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Accurate Polyatomic Quantum Dynamics Studies of Combustion Reactions

Final Progress Report (7/1/1994–6/30/1998)

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Program scope:

This program is designed to develop accurate yet practical computational methods, primarily based on time-dependent quantum mechanics, for studying the dynamics of polyatomic reactions beyond the atom-diatom systems. Efficient computational methodologies are developed and the applications of these methods to practical chemical reactions relevant to combustion processes are carried out. The program emphasizes the practical aspects of accurate quantum dynamics calculations in order to understand, explain and predict the dynamical properties of important combustion reactions.

The aim of this research is to help provide not only qualitative dynamics information but also quantitative prediction of reaction dynamics of combustion reactions at the microscopic level. Through accurate theoretical calculations, we wish to be able to quantitatively predict reaction cross sections and rate constants of relatively small gas-phase reactions from first principles that are of direct interest to combustion. The long-term goal of this research is to develop practical computational methods that are capable of quantitatively predict dynamics of more complex polyatomic gas-phase reactions that are of interest to combustion.

Progress report:

Rigorous time-dependent (TD) quantum dynamical treatment for generic four-atom reactions of the type $AB + CD \rightarrow A + BCD$ has been developed. The three versions of the treatment, rigid-bond 5D (RB5D), potential-averaged 5D (PA5D) and the exact 6D, have been tested on the benchmark $H_2 + OH$ reaction and its isotopically substituted reaction, all capable of giving accurate results. In particular, the PA5D treatment can essentially reproduces the exact 6D result but at a fraction of the computational cost. We also developed a new scheme to calculate reaction probabilities for reactions that require a large number of basis functions. The new scheme (normalized angular quadrature scheme) enables one to obtain stable and accurate reaction probabilities without the need to store large matrices in the computer memories and to perform large

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matrix multiplications. Using this scheme, the benchmark H_2 + OH and its isotopic reaction HD + OH can now be calculated efficiently on a medium sized workstation without the need of a large-memory supercomputer.

We successfully computed reaction probabilities, cross sections and rate constants for the D_2 + OH and HD + OH reactions. Our accurate TD calculation determined the branching ratio for the HD + OH reaction and, in addition, provided direct insight on the steric effect in direct reactions such as HD + OH. Also, our enhanced TD method has been applied successfully to the HO + CO reaction using the PA5D (potential averaged 5D) implementation which is essentially indistinguishable from the exact 6D treatment. Rich resonances have been found in reaction probabilities from this calculation, and previous results based on reduced-dimensionality methods have been assessed based on our new result. New development is in progress to calculate complete state-to-state reaction dynamics, and the result of our application to H + O_2 reaction is very encouraging.

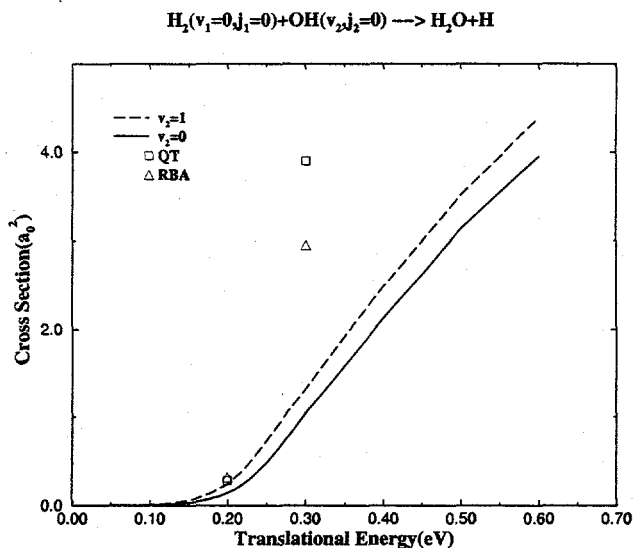$$H_2(v_1=0,j_1=0)+OH(v_2,j_2=0) \longrightarrow H_2O+H$$

Figure 1: Calculated reaction cross sections for the H+2 + OH reaction and comparisons with quasiclassical trajectory (QT) calculation and Reduced dimensinality (RBA) calculation.
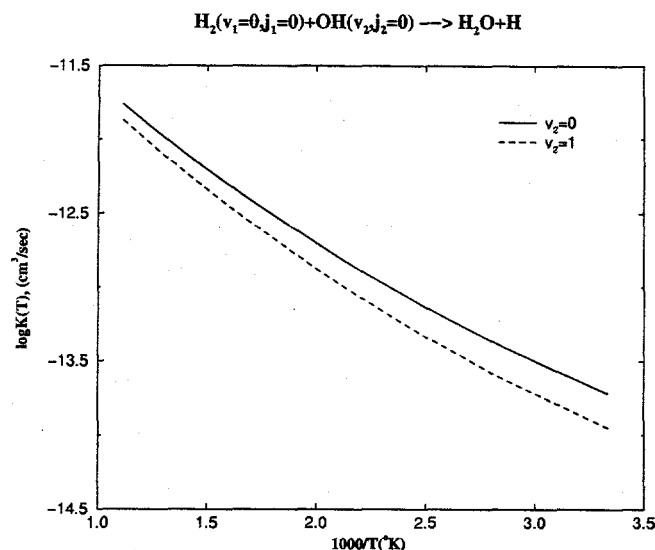
$H_2(v_1=0,j_1=0)+OH(v_2,j_2=0) \longrightarrow H_2O+H$

Figure 2: Calculated reaction rate constant for the H+2 + OH reaction.

We recently reported state-to-state quantum dynamics study for H_2 + OH reaction in full dimensions. The numerical calculations show however that the straightforward TD wavepacket method using a single set of Jacobi coordinates is inefficient for carrying out such state-to-state studies. The computational cost is at least an order of magnitude larger than our previous calculations that do not resolve final states of the product. This leads to the development of a reactant-product decoupling (RPD) approach for general state-to-state dynamics studies. In the RPD approach, the calculation of the full-wavefunction is split into that of reactant and product components. The calculation of the reactant component is independent of that of the product components through the use of absorbing potentials. The calculation of the product component is relatively straightforward because it involves only inelastic scattering calculations. This general RPD approach is efficient to apply to complex reactions with many arrangement channels and with long-range inelastic interactions. Numerical test studies of the RPD approach to three dimensional triatomic reactions demonstrated the efficiency and accuracy of the RPD approach to state-to-state dynamics studies. In particular, the RPD approach is even more efficient to ap-
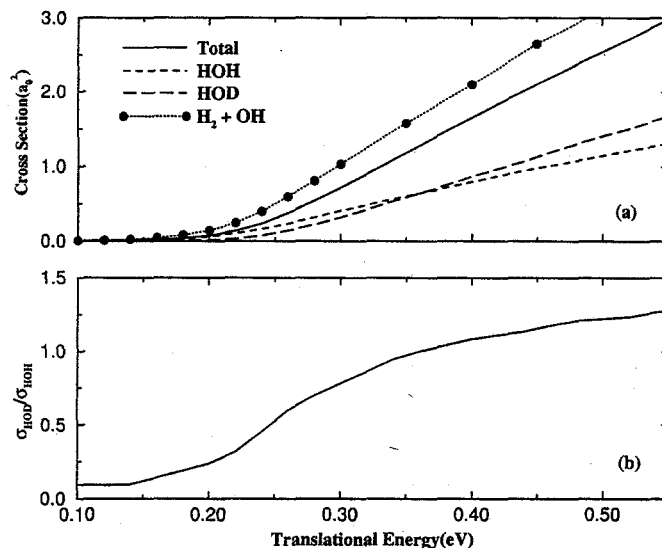
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Figure 3: Calculated reaction cross sections for the reaction of HD + OH → H + DOH, D + HOH.

ply to unimolecular reactions including photo fragmentation dynamics. Work in this area is in progress.

We have recently presented a first full-dimensional quantum dynamics study for the reaction $H_2 + CN \rightarrow H + HCN$ on a new *ab initial* potential energy surface of ter Horst, Schatz and Harding. Our theoretical calculation has obtained the following results.

(1) The PA5D (potential averaged 5D) treatment for the CN bond gives total (final states-summed) reaction probabilities that are indistinguishable from the exact 6D result when both reagents are at ground vibrational state. Small deviations between PA5D and exact 6D results are observed when either diatom is vibrationally excited. Thus as far as the total reaction cross section or rate constant is concerned, the CN molecule can be considered as a spectator.

(2) The vibrational excitation of CN slightly *decreases* the reaction rate while vibrational excitation of H_2 considerably *enhances* the reaction. This is directly related to the structure of the potential saddle point which is "earlier" in the entrance channel with a stretched H_2 bond length but a slightly *shrunk* CN
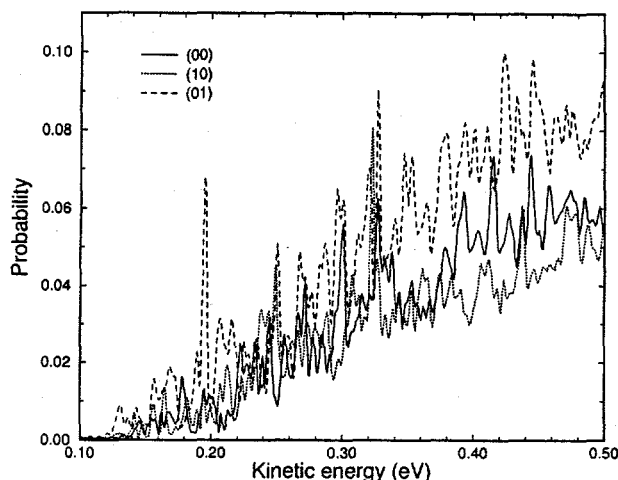
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Figure 4: Calculated reaction probabilities for the reaction of $HO(j_1) + CO(j_2) \rightarrow H + CO_2$, $D + HOH$.

bond length.

(3) The rotational excitations of H_2 and CN increases the *individual* reaction probabilities for fixed total angular momentum J=0. The effect is more pronounced for CN rotations.

4) The comparison of calculated rate constant with experimental data suggests that the *effective* barrier of the TSH3 surface may be too high by about 0.3 kcal/mol.

(5) From both a short reaction time directly observed from the wavepacket propagation and the inactivities of excited vibrational states of CN, we conclude that the H_2 + CN reaction is a direct abstract reaction. Firstly, if the reaction goes through an insertion process to form the H_2CN adduct, one would expect a much longer propagation time due to resonances. Secondly, the insertion mechanism requires contributions from excited CN vibrational states because the H_2CN complex has a much stretched CN bond length (2.30 a_0) clearly supports the mechanism for a direct abstraction reaction.
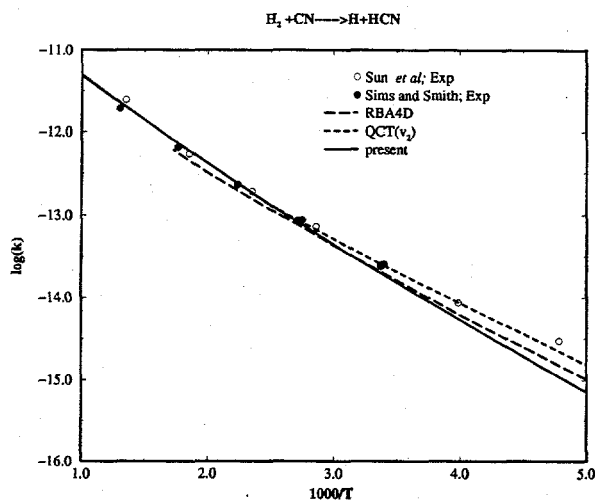
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H₂ +CN---->H+HCN

Figure 5: Comparison of the present theoretical rate constant for the reaction of H_2 + CN at ground state with the experimental thermal rate, the RBA4D quantum calculation, and the QCT calculation with ZPE correction for the bending mode of HCN.

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