Quantum mechanical description of chemical reaction dynamics lies at the center of our understanding of chemical reactivity. With the advent of crossed-molecular beam and laser techniques, it has become possible to interrogate reactive scattering in energy-resolved and initial state-specific manners. These studies have revealed important issues such as tunneling, mode specificity, resonances, and non-adiabaticity.

One of the most detailed measurements of reactivity by a crossed-molecular beam apparatus is the differential cross section (DCS), namely the product internal state distribution in all scattering angles. To quantum mechanically describe the DCS, one needs to compute the S-matrix elements from initial reactant quantum states to final product quantum states.

However, it is very difficult to obtain the S-matrix elements because of the notorious “coordinate problem”, namely the difficulty associated with finding an optimal coordinate system for both the reactant and product arrangement channels. Indeed, the initial wave packet is best represented in the reactant arrangement channels. Specifically, for a diatomic diatomic (AB+CD) and atom-triatom (A+BCD, B+ACD) Jacobi coordinates are often used in the definition of the asymptotes, and they are shown in Figure 1 with the red, blue and green coordinates, respectively.

To understand the state-to-state dynamics, it is convenient to picture a reaction in two steps: the first step is to reach the transition state, and the second step is to dissociate into the products.

Reactant mode specificity

It has long been established that different forms of energy have varying efficacies in promoting a reaction. To illustrate this point, the integral cross sections for the H/F + H2O reactions are displayed in Figure 3 for both the ground and first excited states of H2O. Excitations of the stretching vibrations of the H2O reactant have been found to promote the H + H2O (and Cl + H2O) reaction more strongly than the translational excitation. For the F + H2O reaction, which has an early barrier, theoretical calculations on an accurate PES have indicated that the stretching vibrational modes of H2O also promote the reaction more strongly than the translational mode. This surprising result, which seemingly contradicts Polanyi’s rules, can be understood by the SVP model, which suggests that the vibrational modes have stronger coupling with the reaction coordinate at the transition state than the translational mode. This and other examples suggest that the SVP model is more general, particularly for reactions with more than three atoms.

'Vector Loss’ Effect

In a recent study of the H/Cl + H2O reactions, we have shown that the ratios between the

Figure 1. Jacobi coordinate systems for the AB+CD arrangement (red), the A+BCD arrangement (blue), and the B+ACD arrangement (green).

Figure 2. SVP value calculated by the projections of reactant and product normal mode vectors onto the reaction coordinate at the transition state for the prototypical X + H2O → HX + OH reactions: (a) X= H, (b) X=Cl, and (c) X=F.

Figure 3. Integral cross sections for the H/F + H2O → H/HF + OH reactions with H2O in vibrationally ground and excited states labelled by the vibrational quantum numbers (νs,νa) for the symmetric stretching, bending, and antisymmetric stretching modes.
ground and first excited vibrational states of the 
H\textsubscript{2}/HCl products are not significantly affected by the vibrational excitation in the H\textsubscript{2}O reactant,\textsuperscript{26} even when the total reactivity is greatly increased. The product rotational state distributions also have little influence from initial excitation,\textsuperscript{26} as shown in Figure 4. These are manifestations of the “memory loss” effect, which has also been found in other reactions.\textsuperscript{27-29}

State-to-state Mode Specificity

State-to-state mode specificity is shown in Figure 5 where the DCSs of the D\textsubscript{2} + OH → D + DOH reaction with the OH reactant in the v=0 (a) and v = 1 (b) vibrational states at the collision energies of Ec = 0.25 eV. The 3D DCSs show the product angular distributions with respect to the incoming direction of the OH reactant, i.e. the forward direction of DOH product corresponds to 0° while backward direction to 180°. The radius of the plot represents the product translational energy and arcs with shorter radius correspond to product states with higher internal energies and vice versa.

Conclusions

State-to-state mode specificity can be understood in terms of transition-state control of the reaction dynamics. Using the SVP idea, we point out two limiting cases in state-to-state reactivity. The “memory loss” effect, referring to the insensitivity of the product state distribution to excitations of reactant modes, is due to the facile energy flow from an “active mode” to the reaction coordinate at the transition state. On the other hand, a “spectator mode” sequesters its energy throughout the reaction, leading to a drastic, but predictable changes in the product state distribution. These insights help us to better understand the reaction dynamics in gas phase bimolecular reactions.

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References:

Figure 4. Rotational state distributions of HCl/H\textsubscript{2} and OH products in the Cl+H\textsubscript{2}O→HCl+OH reaction. Rotational state distributions of HCl/H\textsubscript{2} or OH are projected to the side wall by summing the rotational states of the co-product.

Figure 5. 3D polar plots of DCSs for the D\textsubscript{2} + OH → D + DOH reaction with the OH reactant in the v = 0 (a) and v = 1 (b) vibrational states at the collision energies of Ec = 0.25 eV. The 3D DCSs show the product angular distributions with respect to the incoming direction of the OH reactant, i.e. the forward direction of DOH product corresponds to 0° while backward direction to 180°. The radius of the plot represents the product translational energy and arcs with shorter radius correspond to product states with higher internal energies and vice versa.