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Studies in Spectroscopy and Chemical Dynamics***

**Hua-Gen Yu and James T. Muckerman**

*Chemistry Department, Brookhaven National Laboratory, Upton, NY, USA*

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**Chemistry Department**

**Brookhaven National Laboratory**

P.O. Box 5000  
Upton, NY 11973-5000  
[www.bnl.gov](http://www.bnl.gov)

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## GAS-PHASE MOLECULAR DYNAMICS: THEORETICAL STUDIES IN SPECTROSCOPY AND CHEMICAL DYNAMICS

Hua-Gen Yu (hgy@bnl.gov) and James T. Muckerman (muckerma@bnl.gov)  
Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973-5000

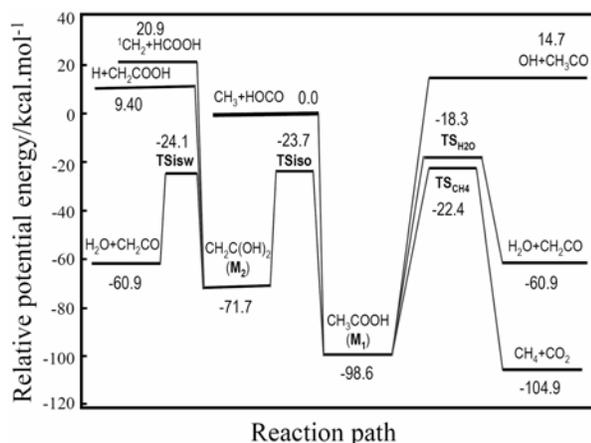
### Program Scope

The goal of this program is the development and application 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 focus is 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

#### Kinetics and dynamics study of the reaction of HOCO radical with CH<sub>3</sub> and ClO radicals

A combined *ab initio* direct dynamics and RRKM (Rice-Ramsperger-Kassel-Marcus) study has been carried out for the reaction of HOCO radicals with CH<sub>3</sub> radicals. It is examined using the coupled cluster method (CCSD(T)) to locate and optimize the critical points on the ground-state potential energy surface as shown in Fig.1. The results show that the CH<sub>3</sub> + HOCO reaction can produce both the H<sub>2</sub>O + CH<sub>2</sub>CO and the CH<sub>4</sub> + CO<sub>2</sub> products through acetic acid (M<sub>1</sub>) and enediol (M<sub>2</sub>) intermediates. Direct *ab initio* dynamics calculations determine the thermal rate coefficients to be  $k(T/K) = 3.24 \times 10^{-11} T^{0.1024}$  in  $\text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$  at  $T \leq 1000$  K for the overall reaction. The product branching ratio of (H<sub>2</sub>O + CH<sub>2</sub>CO) to (CH<sub>4</sub> + CO<sub>2</sub>) is predicted to be  $R_{\text{H}_2\text{O}/\text{CH}_4}(T/K) = 1.52 + (1.95 \times 10^{-4})T$  using the RRKM approach. Both the thermal rate coefficients and the product branching ratios weakly depend on temperature. In addition, the kinetics of the ClO + HOCO reaction has been studied using the variational RRKM theory based on a CCSD(T) potential energy surface. This is a fast reaction leading to a diversity of products *via* an addition or direct hydrogen abstraction reaction mechanism. At room temperature, the thermal rate coefficient is obtained as  $4.26 \times 10^{-12} \text{ cm}^3 \text{molec}^{-1} \text{s}^{-1}$  with the product branching fractions of Cl (0.518), HOCl (0.469), HCl (0.01), and HClO (0.003) at zero pressure. Furthermore, a simple RRKM/master equation simulation indicates that the stabilization of the HOC(O)Cl intermediates is noticeable at moderate



**Figure 1.** CCSD(T)/aug-cc-pVQZ energy diagram for the reaction pathway of the CH<sub>3</sub> + HOCO reaction.

pressures as its thermal rate constant reaches about  $6.0 \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ . This work was done in collaboration with J. Francisco (Purdue).

### **Dynamics study of molecular ion-molecule reaction**

The direct molecular dynamics method was employed to study the reaction of CO with  $\text{H}_3^+$  and  $\text{H}_2\text{D}^+$  using a scaling all correlation second-order Møller–Plesset perturbation theory (SAC-MP2) method with the cc-pVTZ basis set. Results show that total thermal rate coefficients for both the  $\text{CO} + \text{H}_3^+$  and the  $\text{CO} + \text{H}_2\text{D}^+$  reactions have a weakly positive temperature dependence. At room temperature, the rate coefficients are predicted to be  $(1.42 \pm 0.03) \times 10^{-9} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$  with a product branching ratio of  $[\text{HOC}^+]/[\text{HCO}^+] = 0.36 \pm 0.01$  for the  $\text{CO} + \text{H}_3^+$  reaction, and  $(1.26 \pm 0.03) \times 10^{-9} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$  with the product branching ratios:  $0.37 \pm 0.01$  ( $([\text{HOC}^+] + [\text{DOC}^+])/([\text{HCO}^+] + [\text{DOC}^+])$ ),  $0.54 \pm 0.02$  ( $[\text{DCO}^+]/[\text{HCO}^+]$ ), and  $0.49 \pm 0.02$  ( $[\text{DOC}^+]/[\text{HOC}^+]$ ) for  $\text{CO} + \text{H}_2\text{D}^+$ . The product branching ratios have a noticeable temperature dependence as well as a pronounced isotopic effect for the H/DOC<sup>+</sup> product channel.

### **Spherical electron cloud hopping molecular dynamics simulation on dissociative recombination (DR) of protonated water**

The SECH MD method has been applied to study the DR of  $\text{H}_3\text{O}^+$  at zero collision energy. The simulations give several product channels: 0.660 for (OH + 2H), 0.230 for ( $\text{H}_2\text{O} + \text{H}$ ), 0.108 for (OH +  $\text{H}_2$ ), and 0.002 for (O + H +  $\text{H}_2$ ), which are in excellent agreement with the heavy-ion storage ring experimental results. It was noticed that the first excited state of  $\text{H}_3\text{O}$  plays a prominent role in DR of  $\text{H}_3\text{O}^+$ . The OH +  $\text{H}_2$  channel proceeds on this excited state and associated non-adiabatic transitions. Similar dynamics events were also observed by Lester and co-workers in their dynamics measurement of the OH ( $A^2\Sigma$ ) +  $\text{H}_2$  collisions. In addition, two different pathways leading to hydrogen atoms are identified in the  $\text{H}_3\text{O}^+$  DR processes, by analysis of the trajectories, and the bimodal distribution of released kinetic energies of hydrogen atoms.

### **A general program for calculating vibrational spectra of five-atom systems**

Besides the electronic structure and molecular dynamics calculations, our research is also focuses on quantum dynamics studies of molecular spectroscopy. In this project, we aim to develop computational algorithms to accurately calculate the rovibrational spectra of polyatomic molecules, and to assist experimentalists to interpret their observed spectra. By using the two layer Lanczos iterative diagonalization algorithm developed by us previously, we have programmed an exact variational algorithm for calculating vibrational energy levels of pentatomic molecules using a rigorous quantum dynamics method. The algorithm has exploited a common compact Hamiltonian expressed in a set of four orthogonal polyspherical vectors. Since the orthogonal coordinates are a set of scattering coordinates, the large amplitude motions of vibrations and molecular dissociation events are well described. It is possible to study highly excited vibrational states and resonances (metastable vibrational states) of molecules. With the intermediate use of atomic Cartesian coordinates, any functional form can be used for expressing the potential energy surface of the system of interest. In addition, the vibrational states are efficiently solved using a two-layer Lanczos algorithm in a mixed grid/basis representation. A non-direct product basis is used in the angular variables, which avoids the singularity of the Hamiltonian at  $\sin\theta = 0$ . The two-layer Lanczos algorithm solves the whole eigenvalue problem in two consecutive diagonalizations in a five dimensional

manner, and only requires the actions of Hamiltonian on a vector, without explicitly storing the Hamiltonian matrix. Thus, a very large basis set is allowed in calculations, which makes this work feasible. In particular, the algorithm is problem-independent so that it is universal and applicable to most penta-atomic molecules with small and/or large amplitude vibrations. A general code (PetroVib) has been programmed. The program has been successfully applied for calculating the vibrational states of three types of penta-atomic molecules, e.g., semi-rigid CH<sub>4</sub>, floppy H<sub>3</sub>O<sub>2</sub><sup>-</sup>, and the van der Waals complex He<sub>3</sub>Cl<sub>2</sub>, for numerical demonstrations.

## Future Plans

### Kinetics and dynamics study of combustion-related reactions

We will continue to study some important combustion reactions using the direct *ab initio* molecular dynamics program. Our study of a series of reactions involving the HOCO radical will conclude with the disproportionation of the HOCO radical. Here we will address the energies, geometries, and vibrational frequencies of the stationary points on the singlet ground-state surface, and the reaction mechanism. If one HOCO radical abstracts the hydrogen atom from the other, the products would be HC(O)OH and CO<sub>2</sub>. If the two HOCO radicals form an intermediate oxalic acid (HOC(O)C(O)OH) complex, the products could be H<sub>2</sub>O, CO and CO<sub>2</sub>, or two CO<sub>2</sub> and H<sub>2</sub>. The dynamics will be carried out using a dual level *ab initio* method. The aim of this research is to determine the mechanism and product branching ratio as well as rate coefficients.

A new direction in the study of combustion-related radical reactions using the direct *ab initio* molecular dynamics program will focus on the kinetics and dynamics of cyclic, N- and O-containing fuel molecules. The concentration of cyclic compounds in diesels and other future transportation fuels, produced largely from non-traditional sources such as oil shales and sand oils, are much higher than those in current fuels. There are only limited kinetics data on cyclic fuel molecules, yet they are required to design future internal combustion engines using such fuels. A new unique step in the chemistry is the ring-opening processes resulting in, for example cyclopentoxy (cyc-C<sub>5</sub>H<sub>9</sub>O) radicals discussed by us before. Such radicals may well contribute to enhanced formation of soot without a ring-opening reaction. In this work, we will start this project with the reactions of morpholine (1-oxa-4-aza-cyclohexane, i.e. cyclic -OCH<sub>2</sub>CH<sub>2</sub>NHCH<sub>2</sub>CH<sub>2</sub>-) and its derivatives with small radicals such as O<sub>2</sub>, HO<sub>2</sub> and OH. Westmoreland et al. have recently demonstrated that morpholine is an ideal compound for modeling those hydrocarbon, oxygenated and N-containing fuels. Here, we will address the energies, geometries, and vibrational frequencies of the stationary points on the ground-state surfaces, and the reaction mechanism. The dynamics will be carried out using the DualOrthGT program, together with variational RRKM theory.

### Vibronic spectrum calculations of CH<sub>2</sub> and its interactions with He

In our GPMD group, Sears and Hall have observed rich and complicated rovibronic levels of CH<sub>2</sub> near the C + H<sub>2</sub> and CH + H dissociation limits. They provide a challenge for multiple surface dynamics theory, with relevance to the reactive system as well as CH<sub>2</sub> spectroscopy. We have calculated five low-lying electronic potential energy surfaces of CH<sub>2</sub> using a multireference CI (MRCI) method. The adiabatic surfaces will be transformed into a set of diabatic ones using the quasi-adiabatic approximation of

Koppel et al. Full-dimensional quantum dynamics will then be performed on the five coupled surfaces. The principal interest is in the energy levels and non-adiabatic coupling effects, for detailed comparison with experimental observations. In addition, we also plan to calculate the singlet and triplet potential energy surfaces of the He-CH<sub>2</sub> (*X/A*) interaction system using the CCSD(T)/aug-cc-pVQZ level of theory. The surfaces will be used for investigating the dynamics of singlet and triplet states of CH<sub>2</sub> in collaboration with Tscherbul at Harvard, and rotationally inelastic scattering calculations in collaboration with Dagdigian and Alexander at Johns Hopkins and Maryland.

### **Non-adiabatic molecular dynamics studies of polyatomic molecular reactions**

Electronically excited species such as <sup>1</sup>CH<sub>2</sub> also play an important role in combustion chemistry. However, the studies of their reactivity are rather limited, partially due to the non-adiabatic dynamics effects because those reactions often occur on multiple potential energy surfaces. In this research, we will extend the surface hopping direct *ab initio* molecular dynamics algorithm, developed for the SECH MD studies, to simulate the bimolecular reactions and the photo-dissociation chemistry. The first application would be the photodissociation dynamics of acetone at 193-230 nm. This system has been investigated by Suits et al. using an universal ion imaging technique. The photon excited acetone produces two major types of products: CH<sub>3</sub>CO + CH<sub>3</sub> and CO + 2CH<sub>3</sub>. The latter products result from poorly understood dissociation mechanisms. Here we will attempt to explore the dissociation pathways of acetone on its three low-lying electronic states.

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