

I-P 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 dynamics methods, and classical trajectory methods.

I-P-1 Quantum Scattering Calculations of the $O(^1D) + N_2(X^1\Sigma_g^+) \rightarrow O(^3P) + N_2(X^1\Sigma_g^+)$ Spin-Forbidden Electronic Quenching Collision

TAKAYANAGI, Toshiyuki
(JAERI and IMS)

[*J. Phys. Chem. A* **106**, 4914 (2002)]

Three-dimensional quantum scattering calculations have been carried out for the $O(^1D) + N_2 \rightarrow O(^3P) + N_2$ spin-forbidden electronic quenching process using a simplified collision model, in which only the lowest singlet surface and one triplet surface are taken into account. The standard close-coupling technique has been used to obtain nonadiabatic transition probabilities and the coupled-state approximation was applied to calculate the total quenching cross section. The results of the close-coupling calculations have been compared to the results of quasiclassical trajectory surface hopping method. It has been found that the trajectory surface hopping method give too large quenching probabilities compare to the quantum results, in which the quenching dynamics is exclusively resonance-dominated. Detailed analyses of the quantum results show that a curve crossing picture cannot be employed to describe the present nonadiabatic collision. The calculated quenching cross sections have been also compared to experimental data as well as previous theoretical results.

I-P-2 Translational Energy Dependence of NO + NO / $N_2 + O_2$ Product Branching in the $O(^1D) + N_2O$ Reaction: a Classical Trajectory Study on a New Global Potential Energy Surface for the Lowest $^1A'$ State

TAKAYANAGI, Toshiyuki¹; AKAGI, Hiroshi²
(¹IMS and JAERI; ²JAERI)

[*Chem. Phys. Lett.* **363**, 298 (2002)]

An analytical potential energy surface of the lowest singlet $^1A'$ state for the $O(^1D) + N_2O \rightarrow NO + NO / N_2 + O_2$ reaction has been developed on the basis of extensive ab initio electronic structure calculations at the CASPT2/cc-pVDZ level of theory within C_s constraint. A many-body expansion type function was employed to fit the calculated ab initio points. Classical trajectory calculations have been carried out using the newly developed potential energy surface. We found that the initial orientation angle significantly affect the NO +

NO / $N_2 + O_2$ product branching and the branching ratio decreases as the relative translational energy increases.

I-P-3 A CASPT2 Study of the Doublet Potential Energy Surface for the $CH(X^2\Pi) + N_2(X^1\Sigma_g^+)$ Reaction

TAKAYANAGI, Toshiyuki
(JAERI and IMS)

The $HCN_2 \rightarrow H + NCN(^3\Sigma_g^-)$ reaction, which is a key process in the $CH(^2\Pi) + N_2$ reaction mechanisms, has been studied using the ab initio electronic structure method at the CASPT2 level theory. First, we calculated two-dimensional potential energy surfaces as a function of two appropriate coordinates in order to understand overall mechanisms. Then, full-dimensional stationary point searches have been carried out using locally interpolated potential energy surfaces. Our calculations strongly support the recent proposal of Lin and co-workers that the $CH(^2\Pi) + N_2$ reaction does not yield spin-forbidden $N(^4S) + HCN$ products but yield spin-allowed $H(^2\Sigma) + NCN(^3\Sigma_g^-)$ products.