VII-F Theoretical Studies on Electronic Structure and Dynamics of Electronically Excited States

VII-F-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

HARADA, Kensuke[1]; TANAKA, Keiichi[1]; TANAKA, Takehiko[1]; NANBU, Shinkoh
([1]Kyusyu Univ.)

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 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.

VII-F-2 Ab Initio Study of the Complexation Behavior of *p*-Tert-Butylcalix[5]arene Derivative toward Alkyl Ammonium Cations

CHOE, Jong-In[1]; LEE, Sang Hyun[1]; OH, Dong-Suk; CHANG, Suk-Kyu[1]; NANBU, Shinkoh
([1]Chung-Ang Univ.)

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The structures and complexation energies of penta-O-tert-butyl ester of *p*-tert-butylcalix[5]arene toward a series of alkyl ammonium guests have been optimized by ab initio HF/6-31G method. The calculated complexation efficiencies of the ester for alkyl ammonium guests have been found to be similar to the values of previously reported debutylated-calix[5]arene. Calculation results show that both of the calyx[5]aryl alkyl ammonium guests. The structural characteristics of the calculated complexes are discussed as a function of the nature of the alkyl substituents of the ammonium guests.

VII-F-3 Theoretical Transition Probabilities for the $\tilde{A}\ ^2A_1$–$\tilde{X}\ ^2B_1$ System of H_2O^+ and D_2O^+ and Related Franck-Condon Factors Based on Global Potential Energy Surfaces

TOKUE, Ikuo[1]; YAMASAKI, Katsuyoshi[1]; NANBU, Shinkoh
([1]Niigata Univ.)

In order to elucidate the ionization dynamics, in particular the vibrational distribution, of $H_2O^+(\tilde{A})$ produced by the photoionization and the Penning ionization of H_2O and D_2O with $He^*(2^3S)$ atoms, the Franck-Condon factors (FCFs) were presented for the $H_2O(\tilde{X}) \rightarrow H_2O^+(\tilde{X},\tilde{A})$ ionization and the transition probabilities were presented for the $H_2O^+(\tilde{A}–\tilde{X})$ system. The FCFs were obtained by quantum vibrational calculations using the three-dimensional potential energy surfaces (PESs) of $H_2O(\tilde{X}\,^1A_1)$ and $H_2O^+(\tilde{X}\,^2B_1, \tilde{A}\,^2A_1, \tilde{B}\,^2B_2)$ electronic states. The global PESs were determined by the multi-reference configuration interaction calculations with the Davidson correction and the interpolant moving least squares method combined with the Shepard interpolation. The obtained FCFs exhibit that the $H_2O^+(\tilde{X})$ state primarily populates the vibrational ground state since its equilibrium geometry is almost equal to that of $H_2O(\tilde{X})$, while the bending mode (ν_2) is strongly enhanced for the $H_2O^+(\tilde{A})$ state; the maximums in the population of H_2O^+ and D_2O^+ are around ν_2 = 11–12 and 15–17, respectively. These results are consistent with the distributions observed by photoelectron spectroscopy. Transition probabilities for the $\tilde{A}–\tilde{X}$ system of H_2O^+ and D_2O^+ show that the bending progressions consist of the great part of the $\tilde{A}–\tilde{X}$ emission and that combination bands from the (1, ν_2' = 4–8, 0) state are next important.

VII-F-4 Analysis of the Ultraviolet Absorption Cross Sections of Six Isotopically Substituted Nitrous Oxide Specie Using 3D Wavepacket Propagation

NANBU, Shinkoh; JOHNSON, Matthew S.[1]
([1]Univ. Copenhagen)

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The ultraviolet absorption cross sections of six isotopically substituted nitrous oxide species ($^{14}N^{14}N^{16}O$, $^{14}N^{14}N^{17}O$, $^{14}N^{14}N^{18}O$, $^{14}N^{15}N^{16}O$, $^{15}N^{14}N^{16}O$, and $^{15}N^{15}N^{16}O$) were computed using the wavepacket propagation technique to explore the influence of excited state dynamics, transition dipole surface and initial vibrational state. Three-dimensional potential energy surfaces for the electronic states of N_2O related to the experimentally observed photoabsorption between 170 and 220 nm were calculated using the *ab initio* molecular orbital (MO) configuration interaction (CI) method. The transition dipole moment surfaces between these states were also calculated. Numerous wave packet simulations were carried out and used to calculate the temperature-dependent photodissociation cross sections of the six isotopically substituted species. The photolytic isotopic fractionation constants determined using the calculated cross sections are in good agreement with recent experiments. The results show that in addition to the effect of the changed shape of the ground state vibrational wavefunction with isotopic substitution, photodissociation dynamics play a central role in determining isotopic fractionation constants.

VII-F-5 Coarse-Grained Picture for Controlling Quantum Chaos

TAKAMI, Toshiya; FUJISAKI, Hiroshi[1]; MIYADERA, Takayuki[2]
([1]Boston Univ.; [2]Tokyo Univ. Sci.)

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We propose a coarse-grained picture to analyze control problems for quantum chaos systems. Using optimal control theory, we first show that almost perfect control is achieved for random matrix systems and a quantum kicked rotor. Second, under the assumption that the controlled dynamics is well described by a Rabi-type oscillaion between unperturbed states, we derive an analytic expression for the optimal field. Finally we numerically confirm that the analytic field can steer an initial state to a target state in random matrix systems.

VII-F-6 Coarse-Grained Picture for Controlling Complex Quantum Systems

TAKAMI, Toshiya; FUJISAKI, Hiroshi[1]
([1]Boston Univ.)

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We propose a coarse-grained picture to control complex quantum dynamics, *i.e.*, multi-level-multi-level transition with a random interaction. Introducing a Rabi-like-oscillating state between two time-dependent states, we derive an analytic optimal field as a solution to optimal control theory. For random matrix systems, we numerically confirm that the analytic optimal field actually steers an initial state to a target state, which both contain many eigenstates.