

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

VII-F-1 Encapsulation of Hydrogen Atoms by Fullerenes and Carbon Nanotubes with the Use of Nonadiabatic Transition

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An aggressive usage of the non-adiabatic phenomenon is proposed. In this proposal, atomic hydrogen is encapsulated by the transmission through five-membered rings of fullerenes with the help of the non-adiabatic tunneling phenomenon. Cyclopentadienyl radical (C₅H₅) and corannulene (C₂₀H₁₀) are used to model a pentagonal moiety of fullerenes. To demonstrate the proposal, the first principles calculations are performed for the non-adiabatic dynamics on the potential energy surfaces determined by multi-reference configuration interaction (MRCI) method. The results show that the non-adiabatic transitions between ground and excited states essentially control the hydrogen atom transmission through the five-membered ring of corannulene. This transmission is found to occur more than once out of four incidences when the five carbons which surround the five-membered ring are replaced by borons. This phenomenon can be interpreted in terms of the Zhu-Nakamura semiclassical theory of non-adiabatic transition.

VII-F-2 Ab Initio Calculated Structures of Conformers for 1,3-Dimethoxy-p-tert-Butylcalix[4] Crown-5-Ether Complexed with Potassium Cation

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Stable molecular conformations were calculated for the 1,3-dimethyl ether of p-tert-butylcalix[4]crown-5-ether (**1**) in the various conformers and their potassium-ion complexes. The structures of three distinct conformation have been optimized using ab initio RHF/6-31G methods. After geometry optimizations, B3LYP/6-31+G(d,p) single point calculations of the final structures are done to include the effect of electron correlation and basis set with diffuse function and polarization function. Relative stability of free host **1** is in following order: cone (most stable) > partial-cone > 1,3-alternate conformer. For two different kinds of complexation mode, the potassium cation in the crown-5-ether moiety (*cr*) has much better complexation efficiency than in the benzene-rings (*bz*) pocket for all three kinds of conformation of host molecule **1**. The relative stability of complex (**1** + K⁺) in the *cr*-binding mode is in following order: cone ~ 1,3-alternate > partial-cone conformer.

VII-F-3 Theoretical Transition Probabilities for the $\tilde{A}^2A_1-\tilde{X}^2B_1$ System of H₂O⁺ and D₂O⁺ and Related Franck-Condon Factors Based on Global Potential Energy Surfaces

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In order to elucidate the ionization dynamics, in particular the vibrational distribution, of H₂O⁺(\tilde{A}) produced by the photoionization and the Penning ionization of H₂O and D₂O with He*(2³S) atoms, the Franck-Condon factors (FCFs) were presented for the H₂O(\tilde{X}) → H₂O⁺(\tilde{X} , \tilde{A}) ionization and the transition probabilities were presented for the H₂O⁺($\tilde{A}-\tilde{X}$) system. The FCFs were obtained by quantum vibrational calculations using the three-dimensional potential energy surfaces (PESs) of H₂O(\tilde{X}^1A_1) and H₂O⁺(\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 H₂O⁺(\tilde{X}) state primarily populates the vibrational ground state since its equilibrium geometry is almost equal to that of H₂O(\tilde{X}), while the bending mode (ν_2) is strongly enhanced for the H₂O⁺(\tilde{A}) state; the maximums in the population of H₂O⁺ and D₂O⁺ are around $\nu_2 = 11$ –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 H₂O⁺ and D₂O⁺ show that the bending progressions consist of the great part of the $\tilde{A}-\tilde{X}$ emission and that combination bands from the (1, $\nu_2' = 4$ –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

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The ultraviolet absorption cross sections of six isotopically substituted nitrous oxide species (¹⁴N¹⁴N¹⁶O, ¹⁴N¹⁴N¹⁷O, ¹⁴N¹⁴N¹⁸O, ¹⁴N¹⁵N¹⁶O, ¹⁵N¹⁴N¹⁶O, and ¹⁵N¹⁵N¹⁶O) 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 N₂O 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 Theoretical Study of the Oxidation Reaction for the H Atom-Induced Water-Terminated Si Surface $2\text{H}+\text{H}_2\text{O}/\text{Si}(100)-(2\times 1)$

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The reported oxidation reaction observed by BML-IRRAS spectra on the silicon surface system, $2\text{H} + \text{H}_2\text{O}/\text{Si}(100)$, has been studied by an *ab initio* molecular orbital method. The highest transition state is found at $\approx +25$ kJ/mol from the reactant energy level, and the oxidation occurs easily under the experimental condition. The present study also accounts for the reactivity deduced from the absorption bands in the IR spectra. It is noted that the quenching of the reaction by thermal relaxation is impossible because the surface is not trapped into the meta-stable states located much lower in energy than the reactant.