ABSTRACT. This introductory paper presents a brief version of those areas of molecular reaction dynamics relevant to the subject of the Workshop. These include the following: influence of reagent's electronic, vibrational and rotational states upon reactivity; spin-orbit effects in elementary reactions, and dynamical aspects of stereochemistry, with special emphasis on orientation and alignment effects in chemical reactions.

Selectivity with respect to reagents leads to specificity with respect to products, exemplified by non-statistical branching ratios, anisotropy of angular distribution and "surprising" product state distributions. The importance of vector correlations (from crossed beam experiments with polarized laser-induced fluorescence detection) is touched upon, as well as the subject of polarized laser photofragmentation dynamics (half-collisions) leading to (non-statistical) specificity in product polarizations.

An important subject of this paper is that of reagent preparation and stereoselectivity. Experimental techniques for production of oriented (and of aligned) molecules and their theoretical description are outlined. Reactive asymmetry experiments using oriented molecule beams are briefly reviewed, and new approaches described. Results are presented of recent experiments which take advantage of the inherent mutual orientation of the molecules in a van der Waals complex, i.e., "precursor geometry-limited" bimolecular reactions. Finally, a new technique is described for real time, picosecond, clocking of the collision complex in such bimolecular reactions. Results are reported for the time-dependent birth of OH from H + CO₂.

1. INTRODUCTION

State-selectivity is indeed a central theme in molecular reaction dynamics [1]. This was already clear by 1974, the date of publication of "Molecular Reaction Dynamics" [2]. In 1977 it became "official" with the publication of the American Chemical Society Symposium Volume "State-to-State Chemistry" [3]. The writer presented the introductory paper at the symposium, entitled "State-to-State Cross Sections and Rate Constants for Reactions of Neutral Molecules" [4]. The symposium offered a truly impressive array of speakers and topics, covering many of the subjects of the present Workshop. Reading over the volume a decade later is not a waste of time.
It was already fully understood that state-selectivity with respect to reagents leads to state-specificity of products, via the principle of microscopic reversibility (which relates state-to-state cross sections and rates for the forward and reverse reactions at the same total energy [5]). Most of the attention was directed to the product side, e.g. angular and velocity distributions of reactive scattering of crossed molecular beams [6], product state distributions via ir, vis and uv chemiluminescence [7], and laser-induced fluorescence [8], and both ground- and excited-electronic state product branching ratios [9], but the importance of reagent energy and its effect on product energy partitioning was recognized [10]. However, the main excitement was in the "surprising" energy partitioning in elementary exoergic reactions typified by pronounced population inversions, of importance in connection with chemical lasers (both ir and visible) [11]. The interweaving of the fields, chemical lasers and laser chemistry, was already accomplished [12], via the bell-wether reaction of \( \mathrm{F} + \mathrm{H}_2 \) [13], and soon laser-induced selective chemistry took precedence over chemical lasers [14].

Already familiar a decade ago was the information-theoretic approach [15] to the characterization of disequilibrium population distributions and the applicability of surprisal analysis to non-statistical quantum state distributions and branching ratios [16].

With regard to the reactants' side, there was a considerable body of results on the translational energy dependence of the reaction cross section [17], vibrational energy dependence [18], rotational energy dependence [19], and electronic state selectivity [20], including spin-orbit effects [21].

There were also significant experiments [22] on state-to-state rotational excitation using the electrostatic quadrupole lens for state selection and analysis (a technique confined to polar diatomic molecules), and, subsequently inelastic state-to-state cross sections measured by the more general time-of-flight (TOF) method [23].

From the chemical viewpoint, an interesting development was the introduction in 1965 of the electrostatic hexapole lens [24] for producing beams of oriented symmetric top molecules, suitable for use as reagents in crossed beam reactions. The first such "reactive asymmetry" experiments succeeded in demonstrating the orientation dependence of the reactivity of \( \mathrm{CH}_3\mathrm{I} \) with alkali atoms [25]:

\[
\text{CH}_3\text{I} + \mathrm{M} \rightarrow \text{MI} + \text{CH}_3 \quad (1)
\]

Large differences in reactivity were observed for "heads" vs. "tails" orientations. However, the results were only qualitative and no useful theoretical framework for describing the reactive asymmetry was yet available.

A significant breakthrough on the alignment effect (on reactivity) came from the introduction of polarized laser excitation techniques in 1978 [26]. Linearly polarized laser light can selectively excite a homonuclear (as well as a heteronuclear) diatomic molecule so as to align its rotational angular momentum \( \mathbf{j} \), i.e. achieve ±\( m_j \) quantum number selectivity. Of course since the populations of the + and - \( m_j \) states are equal, there is no true orientation, only alignment of the angular momentum vector \( \mathbf{j} \) in space. Nevertheless there is found to be a significant influence of this \( \mathbf{j} \) alignment (with respect to the relative velocity vector \( \mathbf{v} \)) upon reactivity; e.g. for the reaction

\[
\text{Sr} + \text{HF} \quad (\nu=1, j=1; m_j) \rightarrow \text{SrF} + \text{H} \quad (2)
\]