



## Preface

There is no chemistry without collisions. Molecular collisions are the starting point of all chemical reactions: they cause molecular and geometrical rearrangements, induce energy transfer to specific quantum states or simply cause a molecule to fall apart. In everyday life these processes are “non-directional”. Specific orientations do not play a role as all orientations are present within an ensemble. Nevertheless, one expects that nature will have directional preferences. An OH radical, for example, will behave differently when sticking out its head (H-atom) or its bottom (O-atom) in a collision. It is because of the remarkable advances in experimental and theoretical approaches in the last years that such directional processes can now be studied up to the level of individual quantum states. Careful initial molecular state preparation, using sophisticated molecular beam techniques, allows experiments with quantum-number controlled molecules, and high-resolution and sensitive spectroscopic probes make it possible to study reaction products state specifically.

This special issue on ‘Stereodynamics of Chemical Reactions’ deals with the state-of-the-art in the field. It contains a collection of papers submitted in association with the most recent Stereodynamics meeting held in December 2002 in The Netherlands. This meeting is an international bi-annual event that started in 1986, when Prof. R.D. Levine initiated the series in Jerusalem. As in previous occasions [Jerusalem 1986, Bad Honnef 1988, Santa Cruz 1990, Assisi 1992, Gif-sur-Yvette 1994, Bielefeld 1996, Leeds 1999 and Madrid 2000] the main goal was to bring together physicists and chemists working with beams, photons and Hamiltonians to get in ‘touch’ with the vectorial nature of bond making and breaking in molecules and at surfaces in collisional and photo-induced processes. The sequence of the 16 papers that are presented in this special issue is arranged according to subjects that form a focus within the field.

*New tools*, both experimentally and theoretically, are steadily developed to improve and to analyze state preparation, alignment and orientation. Wodtke and coworkers show in their contribution that hexapole focusing can be combined with stimulated emission and Frank–Condon optical pumping techniques. This new method allows the control of rovibronic and orientational properties of molecules and is demonstrated here

on the example of vibrationally excited species. Much effort has been put in the generation and study of *new molecular systems*. A new class of molecules of the form HRgX, for example HXeCl, is generated in photodissociation experiments reported by Buck and coworkers of hydrogen halide molecules on rare gas clusters. They discuss the possibility to produce and successively orient these molecules applying both strong laser and weak electric fields. The structural properties of special transition metal–benzene complexes involving Ti, V, Co and Ni are discussed in a contribution by Kasai et al. who employ electric hexapole and laser vaporization techniques to select and to determine permanent dipole moments. Detailed calculations for *depolarization effects* typically on the time scale of an experiment are discussed by Rutkowski and Zacharias for interactions of the angular momentum vector with the nuclear spin of the molecules and it is concluded that strong dependencies exist particularly for low values of the angular momentum.

Several contributions focus onto the stereodynamic features of *photodissociation* and *unimolecular reactions*. Suits et al. present results on the orbital polarization of S(<sup>1</sup>D<sub>2</sub>) fragments resulting from the photo-dissociation of ethylene sulfide with the novel technique of DC slice imaging, deriving the full absolute speed- and angle-dependent angular momentum as well as alignment-free population distributions. Slice imaging is also used by Kitsopoulos and coworkers in an improved REMPI scheme to study the complete angular distribution of the H-atom photofragments from the photo-dissociation of HBr. From the images they derive branching ratios for Br(<sup>2</sup>P<sub>1/2</sub>): Br(<sup>2</sup>P<sub>3/2</sub>). In a joint experimental and theoretical study the recoil velocity dependent spin–orbit state distribution of Cl<sup>−</sup> fragments as produced in the photodissociation of CsCl<sub>2</sub> has been studied by Gericke, Vasyutinskii et al. In this study the molecular states that are involved in the photo-dissociation process are presented which allows a qualitative explanation of the observed non-statistical population of the spin–orbit states of the Cl fragments.

*Excited state dynamics* of tetrakis(dimethyl-amino)ethylene solvated by Ar atoms has been studied with ultrafast femto second pump–probe laser pulse techniques. Soep and coworkers find that compared to



Fig. 1. An artist's impression of the stereodynamic process addressing the rotationally inelastic scattering of a NO molecule. The construction of the two balls, symbolizing the NO molecule, will rotate, when it is hit by the third ball. In this virtual billiard game, the player can aim at the red or the white ball. However, the resulting amount of rotation of the 'molecule' will not depend on which ball was hit. In the scattering experiments, the discrimination between N-end and O-end collisions was obtained by the orientation of the NO molecule before the collision. Although a NO molecule looks rather similar to two bonded billiard balls, surprisingly large differences between rotational excitation by collisions at the N-end and at the O-end have been observed. More details are available from this special issue.

the free molecule the influence of the Ar-environment causes a slow down of the wavepacket movement – different from a standard cage effect – and an increase of the time scale of the energy transfer.

Progress in understanding the *stereodynamic dependence of bimolecular reactions* is presented by two papers in this special issue. The rotational state distributions of nascent HCl products of the reactions of ground spin-orbit state Cl atoms and CH<sub>4</sub> and CH<sub>3</sub>X (X = F, Cl, Br and I) molecules are reported by Orr-Ewing and coworkers and compared to the outcome of ab initio calculations. Aldegunde, Aquilanti et al. present a theoretical study of the quantum stereodynamics of the F + H<sub>2</sub> → HF + H reaction, using an alternative representation of the stereo-directed S-matrix. They identify clear stereodynamical effects in which the F-atom favours to attack the hydrogen molecule at the transition state (bent) geometry, while for the exit channel the H-atom departs in a collinear geometry from the H-end side of HF.

One molecule that is often used to study *stereodynamic dependence of rotational energy transfer* is the open shell species NO. In a detailed study Wade, Chandler, Cline and coworkers present ion imaging

studies of product rotational alignment in inelastic collisions of NO with Ar. The theoretical and alignment corrected differential cross sections show excellent agreement as do the theoretical and experimental alignment moments for low  $\Delta j$ . For high  $\Delta j$  values, sampling the hard wall of the potential energy surface, this agreement is much less. In two subsequent experiments in which counter-propagating pulsed beams of NO and He (Ne) meet each other at the collision center, Kim and Meyer present a REMPI time-of-flight analysis in which alignment and quantum interference effects are discussed in detail. They show that the alignment of the scattered NO is consistent with that predicted by the apse models. The sign of the steric asymmetry in rotational inelastic state resolved atom–molecule collisions is questioned by Stolte and coworkers on the example of NO–Ar scattering in their contribution. From a careful analysis of the quantum mechanical derivation of this effect it is concluded that the sign of the theoretically predicted value is actually opposite to the experimental one (see Fig. 1).

Finally, progress of stereodynamics in *surface scattering* is reported in the two last papers of this special issue. A beam of oriented NO molecules has been scattered from a Ru(0001)-(1×1)H surface. Kleyn and coworkers find both a strong orientation and lateral dependence: in the chemisorbing region of the unit cell the N-end is strongly bonding, while the O-end is essentially repulsive. The dissociative adsorption of hyperthermal O<sub>2</sub> molecules on Cu(100) is reported by Kasai et al. using synchrotron delivered X-ray photoemission spectroscopy. Whereas the dissociative adsorption at 0.6 eV is expected to occur mainly along a side-on collision geometry, for higher values the observed take up curve suggests that the dissociative adsorption might be dominated by a head on collision geometry.

Coming to the end of this preface, we wish to express our gratitude to all authors who participated in this stimulating project. They have shown what is possible nowadays in the field of stereodynamics and we think that the present issue reflects the way to follow for the future. Finally, we thank Professor Trommsdorff (Grenoble) for providing us with the platform for this Special Issue.

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