Computer Center

VIII-HH Computer Simulation of Quantum Systems in Condensed Phase

VIII-HH-1 An Analysis of Molecular Origin of Vibrational Energy Transfer from Solute to Solvent Based upon Path Integral Influence Functional Theory

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Molecular process of vibrational energy relaxation of CN^- ion in the aqueous solution has been investigated based upon path integral influence functional theory. In order to obtain a molecular-based picture, bath normal coordinates were retransformed to Cartesian coordinate, Eulerian coordinate, and intramolecular vibrational coordinate of the solvent molecule. Then, based upon this retransformation matrix, coupling of the solute with the normal modes may be assigned to the couplings with the solvent molecules. Further, with respect to two-phonon process which is dominant in the relaxation of the present system, the relaxation may be divided into single- and dual-molecular processes. We show that the single-molecular relaxation is dominant in the relaxation. Further, water molecules in the first hydration shell play an essential role in the relaxation, whereas the solvent molecules outside the first hydration shell make little contribution. The solvent molecules located in the direction of CN^- bond axis were found to make great contribution to the relaxation.

VIII-HH-2 Mixed Quantum-Classical Molecular Dynamics Study of Vibrational Relaxation of CN^- Ion in Water: An Analysis of Coupling as a Function of Time

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Mixed quantum-classical molecular dynamics method has been applied to vibrational relaxation of CN^- in water. The calculated relaxation time was in good agreement with that based upon Fermi’s golden rule with classical interaction. Flexible water model adopted here enhanced the relaxation rate by a factor of about 5 compared with the rigid rotor model. This supports our previous result of path integral influence functional theory that intramolecular bending of water plays an essential role in the relaxation. Time-dependent interaction between the solute vibrational degree of freedom and the solvent water shows random-noise-like behavior, no collisional or stationary coupling observed in gas or solid, respectively, being found in the liquid. The interaction has been analyzed in detail defining the effective coupling for the relaxation. The relaxation mechanism in the liquid may be described by a variety of effective couplings, *i.e.*, relaxing and exciting as well as strong and weak, which arise successively as a function of time.

VIII-II Molecular Dynamics Study of Classical Complex Systems

VIII-II-1 A Molecular Dynamics Study of Single Molecular Manipulation by AFM Cantilever—Mechanical Extension of Polyalanine—

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Potential of mean force of polyalanine in water has been calculated as a function of molecular length by molecular dynamics calculations simulating mechanical extension of the molecule by AFM cantilever. When the molecule keeps alpha helix structure, it behaves like a spring following Hooke’s law. After the helix is broken, the force becomes large with increasing extension. Hydrophobic interaction and conformational entropy must play an important role for this force-extension curve. At the extension of about 100%, the force curve rises sharply, showing the increase of molecular bending energy of all trans conformation.

VIII-JJ Development of Simulation Algorithms for Quantum Many-Body Systems

VIII-JJ-1 Path Integral Hybrid Monte Carlo Algorithm for Correlated Bose Fluids

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Path integral hybrid Monte Carlo (PIHMC) algorithm for strongly correlated Bose fluids has been developed. This is an extended version of our previous method applied to a model system consisting of non-interacting bosons. Our PIHMC method for the correlated Bose fluids is constituted of two trial moves to sample path-variables describing system coordinates along imaginary time and a permutation of particle labels giving a boundary condition with respect to imaginary time. The path-variables for a given permutation are generated by a hybrid Monte Carlo method based on path integral molecular dynamics techniques. Equations of motion for the path-variables are formulated on the basis of a collective coordinate representation of the path, staging variables, to enhance the sampling efficiency. The permutation sampling to satisfy Bose-Einstein statistics is performed using the multilevel Metropolis method developed by Ceperley and Pollock. Our PIHMC method has successfully been applied to liquid helium-4 at a state point where the system is in a superfluid phase. Parameters determining the sampling efficiency are optimized in such a way that correlation among successive PIHMC steps is minimized.

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

VIII-KK-1 Millimeter-Wave Spectroscopy of the Internal-Rotation Band of the X-HCN Complex (X = He, Ne, and Ar) 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 X-HCN (X = He, Ne, and Ar) in the frequency region of 95–125 GHz. 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. Regarding the He complex, 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. The energy level diagram is consistent with the millimeter-wave observation. And now, we are trying to measure the stretching motion located just below the dissociation limits.

VIII-KK-2 Theoretical Study of Vibrational Spectra of *p*-Tert-Butylcalix[4]crown-6-Ether Complexed with Ethyl Ammonium Cations

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Theoretical infrared (IR) absorption spectra were calculated for *p-tert*-butylcalix[4] crown-6-ether (1) in the cone conformer and its ethyl ammonium complex. The IR spectra were obtained by restricted Hartree-Fock (RHF) calculations with the 6–31 G basis set. For the purpose of an absorption band assignment on the host molecule, guest molecule, and complexes thereof, we discussed a way to distinguish a specific molecule by comparing the calculated vibrational spectra. The theoretical result for the host molecule and its ethyl ammonium complex were preliminarily compared with the experimental result, and found that the calculated result agrees well with the features of the experimental spectra.

VIII-KK-3 He*(2^3S) Penning Ionization of H_2S I. Theoretical Franck-Condon Factors for the $H_2S(X^1A_1, v' = 0) \rightarrow H_2S^+ (X^2B_1, A^2A_1)$ Ionization and the H_2S^+ (A-X) Transitions

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

In order to elucidate the ionization dynamics, in particular the vibrational distribution, of $H_2S^+(\tilde{A})$ produced by the Penning ionization of H_2S with He*(2^3S) atoms, the Franck-Condon factors (FCFs) were presented for the $H_2S(\tilde{X}) \rightarrow H_2S^+(\tilde{X}, \tilde{A})$ ionization and the $H_2S^+(\tilde{A}–\tilde{X})$ transition, and Einstein's A coefficients were presented for the latter transition. The FCFs were obtained by quantum vibrational calculations using the global potential energy surfaces (PESs) of $H_2S(\tilde{X}\,^1A_1)$ and $H_2S^+(\tilde{X}\,^2B_1, \tilde{A}\,^2A_1, \tilde{B}\,^2B_2)$ electronic states. The global PESs were determined by the multi-reference configuration interaction calculations with the Davidson correction (MRCI+Q) and the interpolant moving least squares (IMLS) method combined with the Shepard interpolation. The obtained FCFs exhibit that the $H_2S^+(\tilde{X})$ state primarily populates the vibrational ground state since its equilibrium geometry is almost equal to that of $H_2S(\tilde{X})$, while the bending mode (ν_2) is strongly enhanced for the $H_2S^+(\tilde{A})$ state; the maximum in the population is around v_2 = 6–7. In the same manner, the bending progressions are expected to consist of the great part of the $H_2S^+(\tilde{A}–\tilde{X})$ emission. A detailed comparison with the experimental study for this system is reported in the accompanying paper, Paper II.

VIII-KK-4 He*(2^3S) Penning Ionization of H_2S II. Formation of $SH^+(A^3\Pi)$ and H_2S^+ (A^2A_1) Ions

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

Emissions in the 200–750 nm region produced by the collision of He(2^3S) with H_2S were studied under single-collision conditions. The hydrogen Balmer lines and the $SH^+(A^3\Pi–X^3\Sigma^-)$ and $H_2S^+(\tilde{A}^2A_1–\tilde{X}^2B_1)$ bands were assigned. The total emission cross section (σ_{em}) was evaluated to be $(1.7 \pm 0.3) \times 10^{-20}$ m^2 at a collision energy of 150 meV. The σ_{em}'s of the $SH^+(A–X)$ and $H_2S^+(\tilde{A}–\tilde{X})$ bands decreased with increase in the collision energy in the 115–200 meV range, indicating that attractive forces are effective for the incident channels with regard to the formation of these species. The rotational distribution of $SH^+(A^3\Pi, v' = 0)$ is represented by a Boltzmann temperature of 870 ± 80 K. The $H_2S^+(\tilde{A}^2A_1–\tilde{X}^2B_1)$ emission, which was assigned for the first time in the Penning ionization of H_2S, primarily consists of the bending progressions. The internal populations of $H_2S^+(\tilde{A})$ were analyzed using the vibrational energies and Einstein's *A* coefficients calculated in this study. The details of the calculation and derived spectroscopic constants are reported in the accompanying paper, Paper I. The populations obtained for the bending vibration (ν_2') of $H_2S^+(\tilde{A})$ show an inverted distribution with a peak at $v_2' = 3$. This distribution is shifted lower compared that with a peak at $v_2' = 4–5$ observed by He(2^3S) Penning ionization electron spectroscopy and that with a peak at $v_2' = 6–7$ predicted by the theoretical Franck-Condon factors (FCFs) for the $H_2S(\tilde{X})$–$H_2S^+(\tilde{A})$ ionization. The origin of the difference is discussed concerning the formation mechanism of $H_2S^+(\tilde{A}^2A_1)$.

VIII-KK-5 Theoretical Analysis of the Oxygen Insertion Process in the Oxidation Reactions of H_2O + H/Si(100) and 2H + H_2O/Si(100); Calculation of an Ab Initio Molecular Orbital Method and an Analysis of the Tunneling Reaction

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[*Chem. Phys. Lett.* submitted]

The reaction paths were analyzed, by an ab initio molecular orbital method, for the surface reaction systems, 2H + H_2O/Si(100)-(2×1) and H_2O + H/Si(100)-(2×1), in which SiH_2 species with one or two oxygen atom-inserted back bonds have been observed as new stable reaction products. It was found that common metastable states exist in both systems, and the initial energy is sufficiently higher than all transition state energies in the former system, while in the latter system, the energy of the highest transition state is much higher than the initial energy, and thus a tunneling effect plays an important role.

VIII-KK-6 Optimal Control of Quantum Chaotic Dynamics

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We numerically investigate how chaos affects controllability of wavepacket dynamics using the monotonically convergent method of optimal control theory introduced by Zhu, Bonita, and Rabitz [*J. Chem. Phys.* **108**, 1953 (1998)]. We find that a quantized kicked rotor in a bounded phase space is successfully controlled with the method, *i.e.*, an initial Gaussian wavepacket can be steered to a target Gaussian wavepacket with a high probability, even in strongly chaotic regions when the target time T is larger than a minimal time $T_{\min}$. We also find that $T_{\min}$ saturates to a certain value as the system becomes a random matrix system.