H.-J. Werner, A. Aguado, F. J. Aoiz, V. Saez-Rabanos, E. Verdasco, J. F. Castillo
New ab initio potential energy surface for the $Li+HF$ reaction
J. Chem. Phys. (in preparation).
Teams involved: MADRID – STUTTGART
14. F. J. Aoiz, L. Bañares, M. Brouard, J. Castillo, D. Minayev, P. O'Keeffe, C. Vallance
The dynamics of the $H + D_2O$ abstraction reaction at 2.5eV
J. Chem. Phys. (in preparation).
Teams involved: MADRID – OXFORD(Expt)
15. P. Quintana, R. F. Delmdahl, D. H. Parker, B. Martínez-Haya, F. J. Aoiz, L. Bañares and E. Verdasco
Velocity map imaging and REMPI study of the photodissociation of CH_3SCH_3 from the first absorption band
Chem. Phys. Lett., **325**, 146-152 (2000).
Teams involved: MADRID – NIJMEGEN
16. F. J. Aoiz, L. Bañares, J. F. Castillo, M. Menéndez, D. Skouteris, H.-J. Werner
A quantum mechanical and quasi-classical trajectory study of the $Cl+H_2$ reaction and its isotopic variants. Dependence of the integral cross section on the collision energy and reagent rotation
J. Chem. Phys. **115**, 2074-2081 (2001).
Teams involved: MADRID – STUTTGART
17. **G. Capecchi**, U. Manthe, J.-H. Werner
Quantum calculations of rate constants for the $Cl+H_2$ reaction
J. Chem. Phys. or **Chem. Phys. Lett.** (in preparation)
Teams involved: STUTTGART - MUENCHEN
18. M. H. Alexander, D. E. Manolopoulos, and H. -J. Werner
An investigation of the $F+H_2$ reaction based on a full ab initio description of the open-shell character of the $F(^2P)$ atom
J. Chem. Phys. **113**, 11084-11100 (2000).
Teams involved: OXFORD (Theory) - STUTTGART

19. E.J. Rackham, **F. Huarte-Larranaga**, D.E. Manolopoulos
Coupled-channel statistical theory of the $N(^2D)+H_2$ and $O(^1D)+H_2$ insertion reactions
Chem. Phys. Lett. **343**, 356 (2001).
Teams involved: OXFORD(theory) – MUENCHEN

List of publications containing acknowledgments to the Network - several having a YR financed by the Network as co-author (indicated in **bold**):

PERUGIA:

- 1a. A. Bergeat, L. Cartechini, N. Balucani, G. Capozza, L. F. Phillips, P. Casavecchia, G.G. Volpi, L. Bonnet, J.-C. Rayez
A crossed beam study of the reaction $C(^1D) + H_2(X^1\Sigma^+, v=0) \rightarrow CH(X^2\Pi, v') + H(^2S)$
Chem. Phys. Lett. **327**, 197-202 (2000)
- 2a. N. Balucani, M. Alagia, L. Cartechini, P. Casavecchia, G.G. Volpi, L. A. Pederson, G. C. Schatz
Dynamics of the $N(^2D)+D_2$ reaction from crossed-beam and quasiclassical trajectory studies
J. Phys. Chem. A **105**, 2414-2422 (2001)
- 3a. P. Casavecchia, N. Balucani, L. Cartechini, G. Capozza, A. Bergeat, G.G. Volpi
Crossed beam studies of elementary reactions of N and C atoms and CN radicals of importance in combustion
Faraday Discuss. **119**, 27-49 (2001)
- 4a. V. Piermarini, S. Crocchianti, and A. Lagana`
Calculated versus measured cross sections: the $Li + HF$ reaction
Journal of Computational Methods in Sciences and Engineering (submitted 15 April 2002)

OXFORD (Expt):

- 5a. M. Brouard, S.D. Gatenby, D.M. Joseph, G.A.J. Markillie, D. Minayev, P. O'Keeffe and C. Vallance
The stereodynamics of the reactions $H + H_2O(D_2O) \rightarrow OH(OD) + H_2(HD)$
J. Chem. Phys. **114**, 6690 (2001)
- 6a. M. Brouard and C. Vallance
The stereodynamics of a light atom transfer reaction: $O(^3P) + HBr \rightarrow OH + Br(^2P)$
Phys. Chem. Chem. Phys. **3**, 3602 (2001)
- 7a. M. Brouard, P. O'Keeffe, C. Vallance
The state-resolved dynamics of elementary reactions
J. Phys. Chem. A, Feature Article, **106** 3625 (2002)
- 8a. M. Bass, M. Brouard, A.P. Clark, and Claire Vallance
Fourier moment analysis of velocity map ion-images
J. Chem. Phys. (Submitted for publication).

NIJMEGEN:

- 9a. M.C. van Beek, G. Berden, H.L. Bethlem and J.J. ter Meulen
Molecular reorientation in rotationally elastic collisions of OH + Ar
Phys. Rev. Lett. **86**, 4001 - 4004 (2001)
- 10a. M.C. van Beek and J.J. ter Meulen
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- 11a. M.C. van Beek and J.J. ter Meulen
An intense pulsed electrical discharge source for OH molecular beams
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- 12a. **D.R. Cireasa**, A. Moise, N.J. Dam and J.J. ter Meulen
Inelastic state-to-state scattering of oriented OH by HCl
J. Chem. Phys. (in preparation)

MADRID:

- 13a. F. J. Aoiz, L. Bañares, J. F. Castillo, B. Martínez-Haya, M. P. de Miranda
The stereodynamics of the O(¹D)+HD reaction on the ground 1A' and excited 11A'' potential energy surfaces
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- 14a. J. F. Castillo, F. J. Aoiz, L. Bañares
A quasiclassical trajectory study of the H+H₂O OH + H₂ reaction dynamics at 1.4 eV collision energy on a new ab initio potential energy surface
Chem. Phys. Lett. **356**, 120 (2002)
- 15a. F. J. Aoiz, L. Bañares, J. F. Castillo, V.J. Herrero, B. Martínez-Haya, P. Honvault, J. M. Launay, X. Liu, J.J. Lin, S. A. Harich, C.C. Wang nad X. Yang
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J. Chem Phys. Accepted for publication (submitted 6 February 2002)

OXFORD (Theory):

- 16a. K. Liu, R. T. Skodje and D. E. Manolopoulos
Resonances in bimolecular reactions.
Phys. Chem. Comm. **5**, 27-33 (2002).
- 17a. T. Xie, D. Wang, J. M. Bowman and D. E. Manolopoulos
Resonances in the O(³P)+HCl reaction due to van der Waals minima.
J. Chem. Phys. **116**, 7461-7467 (2002).
- 18a. E. J. Rackham, **T. Gonzalez-Lezana** and D. E. Manolopoulos
Coupled-channel statistical study of the H + O₂ combustion reaction.
(in preparation).

STUTTGART:

- 19a. M. H. Alexander, **G. Capecchi**, and H.-J. Werner
Theoretical Study of the Validity of the Born-Oppenheimer Approximation in the Cl + H₂ → HCl + H reaction
Science **296**, 715 (2002)
- 20a. **G. Capecchi** and H.-J. Werner
Coupled potential energy surfaces for the Cl(²P_{3/2,1/2}) + H₂ reaction
J. Chem. Phys. (in preparation)

- 21a. **G. Capecchi, D. Skouteris**, M. H. Alexander, and H.-J. Werner
Quantum reactive scattering calculations of differential cross sections on coupled potential energy surfaces for the $Cl(^2P_{3/2,1/2}) + H_2$ reaction
J. Chem. Phys. (in preparation)

MUENCHEN:

- 22a. **F. Huarte-Larranaga** and U. Manthe
Quantum Dynamics of the $CH_4 + H \rightarrow CH_3 + H_2$ Reaction: Full-Dimensional and Reduced Dimensionality Rate Constant Calculations
J. Phys. Chem. A **105**, 2522 (2001)
- 23a. Joel M. Bowman, Donyou Wang, Xinchuan Huang, **F. Huarte-Larranaga**, and U. Manthe
The importance of an accurate CH_4 vibrational partition function in full dimensional calculations of the $CH_4 + H \rightarrow CH_3 + H_2$ reaction
J. Chem. Phys. **114**, 9683 (2001)
- 24a. U. Manthe and **F. Huarte-Larranaga**
Partition functions for reaction rate calculations: statistical sampling and MCTDH propagation
Chem. Phys. Lett. **349**, 321 (2001)
- 25a. **F. Huarte-Larranaga** and U. Manthe
Vibrational excitation in the transition state: the $CH_4 + H \rightarrow CH_3 + H_2$ reaction rate constant in an extended temperature interval
J. Chem. Phys. **116**, 2863 (2002).

PART B - COMPARISON WITH THE PROJECT PROGRAMME

B.1 Project Objectives

The research objectives, as set down in the project programme, may be summarised as follows:

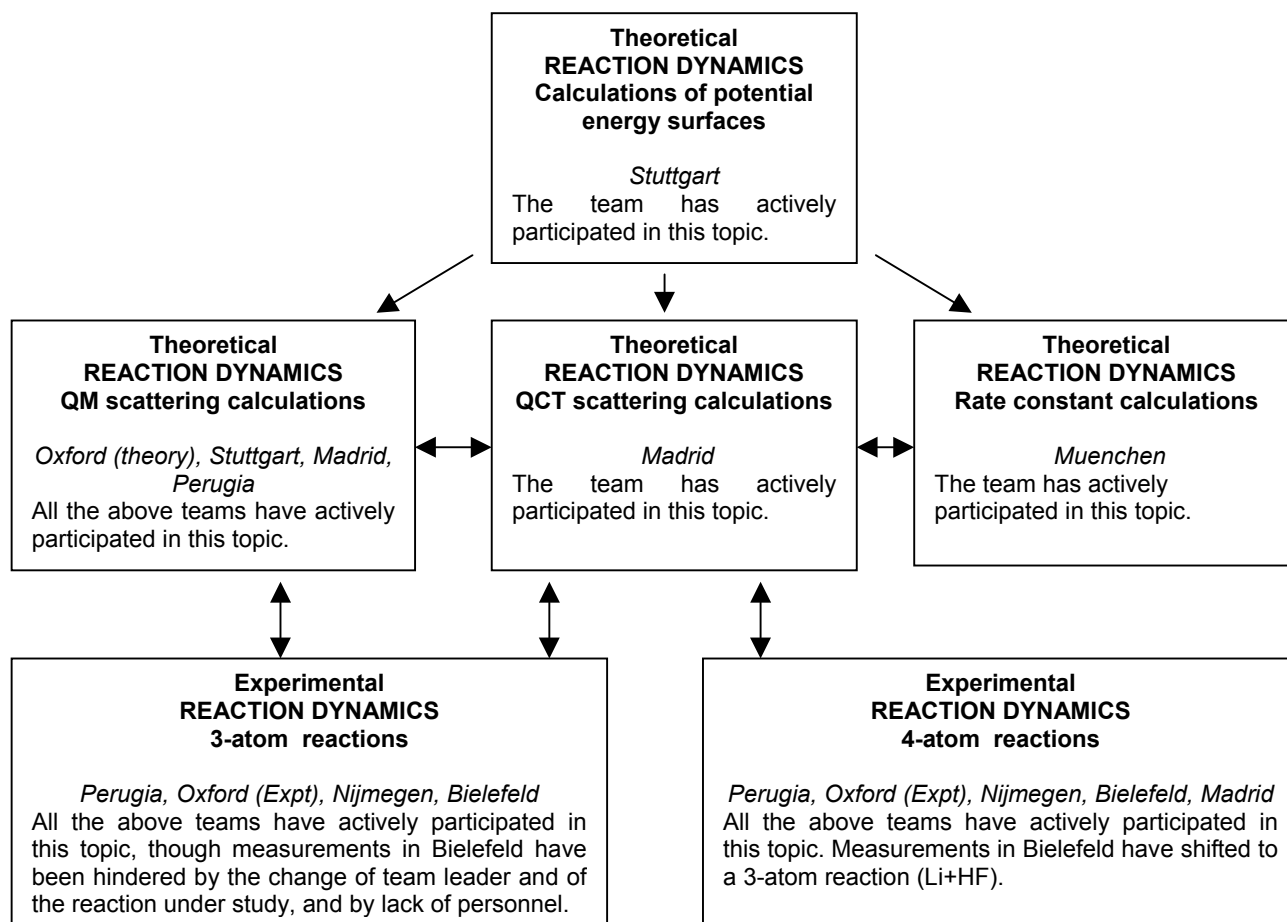
1. Experimentalists will employ novel complementary techniques, which have been implemented and are only available in their laboratories, to study the detailed dynamics of important elementary reactions of relevance from both fundamental and practical points of view.
2. Theoreticians will employ novel quantum chemical methods, developed in their laboratories, to calculate the potential energy surfaces (PESs) which describe the reactions studied experimentally, and to carry out on these potential surfaces scattering calculations using quantum mechanical as well as classical methods, in order to predict the quantities which are experimentally measured. The theoreticians will also develop new theoretical approaches to treat chemical reactions occurring on multiple PESs with inclusion of non-adiabatic couplings, and will implement new methods to overcome the dimensionality problem in the treatment of reactions involving more than three atoms.

All of these objectives are still relevant and have **already been substantially achieved**, and the Network will continue to reinforce this success in order to fulfil our main aim, **to improve substantially our level of understanding of molecular reactive collisions and then of the forces that drive chemical reactivity, a central theme of chemistry.**

B.2 Research Method and Work Plan

The Network's methodology has closely followed that laid down in the contract, where the overall strategy was to bring together a group of researchers with diverse interests, all of whom could make a distinctive and important contribution to solving problems in chemical reaction dynamics, combining (1) Experiments and (2) Theoretical Calculations.

The programme of work was divided into two main areas, the first one (Experimental studies of reaction dynamics) comprising two sub-areas (Three-atom reactions, Four-atom reactions), and the second one (Theoretical studies of reaction dynamics) comprising four sub-areas (Ab initio calculations of potential energy surfaces, Quantum scattering calculations, Quasiclassical trajectory scattering calculations, Rate constant calculations), as detailed in Section A.1. These, along with the respective teams *as envisaged in the contract*, are shown in the following diagram.



Each topic was split down into a set of tasks, and progress towards completing these tasks is detailed in the following table.

Task List	% COMPLETION to date					Teams Involved	Comments/Changes from Contract
	20	40	60	80	100		
1. Experimental studies of 3-atom reactions							
1.1 Reaction $O(^1D) + H_2$						Oxford(Expt), Perugia	One joint publication out and two in progress.
1.2 Reaction $Cl(^2P) + H_2$						Perugia	Two joint publications out and one in preparation.
1.3 $N(^2D) + H_2$						Perugia	One publication on $N(^2D)+D_2$ out and one joint on $N(^2D)+H_2$ in press. More measurements planned.
1.4 Reaction $C(^1D) + H_2$						Perugia	One publication out and one joint in preparation. Measurements on $C(^1D)+D_2$ starting soon.
1.5 Reaction $O(^3P)+H_2(v=1)$ (t.p.)						Bielefeld	Replaced by study of the reaction $Li+HF$, for which measurements are under way (see Section B.2.1-2).
1.6 Beam characterization						Perugia, Nijmegen	Nijmegen measurements highly successful, and now completed. In progress in Perugia.
2. Experimental studies of 4-atom reactions							
2.1 Reaction $OH + CO$						Perugia	Sensitivity apparatus improved. Measurements will start soon.
2.2 Reaction $H + CO_2$						Oxford (Expt)	Study completed at the beginning of network. Neglected to put acknowledgments. Effort has concentrated on the reaction $O(^3P)+HBr$ and on developing an ion-imaging version of the photoinitiated technique, both subjects initially not envisaged in contract.
2.3 Reaction $OH + H_2$						Perugia, Bielefeld	Measurements being planned in Perugia. Bielefeld has concentrated on $Li + HF$ (see Section B.2.1-2).
2.4 Reaction $OH + H_2(v=1)$						Bielefeld, Nijmegen	Replaced in Bielefeld by detailed studies of the reaction $Li + HF$ (see section B.2). Still of interest in Nijmegen, though delayed.
2.5 Reaction $H + H_2O$						Oxford (Expt)	$H+D_2O$ also studied. One publication out, more in preparation.
2.6 Reaction $NH + NO$ (time permitting)						Perugia	Will eventually be attempted towards the end of contract.
2.7 Reaction $H + N_2O$						Oxford (Expt)	As for task 2.2 (reaction $H + CO_2$).
2.8 Reaction $OH + HCl$						Nijmegen	Inelastic scattering with non-oriented OH completed. Measurements with oriented OH under way. Reactive scattering in preparation.
2.9 Inelastic $OH + CO$						Nijmegen	Completed and published.
2.10 Inelastic $OH + H_2(v=1)$						Nijmegen	Work delayed to later stage, but programme goals should be met. As replacement $OH + HCl$ has been anticipated.
2.11 Development of OH source						Bielefeld	Substituted with development of Li source for study of $Li+HF$ (see Section B.2.1-2). Li source developed.
2.12 Pump-Probe apparatus test						Madrid	Completed successfully.
3. Theoretical calculations of PESs							
3.1 Reaction $Cl(^2P) + H_2$						Stuttgart	Project completed very successfully. Numerous publications (of which one in <i>Science</i>).

3.2 Reaction $O(^1D) + H_2$		Stuttgart	Done elsewhere. Concentrated on the reaction Li+HF, initially not envisaged in the contract. PES for Li+HF completed. Publication in preparation. (see Section B.2.3)
3.3 Reaction $N(^2D) + H_2$ (t.p.)		Stuttgart	Done elsewhere. Concentrated on the reaction Li+HF, initially not envisaged in the contract.. PES for Li+HF completed. Publication in preparation. (see Section B.2.3)
3.4 Reaction $C(^1D) + H_2$		Stuttgart	Done elsewhere. Concentrated on the reaction Li+HF, initially not envisaged in the contract.. PES for Li+HF completed. Publication in preparation. (see Section B.2.3)
3.5 Direct dynamics $OH + H_2$		Stuttgart	Programme goals should be met.
4. QM calculations			
4.1 Set-up of programs		Oxford (theory)	Completed for abstraction reactions. Under way for insertion reactions.
4.2 Reaction $Cl(^2P) + H_2$		Oxford (theory)	Carried out also in Stuttgart (especially), Madrid and Perugia. Copious number of publications.
4.3 Reaction $O(^1D) + H_2$		Oxford (theory)	Work in progress in Oxford. Developed also statistical theory and applied also to $N(^2D)+H_2$.
4.4 Reaction $C(^1D) + H_2$		Oxford (theory)	Work in progress in Oxford.
4.5 Reaction $OH + H_2, CO$		Stuttgart	Efforts under way.
5. QCT calculations			
5.1 Set-up of programs		Madrid	Completed for both 3-atom and 4-atom reactions
5.2 Simulation of experiments		Madrid	Completed for experiments done so far on $Cl(^2P) + H_2/D_2, O(^1D)+H_2/D_2, N(^2D)+H_2, C(^1D)+H_2$
5.3 Comparison with QM calculations		Madrid	Completed for QM results available so far for $Cl(^2P) + H_2/D_2, O(^1D)+H_2/D_2, N(^2D)+H_2, C(^1D)+H_2$
6. Rate constant calculations			
6.1 Reaction $Cl(^2P) + H_2$		Muenchen	Completed. Publication in progress.
6.2 Reaction $OH + H_2$		Muenchen	Not done because studied in detail elsewhere (see Section B.2.6). In substitution, done successful applications to the polyatomic reaction $H + CH_4$ (Numerous publications).
6.3 Reaction $OH + HCl$		Muenchen	Work in progress.

No major discrepancies in the overall tasks (1—6) allocated in the contract have occurred. Changes in the Bielefeld projects, justified by the change of Team Leader, have led to a very collaborative project involving several teams (see below). Minor differences will always arise in a detailed scientific programme, but we will attempt to address also these, below, under each of the six main task headings.

1. Experimental studies of 3-atom reactions

Task 1.5 concerning the reaction $O(^3P)+H_2$ ($v=1$) to be studied in Bielefeld by the Rydberg tagging technique, cannot be met because of the changes occurred following the premature death of the initial Bielefeld Team leader. This task, which was envisaged only time permitting, as well as **tasks 2.3 and 2.4** (see below) has been replaced by a large collaborative project on the prototypical, asymmetric 3-atom reaction $Li + HF$, which has attracted a great theoretical interest in the Network (Stuttgart has calculated an *ab initio* PES, Madrid and Perugia are carrying out both QM and QCT dynamics calculations) and for which the only laboratory able to produce detailed experimental data is that of Bielefeld in the group of Prof. J. Loesch, the new Team leader. The dynamics of this reaction is a topic of great interest in the field of Reaction Dynamics, not foreseen initially in the programme, since it represents the prototypical 3-atom reaction involving 3 different atoms that is amenable to detailed theoretical and experimental investigation.

2. Experimental studies of 4-atom reactions

Task 2.3 and 2.4 envisaged the study in Bielefeld of the reaction $\text{OH} + \text{H}_2$ and $\text{OH} + \text{H}_2(v=1)$ using the Rydberg tagging technique. The same comment described above for **task 1.5** holds. However, the reaction $\text{OH} + \text{H}_2(v=1)$ has become a project of interest in Nijmegen, although originally only the inelastic scattering was planned.

Task 2.10 envisaged the inelastic scattering $\text{OH} + \text{H}_2(v=1)$ in Nijmegen. This project has been delayed, for technical reasons, to a later stage (later in the 3rd year), while the $\text{OH} + \text{HCl}$ project, initially planned in Nijmegen at the beginning of the 4th year, has been anticipated to the 2nd year.

3. Theoretical calculations of PESs

Tasks 3.2- 3.3 and 3.4 envisaged calculations in Stuttgart of the PES for the reactions $\text{O}(^1\text{D}) + \text{H}_2$, $\text{N}(^2\text{D}) + \text{H}_2$ and $\text{C}(^1\text{D}) + \text{H}_2$, respectively. Since during these last few years the PESs for these systems have been calculated in other laboratories (outside the Network) at an accurate level, there was no point to re-calculate them. However, all the other aspects of theoretical work on $\text{O}(^1\text{D}) + \text{H}_2$, $\text{N}(^2\text{D}) + \text{H}_2$ and $\text{C}(^1\text{D}) + \text{H}_2$, namely the QM and QCT scattering calculations to be compared with experiment, remain a very active theme in the network, simply the calculations have been performed on the relevant PESs taken from the literature. As replacement, at the light of the shift of interest in Bielefeld from the reaction $\text{OH} + \text{H}_2$ to the reaction $\text{Li} + \text{HF}$, attention in Stuttgart has been focused on the *ab initio* calculation of a state-of-the-art PES for $\text{Li} + \text{HF}$. This is particularly relevant in this Network since $\text{Li} + \text{HF}$ is a "truly" 3-atom A+BC reaction, where all 3 atoms are different. Other teams of the Network have the capability to perform detailed dynamics calculations on this reaction, both quantum and quasiclassical. This has stimulated a very synergistic collaborative effort within the Network that involves four different teams (Stuttgart, Bielefeld, Madrid and Perugia). In this way, it has become possible to extend the very spirit of the Network (combined experimental and theoretical studies of elementary reactions) to a truly A+BC reaction. Therefore **Tasks 3.2-4** can be renamed as "Reaction $\text{Li} + \text{HF}$ " and it has been completed (a publication is in preparation about the PES). Dynamics calculations on $\text{Li} + \text{HF}$ using this new PES will be carried out to compare with previous results on different PESs and with experimental results (past, current and future) from Bielefeld.

4. QM calculations

Programme goals should be met or exceeded.

5. QCT calculations

The programme goals should be met.




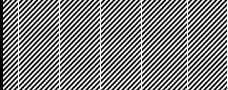


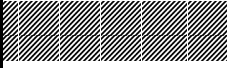
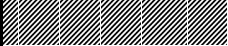
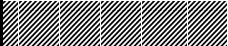


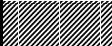






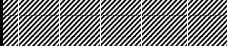
6. Rate constant calculations

Task 6.2 envisaged during the 2nd year the calculation of rate constant for the reaction $\text{OH} + \text{H}_2$. This project has been replaced as a research objective: In fact, starting during the first year of the network, D. H. Zhang et al. published a series of articles on the $\text{H}_2 + \text{OH}$ reaction: *Science* 290, 961 (2000); *J. Chem. Phys.* 114, 4759 (2001); *J. Chem. Phys.* 114, 8733 (2001); *J. Chem. Phys.* 115, 174 (2001); *J. Chem. Phys.* 116, 2388 (2002). They developed a new, high quality potential energy surface and presented numerous quantum dynamical calculations including reaction rate calculations. This work resolved the questions which we intended to address with our planned work on the $\text{H}_2 + \text{OH}$ reaction. As a replacement for the $\text{H}_2 + \text{OH} \rightarrow \text{H} + \text{H}_2\text{O}$ system, the $\text{H} + \text{CH}_4 \rightarrow \text{H}_2 + \text{CH}_3$ has been studied. As a first step, accurate reaction rate calculations have studied the reaction dynamics of this systems on an existing semiempirical potential energy surface. In parallel, a new high quality potential energy surface is being developed for this system in collaboration with the Stuttgart group. Then reaction rate calculations will provide accurate thermal rate constants and cumulative reaction probabilities for this reaction.

B.3 Schedule and Milestones

Please refer to the chart (Section B.2) showing progress towards completion to date of the Schedule laid down in the Project Programme. The following chart shows the milestones which were envisaged at this stage (mid-term) in the project programme, along with a bar chart of their approximate % completion at the current date (end of May, 2002).

Milestones (under originally envisaged dates)	% COMPLETION to date					Comments/Changes from Contract
	20	40	60	80	100	
6 months						
Recruitment of majority of Young Researchers	████████	████████	████████	████████	████████	Took much longer than 6 months. All partners have now been able to employ a young researcher.
14-18 months						
Experiments on $\text{Cl}(^2\text{P}) + \text{H}_2(\text{D}_2)$ and $\text{O}(^1\text{D}) + \text{H}_2(\text{D}_2)$ completed (or nearly).	████████	████████	████████	████████	████████	Completed.
Calculation of PES for $\text{Cl}(^2\text{P}) + \text{H}_2$ completed and for $\text{O}(^1\text{D}) + \text{H}_2$ near completion	████████	████████	████████	████████	████████	Calculations of ground state adiabatic PES for $\text{Cl} + \text{H}_2$ completed. Calculations of multiple PES, including non-adiabatic and spin-orbit coupling, for $\text{Cl} + \text{H}_2$ nearly completed. No calculations performed for $\text{O}(^1\text{D}) + \text{H}_2$ (see Section B.2); attention focused on another reaction: $\text{Li} + \text{HF}$.
Calculation of rate constants for $\text{Cl}(^2\text{P}) + \text{H}_2(\text{D}_2, \text{HD})$ completed	████████	████████	████████	████████	████████	Completed on ground state PES.
Beam source of OH developed	████████	████████	████████	████████	████████	Completed in Nijmegen. In Bielefeld replaced by development of source of Li atoms (see Section B.2)
Inelastic scattering of $\text{OH} + \text{H}_2(v=1)$ and $\text{OH} + \text{CO}$ initiated	████████	████████	████████	████████	████████	Work on $\text{OH} + \text{CO}$ completed, on $\text{OH} + \text{H}_2(v=1)$ delayed (see Section B.2).
Programs by QCT methods for 3-atom multipotential and 4-atom single-potential reactive scattering calculations set-up (or nearly)	████████	████████	████████	████████	████████	Completed
Programs for 3-atom multipotential reactive scattering calculations by QM methods set-up.	████████	████████	████████	████████	████████	Completed
Test of pump-probe apparatus with REMPI detection completed.	████████	████████	████████	████████	████████	Completed
24-28 months – Mid-Term Review						
Experiments on $\text{C}(^1\text{D}) + \text{H}_2$ completed and on $\text{N}(^2\text{D}) + \text{H}_2$ nearly completed.	████████	████████	████████	████████	████████	Completed ahead of schedule. Will also do $\text{C}(^1\text{D}) + \text{D}_2$.
Experiments on $\text{H} + \text{H}_2\text{O}$ completed and on $\text{H} + \text{CO}_2$, $\text{H} + \text{N}_2\text{O}$, $\text{OH} + \text{H}_2$ initiated	████████	████████	████████	████████	████████	Program goals should be met, with the exception of $\text{OH} + \text{H}_2$ work in Bielefeld (see Section B.2)
Atomic and radical beams characterized spectroscopically	████████	████████	████████	████████	████████	Work completed for pulsed OH beams. Under way for continuous beams.
Inelastic scattering of $\text{OH} + \text{H}_2(v=1)$ and $\text{OH} + \text{CO}$ completed and reactive scattering of $\text{OH} + \text{H}_2(v=1)$ initiated.	████████	████████	████████	████████	████████	Work on $\text{OH} + \text{CO}$ completed. Work on $\text{OH} + \text{H}_2(v=1)$ replaced with work on the reaction $\text{Li} + \text{HF}$ in Bielefeld, delayed in Nijmegen. (see Section B.2)
Calculations of PES for $\text{C}(^1\text{D}) + \text{H}_2$ (or $\text{N}(^2\text{D}) + \text{H}_2$) initiated; direct dynamics calculations for $\text{OH} + \text{H}_2$ initiated.	████████	████████	████████	████████	████████	Calculations on $\text{C} + \text{H}_2$ and $\text{N} + \text{H}_2$ will not be done (see Section B.2). In substitution, calculations completed for $\text{Li} + \text{HF}$. Programs for direct dynamics set-up; tests in progress.
Calculations of rate constants for $\text{OH} + \text{H}_2$ performed.	████████	████████	████████	████████	████████	Replaced with the system $\text{H} + \text{CH}_4$ (see Section B.2), done completely.
QM calculations for $\text{Cl}(^2\text{P}) + \text{H}_2$ completed and for $\text{O}(^1\text{D}) + \text{H}_2$ initiated	████████	████████	████████	████████	████████	Completed.
QCT calculations on reactions studied experimentally completed ($\text{Cl}(^2\text{P}) + \text{H}_2$, $\text{O}(^1\text{D}) + \text{H}_2$) or initiated ($\text{N}(^2\text{D}) + \text{H}_2$, $\text{C}(^1\text{D}) + \text{H}_2$, $\text{OH} + \text{H}_2$)	████████	████████	████████	████████	████████	Work on all 3-atom reactions completed.
Comparison between QM and QCT results and simulations of experiments so far performed, completed.	████████	████████	████████	████████	████████	Completed.
36-38 months						
Experiments on $\text{OH} + \text{H}_2$ and $\text{OH} + \text{CO}$ completed	████████	████████	████████	████████	████████	

Experiments on NH+NO possibly initiated		Unlikely to be addressed in timescale available.
Experiments on H + CO ₂ completed, and on H + N ₂ O near completion		
Experiments on OH+H ₂ (D ₂) (v=1) completed and on O(³ P)+H ₂ (v=1) initiated		Will not be met (See Section B.2)
Experiments on OH + HCl initiated		
Calculations of PESs for selected reactions completed		
QM calculations on selected reactions and QCT calculations on nearly all studied reactions completed (or near to completion); comparison with experiments completed or near completion.		
Calculations of inelastic scattering completed		
45 months		
Experiments completed.		
QM and QCT scattering and rate constant calculations completed.		
Comparisons between experiments and theory completed.		
48 months – End of Grant Period		
3-atom reaction (experiment and theory)		
4-atom reactions (experiment and theory)		
PESs for multi-surface 3-atom reactions		
PESs for single-surface 4-atom reactions (improvements)		
QM and QCT calculations for selected single-surface 3-atom reactions		
QM and QCT calculations for selected multi-surface 3-atom reactions		
Non-adiabatic effects in reaction dynamics		
QCT calculations for single-surface 4-atom reactions		
Direct dynamics for 4-atom reactions		
QM calculations of inelastic scattering for 4-atom systems		
Rate constant calculations for 3-atom and 4-atom reactions.		

B.4 Research Effort of the Participants

The following table shows the research effort foreseen to date, compared with the actual situation to date. The foreseen effort by young researchers (YRs) to be financed by the contract was calculated on a pro-rata basis assuming a 6-month recruitment period at the start of the network, i.e. 21 months from 1 September 2000 to 31 May 2002, against 42 months 1 September 2000 to 28 February 2004.

Participant	Foreseen Professional Research Effort (man-months, pro-rata for 21/42 months for YRs) (man-months, pro-rata for 27/48 for others)			Actual Total Professional Research Effort to date (man-months)		
	by young researchers to be financed by the contract (a)	By researchers to be financed from other sources (b)	Total research effort (a + b)	by young researchers financed by the contract (a')	by researchers financed from other sources (b')	Total research effort (a' + b')
1. Perugia	18	57	75	13	90	103
2. Oxford (expt)	18	74	92	3	87	90
3. Nijmegen	18	44	62	24	44	68
4. Bielefeld	18	25	43	2	25	27
5. Madrid	18	111	129	9	120	129
6. Oxford (Th)	18	40	58	23	48	71
7. Stuttgart	18	40	58	18	62	80
8. Muenchen	18	52	70	23	59	82
<u>TOTAL</u>	144	443	587	115	535	650

As can be seen from the table, the Network meets and exceeds its targets for total professional research effort. The following variations should be commented upon:

1. *Oxford (Expt)* and *Bielefeld* young researcher effort is particularly low, but both places have now a YR (pre-doc) in place who is committed to the project. According to advanced contacts, in Oxford another pre-doc will be employed from september/october 2002 and in Bielefeld also a post-doc from 1/11/2002. Although employment of further YRs will be required, both teams are well on their way to provide all the training they agreed to by the end of the contract.
2. *Madrid* YR effort is also somewhat low, but they now have (since 1/9/2001) a YR who is very committed to the project and they will be able to provide all the training they agreed to by the end of the contract.

B.5 Network Organisation and Management

The Network is co-ordinated from *Perugia* by Prof Piergiorgio Casavecchia, the Co-ordinator and Scientific Director of the *Perugia* team. As envisaged in the Project Programme, email has been extensively used for communication by the Co-ordinator with Network members, Young Researchers, and Scientific Directors. The Co-ordinator has separate email databases for all these categories. Indeed, the Network administration is largely paperless.

Shared objectives and common goals, combined with modern email communications, have permitted an exciting progress of the Network, with Team leaders and young researchers reporting directly to the Co-ordinator.

Assisted by the *Perugia* team member Dr Nadia Balucani, the Co-ordinator set up the Network website in 2000 (with further refinements in 2001 and 2002). This is used to provide information and publicity about the aims and objectives of the Network, and its teams, to advertise job positions (especially in view of the condition of the EU Cordis website), and to disseminate information such as programmes for network meetings.

The detailed network home page is at http://www.chm.unipg.it/chimgen/Reaction_Dynamics.html and is maintained by the *Perugia* team member Dr Nadia Balucani.

The Co-ordinator has organised or co-organised a total of three Network meetings, including the mid-term review / network meeting.

The **inaugural meeting** for the Network was held from May 12-14, 2000, at the University of *Perugia*, and organised by the Network Co-ordinator, Piergiorgio Casavecchia. Seven scientific directors were present, as well as a number of

other staff and students from the Participants, including a RTN fellow then in post and two others to be appointed the following month, and numbering 28 in all. Scientific progress reports were given by each Participant, and discussions were held on topics including Network Administration and Future Meetings.

The Network Co-ordinator, Piergiorgio Casavecchia, organised, along with the invaluable assistance of Mark Brouard (of the Oxford team) who acted as local organizer, the **first full annual Network Meeting**, from Wednesday March 28—Sunday April 1, 2001 at the University of Oxford, in Jesus College, Oxford, GB. There were 30 non-local scientific participants, along with three invited speakers and a number of local attendees. All of the then-current RTN fellows gave talks, along with all of the 8 Scientific Directors of the Network, as well as several students. A full day was devoted to a "short course" for the YRs in which 7 tutorial lectures were given by world experts in their respective fields. This "short course" has represented an invaluable training experience for the YRs. Discussions were held on topics including Network Administration and Future Meetings.

The **second full annual Network Meeting** has been organised by the Network Co-ordinator, Piergiorgio Casavecchia, along with the invaluable assistance of Javier Aoiz (of the Madrid team) acting as local organizer, at the Parador de Segovia, Segovia, Spain, from Wednesday June 19—Saturday June 22, 2002, to include the Mid-Term Review meeting on the Friday, June 21. All 8 Scientific Directors will once again be present, along with all Young researchers currently financed by the Network, and an ex-YR fellow. In excess of 35 participants are expected, including three invited speakers and five tutorial lecturers for another "short course", similar in format to the successful one held in Oxford in 2001. For Year 3, in June 2003 all the YRs are expected to attend the school on "Reaction Dynamics" that Prof. Miguel Gonzalez will be organizing in Barcelona (Spain), following the COMET XVIII and the Quantum Reactive Scattering Workshop that F. J. Aoiz will be organizing in Madrid.

B.6 Cohesion with Less Favoured Regions and Associated States

There are not Network partners from less favoured regions of the community or from Associated States.

B.7 Connections to Industry

This network is concerned with basic science and has no direct connections to industry.

PART C - TRAINING

C.1 Appointment of Young Researchers

The following table shows the situation regarding employment of young researchers up until May 31, 2002, compared with the 'Contract deliverable' to the end of the Network (28/2/2004).

Participant	Young researchers financed by the contract so far (man-months)			Contract deliverable of young researchers to be financed by the contract (man-months)		
	Pre-doc (a)	Post-doc (b)	Total research (a + b)	Pre-doc (a)	Post-doc (b)	Total research (a + b)
1. Perugia		13	13		36	36
2. Oxford (Expt)	3		3		36	36
3. Nijmegen		24	24	18	18	36
4. Bielefeld	2		2		36	36
5. Madrid		9	9		36	36
6. Oxford (theory)		23	23		36	36
7. Stuttgart		18	18		36	36
8. Muenchen		23	23		36	36
<u>TOTAL</u>	5	110	115	18	270	288

With 21 months left until the end of the contract, and young researchers recruited for most positions, most partners are expected to be able to fulfil their obligations, at least within one or two man-months. A few points are worthy of note:

- As noted in Sections B.4 and B.5, the teams in *Oxford (Expt)* and *Bielefeld* have had difficulty in recruitment. However, both places have now (from the beginning of the 3rd year) a YR (pre-doc) in place who is committed to the project. **Change from a post-doc to a pre-doc** position was required in both places due to the difficulty of finding a post-doc. The option was chosen of keeping the same budget and correspondingly increasing the number of person-months, as discussed via e-mail with the EC Scientific Officer and detailed in a fax-letter to her in date 2 May 2002. According to advanced contacts, in Oxford another pre-doc will be employed from september/october 2002 and in *Bielefeld* also a post-doc from 1/11/2002. Although employment of further YRs will be required to meet their contract deliverables, both teams are well on their way to provide all the training they agreed to by the end of the contract. In both cases the positions have been amply publicized by the Scientific Directors and on the Network website, Cordis website, mailbases, at conferences, in informal communications, etc.
- Madrid* has employed a post-doc from 1/9/2001. The YR is very committed to the project and they would like to keep him for 36 months. This, however, would exceed of 6 months the agreed duration of the Network, so, unless an extension of the Network of 6-months (at zero cost) will be agreed upon, *Madrid* will need to employ another post-doc for 6 months to meet their training deliverables.
- Nijmegen* had initially envisaged 18 months of post-doc and 18 months of pre-doc. Having *Nijmegen* employed a post-doc shortly afterward the start of the Network, and being the post-doc very committed to the project, it was decided to **change the pre-doc months into post-doc months** and keep the same person as post-doc for a total of 30 months (as detailed in the letter of May 2, 2002 to the Project Scientific Officer, mentioned above). In this case, remaining the budget the same, the number of person-months have decreased with respect to the case of *Oxford(Expt)* and *Bielefeld*, where they have instead increased.
- Considering the initial difficulties of employing a post-doc in *Oxford (expt)*, *Bielefeld*, and also *Madrid* (to some extent), and considering the change from post-doc to pre-doc months in the former two places which increases the number of deliverable person-months (the budget remaining the same), it will be necessary in these places to have two or three YRs overlapping for some time in order to meet the contract deliverables (as it was done in Perugia, for instance, where two post-docs are currently in place). A possibility may arise that an extension of the contract of 6 months (at zero cost) beyond the present ending date of 28/2/2004 may facilitate the fulfillment of the training-months time committed on in the contract. For instance, with a 6-months contract extension, Madrid could keep the present post-doc for the entire period of 36 months.

C.2 Training Programme

The general training programme can be summarised under three headings:

Employment and Visits All of the Young researchers (YRs) are employed in an EU country other than their country of citizenship and spend, on average, one month per year in one of the other laboratories of the Network. The visits to other teams are not only of great benefit to the YRs undertaking them, they also cement the collaborative aspects of the programme. So far, limited secondments have occurred, due to the initial difficulties in the recruitment of YRs, but an intense secondment activity is foreseen during the 3rd and 4th year.

Reports and Meetings Whilst in their home laboratories, the YRs take primary responsibility for day-to-day informal contacts with their peers in the other teams and for the preparation of reports. The YRs have attended and given presentations at the yearly meetings. In addition, they are sent to appropriate national and international scientific meetings to present their research and relate it to the work of the Network as a whole. These activities give them experience in the co-ordination and management of a large research project, as well as improving their oral and written presentational skills.

Institutions Each of the team members is engaged in performing high-quality research in a large and diverse research group located in a research institution of high international standing. This is important from the standpoint of the education and training of the YRs, since it means that they are immersed in an active and dynamic research environment. Each of these establishments have programmes in place to ensure that their young researchers receive a training which is broad as well as deep. The YRs employed by the Network are expected to participate fully in these programmes.

The following **exchange visits** have taken place to date.

Perugia

The YRs have only recently started work in Perugia. Plans for secondements and visits have already been agreed on. Dimitris Skouteris will spend one month (July 2002) in *Stuttgart* working on quantum scattering calculations of reaction dynamics. Rolf Bobbenkamp will spend one month in *Bielefeld* (where he has already made a short visit) during the summer working on reactive scattering experiments.

Oxford (Expt)

The YR Sarandis Marinakis has only very recently started work in *Oxford*. Options for his training visit will be explored at the Network meeting in Segovia.

Nijmegen

No exchange visits have yet been made due to unexpected technical difficulties occurred in the laboratory. However, the YR Raluca Cireasa will make one-month secondment in *Perugia* in September 2002, working on the characterization of continuous OH beams and on crossed beam studies of the 4-atom reaction OH+CO, for which she has studied the inelastic scattering in *Nijmegen*.

Bielefeld

The YR Andrea Russo has only very recently started work in *Bielefeld*. Options for his training visit will be explored at the Network meeting in Segovia.

Madrid

The YR Jonathan Barr will spend one-month in *Oxford(Expt)* during the summer 2002 to foster collaboration on the ion-imaging technique for studies of reaction dynamics.

Oxford(Theory)

The YR Tomas Gonzalez-Lezana has spent one month (May 2001) in *Madrid* working on QCT as well as QM scattering calculations.

Stuttgart

The YR Gabriella Capecchi has spent about a week in *Muenchen* collaborating to rate constant calculations on the Cl+H₂ reaction, and about a week in Perugia collaborating to the simulation of experimental scattering results with QM results on her *ab initio* ClH₂ PES. She could not do a planned one-month secondment in *Oxford(Theory)* because of a pregnancy.

Muenchen

The YR Fermin Huarte-Larranaga has spent one-month secondment (from 28/3/2001 until 1/5/2001) with the team of David Manolopoulos (*Oxford(Theory)*), working on a statistical theory for insertion reactions. He is planning to do another secondment in *Madrid* during the 3rd year.

C.3 Factual Information on the Young Researchers

Participant / Place of work / Country	Name of YR	Nationality	Age at time of appointment	Start / (likely) end date of appointment	Category of Researcher	Scientific specialty	Previous work / study at another Network Partner?
1. Perugia, IT	Dimitris SKOUTERIS	GR	28	01.09.01—31.08.02	Post-doctoral	C-06	Yes, Oxford (postdoc from 1999 until Feb 2000) and Stuttgart (postdoc from March 2000 to August 2001)
	Rolf BOBBENKAMP	DE	32	01.02.02—31.01.04	Post-doctoral	P-03 C-03	Yes, Bielefeld (obtained PhD in January 2002)
2. Oxford (Expt), GB	Sarandis MARINAKIS	GR	27	01.03.02—28.02.04	Pre-doctoral (PhD)	C-03	No
3. Niemegeen, NL	Dana Raluca CIREASA	RO	32	01.06.00—31.12.02	Post-doctoral	P-03 C-03	No
4. Bielefeld, DE	Andrea RUSSO	IT	26	08.04.02—28.02.04	Pre-doctoral	P-03	No
5. Madrid, ES	Jonathan BARR	GB	27	01.09.01—28.02.04	Post-doctoral	C-03	No
6. Oxford (Expt), GB	Tomas GONZALEZ-LEZANA	ES	29	01.07.00—30.06.03	Post-doctoral	C-06	No
7. Stuttgart, DE	Gabriella CAPECCHI	IT	28	01.03.00—31.08.01	Post-doctoral	C-06	Yes, Perugia (obtained PhD in 1999).
8. Muenchen, DE	Fermin HUARTE-LARRANAGA	ES	29	01.07.00—30.06.03	Post-doctoral	C-06	No

PART D - SKETCHES OF THE YOUNG RESEARCHERS

Included here are sketches written entirely by the young researchers themselves, with only minor editing by the Network Co-ordinator (typographic errors only).

Perugia: Dimitris Skouteris

Previous experience: I obtained my D. Phil. in 1999 on 'Structure and Dynamics of Weakly Bound Complexes', having worked with Prof. B.J. Howard in the Physical and Theoretical Chemistry Laboratory of the University of Oxford. I subsequently did a postdoc with Dr. D.E. Manolopoulos in the same laboratory on the quantum theory of chemical reactions. In March 2000 I went to Stuttgart to work with Prof. H.-J. Werner on wavepacket methods to study photodissociation of stable triatomic molecules on more than one potential energy surface, as well as perform some time-independent single-surface calculations on the Cl+H₂ reaction.

Responsibility in the network: In September 2001 I joined the Perugia team, led by Prof. P. Casavecchia, as a YR financed by the network and started to work on the theoretical side of the project in close collaboration with the team member Prof. A. Lagana' who acted as my tutor. Specifically, I worked on wavepacket methods to study reaction dynamics of 3-atom systems, with the possibility of working on multiple electronic potential energy surfaces. We developed a time-dependent wavepacket propagation program for this purpose, which utilises the modified propagator f(H) originally developed by Balint-Kurti and coworkers but with the added option of working on multiple surfaces. We have tested this program on the Cl + H₂ reaction system, using a single surface based on the new potential energy surfaces developed by Capecchi and Werner in Stuttgart.

On the network: I found my experience of working in the network extremely rewarding. Apart from the fact of advancing my experience with time-dependent wavepacket calculations, the network has also given me the opportunity to collaborate with other well-known groups on the subject. Furthermore, it has been a pleasure to work in the Perugia group, both in terms of the expertise and of the working atmosphere.

Perugia: Rolf Bobbenkamp

Before starting my position in the RTN network I worked with Prof. P. Andresen in the Applied Physics Department of the University of Bielefeld where I obtained my PhD in January 2002 on the "Development of a New Time and Position Sensitive Detector for Laser Diagnostics of Chemical Reactions". This new detector allows to measure simultaneously time and 2D spatial information for a nearly unlimited number of spatial separated 'events' hitting the detector surface. One of the many tests performed with this detector was the study of the photodissociative process H₂ → H+H in the group of Prof. W. van der Zande (FOM Institute, Amsterdam), where we obtained good results using this detector. Especially the efficiency of the measurements was improved significantly.

I have recently been appointed to the network and started my postdoctoral position as a RTN fellow in Prof. Casavecchia's group in Perugia from February 2002. The goal of my research in Perugia is to study the reaction dynamics of some simple 3-atom and 4-atom systems by using the technique of crossed molecular beams with mass spectrometric detection. The focus is on the prototype reactions C(¹D) + D₂ and OH + CO. During these first few months we have completed the set-up of an improved, higher sensitivity experimental arrangement, and we have started, very successfully, measurements on the reaction C(¹D) + D₂ → CD + D, for which in Madrid dynamical calculations on a new *ab initio* potential energy surface will soon be performed for comparison with experiment. During these first few months I had also a short stay in the group of Prof. H.J. Loesch in Bielefeld, where the reaction Li + HF is studied using the same technique of crossed molecular beams, but with surface ionization detection. In the Perugia and Bielefeld laboratories similar new approaches are being attempted to vary the collision energy down to very low and very high values by changing the beams intersection angle from 90° to 45° and 135°, respectively. It will be extremely useful to transfer information and expertise between the two laboratories in regard. I intend to do a secondment in Bielefeld for one month later in the year.

During the few months I have worked in this network I found my experiences extremely interesting and rewarding for my future career prospects. The network has given me the opportunity to collaborate with well-known and experienced groups in the field.

Oxford (expt): Sarandis Marinakis

I entered the Department of Chemistry at the National and Capodistrian University of Athens in 1992. I continued my studies having been placed top in the Physical Chemistry written examinations. I obtained my master degree, which in Greece is two years in 1999. My Masters Thesis was entitled 'Computer Simulation Study of the Mixture Xenon and Nitrogen in the Supercritical Region'. During the period of my masters work, I also had the opportunity to demonstrate Physical Chemistry experiments to undergraduate students, to teach the relevant theory for one year, and to give lessons to the undergraduate about Microsoft Office programs and Internet. Then, I completed my military service (18 months). During that period, among many other things, I worked as a chemist in various Military Factories that produced dyes, shoe polish, plastics and oxygen.

I have been appointed at my post (as pre-doc) in the Network from 1 March 2002, in the group of Dr. Mark Brouard at Oxford, where I am pursuing my PhD studies. Dr. Mark Brouard's group uses state-of-the art laser pump and probe techniques to elucidate the mechanisms of simple photochemical and bimolecular reactions. We use (i) polarized laser photolysis to start a reaction, (ii) polarized laser induced fluorescence to probe the products of the reaction. We have already implemented the technique to calculate the cross section for the reaction $\text{H} + \text{H}_2\text{O} \rightarrow \text{OH} + \text{H}_2$, which is of fundamental theoretical importance. We shall continue our studies recording some Doppler-resolved spectra from the products of this reaction.

I am satisfied with the equipment and research infrastructure, the intellectual environment, the pay and related conditions. I also consider that the research I have been given to carry out is very interesting and the impact of my appointment on my career prospects will be very rewarding.

Nijmegen: Raluca Cireasa

I have a degree in Physics with a specialisation in nonlinear optics and a PhD in molecular spectroscopy. I have obtained the PhD degree in 1999 from the University of Paris XI (France) with a thesis about the (Fourier Transform) spectroscopy of silicon carbide free radicals, supervised by Dr. Michel Vervloet.

Previously to my current appointment my scientific background was in material science and molecular spectroscopy. Since June 2000 I joined as a postdoc the group of Professor J.J. ter Meulen in Nijmegen to work on reactive and inelastic scattering of oriented and state selected OH radicals. This group has a long and fruitful experience on measurements of orientation dependent integral state-to-state cross sections. My task was to extend the studies of the orientation effects on the outcome of the scattering processes to the study of chemical reactions. The techniques used to select a particular rotational state of the OH radical and to orient it before undergoing a single collision make the experiments very complex and consequently, implies a lot of constraints for the detection method and for its technical implementation.

The many technical problems encountered, the difficulty of the experiments, the difference between my scientific background and the one needed for these experiments made sometimes the advancement of the project quite slow, but gave me the possibility to learn at both technical and phenomenological level, to achieve a lot of experience and to know in very detail the whole experimental set-up.

The first system we had tried study was $\text{OH} + \text{HCl}$, which according to the theoretical calculations would exhibit a high reactive cross section, but the detection method proved to not be sensitive enough. With the concern of getting some information about the reactive behaviour of the $\text{OH} + \text{HCl}$ system we had performed studies of the orientational dependence of the inelastic cross sections. We are also quite confident that the new detection scheme we are implementing we will finally succeed to obtain results for the reactive scattering of the above mentioned system and of those included in our project.

I appreciate that the experience I have obtained since I start working in this network is very interesting and rewarding through all the aspects that a team "net"work suppose: scientific collaboration, intellectual environment, scientific challenge. Therefore I estimate that the quality and the quantity of the knowledge I have acquired and the opportunity of collaboration with well known groups in the field of Molecular Dynamics will be extremely valuable for my career evolution.

Bielefeld: Andrea Russo

I completed my M.Sc. studies in Physics at the University of Bari (Italy) in December 2001. My thesis job focused on measurements of the non linear refractive index and two photon absorption coefficient on samples of lithium niobate by using the two color Z-scan technique. I also performed time resolved measurements of the optical non linearity of the samples with the purpose of investigating the different physical causes of the non linearity. A picosecond Nd:YAG laser source was used for exciting the material.

On April 8th I joined the "Reaction Dynamics" Network under the supervision of Prof. Loesch (Univ. of Bielefeld). My main task is to perform experiments on the reaction $\text{Li} + \text{HF}$ by using the crossed beam technique with surface ionization detection and time of flight analysis. Specifically, we plan to measure the excitation function down to very low collision energies, a range where theory predicts a peak structure. However, different potential energy surfaces (PES) predict the peak structure with different positions and magnitude. The experimental determination of both quantities would furnish a sensitive test on both the PES and the employed dynamical approximation for calculating the cross sections. At this initial stage I am getting acquainted with the experimental apparatus and with the underlying problematic.

I find the field of reaction dynamics intellectually stimulating and experimentally challenging. I am impressed with the experimental equipment in the laboratory of Prof. Loesch and I am very excited about the possibility of performing state-of-the-art experiments on the fundamental $\text{A} + \text{BC}$ reaction $\text{Li} + \text{HF}$. I like the intellectual environment in the Department of Physics in Bielefeld, and the pay as pre-doc and the conditions of employment are very satisfactory. Furthermore, I am very excited about the possibility of working in a European Network involving chemists and physicists in leading laboratories, with the possibility of a close interaction through secondements and meetings. I look forward to my first upcoming annual Network meeting which will give me the possibility to enter more in depth in the

spirit of the Network. I feel that working in this Network should have a very positive impact for my future career. In particular, I am considering the possibility of embarking in PhD studies in Physics at the University of Bielefeld.

Madrid: Jonathan Barr

Immediately after graduating from Salford University (UK) in 1997 with a BSc(Hons) degree in Chemistry I began my PhD in physical chemistry under the supervision of Professor John Dyke at The University of Southampton (UK). My thesis was concerned with three main areas: (1) The electronic structure of diatomic molecules (generally unstable, e.g. OH, O₃) studied by photoelectron spectroscopy, using both conventional atomic emission UV sources and also synchrotron radiation at the Daresbury source (UK). (2) Laser spectroscopy of Van der Waals molecules (e.g. Ar·NO, N₂·NO). (3) The elucidation of detection limits in ion trap mass spectrometry. The goal of the spectroscopic work was to accurately determine spectroscopic parameters that can be used, with the aid of high level ab initio calculations, to propose viable reaction sequences occurring in the atmosphere. Regarding the ion trap mass spectrometry work, this was part of a student exchange programme between the University of Southampton and The Chemical and Biological Defence Establishment at Porton Down (UK) (known as CBDE-Porton). At Porton I gained valuable experience in various mass spectrometric techniques whilst pursuing the project aim that was to determine statistically the number of ions stored by an ion trap mass spectrometer for a given set of experimental parameters.

After completing my PhD in 2000 I returned to CBDE-Porton (UK) to take up a 1-year postdoctoral position. The project was again concerned with ion trap mass spectrometry, investigating the break down of selected organophosphate molecules that were subject to collisions with rare gas atoms.

In September 2001 I moved to 'Universidad Complutense de Madrid', in the group of Prof. F. J. Aoiz, where I am currently contracted to the EU research network 'Reaction Dynamics'. Here I have been able to apply the laser spectroscopic experience that I gained during my PhD to the rather different problems that are encountered in photodissociation dynamics. I am delighted with the warm welcome that I have received from everyone in the group, without which it would have been difficult to adjust to life in a foreign university. The facilities here are very good, with a well equipped laboratory together with excellent literature searching facilities. In July of this year I will be visiting the group of Mark Brouard in Oxford University, where I hope to benefit from their knowledge with a view, in the near future, to building a new ion-imaging apparatus in Madrid. I believe this sharing of scientific knowledge is the essence of the network idea, which I know will be of great advantage to me as I embark on my chosen scientific career.

Oxford(Theory): Tomás González Lezana

I obtained my PhD in 1999 (June), being my supervisor Prof. Pablo Villarreal Herran at the Instituto de Matemáticas y Física Fundamental of the CSIC (Madrid). The subject of my scientific research was the study of photodissociation of van der Waals clusters X-Y₂ where X is a rare gas atom and X₂ is a halogen diatom. I also studied the energetics and geometrical structure of He₃ trimers and clusters formed by a Helium dimer and small atoms such as Li, Na, H. The interest of such complexes is the extremely small binding energies which characterised these clusters.

I started my postdoctoral position as a RTN-fellow in Dr. Manolopoulos' group at the PTCL (Oxford University) in July 2000. Since then I have been working on different aspects of Reaction Dynamics. The main goal of my research here is to develop a hybrid method between the ABC program conceived by D.E. Manolopoulos, J.F. Castillo and D. Skouteris and the APH method developed by J.M. Launay and collaborators. In its present form, the ABC program can not treat atom-diatom insertion reactions that proceed over deep potential energy wells with a large number of classically allowed surface eigenvalues in the small ρ region. One of the possible ways to avoid these difficulties involves a complementary use of the APH method for this small ρ region combined with the ABC program for larger values of ρ where it is more efficient compared with the APH treatment in terms of calculation time and number of basis functions to employ. We are now in a very good position to present interesting results on some of the reactions under study such as H+O₂.

I am also currently working on the development of the necessary technical tools to study the relevance of resonances in this kind of A+BC chemical reactions. This was for instance the purpose of my short stay in Prof. J. Aoiz and Prof. L. Bañares' group at the Facultad de Químicas of the Universidad Complutense de Madrid last year, where we studied the possible existence of resonances in the H+D₂ reaction.

I personally find the Research Training Network extremely interesting and rewarding for my future career prospects. Apart from giving me the opportunity of being in close contact with some of the most prestigious groups in the field, I have been involved in the development of new theoretical techniques to study atom-diatom reaction dynamics.

Stuttgart: Gabriella Capecchi

I graduated in Chemistry with an experimental Thesis in Biochemistry ("Ribonucleas T1 refolding intermediates characterisation via mass spectrometry methods"; Supervisors: Prof. Piero Pucci and Prof. Gennaro Marino, Naples University), and after I enlarged my background moving towards theoretical research thanks to a Ph.D. work ("Hyperspherical approach to proton transfer in simple and complex systems") with Prof. Vincenzo Aquilanti from the University of Perugia. Following the Ph.D. work, I was offered a post-Doc position by Prof. Hans Joachim Werner from Stuttgart University, within the European Network "Reaction dynamics".

The network project concerned a full quantum mechanical study of reactions involving open shell systems. The activity started with the ab initio calculations and the fitting of coupled potential energy surfaces for the Cl ($^2P_{3/2}$, $^2P_{1/2}$) + H₂ reaction, and then dynamical calculations were performed in collaboration with Prof. Millard Alexander (University of Maryland), in order to provide comparison with experiments (from Piero Casavecchia's group in Perugia and Kopin Liu's group in Taiwan).

This experience proved to be really stimulating and offered me the occasion of learning some of the most advanced ab initio and quantum dynamics techniques, giving me the opportunity of cooperating with other groups within the Network.

At present I'm teaching science and mathematics in a secondary school and I'm waiting for a collaboration contract with a theoretical chemistry group at the University of Torino.

I would suggest to any young researcher an experience in a European Network, not only to learn new techniques, but also to improve communication skills.

Muenchen: Fermín Huarte Larranaga

Before becoming a member of the Munich group I had done my PhD Thesis in the "*Universitat de Barcelona*", also in reaction dynamics but in a somewhat different field. In Barcelona we mainly did reactive scattering calculations on very simple (triatomic) systems while here in Munich I have had the opportunity to employ state-of-the-art methodology to very interesting systems.

I started my Post-Doc in Munich with Dr. U. Manthe in January 12th 2000 and became RTN fellow in July of the same year. Together with Dr. Manthe we have applied the flux-correlation function and MCTDH schemes to the study of polyatomic reactions, in particular H + CH₄ and O + CH₄.

Besides the actual scientific project I have been involved, during this period as a RTN fellow, one of the most valuable aspects I have learned to appreciate is the chance of being part of a Network of high-level laboratories. I have myself experienced how collaboration between laboratories of different countries can prove extremely fruitful. In this sense, I had the chance of visiting the Oxford Theoretical Laboratory on April last year and work together with Dr. D.E. Manolopoulos and, in the next future I expect to benefit also from collaboration with the Madrid group.

PART E - NETWORK FINANCING

The table below compares the projected costs for the Network taken from the proposal (and the tables following the signatures in the contract) with the actual (estimated) costs to the end of May 2002. All figures are in kEURO apart from the bottom row, which is given in %.

Team	A (Personnel):		B (Networking):		D (Overheads):		TOTAL / kECU		% spent
	Prop	Actual	Prop	Actual	Prop	Actual	Prop	Actual	
1 Perugia, IT	116	44	42	24.5	31.25	13.7	189.25	82.2	43.4
2 Oxford (Expt), GB	144	5.3	15	5.5	27	1.8	186	12.6	6.8
3 Nijmegen, NL	135.171	105.8	31.288	20.4	33.291	25.2	199.75	151.4	75.8
4 Bielefeld, DE	156	6.4	20	6	20	1.4	196	13.8	7.0
5 Madrid, ES	100	25.6	25	10.1	25	7.1	150	42.8	28.5
6 Oxford (Th), GB	144	68.2	15.2	5.5	27	12.5	186	86.2	46.3
7 Stuttgart, DE	156	70.1	15	5.3	25	11.0	196	86.4	44.1
8 Muenchen, DE	156	96	15	4	25	14.6	196	114.6	58.5
TOTAL / kEURO	1107.171	421.4	178.488	81.3	213.541	87.3	1499	590.0	39.4
% of total	73.86	71.42	11.89	13.78	14.25	14.80	100	100	

All of the actual expenditure falls within the limits of the appropriate cost headings, as can be seen from the table. Personnel costs, and consequently total expenditures are low for some partners who have only recently hired a YR (e.g., Oxford(Expt) and Bielefeld).

PART F - PROPOSED REVISION TO THE CONTRACT

No major revisions are proposed, beyond the request for some flexibility regarding scientific objectives and the possible extension in duration of six month, at zero cost, to ensure the fulfillment of the training deliverables, if difficulty should arise in employing more YRs in Oxford(Expt) and Bielefeld..

Annex A: Joint publications with abstracts where available

These appear in order of citation in section A.1, *not* in order of importance (YRs are indicated in bold).

1. N. Balucani, L. Cartechini, P. Casavecchia, G. G. Volpi, F. J. Aoiz, L. Bañares, M. Menéndez, W. Bian and H.-J. Werner

Dynamics of the Cl+D₂ reaction: a comparison of crossed molecular beam experiments with quasi-classical trajectory calculations on a new ab initio potential energy surface

Chem. Phys. Lett., **328**, 500-508 (2000).

Teams involved: PERUGIA - MADRID – STUTTGART

Abstract. The dynamics of the Cl + D₂ reaction has been studied experimentally at the collision energies 4.9 kcal/mol and 6.3 kcal/mol by the crossed molecular beam technique. The experimental results have been compared with theoretical predictions based on quasi-classical trajectory (QCT) calculations on the new BW potential energy surface (PES), and a good general agreement has been obtained. The QCT results obtained on the BW PES have been compared with those obtained on the previous semiempirical G3 PES, and striking differences regarding the effect of reagent rotation *j* on the reactivity have been found.

2. D. Skouteris, H.-J. Werner, F. J. Aoiz, L. Bañares, J. F. Castillo, M. Menéndez, N. Balucani, L. Cartechini, P. Casavecchia, G. G. Volpi

Experimental and theoretical differential cross sections for the reactions Cl+H₂/D₂

J. Chem. Phys. **114**, 10662-10672 (2001).

Teams involved: PERUGIA - MADRID – STUTTGART

Abstract. Experimental and theoretical differential cross sections for the reactions between Cl atoms and two isotopic variants of molecular hydrogen (H₂ and D₂) are presented. The experimental results have been obtained by using the crossed molecular beam method with mass spectrometric detection. The theoretical results have been computed using both the quasiclassical trajectory and quantum mechanical (QM) methods. The potential energy surface employed for the calculations is the ab initio BW2 surface by Bian and Werner [J. Chem. Phys. **112**, 220 (2000)]. The theoretical results have been directly compared to the experiments in the laboratory frame at a collision energy (*E_c*) of 4.25 and 5.85 kcal/mol for the Cl+H₂ reaction and of 4.9 and 6.3 kcal/mol for the Cl+D₂ reaction. The agreement between QM results and experiment is quite satisfactory for the Cl+D₂ reaction, especially for the low collision energy, while for Cl+H₂ is less good, especially when considering data at the lower *E_c*.

3. D. Skouteris, A. Lagana', G. Capecchi, H.-J. Werner

Wavepacket calculation for the Cl+H₂ reaction

Journal of Computational Methods in Sciences and Engineering (submitted 15 April 2002).

Teams involved: PERUGIA - STUTTGART

Abstract. Time-dependent quantum mechanical calculations have been carried out to estimate the convergence with the total angular momentum quantum number *J* of the reactive cross sections for the reaction Cl + H₂ using product Jacobi coordinates. The potential energy surface used for the calculations is that of Capecchi and Werner developed recently. The theoretical predictions are compared with experimental results and with results of previous theoretical studies.

4. G. Capecchi, D. Skouteris, H.-J. Werner, N. Balucani, P. Casavecchia

Theoretical simulations of molecular beam experiments for the Cl(²P_{3/2,1/2}) + H₂ reaction based on quantum reactive scattering calculations on coupled potential energy surfaces

J. Chem. Phys. or Chem. Phys. Lett. (in preparation)

Teams involved: STUTTGART - PERUGIA

Abstract unavailable.

5. N. Balucani, L. Cartechini, G. Capozza, E. Segoloni, P. Casavecchia, G. G. Volpi, F. J. Aoiz, L. Banares, P. Honvault, J.-M. Launay

Quantum effects in the differential cross sections for the insertion reaction $N(^2D)+H_2$

Phys. Rev. Letters (accepted 22 May 2002, in press).

Teams involved: PERUGIA - MADRID

Abstract. The quantum (QM) scattering theory has been difficult to apply to the family of insertion reactions and the approximate quasiclassical trajectory (QCT) method or statistical calculations were mostly applied. In this letter, we compare the experimental differential cross sections for the title insertion reaction with the results of QM and QCT calculations on an ab initio potential energy surface. The QM results reproduce well the crossed beam experiment while a small, but significant, difference in the QCT ones points to quantum effects, possibly the occurrence of tunneling through the combined potential and centrifugal barrier.

6. N. Balucani, L. Cartechini, G. Capozza, P. Casavecchia, G. G. Volpi, F. J. Aoiz, L. Bañares, P. Honvault, J.-M. Launay

Experimental differential cross sections for the reaction $C(^1D)+H_2$ versus accurate quantum and quasiclassical trajectory scattering calculations on an ab initio potential energy surface

J. Chem. Phys. (in preparation).

Teams involved: PERUGIA - MADRID

Abstract unavailable.

7. N. Balucani, L. Cartechini, G. Capozza, E. Segoloni, P. Casavecchia, G. G. Volpi, F. J. Aoiz, L. Bañares, P. Honvault, J.-M. Launay

Experimental differential cross sections for the reaction $O(^1D)+H_2$ versus accurate quantum and quasiclassical trajectory scattering calculations on an ab initio potential energy surface

J. Chem. Phys. (in preparation).

Teams involved: PERUGIA - MADRID

Abstract unavailable.

8. N. Balucani, P. Casavecchia, F. J. Aoiz, L. Bañares, J. F. Castillo, M. Brouard, W. Denzer, C. Vallance
Differential cross sections and rotational distributions for the reaction $O(^1D)+D_2$ compared to quasiclassical trajectory scattering calculations on an ab initio potential energy surface

Phys. Chem. Chem. Phys. (in preparation)

Teams involved: PERUGIA - MADRID - OXFORD(expt)

Abstract unavailable.

9. F. J. Aoiz, L. Bañares, J. F. Castillo, M. Brouard, W. Denzer, C. Vallance, P. Honvault, J.-M. Launay, A. J. Dobbyn and P. J. Knowles

Insertion and Abstraction Pathways in the Reaction $O(^1D)+H_2 \rightarrow OH+H$

Phys. Rev. Lett., **86**, 1729-1732 (2001).

Teams involved: MADRID – OXFORD (Expt)

Abstract. Rigorous quantum dynamical calculations have been performed on the ground $1^1A'$ and first excited $1^1A''$ electronic states of the title reaction, employing the most accurate potential energy surfaces available. Product rovibrational quantum state populations and rotational angular momentum alignment parameters are reported, and are compared with new experimental and quasiclassical trajectory calculated results. The quantum calculations agree quantitatively with experiment, and reveal unequivocally that the $1^1A''$ excited state participates in the reaction.

10. P. Honvault, J.-M. Launay, M. Brouard, W. Denzer, C. Vallance, F. J. Aoiz, L. Bañares, J. F. Castillo
The role of the A'' excited state in the $O(^1D)+H_2$ reaction: experiment versus theory

J. Chem. Phys. (in preparation)

Teams involved: MADRID – OXFORD (Expt)

Abstract unavailable.

12. F. J. Aoiz, L. Bañares, M. Brouard, J. F. Castillo and V. J. Herrero
The dynamics of the $O(^1D)+HD$ reaction: a quasiclassical trajectory multisurface study
J. Chem. Phys. **113**, 5339-5353 (2000).

Teams involved: MADRID – OXFORD (Expt)

Abstract. Integral and differential cross sections for the $O(^1D)+HD$ reaction have been obtained from adiabatic and nonadiabatic quasiclassical trajectory calculations performed on new *ab initio* versions of the $1A'$, $1A''$ and $2A'$ potential energy surfaces at the collision energies of 0.089 and 0.196 eV (2.05 and 4.53 kcal/mol, respectively). Results are reported for both the OH+D and OD+H exit channels of the reaction. The new data are compared with those from previous theoretical studies employing other potential energy surfaces, and are also used to simulate experimental differential cross sections obtained from recent molecular beam measurements, which are partially resolved in the internal states of the products. The comparison provides evidence that excited electronic states do participate in the title reaction at 0.196 eV, but that their contribution, particularly that of the A'' state, is overestimated by the quasiclassical trajectory (QCT) calculations employing the latest, and most accurate, potential energy surfaces.

12. M. Bass, M. Brouard, A.P. Clark, B. Martinez-Haya and C Vallance
Angular momentum alignment in the 308nm photolysis of Cl_2 using Fourier moment velocity-map imaging

J. Chem. Phys. or **Chem. Phys. Lett.** (in preparation).

Teams involved: OXFORD(Expt) – MADRID

Abstract unavailable.

13. M. Paniagua, H.-J. Werner, A. Aguado, F. J. Aoiz, V. Saez-Rabanos, E. Verdasco, J. F. Castillo
New ab initio potential energy surface for the $Li+HF$ reaction

J. Chem. Phys. (in preparation).

Teams involved: MADRID – STUTTGART

Abstract unavailable.

14. F. J. Aoiz, L. Bañares, M. Brouard, J. Castillo, D. Minayev, P. O'Keeffe, C. Vallance
The dynamics of the $H + D_2O$ abstraction reaction at 2.5eV

J. Chem. Phys. (in preparation).

Teams involved: MADRID – OXFORD(Expt)

Abstract unavailable.

16. P. Quintana, R. F. Delmdahl, D. H. Parker, B. Martínez-Haya, F. J. Aoiz, L. Bañares and E. Verdasco
Velocity map imaging and REMPI study of the photodissociation of CH_3SCH_3 from the first absorption band

Chem. Phys. Lett., **325**, 146-152 (2000).

Teams involved: MADRID – NIJMEGEN

Abstract. The photodissociation of dimethyl sulfide (CH_3SCH_3) at 229 nm has been studied employing a combination of velocity map imaging and time-of-flight resonance-enhanced multiphoton ionization techniques to detect the CH_3 product. Translational energy and recoil angle distributions as well as rotational state populations have been determined for the CH_3 photofragments formed in the ground vibrational state. The electronic excitation of CH_3SCH_3 to the first absorption band is found to produce

fast $\text{CH}_3\text{S} + \text{CH}_3(v=0)$ recoiling products with a negative spatial anisotropy parameter of $\beta = -0.85 \pm 0.05$. The $\text{CH}_3(v=0)$ products are rotationally cold, the rotational distribution peaking at $N''=3-4$.

16. F. J. Aoiz, L. Bañares, J. F. Castillo, M. Menéndez, D. Skouteris, H.-J. Werner
A quantum mechanical and quasi-classical trajectory study of the $\text{Cl} + \text{H}_2$ reaction and its isotopic variants. Dependence of the integral cross section on the collision energy and reagent rotation
J. Chem. Phys. **115**, 2074-2081 (2001).

Teams involved: MADRID – STUTTGART

Abstract. Quantum mechanical (QM) and quasiclassical trajectory (QCT) calculations have been performed for the $\text{Cl} + \text{H}_2$, $\text{Cl} + \text{D}_2$, $\text{Cl} + \text{HD} \rightarrow \text{HCl}(\text{DCl}) + \text{D}(\text{H})$ reactions in order to determine integral cross sections as a function of collision energy and for different reagent rotational quantum numbers using the recent *ab initio* BW2 potential energy surface (PES) by Bian and Werner [J. Chem. Phys. **112**, 220 (2000)]. The results are compared with experimental data obtained by using the Doppler-selected time-of-flight technique. It has been found theoretically by both the QM and QCT methods that reagent rotation enhances reactivity in agreement with experiment. The QM results are found to be in quantitative agreement with the experimental excitation functions for the $\text{Cl} + p\text{-H}_2$ and $\text{Cl} + n\text{-H}_2$ reactions, whereas those obtained quasiclassically fail to reproduce the experimental data. These results are in strong contrast with those reported on the previous G3 PES, in which QM and QCT calculations predicted that reactivity decreases with reagent rotation. The intermolecular isotope effect, i.e., the ratio between the cross sections of the $\text{Cl} + n\text{-H}_2$ and $\text{Cl} + n\text{-D}_2$ reactions, $\Gamma_{\text{inter}}(\text{Cl} + n\text{-H}_2 / \text{Cl} + n\text{-D}_2)$, predicted by QM calculations on the BW2 surface is notably larger than that obtained experimentally.

17. G. Capecchi, U. Manthe, J.-H. Werner
Quantum calculations of rate constants for the $\text{Cl} + \text{H}_2$ reaction
J. Chem. Phys. or Chem. Phys. Lett. (in preparation)

Teams involved: STUTTGART - MUENCHEN

Abstract unavailable.

18. M. H. Alexander, D. E. Manolopoulos, and H. -J. Werner
*An investigation of the $\text{F} + \text{H}_2$ reaction based on a full *ab initio* description of the open-shell character of the $\text{F}(^2\text{P})$ atom*
J. Chem. Phys. **113**, 11084-11100 (2000).

Teams involved: OXFORD (Theory) - STUTTGART

Abstract. Expanding on an earlier Communication [M.H. Alexander, H.-J. werner, and D.E. Manolopoulos, J. Chem. Phys. **109**, 5710 (1988), we present here the full framework for the quantum treatment of reactions of the fluorine atom with molecular hydrogen. This involves four potential energy surfaces (PESs) and two, coordinate-dependent spin-orbit interaction terms, all of which were fitted to the results of *ab initio* calculations. Quantum scattering calculations, based on a time-independent method formulated in hyperspherical coordinates, were carried out to determine initial and final state-resolved reactive cross sections, for reactions of F in its ground ($^2\text{P}_{3/2}$) and excited ($^2\text{P}_{1/2}$) spin-orbit state with H_2 in $j=0$ and $j=2$ ($p\text{-H}_2$) and $j=1$ ($o\text{-H}_2$). The overall reactivity of the excited state of F, which can occur only through nonadiabatic transitions, is found to be small, at most 25% of the reactivity of the ground spin-orbit state, which is adiabatically allowed. In addition, when compared with results of earlier calculations, based on a single, electronically adiabatic, PES, our calculations show that even fine details of the dynamics of the $\text{F} + \text{H}_2$ reaction will be well described by calculations on a single PES. The contribution of the excited spin-orbit state can be seen most clearly in the formation of HF products in the $v=3$ vibrational manifold, which are nearly thermoneutral (or even slightly endoergic) in the reaction of ground-state F atoms. The cross sections for the near resonant electronic-rotational process [$\text{F}^* + \text{H}_2(j=0) \rightarrow \text{F} + \text{H}_2(j=2)$] is found to be large, in confirmation of earlier work.

19. E.J. Rackham, F. Huarte-Larranaga, D.E. Manolopoulos
Coupled-channel statistical theory of the $\text{N}(^2\text{D}) + \text{H}_2$ and $\text{O}(^1\text{D}) + \text{H}_2$ insertion reactions
Chem. Phys. Lett. **343**, 356 (2001).

Teams involved: OXFORD(theory) – MUENCHEN

Abstract. A detailed statistical theory of atom-diatom insertion reactions is derived by combining the early statistical ideas of Pechukas and Light with the couple-channel capture theory of Clary and Henshaw. The theory is applied to the $N(^2D)+H_2$ and $O(^1D)+H_2$ reactions and found to give results in good agreement with the exact quantum mechanical integral cross sections reported recently by Honvault and Launay.

Annex A: Invitations 1 (List of Invited Talks and Oral Contributions)**PERUGIA*****Invited talks:***

- P. Casavecchia
Recent progress on crossed-molecular-beam studies of atom and radical reaction dynamics, *Gordon Conference on Atomic and Molecular Interactions*, 2-7 July 2000, New London, N.H., USA
- P. Casavecchia
Recent progress in crossed beam studies of reaction dynamics, *Gordon Research Conference on Molecular Energy Transfer*, 14-19 January 2001, Ventura, CA, USA
- P. Casavecchia, N. Balucani, L. Cartechini, G. Capozza, A. Bergeat, G.G. Volpi
Crossed beam studies of elementary reactions of N and C atoms and CN radicals of importance in combustion, *Faraday Discussion 119 "Combustion chemistry: Elementary reactions to macroscopic processes"*, 9-11 July 2001, Leeds, UK

Selected oral contributions:

- M. Alagia, N. Balucani, L. Cartechini, P. Casavecchia, G. G. Volpi
A crossed beam dynamical study of the reactions $N(^2D)+D_2$ and $N(^2D)+H_2O$, *16th International Symposium on Gas Kinetics*, Cambridge, UK, 23-27 July 2000
- N. Balucani, L. Cartechini, M. Alagia, P. Casavecchia, G. G. Volpi
A crossed beam dynamical study of the reactions $N(^2D)+D_2$ and $N(^2D)+H_2O$, *13th European Conference on Dynamics of Molecular Collisions*, Jerusalem, Israel, 17-22 September 2000
- N. Balucani, L. Cartechini, P. Casavecchia, G. G. Volpi, F. J. Aoiz, L. Banares, J. F. Castillo, M. Menendez, D. Skouteris, W. Bian, H.-J. Werner
Dynamics of the $Cl+H_2/D_2$ reaction: A comparison of crossed molecular beam experiments with quasiclassical trajectory and quantum dynamical calculations on a new ab initio potential energy surface, *Stereodynamics 2000 - Stereodynamics of chemical reactions*, El Escorial, Spain, 1-5 December 2000

OXFORD (Expt)***Invited talks:***

- M. Brouard
Dynamical studies of elementary photon-initiated processes, *IBER 2002*, Lisbon, Portugal, March 2002.
- M. Brouard
Stereodynamical studies of hot atom reactions, *XIX International Symposium on Molecular Beams*, Rome, Italy, June 2001.
- M. Brouard
Elucidating the mechanism of elementary bimolecular reactions using polarized light, *16th International Symposium on Gas Kinetics*, Cambridge, UK, July 2000.
- M. Brouard
Orientation and alignment in the products of elementary photon-induced processes, *Stereodynamics 2000 - Stereodynamics of chemical reactions*, El Escorial, Spain, 1-5 December 2000

NIJMEGEN***Invited talks:***

- J.J. ter Meulen
Collisions of oriented OH radicals, *26st International Symposium on Free Radicals*, Assisi, Italy, 3-7 September 2001
- D. Parker
Imaging methods in Reactive Scattering Studies, *International Workshop on Reaction Dynamics*, Oxford, UK, 30 March 2001
- D. Parker

Velocity Map Imaging, *European Conference on Atomic and Molecular Physics (ECAMP)*, Berlin, Germany, April 2001

- D. Parker
Velocity Map Imaging, *ISL/OSA meeting, Long Beach, CA, USA, October 2001*

Selected oral contributions:

- D. Parker
Photodissociation of the OH radical, *26st International Symposium on Free Radicals*, Assisi, Italy, 3-7 September 2001

BIELEFELD

- O. Höbel, M. Menendez, H.J. Loesch
New experimental results on the benchmark reaction $\text{Li}+\text{HF} \rightarrow \text{LiF}+\text{H}$, *13th European Conference on Dynamics of Molecular Collisions*, Jerusalem, Israel, 17-22 September 2000
- O. Höbel, M. Menendez, H.J. Loesch
New experimental results on alignment and energy effects in the benchmark reaction $\text{Li}+\text{HF} \rightarrow \text{LiF}+\text{H}$, *Stereodynamics 2000 - Stereodynamics of chemical reactions*, El Escorial, Spain, 1-5 December 2000

OXFORD (Theory)

Invited talks:

- D. E. Manolopoulos
Some recent developments in chemical reaction dynamics, *Gordon Research Conference on Molecular Energy Transfer*, 14-19 January 2001, Ventura, CA, USA
- D. E. Manolopoulos
Some recent developments in chemical reaction dynamics, *18th Conference on the Dynamics of Molecular Collisions*, Copper Mountain, Colorado, USA, July 2001
- D. E. Manolopoulos
Some recent developments in chemical reaction dynamics, *Frontiers of Theoretical Chemistry: Theory and Applications*, Okazaki, Japan, December 2001
- D. E. Manolopoulos
Some resonances in bimolecular reactions, *ACS (American Chemical Society) National Meeting: Symposium on Chemical Dynamics*, Orlando, Florida, April 2002

STUTTGART

Invited talks:

- H.-J. Werner
Quantum Mechanical Study of the $\text{H}_2 + \text{Cl}(^2\text{P}_{1/2}, ^2\text{P}_{3/2})$ Reaction on new Coupled Potential energy Surfaces, *221st National Meeting of the ACS (American Chemical Society), Symposium on the "Accurate Description of Low-Lying Molecular States and Potential Energy Surfaces"*, San Diego, USA, 1-5 April 2001
- H.-J. Werner
Theoretical studies of chemical Reactions on Coupled Potential Energy Surfaces, *XVIIIth Conference on the Dynamics of Molecular Collisions*, Copper Mountain, Colorado, USA, 15-20 July 2001
- H.-J. Werner
Theoretical treatment of chemical Reactions on Coupled Potential Energy Surfaces, *37th Symposium on Theoretical Chemistry*, Bad Herrenalb, Germany, Sept. 23-27, 2001

MUENCHEN

Invited talks:

- U. Manthe
Quantum dynamics of non-adiabatic processes: System-bath separation and mixed quantum-classical dynamics, *CECAM workshop: Methods for computer simulation of non-adiabatic charge transfer processes in condensed phase*, Lyon, France 22-24 April 2002
- U. Manthe
Quantum dynamics of polyatomic systems: quantum-classical and system-bath approaches, *International Seminar on Quantum Dynamical Concepts: From Diatomics to Biomolecules*, Dresden, Germany, 2-5 April 2002
- U. Manthe
Quantum Molecular Dynamics with Wave Packets, *Quantum Simulations of Complex Many-Body Systems: From Theory to Algorithms*, Kerkrade, Germany, 25.2.-1.3.2002

- U. Manthe
A multi-configuration Hartree approach to reaction dynamics, *4th European workshop on time-dependent methods in gas-surface Dynamics*, Freising, Germany, 24.-27.6.2001
- U. Manthe
Accurate quantum calculations of reactions rates: beyond four atom systems, *Time-dependent Quantum Dynamics*, Bristol, UK, 9.4.-12.4.2001
- U. Manthe
Thermal rate constants of polyatomic reactions, *Chemical Dynamics*, Berkeley, CA, USA, 28.3.-31.3.2001
- U. Manthe
Thermal rate constants of organic reactions, *Workshop on Quantum Reaction Dynamics*, Pasadena, CA, USA, 10.1.-13.1.2001
- U. Manthe
Quantum effects on reaction rates, *36th Symposium for Theoretical Chemistry*, Litschau (A), 10.9.-14.9.2000
- U. Manthe
Dissipative dynamics in vibronically coupled systems, *TSRC Workshop: Theory of nonadiabatic processes*, Telluride (CO, USA), 30.7.-5.8.2000
- U. Manthe
Quantum dynamics of reaction processes: reaction rates, *Xth International Congress of Quantum Chemistry*, Menton (FR), 5.6.-10.6.2000

Annex A: Invitations 2 (List of Invited Talks at Future Meetings)

- D. E. Manolopoulos (Oxford)
11th International Congress of Quantum Chemistry
July 2003, Bonn, Germany.
- M. Brouard (Oxford)
XIV European Conference on Molecular Collisions (MOLEC XIV)
Istanbul, Turkey, September 2002
- F. J. Aoiz (Madrid)
Gordon Conference on Atomic and Molecular Interactions
New London, New Hampshire, USA, July 2002
- U. Manthe (Muenchen)
12th European Seminar on Computational Methods
Zeist (NL), 18.-22.9.2002
- U. Manthe (Muenchen)
Welch Conference: Advances in Quantum Chemistry
Houston (USA), 28.-29.10.2002
- U. Manthe (Muenchen)
Multidimensional Quantum Reaction Dynamics
Berlin (Germany), 16.-17.7.2003

Annex B: Names of participants

The official names of the participants have not been used in the text of this report, for the sake of clarity. These are given below:

Official name	Name used in report
UPER.DC	<i>Perugia</i>
UOXF.PTCL	<i>Oxford(Expt)</i>
KUN.AP	<i>Nijmegen</i>
UBIE.EAP	<i>Bielefeld</i>
UCMAD.FQ.DQF	<i>Madrid</i>
UOXF.PTCL	<i>Oxford(Theory)</i>
USTUTT.ITC	<i>Stuttgart</i>
TUMUC.LTC	<i>Muenchen</i>