

## RESEARCH ACTIVITIES VIII Computer Center

### VIII-A Theoretical Studies on Electronic Structure and Dynamics of Electronically Excited States in Polyatomic Molecules

#### VIII-A-1 Theoretical Study on the Spectroscopy and Dynamics of Electronically Excited States of HCP Molecule

NANBU, Shinkoh; KINOSHITA, Tomoko; GRAY, Stephen K.<sup>1</sup>; AOYAGI, Mutsumi  
(<sup>1</sup>Argonne Natl. Lab.)

Quantum mechanical bound-state calculations for the low-lying electronic excited states of HCP molecule,  $1^1A''$ ,  $2^1A'$  and  $2^1A''$ , were performed using the ab initio global potential energy surfaces. The global potential surfaces were determined by the multi-reference configuration interaction (MRCI) method at DZP basis set level. A large direct-product basis coupled with the standard Lanczos iterative method was employed for computing the rovibrational energy levels. An evenly spaced discrete variable representation (DVR) was used to describe the two radial coordinates of Jacobi coordinates, and the Gauss-Legendre quadrature points was used as an angular DVR for the bending coordinate. The results almost reproduced the low-lying vibrational levels for the  $1^1A''$  state measured in the UV absorption spectrum and IR-UV double resonance spectroscopy, and moreover the term energies of the  $1^1A''$  and  $2^1A''$  states with including the zero point vibrational energy were also in good agreement with the experimental data at aug-cc-pVDZ basis set level. We also performed wave packet calculations on ab initio surfaces to investigate the photodissociation dynamics for  $HCP(1^1\Sigma^+) + h\nu \rightarrow H(2S) + CP(X)$ ; where  $X = 1^2\Sigma^+$  and  $2^2\Pi$ . It is found that the non-adiabatic transition between  $1^1A'$  and  $2^1A'$  states in the bent conformations plays an important role in the predissociation process.

#### VIII-A-2 Development of *Ab Initio* MD Method Based on the Direct Evaluation of CAS-SCF Energy Derivatives

KINOSHITA, Tomoko; NANBU, Shinkoh; AOYAGI, Mutsumi

We have been developing an ab initio molecular dynamics programs to investigate the reaction dynamics of large scale problems, *i.e.*, surface reactions, and biological systems. Since we employed parallelized version of McMurchie-Davidson's algorithm to evaluate both AO integrals and derivatives of AO integrals, the most time consuming step of electronic structure calculations has been carried out in a tractable way. At each time steps of MD calculations, we obtain analytical energy derivatives of complete active space (CAS) wavefunctions. We continue to develop the codes for non adiabatic and spin-orbit coupling matrix elements.

Our direct method can easily extend to apply a number of interesting problems including non adiabatic reactions and spin forbidden processes.

#### VIII-A-3 Theoretical Study on the Unimolecular Reaction Dynamics of Acetyl Radical $CH_3CO \rightarrow CH_3 + CO$

ITO, Masakatsu; NANBU, Shinkoh; AOYAGI, Mutsumi

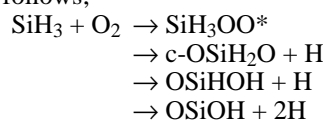
We investigate the dissociation dynamics of acetyl radical with the classical trajectory method using the electronic model hamiltonian based on our ab initio calculations. At each time step in our classical trajectory calculations, the electronic hamiltonian is diagonalized to obtain the instantaneous adiabatic states and then the Hellmann-Feynmann forces are evaluated to drive the nuclear coordinates. Our hamiltonian is based on the valence bond (VB) description of the electronic wavefunctions. Since acetyl radical and its dissociative products have different bonding characters, the wavefunctions along the dissociation process are approximately expanded by two corresponding VB bases states. We found that the energy of the CCO bending excitation does not efficiently transfer into the dissociation coordinate (C-C) over the time period of 30 ps. It is suggested that this slow transfer or redistribution of internal energy could be one of the important sources for the discrepancy between the RRKM rate constants and the experimental results.

#### VIII-A-4 *Ab Initio* Molecular Orbital Studies of Isomerization Reaction from *c*-OSiH<sub>2</sub>O to *t*-OSiHOH

KONDO, Shigeo<sup>1</sup>; TOKUHASHI, Kazuaki<sup>1</sup>; NAGAI, Hidekazu<sup>1</sup>; TAKAHASHI, Akifumi<sup>1</sup>; SUGIE, Masaaki<sup>1</sup>; AOYAGI, Mutsumi  
(<sup>1</sup>Natl. Inst. Mater. Chem. Res.)

[*J. Mol. Struct. (THEOCHEM)* **469**, 25 (1999)]

We have suggested in a previous study that the reaction route from  $SiH_3 + O_2$  to  $OSiOH + 2H$  is a key to understand the spontaneous ignition at room temperature. The whole route of this reaction was found as follows;



In this study, the isomerization reaction from *c*-OSiH<sub>2</sub>O to *t*-OSiHOH, a vital reaction to understand the

spontaneous ignition of Silane, has been reinvestigated with Gaussian-2 theory and CAS(6,6) method. It was found that the reaction proceeds through two consecutive steps; *i.e.*, *c*-OSiH<sub>2</sub>O undergoes isomerization to yield *w*-OSiH<sub>2</sub>O, and then the latter is converted to *t*-OSiHOH. The G-2 energy of the transition state of the latter process is 4.3 kcal/mol higher than that of the former. However, the G-2 energy of this higher transition state plus H atom is still 4.8 kcal/mol lower than that of the original reactants of SiH<sub>3</sub> + O<sub>2</sub>.

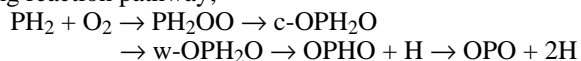
#### VIII-A-5 *Ab Initio* Study of PH<sub>2</sub> + O<sub>2</sub> Reaction Relevant to the PH<sub>3</sub> Combustion

KONDO, Shigeo<sup>1</sup>; TOKUHASHI, Kazuaki<sup>1</sup>; TAKAHASHI, Akifumi<sup>1</sup>; SUGIE, Masaaki<sup>1</sup>; AOYAGI, Mutsumi

(<sup>1</sup>Natl. Inst. Mater. Chem. Res.)

[*J. Phys. Chem. A* in press]

*Ab initio* calculations have been carried out for the PH<sub>2</sub> + O<sub>2</sub> reaction by using Gaussian-2 theory, which is considered as a key reaction to understand low temperature phosphine combustion. This reaction consists of two main branching routes at low temperatures. One is the reaction to yield OH radicals, and the other to yield hydrogen atoms. Of the two reactions, we found that a long reaction pathway;



has been concluded to be the chain branching process, which enables the spontaneous ignition of phosphine at room temperature.

#### VIII-A-6 Semiclassical Study of Nonintegrable Systems

TAKAMI, Toshiya

We study nonadiabatic processes in highly excited states of molecules. Although a lot of theoretical works have been published on the subject so far, many of the authors have considered the problem under assumption that avoided crossings are sufficiently small. In the highly excited states, however, the assumption is not always validated. A new approach is desirable in order to study dynamical processes in systems with many levels interacting each other.

Our approach for the problem starts from studying systems with boundaries in the parameter space. We showed that the transition probability in adiabatic limit is dominated by an extra transition on the boundaries, which comes from nonadiabatic couplings between adiabatic states. We also found an iterative method to define a new base in which the extra transition is suppressed and the transition by avoided crossings can be observed locally. The new base can be used to analyze nonadiabatic processes of not only two level systems but also many level ones.

Our final goal is to construct a new framework for investigating many level nonadiabatic transition in realistic systems by using the new base instead of the usual adiabatic or diabatic base, as well as to develop

the higher order asymptotic theories in nonintegrable dynamical systems.

#### VIII-A-7 A Theoretical Study on Structures and Vibrational Spectra of C<sub>84</sub> Fullerene Isomers

NISHIKAWA, Takeshi; KINOSHITA, Tomoko; NANBU, Shinkoh; AOYAGI, Mutsumi

[*J. Mol. Struct. (THEOCHEM)* **461-462**, 453 (1999)]

The C<sub>2</sub>, D<sub>2</sub>, and D<sub>2d</sub> isomers of C<sub>84</sub> fullerene were investigated by *ab initio* molecular orbital calculations. Optimized geometries, relative stabilities, and vibrational spectra of eleven isomers are determined by restricted Hartree-Fock (RHF) calculations with STO-3G, 3-21G, and D95V basis sets. For the purpose of an assignment on the C<sub>84</sub> structures, we discussed a way to distinguish a specific isomer by comparing the calculated vibrational spectra.

We found that the peaks located at higher than 1300 cm<sup>-1</sup> are all belonging to the on-surface mode where each carbon atom moves on the surface of C<sub>84</sub> skeleton. On the other hand, the peaks below 1000 cm<sup>-1</sup> correspond to the breathing mode, in which atoms are moving perpendicularly to the surface. There exists a window region (around 1000–1300 cm<sup>-1</sup>) in all calculated spectra, which split a character of normal mode vibrations. In D<sub>2</sub> symmetry, the vibrational spectra of isomer No. 1 has a noticeable difference in the locations of three main peaks. The isomer No. 2 with C<sub>2</sub> symmetry also has characteristic vibrational structure, where numbering scheme introduced by Fowler *et al.* is used. For the rest of other isomers examined, it was hard to clearly predict the structure solely with calculated vibrational spectra. We suggested that the difference in the bands around 650 cm<sup>-1</sup> and 1670 cm<sup>-1</sup> can be used as a finger print of D<sub>2</sub> isomers, and that the vibrational bands below 900 cm<sup>-1</sup> and peak around 1880 cm<sup>-1</sup> can be used to distinguish C<sub>2</sub> species.