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Stereodynamics of Chemical Reactions

Foreword

The chemical change of matter on the microscopic level is governed by close encounters of the molecular reagents, intermediates, products, and solvents. A detailed knowledge about these elementary events is the prerequisite for a thorough understanding of the macroscopic processes and for their simulation, manipulation, and optimization. The supply of experimental data, the conception of models for their theoretical description, and the assessment of the accuracy and sophistication of these models by comparison with observations are among the central goals of chemical reaction dynamics. New experimental methods, improved theoretical schemes, and the continued increase in computer capacity and speed provide more detailed and precise information. The resulting deeper understanding of the molecular encounters will lead to refined computer simulations of macroscopic processes such as combustion, formation of pollutants in engines and heat generators, reactions in the earth's and planetary atmospheres, heterogeneous catalysis, and even reactions in liquids.

One important aspect of molecular encounters, be they reactive or nonreactive, is energetics. Extensive efforts have been made to investigate the influence of the reagents' temperature and, separately, the influence of their translational, rotational, and vibrational energy both on the reaction probability and on the partitioning of the available energy among the various degrees of freedom of the products. In addition to these scalar quantities, molecular collisions are also characterized by vectors; scalar and vector properties provide complementary information on the chemical forces and the dynamics of the interacting particles, and knowledge about both is required to draw a complete picture of the collision. For example, the change in direction of the relative velocity vectors that occurs when the system proceeds from reagents to products interrogates roughly the force exerted on the particles during collision. Therefore, the observable product flux measured as a function of the deflection angle (the angular distribution) is an extremely sensitive probe of the interaction potential. The unit vectors of the reagent molecule's principle axes, which define its orientation relative to the laboratory frame, play a central role. Depending on the prepared orientation, the flux of approaching atoms (molecules) interacts with different areas of the molecular surface and explores the anisotropy of the potential. Various orientation-dependent phenomena (steric effects) may be observed, such as the head vs tail asymmetry of the reaction probability, the branching ratios for various types of products, the energy partitioning among the products' degrees of freedom, or the direction of average product flux. Another vector in the entrance channel is the angular momentum of the reagent molecules. Its magnitude and direction with respect to space- and body-fixed coordinate frames control the directional distribution of the molecular axes. The preparation of specific rotational states thus opens another access to steric effects and anisotropic potential properties. The vectors characterizing the outcome of the collision are the angular momenta of the product molecules and the final relative velocity. Modulus and direction of the former may be dictated by the mass ratio of products as in the case of heavy + heavy−light → heavy−heavy + light reactions, where the angular momentum of the heavy−heavy product is essentially equal to the orbital angular momentum of the reagents. Less extreme mass ratios reduce the predominance of the kinematics, and information about the torques that generate the angular momentum during the interaction can be gained. Further information on the forces and dynamics is contained in the dependence of the product flux on various sets of initial and final vectors (vector correlations). In atom + molecule → molecule′ + atom′ reactions, these range from the correlation of the molecular reagent's and product's angular momenta to the full four-vector correlation involving initial and final relative velocity and angular momenta of reagent and product molecules. Exploration of the role of vector quantities and vector correlations in collision processes lies at the heart of stereodynamics.

For an asymmetric top, the most general type of reagent molecule, full control of molecular orientation requires the preparation of fixed directions for all three axes. However, the orientation of only one axis already furnishes valuable steric information. For linear and symmetric top molecules the orientation of the symmetry axis is sufficient. Experimentally, orientation of polar molecules in a beam can be created by selecting and focusing specific rotational states of symmetric tops or symmetric top like molecules in an electrostatic hexapole field. The importance of this technique, although in use since the beginning of stereodynamics in the 1960s, is still growing;

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in addition to crossed molecular beam scattering, it now finds applications in surface scattering, electron scattering, cluster investigations, and photodissociation experiments. A few years ago, the brute force technique was introduced that utilizes moderately strong homogeneous electric fields. The molecules entering this field experience an external torque that leads to librations of the dipole around the field direction (pendular states) or, at least, enhancement of the tendency of the dipole to point along it. Brute force orientation and pendular states have first been used in reactive scattering but are now applied also in spectroscopic and photodissociation studies. A more recent technique is based on the observation that the angular momenta of molecules in a supersonic beam expansion are polarized. The resulting anisotropic directional distribution of the molecular axis features an inversion center, and consequently, the molecules are aligned rather than oriented. Although the first applications have been devoted to the determination of anisotropic interaction potentials of nonreactive systems, an extension to reactive scattering appears feasible. The preparation of the initial angular momentum has been achieved by using the conventional hexapole field technique, and more recently by various laser methods. The latter are of more general importance because radiation-induced methods are not restricted to beams; applications for reactions in the bulk have already been reported. A disadvantage of the laser methods is that the prepared axis distributions reflect alignment rather than orientation and thus do not access head/tail information. However, recent theoretical investigations indicate that this drawback can be overcome by exploiting coherence effects. Laser methods such as laser-induced fluorescence (LIF) or resonance-enhanced multiphoton ionization (REMPI) are available to interrogate the product states and their polarization; electric deflection fields used in the past are now of minor importance.

This issue of *The Journal of Physical Chemistry A* celebrates advances in the study of stereodynamics that have taken place during the past two years. While many articles represent work that was presented at the Conference on the Stereodynamics of Chemical Reactions held December 1996 in Bielefeld, Germany, authors who were not able to attend the conference have also been asked to contribute. The biannual conferences on stereodynamics which were initiated by Raphael D. Levine and first held in Jerusalem (1986) are devoted to theoretical and experimental investigations of vector properties in molecular collisions that go beyond the more traditionally studied initial−final relative velocity correlation (differential cross section). After the meeting in Jerusalem, conferences were organized in Bad Honnef (1988), Santa Cruz (1990), Assisi (1992), Paris (1994), and eventually in Bielefeld (1996). The latter conference was held at Bielefeld's Center for Interdisciplinary Research (ZiF) together with the opening symposium of the advanced research project titled Interactions of Oriented Molecules. The project will operate until September 1997, allowing about 50 scientists of the community to collaborate on stereodynamical subjects for shorter or more extended periods of time.

The main topics discussed in the conference included steric effects and vector correlations in bimolecular collisions using oriented (Brooks, Kasai, ter Meulen, Möller) and aligned and/or state-selected (Aquilanti, Gericke, Rakitzis, Simons) reagent molecules; vector properties of photodissociation processes (Andresen, Baugh, Dixon, R. E. Miller, Vigué); new techniques for creation and in situ measurement of orientation and alignment (Böwering, Stolte, Vrakking); collision processes with orbitally aligned atoms (Andersen, Campbell, Grosser); and steric aspects of molecule−surface processes, both reactive and nonreactive (Heinzmann, Kleyn, Zacharias). A special section was devoted to molecules in strong laser fields where coherent control of orientation (Shapiro, Vrakking), spectroscopy in high fields (Felker, Friedrich, Girard), and manipulations such as trapping and steering of molecules (Herschbach, Seideman) have been discussed. Other subjects included stereodynamics of clusters (González Ureña), anisotropy of intermolecular interactions (Aquilanti, Vasyutinskii) and mechanisms for reactions (Grice, Soep), and intramolecular energy transfer (Wittig). The extensive experimental activity is accompanied by corresponding theoretical work. Vector correlations and orientation-dependent effects (Aoiz, van der Avoird), the effect of conical intersections and geometric phases to resonances in reactive scattering (Baer), and the full multiple spawning method for treating the stereodynamics of a reaction that is governed by two or more potential energy surfaces (Levine) have been discussed. Further topics include the theory of chemical reaction rates (W. H. Miller) and of time-dependent X-ray diffraction probing the fragments of an optically initiated reaction (Ben-Nun).

The organizer thanks all 39 speakers and authors of the 40 posters for their interesting and pioneering papers representing the state of the art of the field and all participants for their contributions to the lively discussions during the talks and the poster sessions. He also thanks the staff of the ZiF, particularly the conference secretary, Mrs. B. Valentin, for the competent assistance before and during the conference. Financial support by the Deutsche Forschungsgemeinschaft, the ministry of science and research of the federal state Nordrhein-Westfalen, the Westfälisch-Lippische Universitätsgesellschaft, and industry (Janz Computer, Digital Equipment, Merck, Jandel, Pfeiffer) are gratefully acknowledged.

Hansjürgen Loesch