VIII-Y Theoretical Studies on Electronic Structure and Dynamics of Electronically Excited States

VIII-Y-1 Chemical Reactions in the O(^{1}D) + HCl System I. *Ab Initio* Global Potential Energy Surfaces for the 1^1A', 2^1A', and 1^1A" States

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New global *ab initio* potential energy surfaces (PES) are presented for the low-lying 1^1A', 2^1A', and 1^1A" electronic states which are correlated to O(^{1}D) + HCl. These potential energy surfaces are computed by using the multi-reference configuration interaction method with the Davidson correction (MRCI + Q). The reference functions are constructed by the complete active space self-consistent field (CASSCF) calculations using the quadruple zeta + polarization basis set augmented with diffuse functions. The computations are carried out at about 5000 molecular conformations on each three-dimensional potential energy surface. The high accuracy of the computations is confirmed by a comparison with the available most accurate data for the ground state 1^1A'; thus the present work is the first report of the accurate potential energy surfaces for the two excited states. Three low-lying transition states on the excited surfaces, two (TS2 and TS4) on 1^1A" and one (TS3) on 2^1A', are found. Since TS2 and TS3 are as low as 0.07 eV and 0.28 eV, respectively, and correlated to the OH($^2\Pi$) + Cl(^{2}P) product, these excited surfaces are expected to play quite important roles in the reaction dynamics. Possible effects of non-adiabatic couplings among the three PESs are also briefly discussed, although the non-adiabatic couplings have not yet been estimated. The quantum reaction dynamics on these three PESs are discussed in the second and third accompanying paper.

In the present work, we have determined new global three ab initio potential energy surfaces accurately; and furthermore quantum wave packet dynamics calculations have been carried out to obtain the total reaction probabilities. The reaction probability for HCl(v = 0, j = 0) shows that the OH + Cl product channel *via* the 1^1A" state should be opened at the lower collision energy than E_{coll} = 0.529 eV, while the channel *via* 2^1A' should be closed. Although there was the discrepancy between previous theoretical works and experimental results, it was explained by our works including the electronic excited states.

VIII-Y-2 Millimeter-Wave Spectroscopy of the Internal-Rotation Band of the He–HCN Complex and the Intermolecular Potential Energy Surface

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Millimeter-wave absorption spectroscopy combined with a pulsed-jet expansion technique was applied to the measurement of the internal-rotation band of the He–HCN in the frequency region of 95–125 GHz. In total 13 rovibrational lines, split into nitrogen nuclear hyperfine structure, were observed for the fundamental internal-rotation band, j = 1–0. The observed transition frequencies were analyzed including their hyperfine splitting to yield an intermolecular potential energy surface, as improved from the one given by a coupled-cluster single double (triple) *ab initio* calculation. The surface obtained has a global minimum in the linear configuration (He···H–C–N) with a well depth of 30.2 cm^{-1}, and the saddle point located in the anti-linear configuration (H–C–N···He) is higher by 8.174 cm^{-1} in energy than the global minimum. The distance R_m between the He atom and the center of mass of HCN along the minimum energy path shows a strong angular dependence; R_m = 4.169 Å and 4.040 Å in the linear and anti-linear forms, respectively, while it is 3.528 Å in a T-shaped configuration. In the first excited internal-rotation state (j = 1), levels with l less than 4 are bound but not for the one with l = 5, according to the energy level diagram calculated from the present potential energy surface, where l denotes the quantum number for the end-over-end rotation of the complex. The energy level diagram is consistent with the millimeter-wave observation, in which the Δl = 0 transitions with l = 0 ~ 4 were observed but not for those with l equal to or greater than 5. The band origin of the internal-rotation band, 98.70 GHz, as defined to be the same as the frequency of the *R*(*0*) transition, is larger by 11% than the J = 1–0 rotational transition frequency of the free HCN molecule.

VIII-Y-3 Determination of the Global Potential Energy Surfaces and Transition Wave Packet Dynamics for Polyatomic Systems

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Computational algorithm for the determination of the global potential energy surfaces of polyatomic systems are developed with using the interpolant moving least squares scheme, which was proposed by Ishida and Schatz [*Chem. Phys. Lett.* **314**, 369 (1999)]. In this scheme, any derivatives in quantum-chemical calculations are not required to construct the surface and in contrast with previously developed schemes based on Shepard interpolation alone. In our new algorithm, the molecular conformations are generated with the Monte

Carlo sampling, and then the *ab initio* calculations for all of the conformations are performed by parallel computing. Therefore, we have good advantage for computational time for the serial calculations. Application is made to the tetra-atomic systems, the 2OH ↔ H_2O + O reaction.

Regarding to the wave packet dynamics, we are also developing the program code based on the MPI-library to make a time-evolution of the wave packet for the tetra-atomic systems.

VIII-Y-4 *Ab Initio* Study of Conformers of *p-tert*-Butylcalix [4] Crown-6-Ether Complexed with Alkyl Ammonium Cations

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The structures and energies of *p-tert*-butylcalix[4]-crown-6-ether (1) in various conformers and their alkyl ammonium complexes have been calculated by *ab initio* HF/6-31G quantum mechanics method. We have tried to obtain the relative affinity of partial-cone and 1,3-alternate conformers of 1 for alkyl ammonium guests by comparison with its cone-shaped analogue. We have also calculated the relative complexation efficiency of these host-guest complexes focusing on the binding sites of crown-6-ether moiety or benzene-rings pocket of the host molecule 1. These calculations revealed that the crown moiety has better complexation efficiency than upper rim part of calix[4]arene that is in similar trend to the cone-shaped complexes.

VIII-Y-5 *Ab Initio* Study of the Complexation Behavior of Calix[5]arene Derivative toward Alkyl Ammonium Cations

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The structures and complexation energies of penta-O-alkylated 1b and penta-O-tert-butyl ester 1e of p-tert-butylcalix[5]arene and its simplified structures (2b and 2e) toward a series of alkyl ammonium guests have been calculated by semi-empirical AM1 quantum mechanics method. For AM1 calculation, complexation efficiencies of the simplified host 2e are very similar to the values of host 1e. The complexes of simplified host 2e with alkyl ammonium ions have been also optimized by ab initio HF/6-31G quantum mechanics method. The calculated complexation efficiencies for 2e by *ab initio* method have been found to be bigger in magnitude than the values obtained by AM1 calculations for linear alkyl ammonium guests. Calculation results show that all of the calix [5] aryl derivatives investigated in this study have much better complexation ability toward ammonium cation without alkyl group over other alkyl ammonium guests. *Ab initio* calculations also well duplicate the molecular discriminating behaviors of calyx [5] arene derivative 2e between butyl ammonium ions: *n*-$BuNH_3^+$ > *iso*-$BuNH_3^+$ > *sec*-$BuNH_3^+$ > *tert*-$BuNH_3^+$.

VIII-Y-6 Formation of $HCl^+(A^2\Sigma^+)$ and $HBr^+(A^2\Sigma^+)$ Resulting from $He(2^3S)$ Penning Ionization of HCl and HBr

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$He(2^3S)$ Penning ionization of HCl and HBr leading to $HCl^+(A)$ and $HBr^+(A)$ has been studied optically by using a crossed-beam apparatus. The ratios of the vibrational population, $P_{v'}/P_v(v' = 2$ and 3) of $HCl^+(A)$ and P_1/P_0 of $HBr^+(A)$, increase with the collision energy in the region of 120–200 meV. The rotational distributions of $HCl^+(A,v' = 0)$ and $HBr^+(A,v' = 0)$ can be represented by a double-Boltzmann distribution; the temperatures are 200 ± 50 and 700 ± 80 K for $HCl^+(A,v' = 0)$ and 250 ± 50 and 1200 ± 200 K $HBr^+(A)$, and are nearly independent of the collision energy. The model potential surface for He*(Li) + HCl as the entrance channel is nearly isotropic and shows a shallow dip of about 20 meV, while the surface for He + $HCl^+(A)$ as the exit channel is anisotropic and shows a deep minimum of 250 meV in the He–H–Cl collinear direction. These results suggest that at least two processes contribute to formation of these ions; one is the direct Penning ionization and the other is the formation via a temporary complex $[HeHCl(A)]^+$ by orbiting.

VIII-Y-7 Theoretical Study of Vibrational States for AlNC/AlCN

MINAMINO, Satoshi; NANBU, Shinkoh; AOYAGI, Mutsumi

The character of the low-lying electronic states of AlNC strongly depends on the bond distance of Al-NC, because the covalent states are lying closely to the ionic states. Especially, due to the electronic ground state having the ionic character, the bending vibrational motion has a quite strong anharmonicity, and the motion is characterized as a large amplitude motion (LAM). Therefore, in general, the observed spectrum has the complicated vibronic structures and it is difficult to understand the molecular conformation having the LAM. In this study, we determined the global potential energy surfaces of the electronic ground state for the isomerization of AlNC/AlCN, and we elucidated the molecular structure of the complicated vibronic states by solving the exact Schrödinger equation for the nuclear motion.

VIII-Y-8 Boundary Expansion in Time-Dependent Nonadiabatic Problems

TAKAMI, Toshiya

Time-dependent nonadiabatic transitions were studied as an initial value problem in a finite parameter range. We introduced "boundary expansion" by expanding Schrödinger's equation around end points of the parameter. We have shown that extra transitions emerge at the points, and are explained by the terms of the expansion. We have also shown that Berry's superadiabatic base is naturally defined through the expansion. By the use of the superadiabatic base, we performed numerical analysis of multi-level non-adiabatic transitions in systems with a random matrix Hamiltonian.

VIII-Y-9 Optimal Control of Random Matrix Systems with a Parameter

TAKAMI, Toshiya; FUJISAKI, Hiroshi

We studied control of chaotic quantum systems by applying Optimal Control Theory (OCT) to random matrix Hamiltonian systems with a parameter. For simple two-state problems, we have shown that the optimized field obtained by OCT can be classified into several types: (i) oscillating one with a frequency which agrees with the energy split between the inital and the final state; (ii) one which mainly uses transition between diabatic states at an avoided crossing; (iii) one which can be seen as nonadiabatic transition, etc. Although the oscillating solution is always obtained even in many level systems if the final time is large enough, it is difficult to distinguish other types of solution in short time.

We have shown that the distribution of the optimized solutions for short time is affected by dynamical properties of the system. In particular, we examined influence of the strength of chaos or complexity of the system. We have also studied systems with banded random elements.