

Computer Center

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

VIII-L-1 Quantum Reactive Scattering Calculations of the $O(^1D) + HCl$ Reaction Using the Global *ab initio* Potential Energy Surfaces of Electronic Excited States

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The $O(^1D) + HCl(^1\Sigma^+)$ reaction is quite important due to the significant role in stratospheric chemistry. The reaction is correlated with five electronic states, and there are two product channels, $OH(^2\Pi) + Cl(^2P)$ and $ClO(^2\Pi) + H(^2S)$ if its spin-symmetry is kept. Up to now, *ab initio* calculations of the ground PES and quantum wave packet calculations have been carried out along that surface, although at least three electronic potential energy surfaces are involved in this reaction.

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-L-2 Millimeter-Wave Spectroscopy of the Internal-Rotation Band of the He–HCN Cluster and Determination of the Empirical Intermolecular Potential Energy Surface

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Millimeter-wave absorption spectroscopy was applied to the measurement of the internal-rotation band of the He–HCN cluster 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, $j = 1-0$.

In order to determine the empirical intermolecular potential energy surface (PES), the potential parameters were optimized by the Newton-Raphson method; the exact Schrödinger equation for the weakly bound

complex was solved, and then the derivatives were evaluated. The obtained PES has a global minimum in the linear configuration ($He \cdots H-C-N$) with a well depth of 27.827 cm^{-1} , and the saddle point located in the anti-linear configuration ($H-C-N \cdots He$) is higher in energy than the global minimum by 8.174 cm^{-1} . The distance R_m from the He atom to the center of mass of HCN along the minimum energy path shows a large angular dependence; $R_m = 4.211$ Å and 4.104 Å in the linear and anti-linear forms, respectively, and has a minimum value of 3.513 Å in a T-shaped configuration. The rovibrational energies calculated from the empirical PES suggest that the cluster will dissociate at $l = 5$ in the first excited internal-rotation state, $j = 1$, where l denotes the quantum number for the end-over-end rotation of the cluster. This is consistent with the millimeter-wave observation of sudden disappearance of the first excited state of the intermolecular stretching vibration is located just below the dissociation limit, -0.202 cm^{-1} .

VIII-L-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 $2OH \leftrightarrow H_2O + O$ 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-L-4 *Ab Initio* Study of p-tert-Butylcalix[4]crown-6-ether Complexed with Alkyl Ammonium Cations

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The conformations and energies of *p*-tert-butylcalix[4]crown-6-ether (**1**) and its alkyl ammonium complexes have been calculated by *ab initio* (6-31G) quantum mechanics method. The cone conformation was found to be most stable for free host **1**. We have determined the binding site of these host-guest complexes focusing on the crown-6-ether or *p*-tert-butylcalix[4]arene pocket of the cone conformation of host molecule **1**. The primary binding site of host **1** for the recognition of alkyl ammonium guests was confirmed to be the central part of the crown moiety of cone conformation. The complexation energy calculations revealed that the ammonium cation without alkyl group showed the better complexation efficiency when combined with host **1**, that is in satisfactory agreement with the experimental results.

VIII-L-5 Nonadiabatic Process in Nonintegrable Quantum Systems

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We study nonadiabatic processes in classically nonintegrable systems. We have shown that extra-transitions arise from nonadiabatic couplings between eigenstates on the endpoints, and that, paradoxically, the usual adiabatic base is useless in the adiabatic limit to observe Landau-Zener transition. In order to describe the extra-transition theoretically, we introduce "boundary expansion" to obtain higher order terms of the nonadiabatic couplings. By the use of the expansion, we construct a new base which can describe non-adiabatic transition locally even in nonintegrable systems. This base is shown to be an extension of the superadiabatic base which is known as an asymptotic approximation of the exact solution. While our approach above is only for simple time-dependent nonadiabatic systems, we consider in the next applying the super-adiabatic analysis to chemical reactions. In order to analyze nonadiabatic processes on molecules in the adiabatic limit, we introduce the phase-space analysis through the method of the adiabatically renormalized Hamiltonian.

VIII-L-6 Theoretical Study of Endohedral Metalofullerene La@C₇₆

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Endohedral metallofullerenes have attracted interests as new molecules having novel properties. We have carried out DFT calculation to get information on cage structure of La@C₇₆. Two IPR satisfying structures with T_d and D₂ symmetries are possible for C₇₆ cage, while it has known from the ¹³C NMR that empty C₇₆ has D₂ symmetry. The result of geometry optimizations showed

that La@C₇₆ with T_d-cage is more stable. Theoretical IR spectrum of D₂-C₇₆ reasonably reproduced experimental one of sublimed C₇₆ films, although it was difficult to compare it with our measured IR spectra in CS₂.

VIII-L-7 Formation of HCl⁺ (A²Σ⁺) and HBr⁺ (A²Σ⁺) Resulting from He (2³S) Penning Ionization of HCl and HBr

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He (2³S) 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.