I-L Theoretical Studies of Quantum Effects in Chemical Reactions

Although the study of quantum mechanical effects in chemical reactions has its long standing history, quantitative understandings of the importance of quantum effects in reactions have not been achieved. We investigate quantum effects, tunneling, resonances, interference, and electronically nonadiabatic transitions, in simple reaction systems by means of various theoretical approaches, including quantum reactive scattering methods, semiclassical dynamical methods, and classical trajectory methods.

I-L-1 Ab Initio Calculations of Low-Lying Potential Energy Surfaces of the HHeF System

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[*Chem. Phys. Lett.* **371**, 675 (2003)]

The low-lying singlet potential energy surfaces for the HHeF system have been calculated using the ab initio electronic structure method at the multireference configuration interaction level of theory. It is found that the interaction of helium with HF($B^1\Sigma^+$) in the ion-pair electronically excited state is attractive in a wide rage of the orientation angle and that the helium atom strongly stabilize the ion-pair HHe^+F^- complex on the $3^1A'$ surface, which is asymptotically correlating to the HF($B^1\Sigma^+$) state. We also found that the electronically nonadiabatic coupling between the $1^1A'$ ground state and $3^1A'$ state plays an essential role in the topographical features of these two surfaces.

I-L-2 Photodissociation of Cl_2 in Helium Clusters: An Application of Hybrid Method of Quantum Wavepacket Dynamics and Path Integral Centroid Molecular Dynamics

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[*Chem. Phys. Lett.* **372**, 90 (2003)]

The photodissociation dynamics of Cl_2 embedded in helium clusters is studied by numerical simulation with an emphasis on the effect of quantum character of helium motions. The simulation is based on the hybrid model in which Cl–Cl internuclear dynamics is treated in a wavepacket technique, while the helium motions are described by a path integral centroid molecular dynamics approach. It is found that the cage effect largely decreases when the helium motion is treated quantum mechanically. The mechanism is affected not only by the zero-point vibration in the helium solvation structure, but also by the quantum dynamics of helium.

I-L-3 Theoretical Simulations on Photoexcitation Dynamics of the Silver Atom Embedded in Helium Clusters

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Quantum molecular dynamics simulations have been performed to study the photoexcitation $Ag(5p^2P_J) \leftarrow Ag(5s^2S_{1/2})$ in size-selected helium clusters considering electronically nonadiabatic transitions. We employed the hybrid method in which the electronic degree of freedom of $Ag(^2P)$ was treated quantum mechanically while the motions of helium atoms were described by the semiclassical path integral centroid molecular dynamics method in order to take the quantum fluctuation effect into account. It has been found that the dynamics after photoexcitation is dominantly nonadiabatic in all cluster sizes studied, and that nonadiabatic transitions are enhanced by quantum fluctuation of helium motions. Most of the photoexcited AgHen clusters decompose into an isolated Ag atom and free helium atoms within several picoseconds. However, Ag^*He_n ($n = 1 \sim 5$) exciplex formation was also found to occur for all helium cluster sizes studied, although this process is found to be minor.