FINAL PROGRESS REPORT (DE-FG05-86ER13568)

Theoretical Studies of Combustion Dynamics

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We completed a number of projects during this period of time. This resulted in fifty nine publications, which are listed below. The major thrusts of this research are the development and application of quantum methods to the study of fundamental chemical processes of importance in gas-phase combustion. Broadly speaking our work falls into two categories. One is the development and application of reduced dimensionality theories of chemical reactions, and the other into studies of radical-radical reactions that proceed mainly via complex formation. The various projects in these two areas and their intersection are reviewed below.

I. Reduced dimensionality theory of chemical reactions

We demonstrated the accuracy of our reduced dimensionality approaches for the $\text{H}+\text{H}_2$ and $\text{D}+\text{H}_2$ reactions, and made comparisons with experiment over a very large temperature range. We also applied these methods to the $\text{O}(^3\text{P})+\text{H}_2$, D_2 , and HD reactions, where again comparisons with experiment demonstrated the power of the reduced dimensionality method. Both of these sets of calculations made use of high quality *ab initio* potential energy surfaces.

In 1990 we extended our reduced dimensionality methods to diatom+diatom reactions, by using what we termed "hyper cylindrical coordinates". We applied this methodology to the $\text{H}_2(\text{D}_2) + \text{CN}$ reaction using a potential we developed, based on limited *ab initio* calculations of others. Later, we calculated the cumulative reaction probability for the $\text{OH}+\text{H}_2$ reaction for zero total angular momentum. Subsequently Miller and co-workers performed accurate full dimensional calculations of this quantity and the comparison with our earlier calculation is shown below. As seen there is very good agreement between our reduced dimensionality and the full dimensionality calculations. Miller and co-worker then went on to obtain the thermal rate constant using the so-called J-shifting approximation. This approximation was introduced by us in the general context of the reduced dimensionality approach to reactive scattering. It affords an enormous savings in computational effort and its accuracy of 10 - 20% makes it a very attractive, and one that has been adopted by many research groups. We also were among the do quantum calculations of mode-specific effects in this reaction and the $\text{HOD}+\text{H}$ reaction. The comparisons with experiments were very valuable and agreement was generally excellent.

Our most ambitious reduced dimensionality reactive scattering calculation was on the $\text{H}+\text{C}_2\text{H}_2$ reaction. This four-degree-of-freedom calculation was done using a potential that we developed based on *ab initio* calculations of the saddle point. We focused on mode-specific effects in this reaction and also performed a calculation of the thermal rate constant.

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Comparison of full dimensional quantum calculations of Miller and co-workers with our reduced dimensionality quantum calculations of the cumulative reaction for the $\text{OH} + \text{H}_2$ reaction for zero total angular momentum.

II. Resonances in radical-radical systems

We have completed several projects dealing with unimolecular dissociation and collision induced recombination in HCO . Together with Dr. Lawrence Harding of Argonne National Laboratory we developed a potential for this system that has been used by many groups. We calculated resonances in this system using a variety of methods, and we recently examined the effect of rotation on the positions and widths of resonances. A sample of results is shown below. The shifts in resonance energies relative to the $J = 0$ results are shown for the even parity component of $J = 1, K = 1$. The circles are from an exact calculation and the solid line is from an approximation we term the "Adiabatic Rotation Approximation". (As seen, this approximation is quite accurate.) There are significant variations in the shifts as a function of the resonance state. The progression seen for increasing ΔE correlates with increasing bend excitation of the resonance. This causes an increase in the effective A-constant. (HCO is to a good approximation a prolate symmetric top.) Analogous results were also obtained for $J = 1, K = 0$, and also for higher values of J and K .

The adiabatic rotation approximation has been used by a number of groups, especially for radical-radical systems, where J-shifting may not be accurate. These applications have been to recombination in $\text{H} + \text{CO}$, reaction and recombination in $\text{OH} + \text{O}$, and also to dissociation of HOCO . We have done several calculations on the latter system, which is especially challenging, theoretically.

The reaction $\text{OH} + \text{CO} \rightarrow \text{H} + \text{CO}_2$ is known to proceed through formation of the HOCO complex. The calculation of the thermal rate constant is quite difficult and has not been done in full dimensionality. We applied reduced dimensionality theory to this reaction, using as input two-degree-of-freedom quantum scattering calculations of Clary

and co-workers and Schatz and co-workers. After making a slight adjustment to the threshold energy of the cumulative reaction probability we obtained fairly good agreement with experiment, as shown below.

Comparison of exact (—) and Adiabatic Rotation (0) resonance energy shifts relative to $J = 0$ results for $J = K = 1$.

Comparison of reduced dimensionality calculated (solid line) and experimental (+) rate constant for the OH+CO reaction.

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