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***Gas-Phase Molecular Dynamics: Quantum
Molecular Dynamics of Combustion Reactions and
Molecular Spectroscopy Calculations***

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**GAS-PHASE MOLECULAR DYNAMICS: QUANTUM MOLECULAR DYNAMICS OF COMBUSTION
REACTIONS AND MOLECULAR SPECTROSCOPY CALCULATIONS**

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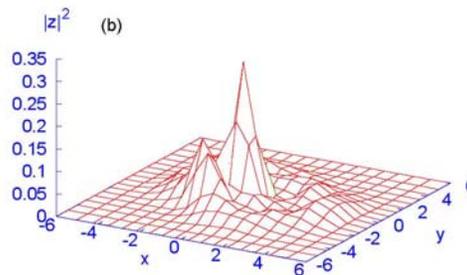
Program Scope

The goal of this program is the development of computational methods for studying chemical reaction dynamics and molecular spectroscopy in the gas phase. We are interested in developing rigorous quantum dynamics algorithms for small polyatomic systems and in implementing approximate approaches for complex ones. Particular focuses are on the dynamics and kinetics of chemical reactions and on the rovibrational spectra of species involved in combustion processes. This research also explores the potential energy surfaces of these systems of interest using state-of-the-art quantum chemistry methods.

Recent Progress

A coherent discrete variable representation method

A coherent discrete variable representation (ZDVR) method has been developed for constructing a multidimensional potential-optimized DVR basis. In this approach, inspired by a coherent-state formalism in momentum and conjugate coordinates, the multidimensional quadrature pivots are obtained by diagonalizing a complex coordinate operator matrix in a finite basis set, which is spanned by the lowest eigenstates of a two-dimensional reference Hamiltonian. Here a *c-norm* condition is used in the diagonalization procedure. The orthonormal eigenvectors define a collocation matrix connecting the localized ZDVR basis functions and the finite basis set. The method has been applied to two vibrational models for computing the lowest bound states. Results show that the ZDVR method provides exponential convergence and accurate energies. In addition, a zeroth order approximation method has been derived and tested.



A typical two-dimensional coherent discrete variable representation (ZDVR) basis function

Vibronic energies of DCCI and HCCI in three low-lying states

Three low-lying electronic states (X^1A' , a^3A'' , A^1A'') and the spin-orbit coupling matrix between the X and a states of HCCI have been calculated with an *ab initio* multi-reference configuration interaction (MRCI) method. The three-dimensional potential energy surfaces are interpolated using a general DVR interpolation technique from 6075 MRCI energy points. The vibronic energy levels of the DCCI and HCCI molecules are computed using a variational K -dependent quantum dynamics approach in hyperspherical coordinates. As a result, the Renner-Teller effect and the spin-orbit coupling in the system are treated in detail. In addition, the relative position of

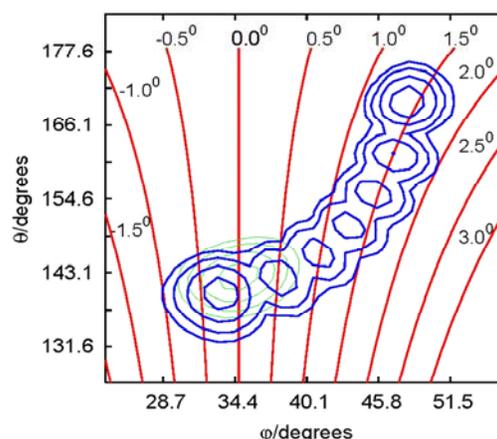
the triplet state of HCCl to the singlet ground state is predicted to be 2122 cm^{-1} (with Sears & Muckerman).

Transition intensity calculation of the $A^1A''-X^1A'$ band of HCCl

Recently, our group has measured several hot bands lying to the red of the origin of the $A^1A''-X^1A'$ transition of HCCl. These new bands may reveal a clue to the fundamental C-Cl stretching frequency of HCCl in the A state. In order to confirm this, following the energy level calculations described above, we further studied the transition intensities of the $A^1A''-X^1A'$ bands based on a MRCI/aug-cc-pVTZ dipole moment surface. In a manner similar to the potential energy surfaces, the dipole moment surface was interpolated from a set of grid points. Results show that there exist apparent intensities for the $A(0, \nu_2, \nu_3)-X(100)$ transitions of HCCl due to the fact that the $X(012)$ vibrational state lies very close in energy to the $X(100)$ state (with Sears).

Exploring the intensity of the parallel sub-bands of the $A(060)-X(000)$ transition of HCB

In our group the rotationally resolved spectrum of the $A(006)-X(000)$ has been recorded recently. The spectrum contains both perpendicular and parallel rotational sub-band structures, where the latter are partially due to axis-switching in the transition as shown in the figure. However, the relative intensity of the parallel rotational bands to the perpendicular ones is not well explained by solely using the axis-switching model. The calculated intensities are substantially smaller than observed. In this work we propose another possible explanation by considering Coriolis coupling in the excited state and the non-adiabatic effect due to the electronic coupling between the B^1A' and X^1A' states, based on the calculated transition dipole moment matrices in four low-lying electronic states included the B^1A' excited state (with Hall & Sears).



Contour plots of the $A(060)$ and $X(000)$ vibrational states for HCB in the hyperangle plane. The axis-switching angles with respect to the equilibrium geometry of the X state are explicitly labeled in the figure.

Quantum molecular dynamics study of radical-radical reactions

We have improved our dual-level *ab initio* direct dynamics program, and applied it to study two combustion-related reactions: the $^1\text{CH}_2 + \text{C}_2\text{H}_2$ and $\text{OH} + \text{HOCO}$ reactions. The $^1\text{CH}_2 + \text{C}_2\text{H}_2$ reaction has been studied using the dual-level “scaling all correlation” (SAC) *ab initio* method of Truhlar et al, i.e., the UCCSD(SAC)/cc-pVDZ theory. Results show that the reaction occurs via long-lived complexes. The lifetime of the cyclopropene intermediate is obtained as 3.2 ± 0.4 ps. It is found that the intermediate propyne can be formed directly from reactants through the insertion of $^1\text{CH}_2$ into one C-H bond of C_2H_2 . However, compared to the major mechanism in which the propyne is produced through a ring-opening of the cyclopropene complex, this reaction pathway is much less favorable.

The dynamics study of the $\text{OH} + \text{HOCO}$ reaction has been carried out using the UMP2(SAC)/6-31G(d) method. This method was selected by minimizing the root-mean-squares errors of the relative SAC energies of the stationary points corresponding to the CCSD(T)/CBS results. The

reaction is shown to proceed through an addition intermediate, HOC(O)OH, which then passes through a four-centered transition state as it produces the products H₂O and CO₂. The energetics suggest that the reaction is effectively barrierless. The calculated thermal rate constant of $1.03 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at room temperature shows that it is a fast radical reaction, and the intermediate HOC(O)OH is short-lived (with Muckerman & J. Francisco).

Future Plans

Kinetics and dynamics study of the reaction of HOCO with oxygen

We will apply our direct *ab initio* molecular dynamics program for studying some important combustion reactions. Currently, of particular interest is the reactivity of the HOCO radical reaction with oxygen atom and molecule. For the O + HOCO reaction, in collaboration with J. Francisco (Purdue), we will address the energies, geometries, and vibrational frequencies of the stationary points on the ground-state doublet potential energy surface, and the reaction mechanism by using a SAC/UCCD method. For the O₂ + HOCO reaction, on the other hand, the *ab initio* direct dynamics study will be carried out using the UB3PW91 density functional theory (DFT). This DFT method is selected by minimizing the errors of the relative energies of the stationary points on the ground-state electronic surface of HOC(O)O₂ with respect to the best *ab initio* values of Poggi and Francisco (*J. Chem. Phys.* 120 (2004) 5073). Besides the kinetics and dynamics studies of the reaction, we also hope to predict the lifetime of the HOC(O)O₂ intermediate produced through the reaction course, and the energy disposal in the HO₂ + CO₂ products. For both reactions, the temperature dependence of the thermal rate constants will be calculated (with Muckerman & J. Francisco).

Rovibrational tunneling spectroscopy of weakly bound molecular clusters

Significant experimental progress has been made on understanding the structure and dynamics of weakly bound clusters from very simple van der Waals molecules, *e.g.*, Ar-H₂ and Ne-HF, to systems of real chemical interest such as the OH⁻(H₂O)_n clusters. These experimental advances present a major challenge to theory both in calculating the potential energy surface of clusters, and in developing the dynamics methods to compute the rovibrational bound states. In the dynamics aspect, the challenge arises from the shallowness of the potential well of the weakly bound molecular clusters that gives rise to strong anharmonic effects in their ground-state dynamics. This consideration precludes the applicability of the widely used vibrational normal mode approach. Furthermore, the vibrational energy level spacings are also very small, and one needs to calculate them to a very high accuracy. In this research, we plan to apply the two-layer Lanczos algorithm for studying the rovibrational spectra of the HF(H₂)_n and OH⁻(H₂O)_n clusters, implemented with the diffusion Monte Carlo technique. In these calculations, we are particularly interested in studying tunneling dynamics in the spectroscopy of the hydrogen-containing molecular clusters (with Z. Bacic and J. Bowman).

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