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学位申請論文

A Theoretical Study on the Electronic
Relaxation in Excited States of
Polyatomic Molecules

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Chapter 1

Introduction

The energy transfer in electronically excited states of molecules is one of the most interesting phenomena in photochemistry. Especially, the processes with no emission, i.e. nonradiative transition, affect the lifetimes of excited states of molecules and serve the starting points for the chemical reactions which rarely occur in the ground states of molecules.

The nonradiative transition has been extensively studied from the experiments in solid, liquid, and gas phases. From the experimental points of view, the existence of nonradiative transition in organic molecules is proved by the lower fluorescence quantum yield than unity and the Kasha's rule[1]. The former shows the existence of the radiationless electronic relaxation process, which is competing with the radiative transition, in the electronic excited states such as the S_1 and T_1 states. The latter rule means that the emission always originates from the lowest excited electronic states of the same multiplicity as that of the states excited by photoexcitation, independent of the exciting wavelength. This rule is accounted for by the occurrence of the fast nonradiative transition between the electronic excited states and is realized for the majority of the organic molecules.

We can also list the energy gap law[2] and the deuterium isotope effect[3] as the important features of nonradiative transition obtained from the experimental studies. The energy gap law indicates that the nonradiative transition rate decreases exponentially with the increase of the energy difference of both the considering electronic states. This is related to the Kasha's rule and is easily understood from the fact that the energy difference between the ground and the first excited states is large compared with that between the excited states. The deuterium isotope effect means that the rate constant diminishes by the deuteration of hydrogen atoms. This implies that the variation of vibrational levels remarkably affects the rate constants of nonradiative transition.

Owing to the development of experimental instruments, e.g. apparatus such as laser or supersonic jet[4], the nonradiative rate constants under the various conditions have been measured in recent years. Especially, the biexponential decay behavior of fluorescence has been observed under collision-free conditions[5] in many polyatomic molecules. These experimental results give us the information on the molecules in the intermediate case of large molecule or in the small molecule limit. The rotational effect to the nonradiative transition has been also investigated extensively in order to shed light on the mechanism of transition in the nonstatistical-limit molecules.

On the other hand, the qualitative understanding for the mechanism of these processes have been obtained theoretically using the models on the basis of the adiabatic approximation.

The qualitative theories introducing medium to elucidate the mechanism of nonradiative transition was proposed, e.g. the Robinson-Frosch theory[6]. In these theories, the medium is treated as the sink to remove the excess energy released in the nonradiative transition and the electronic energy relaxation can be described as the isoenergetic transition. However, the definite forms of the interaction were not derived in these theories. Moreover, it has been clarified that the radiationless transition could occur in isolated molecules from the experiments.

Bixon and Jortner[7] originally proposed the theory on the nonadiabatic transition in an isolated molecule. Assuming that the vibrationally excited states in the decayed electronic state are uniformly spaced and the coupling matrix elements are constant, they derived the wave functions of the molecule expressed as linear combinations of the Born-Oppenheimer adiabatic functions and showed that the probability of finding the adiabatic vibrational states in the newly formed vibrational states exhibits a Lorentzian as a function of energy. The exponential nonradiative decay was pointed out in the case of the excitation of a broad optical source in the statistical limit. They also considered the matrix elements of nonadiabatic coupling and indicated the importance of nonadiabatic Franck-Condon overlaps, which are expressed as the matrix elements of nuclear momentum operator. The Bixon-Jortner theory explains skillfully the mechanism of the radiationless transition qualitatively.

There exists a large number of theoretical studies[8],[9], devoting to the calculations of the nonradiative transition rates mostly based on the Fermi's Golden rule, which is

obtained from the time-dependent perturbation theory, to reproduce the rate constants and to construct the theory for the quantitative discussions about this process. However, the calculated rate constants from these methods, such as generating function method[8], were remarkably different from the experimental ones.

The problems in these theoretical treatments of nonadiabatic transition seem to lie in the calculations of matrix elements of interaction and the enormous number of states, consisted of rotational and vibrational states in the decayed electronic state, necessary to the calculations of Franck-Condon factors etc. and required to the description of relaxation in the dynamics calculations.

In the present thesis, the author develops a new time-dependent method using the reaction path Hamiltonian to estimate a nonadiabatic transition rate constant, in which the matrix elements of nonadiabatic coupling are evaluated from ab initio molecular orbital method based on the adiabatic approximation and the vibrational relaxation in the decayed state can be described, and apply it to the internal conversion from S_1 to S_0 state in formaldehyde.

Dynamics of the photochemical behavior of formaldehyde has received continuous interests from both the experimental and theoretical points of view in the last 30 years[10],[11]. The photochemical reaction of this molecule has been characterized by the initial radiationless transition from the S_1 to S_0 state and the subsequent dissociation into H_2+CO or $H+HCO$ fragments. The vibrational energy redistribution in highly vibrational excited states produced just after the radiationless transition process has been a subject of extensive discussion in recent years, because it is an important factor to understand the dissociation dynamics[13].

The radiationless transition rates from the single vibronic levels of S_1 state formaldehyde were measured minutely by Miller and Lee[15],[16]. The rotational level dependence of the transition rates was also studied to obtain deeper insight to the mechanism of the radiationless transition[17]. On the theoretical ground, Yeung and Moore[14] calculated the nonradiative transition rates from the single vibronic levels of S_1 state with the use of Fermi's Golden rule. Although they could reproduce the initial vibronic level dependence of the rate constants observed experimentally, the absolute values of calculated rates were larger than the experimental ones by a few orders of magnitude. Lin[26] showed that the transition rates estimated by Yeung and Moore could be reduced by two orders of magni-

tude using the electronic matrix elements of vibronic coupling obtained from simple MO calculations. In these previous approaches, the vibrational wave functions of S_0 state were constructed using the harmonic functions and the electronic matrix element of nonadiabatic coupling was assumed to be constant in calculating the rate constant on the basis of Fermi's Golden rule. However, it is noted that the anharmonic effect plays an important role and the vibrational motion is far from the normal modes at highly vibrational excited states[20]. Furthermore, the nonadiabatic coupling matrix elements strongly depend on the nuclear coordinates as will be shown later.

To treat quantum dynamics as a time-dependent problem, several theoretical methods have been developed to propagate the wave packet on the potential surface and to evaluate the Hamiltonian matrix elements in recent years[21]-[25]. Kosloff and Kosloff[21] showed that the fast-Fourier-transformation (FFT) algorithm is a powerful tool for chemical dynamics in a short-time scale. The Chebychev scheme,[23] in which the time propagation operator is approximated by complex Chebychev polynomials, has been used to examine the processes for a relatively long-time scale. The discrete variable representation (DVR)[24] has been employed to calculate the matrix elements of Hamiltonian operator. Marston and Balint-Kurti[22] presented the Fourier grid Hamiltonian method which provides the eigenvalues and eigenfunctions as a special case of DVR using the FFT algorithm.

There have been many examples of dynamics calculations to which the FFT algorithm and DVR method have been applied. Zhang and Zhang[12] carried out a full-dimensional time-dependent wave packet dynamics calculations for diatom-diatom reactions such as the $H_2 + OH$ reaction and calculated the reaction cross sections. Kroes *et al.*[27] studied the photodissociation of $CH_2(\tilde{X}^3B_1)$ into $CH(X^2\Pi)+H(^2S)$ to evaluate the total cross sections resolved with respect to the vibrational and rotational quantum numbers of the CH fragment.

Based on the adiabatic approximation for the electronic states, the nonadiabatic transition among these states is caused by the nonadiabatic coupling terms given by the off-diagonal matrix elements for the nuclear kinetic energy. Lengthfield *et al.*[18] presented the analytical method for the evaluation of electronic nonadiabatic coupling matrix elements using the state-averaged multiconfigurational SCF (SAMCSCF) wave function and calculated these matrix elements for several systems[18],[28].

The purpose of the present study is to develop an efficient time-dependent method to

estimate the nonradiative decay rates of polyatomic systems and to elucidate the mechanism of radiationless transition of S_1 state formaldehyde associated with the vibrational energy redistribution in the S_0 state. The validity of present method will be examined by comparing the calculated results with the available experimental data[16].

In the Chapter 2, the ab initio molecular orbital method to obtain the nonadiabatic coupling matrix elements and the time propagation scheme based on a new time-dependent wave packet dynamics calculation are presented. In the Chapter 3, the proposed method is applied to the problem of the internal conversion from single vibronic levels of S_1 to S_0 state in formaldehyde and estimated the rate constants.

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Chapter 2

Theoretical methods

In the present chapter, we describe the details of quantum mechanical ways used in the subsequent chapter, such as the *ab initio* MO method for the evaluation of matrix elements of nonadiabatic coupling and the time propagation scheme for wave packet.

2.1 Matrix element of nonadiabatic coupling

In the present section, we review the derivation of nonadiabatic coupling terms based on the adiabatic approximation and present an *ab initio* molecular orbital method to obtain the matrix elements of nonadiabatic coupling analytically required to the calculations of radiationless transition rate constants.

Lengthfield *et al.*[1],[2] originally derived the formula for the calculation of electronic nonadiabatic coupling matrix elements with the state-averaged multiconfigurational SCF (SAMCSCF) wave function[3] by developing the energy gradient technique, which was extensively studied to calculate geometrical parameters and vibrational frequencies of polyatomic molecules, about a decade ago. Here, the coupled perturbed state-averaged complete active space (CPSACAS) SCF equations[4], necessary to the analytical calculations for these electronic matrix elements, are derived by the same technique as that of Osamura *et al.*[5] used to obtain the coupled perturbed MCSCF equations.

The remaining part of these matrix elements are evaluated from the Franck-Condon overlaps using the harmonic functions as a basis set for the nuclear motion.

nonadiabatic coupling

The total molecular Hamiltonian has the form

$$H = H_{el} + T_N, \quad (2.1)$$

where

$$H_{el} = \sum_i \left\{ -\frac{\hbar^2}{2m} \nabla_i^2 \right\} + V(\mathbf{r}, \mathbf{R}), \quad (2.2)$$

$$T_N = \sum_k \left\{ -\frac{\hbar^2}{2M_k} \nabla_k^2 \right\}, \quad (2.3)$$

with

$$\nabla_i = \left(\frac{\partial}{\partial x_i}, \frac{\partial}{\partial y_i}, \frac{\partial}{\partial z_i} \right), \quad (2.4)$$

$$\nabla_k = \left(\frac{\partial}{\partial X_k}, \frac{\partial}{\partial Y_k}, \frac{\partial}{\partial Z_k} \right). \quad (2.5)$$

x_i , y_i , and z_i represent the Cartesian coordinate of the i -th electron and m its mass. X_k , Y_k , and Z_k also represent that of the k -th nucleus and M_k its mass. $\mathbf{r}$ and $\mathbf{R}$ denote the sets of electronic and nuclear coordinates, respectively. $V(\mathbf{r}, \mathbf{R})$ is the potential energy of the molecule.

The total molecular wave function $\Psi(\mathbf{r}, \mathbf{R})$ satisfies the Schrödinger equation

$$H\Psi(\mathbf{r}, \mathbf{R}) = E\Psi(\mathbf{r}, \mathbf{R}), \quad (2.6)$$

where E is the total energy of the molecule. Assuming that the electronic wave functions $\Psi_K(\mathbf{r}, \mathbf{R})$ with the corresponding eigenvalue E_K are obtained from the equation

$$H_{el}\Psi_K(\mathbf{r}, \mathbf{R}) = E_K(\mathbf{R})\Psi_K(\mathbf{r}, \mathbf{R}). \quad (2.7)$$

Hereafter, K , L , and M denote the electronic states. We can expand the total molecular wave function $\Psi(\mathbf{r}, \mathbf{R})$ by the electronic wave functions above and the wave functions for the nuclear motion $F_K(\mathbf{R})$ due to the completeness of the electronic wave functions;

$$\Psi(\mathbf{r}, \mathbf{R}) = \sum_K F_K(\mathbf{R})\Psi_K(\mathbf{r}, \mathbf{R}). \quad (2.8)$$

Substituting Eq. (2.8) into Eq. (2.6), we obtain the following equations;

$$\begin{aligned} & \left[T_N + E_K(\mathbf{R}) + \sum_k \left\{ -\frac{\hbar^2}{2M_k} \int \Psi_K^*(\mathbf{r}, \mathbf{R}) \nabla_k^2 \Psi_K(\mathbf{r}, \mathbf{R}) d\mathbf{r} \right\} - E \right] F_K(\mathbf{R}) \\ &= - \sum_{K'(\neq K), k} \left\{ -\frac{\hbar^2}{M_k} \int \Psi_K^*(\mathbf{r}, \mathbf{R}) \nabla_k \Psi_{K'}(\mathbf{r}, \mathbf{R}) d\mathbf{r} \cdot \nabla_k \right\} F_{K'}(\mathbf{R}) \\ & - \sum_{K'(\neq K), k} \left\{ -\frac{\hbar^2}{2M_k} \int \Psi_K^*(\mathbf{r}, \mathbf{R}) \nabla_k^2 \Psi_{K'}(\mathbf{r}, \mathbf{R}) d\mathbf{r} \right\} F_{K'}(\mathbf{R}). \end{aligned} \quad (2.9)$$

The right-hand side of Eq. (2.9) represents the nonadiabatic coupling between the electronic states obtained by Eq. (2.7) and is neglected in the adiabatic approximation. The second term is usually small compared with the first term. Therefore, we concentrate on the evaluation of the first term of nonadiabatic coupling in this section.

electronic states

The state-averaged CASSCF wave function is suitable for the evaluation of electronic matrix elements of nonadiabatic coupling because the molecular orbitals are optimized for both the electronic states with equivalent precision and the orthogonality condition is satisfied between these electronic states[3].

The electronic wave function $\Psi_K(\mathbf{r}, \mathbf{R})$ can be expanded as follows;

$$\Psi_K(\mathbf{r}, \mathbf{R}) = \sum_I C_I^K(\mathbf{R}) \psi_I(\mathbf{r}, \mathbf{R}), \quad (2.10)$$

where

$$\psi_I(\mathbf{r}, \mathbf{R}) = P \prod_{i=1}^N \phi_{I_i}(r_i, \mathbf{R}), \quad (2.11)$$

$$\phi_i(r_i, \mathbf{R}) = \sum_{\mu} C_{\mu}^i(\mathbf{R}) \chi_{\mu}(r_i, \mathbf{R}). \quad (2.12)$$

$\psi_I(\mathbf{r}, \mathbf{R})$, $\phi_i(r_i, \mathbf{R})$, and $\chi_{\mu}(r_i, \mathbf{R})$ are the configurational state function (CSF), the molecular orbital (MO), and the atomic orbital (AO), respectively. $C_{\mu}^i(\mathbf{R})$ and $C_I^K(\mathbf{R})$ are the MO coefficient of the μ -th AO of the i -th MO and the CI coefficient of the I -th CSF of the K -th electronic state. P represents the antisymmetrization operator so that the $\psi_I(\mathbf{r}, \mathbf{R})$ is symmetry adapted CSF. Hereafter, I and J denote the CSFs, i, j, k, l , and m MOs, and μ, ν, ρ , and σ AOs. we also abbreviate $\mathbf{r}$ and $\mathbf{R}$ for simplicity.

In the state-averaged CASSCF procedure, the CI coefficients and the MO coefficients are determined from the following two criteria;

$$\sum_J H_{IJ} C_J^K = C_I^K E_K, \quad (2.13)$$

and

$$\epsilon_{ij} - \epsilon_{ji} = 0, \quad (2.14)$$

where H_{IJ} is the matrix element of electronic Hamiltonian

$$H_{I,J} = \int \psi_I(\mathbf{r}, \mathbf{R}) H_{el} \psi_J(\mathbf{r}, \mathbf{R}) d\mathbf{r} = \langle \psi_I(\mathbf{r}, \mathbf{R}) | H_{el} | \psi_J(\mathbf{r}, \mathbf{R}) \rangle_{\mathbf{r}}$$

$$= \sum_{i,j} h_{ij} \gamma_{ij}^{IJ} + \frac{1}{2} \sum_{ijkl} [ij; kl] \Gamma_{ijkl}^{IJ}, \quad (2.15)$$

and ϵ_{ij} is the matrix element of Lagrangian

$$\epsilon_{ij} = \sum_K^N w_K \epsilon_{ij}(K) \quad (2.16)$$

with

$$\begin{aligned} \epsilon_{ij}(K) &= \sum_{IJ} \sum_k h_{ik} C_I^K C_J^K \gamma_{kj}^{IJ} + \sum_{IJ} \sum_{klm} [ik; lm] C_I^K C_J^K \Gamma_{jklm}^{IJ} \\ &= \sum_k h_{ik} \gamma_{kj} + \sum_{klm} [ik; lm] \Gamma_{jklm}. \end{aligned} \quad (2.17)$$

h_{ij} and $[ij; kl]$ are the one- and two-electron molecular orbital integrals. γ_{ij}^{IJ} and Γ_{ijkl}^{IJ} are the one- and two-electron coupling coefficients. γ_{ij} and Γ_{ijkl} are the one- and two-electron density matrices. w_K and N are the weight for the electronic state K and the total number of the electronic states treated in the state-averaged CASSCF method.

The electronic matrix element of nonadiabatic coupling between the electronic states $\Psi_K(\mathbf{r}, \mathbf{R})$ and $\Psi_{K'}(\mathbf{r}, \mathbf{R})$ with respect to the nuclear coordinate R_a is written by

$$\int \Psi_K^*(\mathbf{r}, \mathbf{R}) \frac{\partial}{\partial R_a} \Psi_{K'} d\mathbf{r} = \langle \Psi_K(\mathbf{r}, \mathbf{R}) | \frac{\partial}{\partial R_a} | \Psi_{K'}(\mathbf{r}, \mathbf{R}) \rangle_{\mathbf{r}}. \quad (2.18)$$

Using the state-averaged CASSCF wave functions as the electronic wave functions, the matrix element above is rewritten in the following[1];

$$\langle \Psi_K(\mathbf{r}, \mathbf{R}) | \frac{\partial}{\partial R_a} | \Psi_{K'}(\mathbf{r}, \mathbf{R}) \rangle_{\mathbf{r}} = \sum_{i,j} \tilde{\gamma}_{ij}^{KK'} d_{ij}^a + \sum_I C_I^K \frac{\partial C_I^{K'}}{\partial R_a}, \quad (2.19)$$

where

$$\tilde{\gamma}_{ij}^{KK'} = \sum_{I,J} C_I^K C_J^{K'} \langle \psi_I | E_{ij} | \psi_J \rangle, \quad (2.20)$$

$$d_{ij}^a = U_{ij}^a + \langle \phi_i | \phi_j^a \rangle, \quad (2.21)$$

with

$$E_{ij} = a_i^+ a_j, \quad (2.22)$$

$$\phi_i^a = \sum_{\mu} C_{\mu}^i \frac{\partial \chi_{\mu}}{\partial R_a}. \quad (2.23)$$

$\tilde{\gamma}_{ij}^{KK'}$ is the square one-particle transition density matrix for states Ψ_K and $\Psi_{K'}$. U_{ij}^a represents the first-order changes with respect to R_a in the molecular orbitals. a_i^+ and a_j are the electron creation and annihilation operators, respectively.

In order to evaluate the electronic matrix element of nonadiabatic coupling analytically for the state-averaged CASSCF wave function, it is necessary to calculate U_{ij}^a and $\frac{\partial C_I^K}{\partial R_a}$ obtained from the coupled perturbed state-averaged (CPSA) CASSCF equations.

CPSACASSCF equations derived as follows;

The perturbation of a geometrical parameter (R_a) causes changes in molecular orbitals, AO integrals, and CI coefficients. Applying the Taylor expansions with respect to the nuclear coordinate and introducing a parameter λ , the expansions of these values are given by

$$\phi_i \rightarrow \phi_i + \lambda \sum_j \phi_j U_{ji}^a + \dots, \quad (2.24)$$

$$\langle \mu|h|\nu \rangle \rightarrow \langle \mu|h|\nu \rangle + \lambda \langle \mu|h|\nu \rangle^a + \dots, \quad (2.25)$$

$$[\mu\nu; \rho\sigma] \rightarrow [\mu\nu; \rho\sigma] + \lambda [\mu\nu; \rho\sigma]^a + \dots, \quad (2.26)$$

$$C_I^K \rightarrow C_I^K + \lambda \sum_{L \neq K} V_L^a(K) C_I^L + \dots, \quad (2.27)$$

where $\langle \mu|h|\nu \rangle$, $[\mu\nu; \rho\sigma]$, $\langle \mu|h|\nu \rangle^a$, $[\mu\nu; \rho\sigma]^a$, and $V_L^a(K)$ are the one-, two-atomic orbital integrals, derivatives of one-, two-atomic orbital integrals, and the first-order change of CI coefficient with respect to R_a , respectively. H_{IJ} , E_K , γ_{ij} , and Γ_{ijkl} are also affected by the perturbation through the changes in the MO and CI coefficients and the following expressions are obtained;

$$H_{IJ} \rightarrow H_{IJ} + \lambda \frac{\partial H_{IJ}}{\partial R_a} + \dots, \quad (2.28)$$

$$E_K \rightarrow E_K + \lambda E_K^a + \dots, \quad (2.29)$$

$$\gamma_{ij} \rightarrow \gamma_{ij} + 2\lambda \sum_K w_K \sum_{L(\neq K)} V_L^a(K) \sum_{IJ} C_I^L C_J^K \gamma_{ij}^{IJ} + \dots, \quad (2.30)$$

$$\Gamma_{ij} \rightarrow \Gamma_{ij} + 2\lambda \sum_K w_K \sum_{L(\neq K)} V_L^a(K) \sum_{IJ} C_I^L C_J^K \Gamma_{ij}^{IJ} + \dots, \quad (2.31)$$

where

$$\frac{\partial H_{IJ}}{\partial R_a} = H_{IJ}^a + \sum_{ij} U_{ij}^a X_{ij}^{IJ}, \quad (2.32)$$

$$\begin{aligned} E_K^a &= \sum_{ij} \gamma_{ij} \sum_{\mu\nu} C_\mu^i C_\nu^j \langle \mu|h|\nu \rangle^a \\ &+ \sum_{ijkl} \Gamma_{ijkl} \sum_{\mu\nu\rho\sigma} C_\mu^i C_\nu^j C_\rho^k C_\sigma^l [\mu\nu; \rho\sigma]^a + 2 \sum_{ij} U_{ij}^a \epsilon_{ij}(K), \end{aligned} \quad (2.33)$$

with

$$X_{ij}^{IJ} = 2 \sum_k h_{ik} \gamma_{jk}^{IJ} + 2 \sum_{klm} [ik; lm] \Gamma_{jklm}^{IJ}, \quad (2.34)$$

$$\begin{aligned} H_{IJ}^a &= \sum_{ij} \gamma_{ij}^{IJ} \sum_{\mu\nu} C_\mu^i C_\nu^j < \mu | h | \nu >^a \\ &+ \frac{1}{2} \sum_{ijkl} \Gamma_{ijkl}^{IJ} \sum_{\mu\nu\rho\sigma} C_\mu^i C_\nu^j C_\rho^k C_\sigma^l [\mu\nu; \rho\sigma]^a. \end{aligned} \quad (2.35)$$

Substituting these expressions into Eq. (2.13) and Eq. (2.14), collecting the first-order in λ , we obtained the following equations in matrix form;

$$\begin{pmatrix} \mathbf{A}^{11} & w_1 \mathbf{A}^{12}(1) & \dots & w_N \mathbf{A}^{12}(N) \\ \mathbf{A}^{21}(1) & \mathbf{A}^{22}(1) & & \mathbf{0} \\ \vdots & & \ddots & \\ \mathbf{A}^{21}(N) & \mathbf{0} & & \mathbf{A}^{22}(N) \end{pmatrix} \begin{pmatrix} \mathbf{U}^a \\ \mathbf{V}^a(1) \\ \vdots \\ \mathbf{V}^a(N) \end{pmatrix} = \begin{pmatrix} \mathbf{B}^1 \\ \mathbf{B}^2(1) \\ \vdots \\ \mathbf{B}^2(N) \end{pmatrix}, \quad (2.36)$$

where $\mathbf{U}^a$ and $\mathbf{V}^a$ are the first-order change vectors of MO coefficients with the component U_{ij}^a and that of CI coefficients with the component $V_K^a(M)$, respectively. The matrix elements of $\mathbf{A}^{11}$, $\mathbf{A}^{21}(M)$, $\mathbf{A}^{12}(M)$, $\mathbf{A}^{22}(M)$, $\mathbf{B}^1$, and $\mathbf{B}^2(M)$ are given by

$$A_{ij,kl}^{11} = Y_{ijkl} - Y_{jikl} - Y_{ijlk} + Y_{jilk} + \delta_{il}\epsilon_{jk} - \delta_{ik}\epsilon_{jl} - \delta_{jl}\epsilon_{ik} + \delta_{jk}\epsilon_{il}, \quad (2.37)$$

$$A_{K,ij}^{21}(M) = \sum_{IJ} C_I^K C_J^M (X_{ij}^{IJ} - X_{ji}^{IJ}) - 2 [\epsilon_{ij}(M) - \epsilon_{ji}(M)] \delta_{KM}, \quad (2.38)$$

$$A_{ij,K}^{12}(M) = \sum_{IJ} C_I^K C_J^M (X_{ij}^{IJ} - X_{ji}^{IJ}), \quad (2.39)$$

$$A_{K,L}^{22}(M) = \sum_{IJ} C_I^K C_J^L H_{IJ} - \delta_{KL} E_M, \quad (2.40)$$

$$\begin{aligned} B_{ij}^1 &= \sum_{m>n} S_{mn}^a (Y_{ijnm} - Y_{jinm} + \delta_{im}\epsilon_{jn} - \delta_{jm}\epsilon_{in}) \\ &+ \frac{1}{2} \sum_m^{occ} S_{mn}^a (Y_{ijmm} - Y_{jimm} + \delta_{im}\epsilon_{jm} - \delta_{jm}\epsilon_{im}) - \epsilon_{ij}^a + \epsilon_{ji}^a, \end{aligned} \quad (2.41)$$

$$\begin{aligned} B_K^2(M) &= - \sum_{IJ} C_I^K C_J^M H_{IJ}^a + \sum_{IJ} C_I^K C_J^M \left(\sum_{i>j} S_{ij}^a X_{ji}^{IJ} + \frac{1}{2} \sum_i S_{ii}^a X_{ii}^{IJ} \right) \\ &+ \left[\sum_{IJ} C_I^M C_J^M H_{IJ}^a - 2 \sum_{k>l} S_{kl}^a \epsilon_{lk}(M) - \sum_k S_{kk}^a \epsilon_{kk}(M) \right] \delta_{KM}, \end{aligned} \quad (2.42)$$

where

$$Y_{ijkl} = h_{ik} \gamma_{jl} + \sum_{mn} ([ik; mn] \Gamma_{jlmn} + 2[im; kn] \Gamma_{jmln}), \quad (2.43)$$

$$\epsilon_{ij}^a = \sum_k \sum_{\mu\nu} C_\mu^i C_\nu^k < \mu | h | \nu >^a \gamma_{jk} + \sum_{klm} \sum_{\mu\nu\rho\sigma} C_\mu^i C_\nu^k C_\rho^l C_\sigma^m [\mu\nu; \rho\sigma]^a \Gamma_{jklm}. \quad (2.44)$$

S_{ij} and S_{ij}^a are the overlap and overlap derivative of molecular orbitals with respect to R_a . Here, we use the relation

$$U_{ij}^a + U_{ji}^a + S_{ij}^a = 0, \quad (2.45)$$

and

$$S_{ij}^a = S_{ji}^a, \quad (2.46)$$

which comes from the orthonormality condition for molecular orbitals. Using the CI coefficient matrix and its transpose matrix, denoted by $\mathbf{C}$ and $\mathbf{C}^+$, and employing the projection method expressed as follows[6];

$$\begin{aligned} & \begin{pmatrix} 1 & & 0 \\ & \mathbf{C} & \\ 0 & \cdots & \mathbf{C} \end{pmatrix} \begin{pmatrix} \mathbf{A}^{11} & w_1 \mathbf{A}^{12}(1) & \cdots & w_N \mathbf{A}^{12}(N) \\ \mathbf{A}^{21}(1) & \mathbf{A}^{22}(1) & & 0 \\ \cdots & & \cdots & \\ \mathbf{A}^{21}(N) & 0 & \cdots & \mathbf{A}^{22}(N) \end{pmatrix} \\ & \cdot \begin{pmatrix} 1 & & 0 \\ & \mathbf{C}^+ & \\ 0 & \cdots & \mathbf{C}^+ \end{pmatrix} \begin{pmatrix} 1 & & 0 \\ & \mathbf{C} & \\ 0 & \cdots & \mathbf{C} \end{pmatrix} \begin{pmatrix} \mathbf{U}^a \\ \mathbf{V}^a(1) \\ \cdots \\ \mathbf{V}^a(N) \end{pmatrix} \\ & = \begin{pmatrix} 1 & & 0 \\ & \mathbf{C} & \\ 0 & \cdots & \mathbf{C} \end{pmatrix} \begin{pmatrix} \mathbf{B}^1 \\ \mathbf{B}^2(1) \\ \cdots \\ \mathbf{B}^2(N) \end{pmatrix}, \end{aligned} \quad (2.47)$$

the resultant CPSACASSCF equations are obtained by

$$\begin{pmatrix} \mathbf{A}^{11} & w_1 \mathbf{A}^{12}(1) & \cdots & w_N \mathbf{A}^{12}(N) \\ \mathbf{A}^{21}(1) & \mathbf{A}^{22}(1) & & 0 \\ \cdots & & \cdots & \\ \mathbf{A}^{21}(N) & 0 & \cdots & \mathbf{A}^{22}(N) \end{pmatrix} \begin{pmatrix} \mathbf{U}^a \\ \frac{\partial \mathbf{C}^1}{\partial R_a} \\ \cdots \\ \frac{\partial \mathbf{C}^N}{\partial R_a} \end{pmatrix} = \begin{pmatrix} \mathbf{B}^1 \\ \mathbf{B}^{2(1)} \\ \cdots \\ \mathbf{B}^{2(N)} \end{pmatrix}, \quad (2.48)$$

where the matrix elements of $\mathbf{A}^{12}(K)$, $\mathbf{A}^{21}(K)$, $\mathbf{A}^{22}(K)$ are given by

$$A_{I,ij}^{21}(K) = \sum_J C_J^K (X_{ij}^{IJ} - X_{ji}^{IJ}) - 2C_I^K [\epsilon_{ij}(K) - \epsilon_{ji}(K)], \quad (2.49)$$

$$A_{ij,I}^{12}(K) = \sum_J C_J^K (X_{ij}^{IJ} - X_{ji}^{IJ}), \quad (2.50)$$

$$A_{I,J}^{22}(K) = H_{IJ} - \delta_{I,J} E_K + C_I^K C_J^K, \quad (2.51)$$

$$\begin{aligned} B_I^{2(1)}(K) &= -\sum_J C_J^K H_{IJ}^a + \sum_J C_J^K \left(\sum_{i>j} S_{ij}^a X_{ji}^{IJ} + \frac{1}{2} \sum_i S_{ii}^a X_{ii}^{IJ} \right) \\ &+ C_I^K \left[\sum_{IJ} C_I^K C_J^K H_{IJ}^a - 2 \sum_{k>l} S_{kl}^a \epsilon_{lk}(K) - \sum_k S_{kk}^a \epsilon_{kk}(K) \right], \end{aligned} \quad (2.52)$$

and $\frac{\partial C^M}{\partial R_a}$ is the vector with the component $\frac{\partial C^M}{\partial R_a}$. These equations should be solved for the pair suffices i, j of U_{ij}^a ; ($i = \text{active}, j = \text{core}$), ($i = \text{active}, j = \text{active}$), and ($i = \text{virtual}, j = \text{active}$) because the unitary transformation between core and virtual orbitals does not change the energy.

Employing the procedure described above, we can obtain the electronic nonadiabatic coupling matrix elements with the state-averaged CASSCF wave functions analytically.

nuclear motion

Using the normal coordinates $\mathbf{Q}$ with the component Q_r for the normal mode r , introducing the vibrational state functions $\chi_u^K(\mathbf{Q})$, which are the products of harmonic functions $\chi_r^K(Q_r)$, instead of $F_K(\mathbf{R})$ as a basis set for the nuclear motion, the matrix element of nonadiabatic coupling is given by

$$-\sum_r \frac{\hbar^2}{\mu_r} \langle \chi_u^K(\mathbf{Q}) | \langle \Psi_K(\mathbf{r}, \mathbf{Q}) | \frac{\partial}{\partial Q'_r} | \Psi_{K'}(\mathbf{r}, \mathbf{Q}') \rangle_{\mathbf{r}} \cdot \frac{\partial}{\partial Q'_r} | \chi_v^{K'}(\mathbf{Q}') \rangle_{\mathbf{Q}}, \quad (2.53)$$

where μ_r represents the reduced mass for the normal mode r and subscript $\mathbf{Q}$ denotes the integration with respect to the normal coordinates. u and v are the indices for the vibrational states, respectively. Hereafter, r and s denote the indices for the normal modes, respectively.

Assuming that the value of electronic nonadiabatic coupling matrix element does not heavily depend on the normal coordinates, the matrix element of nonadiabatic coupling is approximated as follows;

$$\begin{aligned} & -\sum_r \frac{\hbar^2}{\mu_r} \langle \Psi_K(\mathbf{r}, \mathbf{Q}) | \frac{\partial}{\partial Q'_r} | \Psi_{K'}(\mathbf{r}, \mathbf{Q}') \rangle_{\mathbf{r}} \cdot \langle \chi_u^K(\mathbf{Q}) | \frac{\partial}{\partial Q'_r} | \chi_v^{K'}(\mathbf{Q}') \rangle_{\mathbf{Q}} \\ &= -\sum_r \frac{\hbar^2}{\mu_r} \langle \Psi_K(\mathbf{r}, \mathbf{Q}) | \frac{\partial}{\partial Q'_r} | \Psi_{K'}(\mathbf{r}, \mathbf{Q}') \rangle_{\mathbf{r}} \cdot \langle \chi_r^K(Q_r) | \frac{\partial}{\partial Q'_r} | \chi_r^{K'}(Q'_r) \rangle_{Q'_r} \\ & \quad \prod_{s \neq r} \langle \chi_s^K(Q_s) | \chi_s^{K'}(Q'_s) \rangle_{Q'_s}, \end{aligned} \quad (2.54)$$

where subscript Q'_r also denotes the integration with respect to the normal coordinate Q'_r .

Here, it is necessary to calculate the Franck-Condon and the nonadiabatic Franck-Condon overlaps[7] to obtain the matrix element of nonadiabatic coupling. These overlaps can be evaluated without difficulty employing the recurrence equations derived by Kupka and Cribb[8].

2.2 Scheme for dynamics calculation

Recently, time-dependent quantum mechanical methods have been applied to many dynamics calculations for chemical reactions and chemical processes because these methods are easy to implement and give us simple interpretation for the physical mechanism of these systems. In the present section, we briefly review the theory for the time-dependent quantum mechanical dynamics calculations, mainly on the short-time propagation scheme[9] and the representation of state functions[10], which lies at the foundation of a new time-dependent wave packet method to estimate the nonradiative transition rates proposed in the next Chapter.

In time-dependent quantum mechanical methods, we must solve the time-dependent Schrödinger equation:

$$i\hbar \frac{\partial \psi(t)}{\partial t} = \widehat{H}\psi(t). \quad (2.55)$$

For a short-time propagation, dt , the evolution operator $\widehat{U}(dt)$, which would be a good approximation to the correct evolution operator including the awkward time-ordering operator, is expressed as follows;

$$\widehat{U}(dt) = \exp\left(\frac{-i\widehat{H}dt}{\hbar}\right) \quad (2.56)$$

and the time propagation of the wave function is carried out using the equation

$$\psi(t + dt) = \widehat{U}(dt)\psi(t). \quad (2.57)$$

Further, expanding the evolution operators, $\widehat{U}(dt)$ and $\widehat{U}(-dt)$, in Taylor series and preserving the conservation of time reversal symmetry of the Schrödinger equation so as to ensure the stability[11] in the time propagation of wave function, we obtain the second-order propagation scheme, which is usually called the second-order differentiating scheme, described as follows;

$$\psi(t + dt) \cong \psi(t - dt) - 2idt\widehat{H}\psi(t)/\hbar. \quad (2.58)$$

To implement the time-dependent wave packet dynamics calculations using this scheme, we need to evaluate the matrix element of Hamiltonian operator composed of a kinetic energy and a potential energy operators

$$\widehat{H} = \widehat{T} + V(\hat{x}), \quad (2.59)$$

where

$$\hat{T} = \frac{\hat{p}^2}{2m}, \quad (2.60)$$

and m is the mass of the particle. The representations usually used in Hilbert space are the coordinate representation and the momentum representation, of which basic vectors are denoted by $|x\rangle$ and $|k\rangle$, respectively. The matrix of potential operator is diagonal in the coordinate representation

$$\langle x' | \mathbf{V}(\hat{x}) | x \rangle = V(x) \delta(x - x'), \quad (2.61)$$

whereas that of kinetic one is diagonal in the momentum representation

$$\langle k' | \hat{T} | k \rangle = \frac{\hbar^2 k^2}{2m} \delta(k - k'). \quad (2.62)$$

The transformation matrix element between the coordinate and momentum representations is given by

$$\langle k | x \rangle = \frac{1}{\sqrt{2\pi}} \exp(-ikx). \quad (2.63)$$

Using the completeness relation, the transformation matrix described above, and the matrix elements presented in Eq. (2.61) and (2.62), the matrix element of Hamiltonian operator in the coordinate representation is given by

$$\langle x | \hat{\mathbf{H}} | x' \rangle = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{ik(x-x')} \frac{\hbar^2 k^2}{2m} dk + V(x) \delta(x - x'). \quad (2.64)$$

Replacing the continuous range of coordinate values x by a grid of uniformly discrete values x_i , the matrix element of Hamiltonian operator is written by

$$\langle x_i | \hat{\mathbf{H}} | x_j \rangle = \frac{1}{\Delta x} \left\{ \sum_{l=-n}^n \frac{e^{il2\pi(i-j)/N}}{N} \cdot \frac{\hbar^2}{2m} \cdot (l\Delta k)^2 + V(x_i) \delta_{ij} \right\}, \quad (2.65)$$

where N is the total number of grid points. Δx is the uniform spacing between grid points and Δk is the reciprocal grid size in the momentum space determined as follows;

$$\Delta k = 2\pi/N\Delta x. \quad (2.66)$$

The transformation between these grid representations are carried out with the fast Fourier transformation (FFT) algorithm efficiently[12].

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Chapter 3

Internal conversion rate from S_1 to S_0 state in formaldehyde

In the present Chapter, we describe the details of a new time-dependent approach to estimate the nonadiabatic decay rate.

In Sec. I, theoretical methods for the dynamics calculation based on Fermi's Golden rule to obtain the nonadiabatic decay rates are presented. The quantum mechanical reaction path Hamiltonian is utilized in the wave packet propagation on the S_0 surface. The method to reduce the size of Hamiltonian matrix employed in the dynamics calculation is also described. In Sec. II, the results of CASSCF calculations used to construct the reaction path Hamiltonian are given. We also discuss the matrix elements of nonadiabatic coupling calculated for the electronic part analytically with the state-averaged CASSCF wave function and for the vibrational one with the harmonic functions. In Sec. III, the estimated nonradiative decay rates of S_1 state formaldehyde are compared with the experimental results. Based on the wave packet dynamics calculations, the mechanism of radiationless transition is examined. In particular, the importance of vibrational energy redistribution on the S_0 surface is stressed. The discussions and conclusions are summarized in Sec. IV.

3.1 Dynamics calculation

3.1.1 Nonradiative transition rate

Fermi's Golden rule has been conveniently used to estimate the nonradiative transition rate;

$$k_{NR} = \sum_f \frac{2\pi}{\hbar} |\langle \psi_f | \hat{V} | \psi_i \rangle|^2 \delta(E_f - E_i), \quad (3.1)$$

where the suffices i and f stand for the initial S_1 and final S_0 states, respectively. E is the energy of the corresponding state. $\hat{V}$ represents the nonadiabatic coupling operator expressed as follows;

$$\hat{V} = - \sum_{k=1}^N \frac{\hbar^2}{M_k} < \Phi_0 | \nabla_k | \Phi_1 > \cdot \nabla_k, \quad (3.2)$$

and

$$\nabla_k = \left(\frac{\partial}{\partial X_k}, \frac{\partial}{\partial Y_k}, \frac{\partial}{\partial Z_k} \right), \quad (3.3)$$

where X_k , Y_k , and Z_k represent the Cartesian coordinate of k -th nucleus and M_k its mass. $|\Phi_0 >$ and $|\Phi_1 >$ are the electronic wave functions of S_0 and S_1 states, respectively.

In many experimental studies[1], the initial state ($|\psi_i >$) prepared by photoabsorption is a low-lying rovibronic state of S_1 characterized by quasi-periodic motion. On the other hand, the final states ($|\psi_f >$) are highly vibrational excited states on the S_0 surface with the rotational-vibrational energies corresponding to the excitation energy. The nuclear dynamics of such states are characterized by chaotic motion and it is difficult to determine the wave functions ($|\psi_f >$) by diagonalizing the Hamiltonian matrix even for simple molecules such as formaldehyde. We therefore adopt another approach, which does not use those wave functions ($|\psi_f >$) explicitly, to calculate the rate constant given by Eq. (3.1).

Employing the energy-time Fourier transformation of the delta function[2] in Eq. (3.1), we can obtain the equivalent expression to Eq. (3.1) as follows;

$$k_{NR} = \frac{1}{\hbar^2} \int_{-\infty}^{\infty} \exp\left(\frac{iE_it}{\hbar}\right) < \phi(0) | \phi(t) > dt, \quad (3.4)$$

where

$$|\phi(0) > = \hat{V} |\psi_i >, \quad (3.5)$$

and

$$|\phi(t) > = \exp\left(\frac{-i\hat{H}t}{\hbar}\right) |\phi(0) >. \quad (3.6)$$

$\hat{H}$ is the Hamiltonian operator for the nuclear motion on the S_0 potential surface. The advantages to use Eq. (3.4) in evaluating the rate constant is that we need to propagate the wave packet ($|\phi(0) >$) in a short time because the auto-correlation function ($< \phi(0) | \phi(t) >$) is expected to decay rapidly due to fast energy flow among the vibrational modes in the S_0 state.

3.1.2 Hamiltonian for nuclear motion

It would be formidable to carry out full-dimensional quantum mechanical dynamics calculations for a vibrationally highly excited formaldehyde molecule. To simplify the dynamics calculations, we employed the reaction path Hamiltonian model[3] in which the degrees of freedom are classified into the two groups, the small amplitude coordinates and the large amplitude coordinates. The reaction path Hamiltonian model was originally developed for reactive processes proceed along the minimum energy path connecting the reactant and product. We used it to describe the dynamics of polyatomic systems including a large amplitude motion regarding it as the motion along the reaction coordinate. In the present system, the out of plane bending mode undergoes a large displacement in the S_1 to S_0 nonadiabatic transition and is needed to be treated as a large amplitude motion. Although the reaction path Hamiltonian is an approximate model to describe the dynamics of polyatomic systems, it would be a good approximation to the full-dimensional treatment when the dynamics in a short-time scale is considered.

Adopting the reaction path Hamiltonian model, we chose the out-of-plane bending angle (denoted by ρ in Fig. 1) as the reaction path, the large amplitude coordinate. The transverse normal coordinates (Q_i , $i=1\sim 3N-7$) were defined along the reaction path so as to satisfy the relations[4];

$$\frac{\partial V}{\partial Q_i} = 0, (i = 1 \sim 3N - 7). \quad (3.7)$$

It is noted that the transverse normal coordinates are not necessarily orthogonal to the reaction path in contrast to the usual definition[3],[5].

The reaction path Hamiltonian in quantum mechanical form is given by[3]

$$\begin{aligned} \widehat{H} = & \sum_{k=1}^{3N-7} \frac{1}{2} \left[\mu^{1/4} \widehat{P}_k \mu^{-1/2} \widehat{P}_k \mu^{1/4} + \omega_k(\rho)^2 \widehat{Q}_k^2 \right] + V_0(\rho) \\ & + \frac{1}{2} \mu^{1/4} (\widehat{J} - \widehat{\pi}) \cdot \mathbf{G} \cdot \mu^{-1/2} (\widehat{J} - \widehat{\pi}) \mu^{1/4}, \end{aligned} \quad (3.8)$$

where

$$\mathbf{G} = (I_0 + \mathbf{b})^{-1} \cdot I_0 \cdot {}^t(I_0 + \mathbf{b})^{-1}, \quad (3.9)$$

$$\mu = |\mathbf{G}|, \quad (3.10)$$

and N is the number of constituent atoms. In Eq. (3.8), $\widehat{Q}_k$ and $\widehat{P}_k$ are the operator corresponding to the transverse normal coordinate Q_k with the frequency $\omega_k(\rho)$ and the

momentum operator conjugates to $\widehat{Q}_k$. $V_0(\rho)$ is the potential energy along the reaction path. $\widehat{J}$ is the angular momentum vector;

$$\widehat{J} = (\widehat{P}_\rho, \widehat{J}_x, \widehat{J}_y, \widehat{J}_z), \quad (3.11)$$

where $\widehat{J}_x$, $\widehat{J}_y$, and $\widehat{J}_z$ are the components of angular momentum operator representing the overall rotation and $\widehat{P}_\rho$ the momentum operator conjugate to the coordinate ρ . $\widehat{\pi}$ is the four-dimensional vibrational angular momentum vector;

$$\begin{aligned} \widehat{\pi} &= (\widehat{\pi}_\rho, \widehat{\pi}_x, \widehat{\pi}_y, \widehat{\pi}_z) = \widehat{\pi}_1 + \widehat{\pi}_2 \\ &= \sum_{k,k'=1}^{3N-7} B_{k,k'}(\rho) \widehat{Q}_k \widehat{P}_{k'} + \sum_{k'=1}^{3N-7} B_{k'}(\rho) \widehat{P}_{k'}, \end{aligned} \quad (3.12)$$

where

$$B_{k,k'}(\rho) = (B_{k,k'}^\rho(\rho), \mathbf{B}_{k,k'}(\rho)), \quad (3.13)$$

$$B_{k'}(\rho) = (B_{k'}^\rho(\rho), \mathbf{0}), \quad (3.14)$$

with

$$B_{k,k'}^\rho(\rho) = \sum_{i=1}^N \frac{\partial \mathbf{L}_{i,k}(\rho)}{\partial \rho} \cdot \mathbf{L}_{i,k'}(\rho), \quad (3.15)$$

$$\mathbf{B}_{k,k'}(\rho) = \sum_{i=1}^N \mathbf{L}_{i,k}(\rho) \times \mathbf{L}_{i,k'}(\rho), \quad (3.16)$$

$$B_{k'}^\rho(\rho) = \sum_{i=1}^N \sqrt{M_i} \frac{\partial \mathbf{a}_i(\rho)}{\partial \rho} \cdot \mathbf{L}_{i,k'}(\rho). \quad (3.17)$$

$\mathbf{a}_i(\rho)$, $\mathbf{L}_{i,k}(\rho)$, and M_i are the reference configuration of atom i , the displacement vector of atom i corresponding to the transverse normal coordinate Q_k , and the mass of atom i , respectively. I_0 is the 4×4 inertia tensor;

$$I_0 = \begin{pmatrix} S(\rho) & \mathbf{0} \\ \mathbf{0} & \mathbf{I}_0(\rho) \end{pmatrix}, \quad (3.18)$$

where

$$S(\rho) = \sum_{i=1}^N M_i \frac{\partial \mathbf{a}_i(\rho)}{\partial \rho} \cdot \frac{\partial \mathbf{a}_i(\rho)}{\partial \rho} - \sum_k^{3N-7} U_k^2, \quad (3.19)$$

$$\mathbf{I}_0(\rho) = \sum_{i=1}^N M_i [\mathbf{1} \mathbf{a}_i(\rho) \cdot \mathbf{a}_i(\rho) - \mathbf{a}_i(\rho) \mathbf{a}_i(\rho)], \quad (3.20)$$

and

$$U_k = \sum_{i=1}^N \sqrt{M_i} \frac{\partial \mathbf{a}_i(\rho)}{\partial \rho} \cdot \mathbf{L}_{i,k}(\rho). \quad (3.21)$$

$\mathbf{b}$ is the 4×4 centrifugal distortion matrix;

$$\mathbf{b} = \sum_{k=1}^{3N-7} \mathbf{b}_k(\rho) \widehat{Q}_k, \quad (3.22)$$

where

$$\mathbf{b}_k(\rho) = \begin{pmatrix} b_k^{(\rho,\rho)}(\rho) & \mathbf{b}_k^{(\rho)}(\rho) \\ \mathbf{b}_k^{(\rho)}(\rho) & \mathbf{b}_k^{(0)}(\rho) \end{pmatrix}, \quad (3.23)$$

with

$$b_k^{(\rho,\rho)}(\rho) = \sum_{i=1}^N \left(\sqrt{M_i} \frac{\partial \mathbf{a}_i(\rho)}{\partial \rho} \cdot \frac{\partial \mathbf{L}_{i,k}(\rho)}{\partial \rho} - \sum_{l=1}^{3N-7} U_l \mathbf{L}_{i,l}(\rho) \cdot \frac{\partial \mathbf{L}_{i,k}(\rho)}{\partial \rho} \right), \quad (3.24)$$

$$\mathbf{b}_k^{(\rho)}(\rho) = \sum_{i=1}^N \sqrt{M_i} \mathbf{L}_{i,k}(\rho) \times \frac{\partial \mathbf{a}_i(\rho)}{\partial \rho}, \quad (3.25)$$

$$\mathbf{b}_k^{(\rho)}(\rho) = {}^t \mathbf{b}_k^{(\rho)}(\rho) + \sum_{l=1}^{3N-7} U_l \left[\sum_{i=1}^N \mathbf{L}_{i,l}(\rho) \times \mathbf{L}_{i,k}(\rho) \right], \quad (3.26)$$

$$\mathbf{b}_k^{(0)}(\rho) = \sum_{i=1}^N \sqrt{M_i} [\mathbf{1} \mathbf{L}_{i,k}(\rho) \cdot \mathbf{a}_i(\rho) - \mathbf{L}_{i,k}(\rho) \mathbf{a}_i(\rho) \cdot]. \quad (3.27)$$

Assuming that the total angular momentum is equal to be zero[6], adopted in the following calculations, the reaction path Hamiltonian becomes as follows;

$$\widehat{H} = \sum_{k=1}^{3N-7} \frac{1}{2} \left[\widehat{P}_k^2 + \omega_k(\rho)^2 \widehat{Q}_k^2 \right] + V_0(\rho) + \frac{1}{2} (\widehat{P}_\rho - \widehat{\pi}_\rho) \cdot \mathbf{G} \cdot (\widehat{P}_\rho - \widehat{\pi}_\rho) + U, \quad (3.28)$$

where

$$\begin{aligned} U &= -\frac{1}{8} \hbar^2 (I'')^{-2} \sum_{k=1}^{3N-7} \left(\frac{\partial I''}{\partial Q_k} \right)^2 + \frac{1}{4} \hbar^2 (I'')^{-1} \sum_{k=1}^{3N-7} \frac{\partial^2 I''}{\partial Q_k^2} \\ &+ \frac{1}{8} [(\widehat{P} - \widehat{\pi}) \cdot \mathbf{G} \cdot \mathbf{d}\mu] - \frac{1}{32} \mathbf{d}\mu \cdot \mathbf{G} \cdot \mathbf{d}\mu, \end{aligned} \quad (3.29)$$

with

$$I'' = |I_0 + \mathbf{b}|, \quad (3.30)$$

$$\widehat{P} = (\widehat{P}_\rho, \mathbf{0}), \quad (3.31)$$

$$\mathbf{d}\mu = (I'')^{-1} ((\widehat{P}_\rho - \widehat{\pi}_\rho) I'', \widehat{\pi}_x I'', \widehat{\pi}_y I'', \widehat{\pi}_z I''), \quad (3.32)$$

and G is the (1,1) component of $\mathbf{G}$. In evaluating the matrix elements for the Hamiltonian, we expanded Eq. (3.28) by a power of series of the components of $\mathbf{b}$, truncated up to the

second order, and kept the coupling terms up to the second order with respect to $\widehat{Q}_k$ and $\widehat{P}_k$, because the potential energy and the kinetic energy of transverse normal vibrations are also approximated by the second order with respect to $\widehat{Q}_k$ and $\widehat{P}_k$.

3.1.3 Wave packet calculations

To execute the dynamics calculations using the reaction path Hamiltonian for the S_0 state, we introduced the basis set, $|\varphi_{i,m}\rangle$, defined for the S_0 state and expanded $|\phi(t)\rangle$ with this basis set as follows;

$$|\phi(t)\rangle = \sum_{i,m} a_i^m(t) |\varphi_{i,m}\rangle, \quad (3.33)$$

and

$$|\varphi_{i,m}\rangle = |\rho_i\rangle \prod_{k=1}^{3N-7} |\chi_k^{m_k}(Q_k, \rho_i)\rangle, \quad (3.34)$$

$$a_i^m(0) = \langle \varphi_{i,m} | \phi(0) \rangle = \langle \varphi_{i,m} | \widehat{V} | \psi_i \rangle, \quad (3.35)$$

where $|\rho_i\rangle$ is the DVR basis function at the grid point i for the large amplitude motion and $|\chi_k^{m_k}(Q_k, \rho_i)\rangle$ is the harmonic basis function for the transverse normal vibrational mode k with the quantum number m_k at the grid point i . $a_i^m(t)$ is the time-dependent coefficient of $|\varphi_{i,m}\rangle$. Consequently, the time-dependent equation for the coefficients is expressed as follows;

$$\mathbf{a}(t) = \exp\left(\frac{-i\mathbf{H}t}{\hbar}\right) \mathbf{a}(0), \quad (3.36)$$

where $\mathbf{H}$ is the Hamiltonian matrix with the element

$$H_{i,m}^{j,m'} = \langle \varphi_{i,m} | \widehat{H} | \varphi_{j,m'} \rangle, \quad (3.37)$$

and $\mathbf{a}(0)$ is the initial amplitude vector with the component $a_i^m(0)$, respectively.

Even if the rotational angular momentum is equal to be zero, it is too demanding to treat all the vibrational states of S_0 , denoted by m in the basis function $|\varphi_{i,m}\rangle$, explicitly in the dynamics calculations. We therefore separated the basis functions into two manifolds; the manifold(a) which interact with the initial prepared state of S_1 directly through the nonadiabatic coupling ($\widehat{V}$) and are used in the dynamics calculation explicitly, and the manifold(b) which interact indirectly through the vibrational coupling with the manifold(a). We further introduced the effective Hamiltonian,[7]denoted by $\widehat{H}_{eff}$ hereafter, whose imaginary components represent the vibrational transition from the manifold (a) to

(b) through the coupling in the S_0 state. The matrix element of the effective Hamiltonian is given by;

$$(H_{eff})_{i,m}^{j,m'} = H_{i,m}^{j,m'} - i\pi \sum_{k,n} H_{i,m}^{k,n} H_{k,n}^{j,m'}, \quad (3.38)$$

where the suffices $m(m')$ and n stand for the vibrational basis functions belong to the manifold(a) and (b), respectively.

In the present model, the anharmonic coupling between the out of plane bending mode and the remaining degrees of freedom were took into account. Considering that only the out of plane bending motion is highly excited in the S_1 to S_0 nonadiabatic transition and the energy flow from the out of plane bending mode is the dominant process in the initial stage of vibrational relaxation, such the approximation would be appropriate to describe a short-time dynamics. It is noted that the dissociation process into $H_2 + CO$ may affect on the internal conversion rate. However, the effect of such process is considered to be small because the magnitude of second term in Eq. (3.38) is much larger than the line width coming from the dissociation at the energy range considered in the present calculations.

The criterion to determine the manifold(a) was to select all the vibrational states m which fulfill the condition that the maximum value of $|a_i^m(0)|$ with respect to the reaction coordinate exceeds a threshold. We chose the threshold so as to reproduced more than 95% of the amplitude of initial auto-correlation function $\langle \phi(0)|\phi(0) \rangle$. With these classification, the number of the vibrational states in the manifold(a) became several hundreds in the case of H_2CO .

The initial wave function of S_1 state was constructed by the product of the wave function along the ρ coordinate represented by the DVR basis set and the harmonic functions with respect to the transverse normal coordinates at each grid point. The wave functions along the ρ coordinate were calculated by Fourier grid Hamiltonian method[8],[9] using the vibrational adiabatic Hamiltonian given by;

$$\widehat{H} = \sum_{k=1}^{3N-7} \hbar\omega_k(\rho) \left(v_k + \frac{1}{2} \right) + V_0(\rho) + \frac{1}{2}\mu_0^{1/4} \widehat{P}_\rho S(\rho)^{-1} \mu_0^{-1/2} \widehat{P}_\rho \mu_0^{1/4}, \quad (3.39)$$

where

$$\mu_0 = |I_0^{-1}|, \quad (3.40)$$

and v_k is the quantum number of the vibrational mode k .

Time evolution of the wave packets given in Eq. (3.36) was carried out using the second order differentiating (SOD) scheme developed by Kosloff and Kosloff[10]. This propagation

scheme is easy to implement and feasible to evolve the wave packets using the FFT algorithm. We used a grid containing 129 points, which are equally spaced in the range from -90° to 90° for the out-of-plane bending angle ρ , and fixed the time step to be 0.05 a.u.. To ensure the conservation of the norm of wave packets, $|\langle \phi(t) | \phi(t) \rangle|$, we carried out the wave packet dynamics calculations by setting the damping terms in Eq. (3.38) to be zero so as to preserve the hermiticity of Hamiltonian. The norm was conserved with the deviation of less than 0.65% of the initial one for 120 fs propagation.

3.2 Ab initio calculations for S_0 and S_1 states of formaldehyde

3.2.1 Parameters for the reaction path Hamiltonian

We carried out CASSCF calculations to determine all the parameters involved in the reaction path Hamiltonian, Eq. (3.28). In constructing the CASSCF wave functions, 9 active orbitals [$\sigma(C-O)$, $2*\sigma(C-H)$, $\pi(C-O)$, $n(O)$, $\pi^*(C-O)$, $2*\sigma^*(C-H)$, $\sigma^*(C-O)$] were chosen and 10 electrons were distributed among them. In C_1 symmetry, the total number of configuration state functions in the CASSCF wave function was 5292. The Huzinaga-Dunning-Raffenetti[11] (9s5p1d/4s1p)/[3s2p1d/2s1p] double zeta plus polarization basis set was used.

The reference positions of atoms, denoted by $\mathbf{a}_i(\rho)$, in the molecule-fixed coordinate system are shown in Fig. 1. C and O atoms are located in the y - z plane, two H atoms are placed to have C_s symmetry with respect to the y - z plane, and the center of mass is fixed at the origin. These positions are chosen such that the angular momentum of the reference geometry vanishes in the molecule-fixed coordinate system[12].

The potential energy curves along the out-of-plane bending coordinate ρ both for the S_0 and S_1 states are shown in Fig. 2. The potential energy of S_0 state increases monotonously with the increase of ρ , while that of S_1 state is almost constant up to $\rho = 60^\circ$ and increases gradually. The geometric parameters were optimized as the functions of ρ for each state. The equilibrium geometry of S_0 state has C_{2v} symmetry. The calculated CO , CH bond distances (R_{CO} , R_{CH}), and HCH angle ($\angle HCH$) were 1.217, 1.117Å, and 115.1° , respectively. On the other hand, the out-of-plane bending angle was 37.2° at the equilibrium geometry of S_1 state, which has C_s symmetry. The calculated R_{CO} ,

R_{CH} , and $\angle HCH$ were 1.364, 1.107Å, and 117.5°, respectively. These values, except for R_{CO} of the S_1 state which is slightly overestimated, are in good agreement with the experiments[13] ($R_{CO}=1.207\text{Å}$, $R_{CH}=1.117\text{Å}$, $\angle HCH=116.2^\circ$ for the S_0 state and $R_{CO}=1.323\text{Å}$, $R_{CH}=1.098\text{Å}$, $\angle HCH=118.4^\circ$, $\rho=34^\circ$ for the S_1 state). The calculated energy difference between the S_0 and S_1 states was 3.80 eV.

The variations of vibrational frequencies for the transverse normal modes are plotted in Fig. 3. These were obtained by the GF matrix procedure[14] for the five dimensional internal coordinate space excluding the components for the out-of-plane bending angle ρ . The harmonic functions derived by this procedure were used as the vibrational basis functions for the S_0 state and as the vibrational eigenfunctions for the S_1 state. As seen in Fig. 3(a), the frequency of CH asymmetric stretching mode monotonically increases with the increase of ρ , while those of CO stretching and HCH symmetric bending mode decrease. The frequency of HCH asymmetric bending mode has a maximum at $\rho=60^\circ$. The changes of frequencies of S_1 state are relatively small compared to those of S_0 state except for the HCH asymmetric bending mode, as presented in Fig. 3(b).

Figure 4 shows the (1,1) components of the centrifugal distortion matrix $\mathbf{b}$, $b_k^{(\rho,\rho)}$ in Eq. (3.24), and the first components of $\widehat{\pi}_2$, $B_{k'}^\rho$ in Eq. (3.17). $B_{k'}^\rho$ are the most effective terms for the vibrational coupling and are non-zero only for the symmetric (A') vibrational modes. Both $b_k^{(\rho,\rho)}$ and $B_{k'}^\rho$ corresponding to the CO stretching and HCH symmetric bending modes change remarkably in the region of large ρ . It is noted that the value of $B_{k'}^\rho$ corresponding to the CO stretching is large enough to induce strong vibrational coupling in the small ρ region. On the other hand, the CH symmetric stretching is not responsible for the vibrational relaxation so much. The features of the other elements are as follows; in $B_{k,k'}(\rho)$ of Eq. (3.13), the coupling between the HCH asymmetric bending and CH symmetric stretching mode and that between the HCH symmetric bending and CH asymmetric stretching mode are comparatively strong. These coupling elements affect the vibrational relaxation between the symmetric and asymmetric vibrational modes. The values of $S(\rho)$ in Eq. (3.19) are almost constant up to the equilibrium angle of S_1 state and are gradually reduced. At $\rho=75^\circ$, $S(\rho)$ has the minimum value, which is 76% of that at $\rho=0^\circ$.

The results of normal mode analyses at the equilibrium geometries of S_0 and S_1 states are also given in Table 1 along with the experimental frequencies[15]. The ν_4 value of S_1

state is not included, because the potential surface of S_1 state of H_2CO forms the inversion doubling along the coordinate ρ . All the frequencies, except that of CO stretching mode of S_1 state, are slightly overestimated by 2~10% compared with the experimental ones.

The vibrational energy levels of S_1 state were calculated by the Fourier grid Hamiltonian method using the Hamiltonian given by Eq. (3.39). The energies of 4^1 , 4^2 , and 4^3 states were estimated to be 75, 533, and 918 cm^{-1} measured from the ground vibrational state, the 4^0 state. The corresponding experimental values are 125, 542, and 948 cm^{-1} , respectively[16]. The vibrational states are denoted by $1^{v_1}2^{v_2}\dots6^{v_6}$ and the vibrational modes with the zero quantum number are abbreviated for simplicity. The potential barrier height, which exists between two equilibrium points, is low (~ 0.035 eV from the present calculation and ~ 0.015 eV from the experiment[16]). The calculated energy difference including the zero-point energies of S_0 and S_1 states was 3.71 eV and is overestimated by 0.21 eV compared to the experimental value[17].

3.2.2 Nonadiabatic coupling

To obtain the electronic matrix element of nonadiabatic coupling analytically with the state-averaged CASSCF wave function, the first-order change of molecular orbitals (U^a) and CI coefficients ($\frac{\partial C^K}{\partial a}$) with respect to the displacements of nuclear coordinates are required[?]. These values are determined from the coupled perturbed state-averaged CASSCF (CPSA-CASSCF) equations. The details are presented in the Chapter 2. The weights for the S_0 and S_1 states used to construct the state-averaged CASSCF wave function were chosen to be 0.6 and 0.4, respectively.

We calculated the electronic nonadiabatic coupling elements given in Eq. (2.19) between the S_0 and S_1 states along the reaction path for the S_1 state. The elements with respect to the symmetry adapted internal coordinates defined in Ref. [18] are shown in Fig 5. Only the matrix elements for the HCH asymmetric bending and CH asymmetric stretching mode have non-zero values from the symmetry. These values form odd functions along the reaction path with respect to the origin ($\rho = 0$). As seen in Fig. 5, both the matrix elements become large with the increase of out-of-plane bending angle ρ . In particular, the contribution from the HCH asymmetric bending mode increases rapidly at the region of $\rho > 60^\circ$. This may be attributed to the large variation of HCH angle along the reaction path compared to the CH distance.

The remaining part of the matrix elements of nonadiabatic coupling, the vibrational nonadiabatic coupling matrix element, is given by[19];

$$\langle \chi_k^f(Q'_k, \rho) | \frac{\partial}{\partial Q_k} | \chi_k^i(Q_k, \rho) \rangle = \prod_{j \neq k} \langle \chi_j^f(Q'_j, \rho) | \chi_j^i(Q_j, \rho) \rangle. \quad (3.41)$$

Where, $\chi_k^i(Q_k, \rho)$ and $\chi_k^f(Q'_k, \rho)$ are the harmonic functions for the transverse normal coordinate Q_k of S_1 state and those for Q'_k of S_0 state at ρ , respectively. Multidimensional Franck-Condon integrals, which are required to obtain these matrix elements, are evaluated using the method derived by Kupka and Cribb[20], in which the Duschinsky effect[21] is taken into account. We employed about 41,000 vibrational basis functions for the S_0 state, Eq. (3.34), to calculate these matrix elements. With the electronic and vibrational matrix elements of nonadiabatic coupling, the initial wave packets on the S_0 state, i.e. $a_i^m(0)$, were obtained following to Eq. (3.35).

3.3 Transition rate of formaldehyde

3.3.1 Auto-correlation functions

The wave packet propagations were carried out starting from various initial vibrational levels of S_1 state. In addition to the 4^0 , 4^1 , 4^2 , and 4^3 levels, the initial states involve the 2^14^1 , 2^14^3 , 2^24^1 , and 2^24^3 states where both the CO stretching, ν_2 , and out-of-plane bending, ν_4 , modes are excited, and the 5^1 and 2^15^1 ones in which the asymmetric CH stretching mode, ν_5 , is excited in the S_1 state. The squares of the amplitude for the initial wave packet, $\sum_m |a_i^m(0)|^2$, for the 4^0 , 4^1 , 4^2 , and 4^3 states are shown in Figs. 6(a)~(d) as the functions of out-of-plane bending angle ρ . Comparing to the initial wave functions, the locations of maximum tend to shift to the direction of large absolute value of ρ for each state ($\pm 33^\circ \rightarrow \pm 42^\circ$; $\pm 35^\circ \rightarrow \pm 45^\circ$; $0^\circ, \pm 45^\circ \rightarrow \pm 17^\circ, \pm 51^\circ$; and $\pm 20^\circ, \pm 50^\circ \rightarrow \pm 25^\circ, \pm 55^\circ$, for the 4^0 ; 4^1 ; 4^2 ; and 4^3 states, respectively). An important feature is a decrease of the magnitude near the origin because of small electronic nonadiabatic coupling at this region. Figure 7 illustrates the auto-correlation function for the wave packet initiated from the 4^1 state. Both the real and imaginary parts oscillate with the period of 1.7 fs and decay gradually with time. This oscillation period may be attributed to the time scale of out-of-plane bending motion. The main feature of wave packet auto-correlation functions started from the other initial vibrational states were the same as that of 4^1 state, though the oscillation periods become slightly shorter with the excitation of ν_2 and ν_5 modes.

The magnitudes of the auto-correlation functions, $|\langle \phi(0)|\phi(t) \rangle|$, corresponding to the 4^0 , 4^1 , 4^2 , and 4^3 states are given in Fig. 8, where we can see that all the functions show a Gaussian like damping behavior and almost disappear at 5 fs. These magnitudes from the $2^1 4^1$, $2^1 4^3$, $2^2 4^1$, and $2^2 4^3$ states are almost the same as those of 4^1 , 4^3 , 4^1 , and 4^3 states, respectively. The auto-correlation functions for the 5^1 and $2^1 5^1$ states decay more rapidly rather than those of other states. These rapid decays mainly come from the dephasing by many wave packets expanded by the vibrational basis functions of S_0 which propagate with different energies each other.

In order to examine the importance of vibrational relaxation in the S_0 state, we also performed the wave packet calculations with the vibrational adiabatic Hamiltonian expressed in Eq. (3.39). The absolute values of the auto-correlation functions for the case of 4^0 and 4^1 states are shown in Fig. 9 as representatives of the odd and even initial wave packets with respect to the coordinate ρ . The time dependent behaviors of the auto-correlation functions are similar to those in Fig. 9 at the initial stage of the propagation. However, the recurrences were observed at about 41, 58, and 111 fs in the calculations up to 120 fs, whose magnitudes were about 20% of initial ones in both the cases. On the other hand, we found no such recurrences of the auto-correlation functions obtained using the Hamiltonian matrices including the off-diagonal elements and damping terms. Thus the vibrational coupling in the S_0 state is important to diminish the recurrence of auto-correlation function in a long-time scale. We calculated the probabilities of existence of wave packets in the manifold(a) to see the effect of damping terms in the effective Hamiltonian. The calculated probabilities are 23% at 57 fs for the wave packet started from the 4^0 state and 10% at 23 fs for that from the 4^1 state, respectively, indicating that the vibrational energy transfer is a rather slower process compared to the initial decay caused by the dephasing. From these results, it may be concluded that it is indispensable to take the vibrational coupling in the S_0 state into account in evaluating the rate constants of the nonadiabatic transition and we can obtain it by evolving the initial wave packets for a short time (7 or 8 fs) using the effective Hamiltonian.

In the present approach, the nonradiative transition rate is represented by the product of two terms;

$$k_{NR} = \langle \phi(0)|\phi(0) \rangle \cdot \frac{1}{\hbar^2} \int_{-\infty}^{\infty} \exp\left(\frac{iE_it}{\hbar}\right) C(t) dt, \quad (3.42)$$

and

$$C(t) = \frac{\langle \phi(0) | \phi(t) \rangle}{\langle \phi(0) | \phi(0) \rangle}, \quad (3.43)$$

where the first term is the norm of initial wave packet which is determined by the shape of initial state wave function and the nonadiabatic coupling matrix elements and the second term is the Fourier transformation of the normalized auto-correlation function reflecting the quantum dynamics on the S_0 surface. As seen in Fig. 8, the norms of initial wave packets for the 4^0 , 4^1 , 4^2 , and 4^3 states are not in the order of the quantum number of out-of-plane bending vibration; i.e. $4^0 < 4^2 < 4^1 < 4^3$. This is because the wave functions for the 4^0 and 4^2 states have a large amplitude near the origin ($\rho = 0^\circ$), contrasting with those for the 4^1 and 4^3 states. Since the electronic matrix elements of nonadiabatic coupling are odd functions with respect to the coordinate ρ , the amplitudes for the 4^1 and 4^3 states rather than those for the 4^0 and 4^2 states are intensified by these electronic matrix elements. However, the normalized auto-correlation function of 4^1 state decays more rapidly rather than that of 4^2 state and the rate constants consequently become in the order of the quantum number.

3.3.2 Rate constants from single vibronic levels

The calculated transition rates from various single vibronic levels of S_1 state are shown in Fig. 10 and are listed in Table 2 along with the experimental values measured by Miller and Lee[22]. The rate constants from the 4^0 and 4^2 states are not observed experimentally because these are not accessible by the electronic dipole transition. With regard to the values from the 4^0 , 4^1 , 4^2 , and 4^3 states, the calculated rate constants increase with the increase of the quantum number of out-of-plane bending motion. The calculated values were about twice of the experimental ones reported by Miller and Lee for the 4^1 and 4^3 states. For the transitions from the states where the CH asymmetric and CO stretching modes are excited, the rate constants from the 5^1 and 2^15^1 states were almost one third of the experiment. Miller and Lee pointed out that the energy difference between the 5^1 and 1^14^1 states was only 2.7cm^{-1} and these states are considered to be strongly coupled. The experimental rate constants are expected to be those from the mixed states of 5^1 and 1^14^1 states and of 2^15^1 and $1^12^14^1$ states, respectively. Therefore the calculated rate constants for the 5^1 and 2^15^1 states may not be compared with the experimental ones simply. As seen in Table 2, the ratios of calculated rate constants to the experimental ones decrease

with the increase of the quantum number of the CO stretching mode (1.9, 1.1, and 0.6 for the 4^1 , 2^14^1 , and 2^24^1 states; 1.9, 1.5, and 1.2 for the 4^3 , 2^14^3 , and 2^24^3 states). This is because that the harmonic approximation may not be appropriate for the description of CO stretching motion. Taking the approximations introduced in the present calculations and the experimental uncertainties into account, the discrepancies between the present estimated and the experimental rate constants would be acceptable.

Compare the rate constant from the 2^14^1 state to that from the 4^1 state, the values of $\langle \phi(0)|\phi(0) \rangle$ are identical for both the states. Thus the difference of rate constants between these two states comes from the difference of dephasing dynamics. The decay of 2^14^1 state is slightly slower than that of 4^1 state and the transition rate becomes faster. The same situation is also seen between the 2^24^1 and 4^1 , the 2^14^3 and 4^3 , and the 2^24^3 and 4^3 states. As for the transition rates from the 5^1 and 2^15^1 states, the norm of initial wave packet is 3.0×10^{-10} a.u. which is larger than that for the 4^0 state by the factor 2.2. The difference is well correlated to the ratio of rate constants between the 5^1 and 4^0 states.

3.4 Discussion and conclusion

In this chapter, we have presented an efficient time-dependent wave packet method to estimate the nonradiative transition rate and applied it to the internal conversion of formaldehyde as a typical example of polyatomic molecules. Ab initio calculations were carried to construct the reaction path Hamiltonian for the S_0 state with the CASSCF wave functions and to obtain the electronic matrix elements of nonadiabatic coupling between the S_0 and S_1 states with the state-averaged CASSCF wave functions. The time-dependent wave packet dynamics calculations were employed using the FFT algorithm. We showed that the auto-correlation function, used to obtain the rate constants with the Fourier transformation, rapidly decays because of the dephasing between the wave packets in the vibrational basis functions of S_0 and it is necessary to take the vibrational relaxation into account to restrain the recurrences of auto-correlation function after the decay by the dephasing. The calculated nonradiative rate constants were in good agreement with the experimental ones.

In the previous works to estimate the nonradiative rate constants in formaldehyde[18],[23],[24], there exists a problem in determining the wave functions of highly vibrational excited states of S_0 characterized by chaotic motion. Yeung and Moore[18] calculated the nonradiative

decay rates using Fermi's Golden rule formula in which the vibrational eigenfunctions of S_0 state were constructed by the harmonic functions and the anharmonic mixing of vibrational states was assumed to be taken into account by averaging the rate constants over a range of final levels. In the present study, we employed a time-dependent approach and the wave packet dynamics calculations were carried out using the reaction path Hamiltonian.

The difficulty in considering the intramolecular vibrational energy redistribution in polyatomic molecules comes from a large size of Hamiltonian matrix in dynamics calculations due to enormous number of the vibrational states of S_0 . Here, though the initial wave packet is expanded by a large number of the basis functions, the reduction of Hamiltonian matrix is efficiently accomplished by introducing the effective Hamiltonian[7]. Moreover, for the nonadiabatic transition, the wave packet propagation method using the SOD scheme is appropriate to deal with the vibrational relaxation in highly vibrational excited states, which is expected to be an extremely rapid process, because the propagation scheme is stable during such a short time period.

It is also noted that realistic values for the electronic nonadiabatic coupling elements are necessary to obtain the nonradiative transition rate comparable to the experiments. For this purpose, we carried out ab initio calculations for these matrix elements with the CPSCA-CASSCF method which provides these elements analytically.

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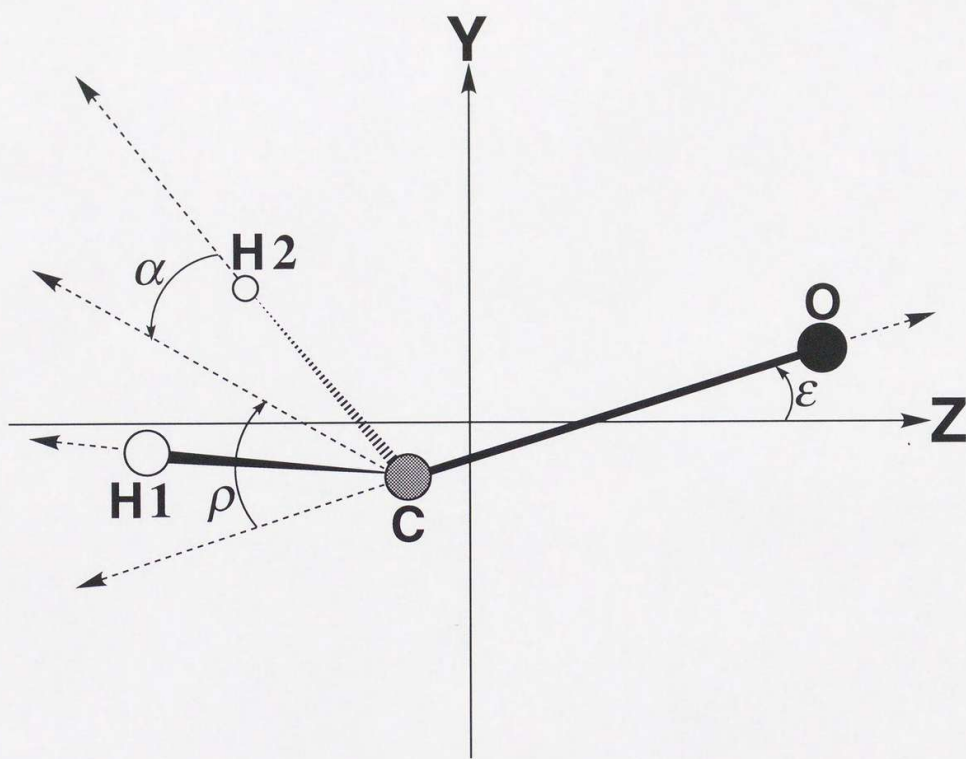


Fig. 1

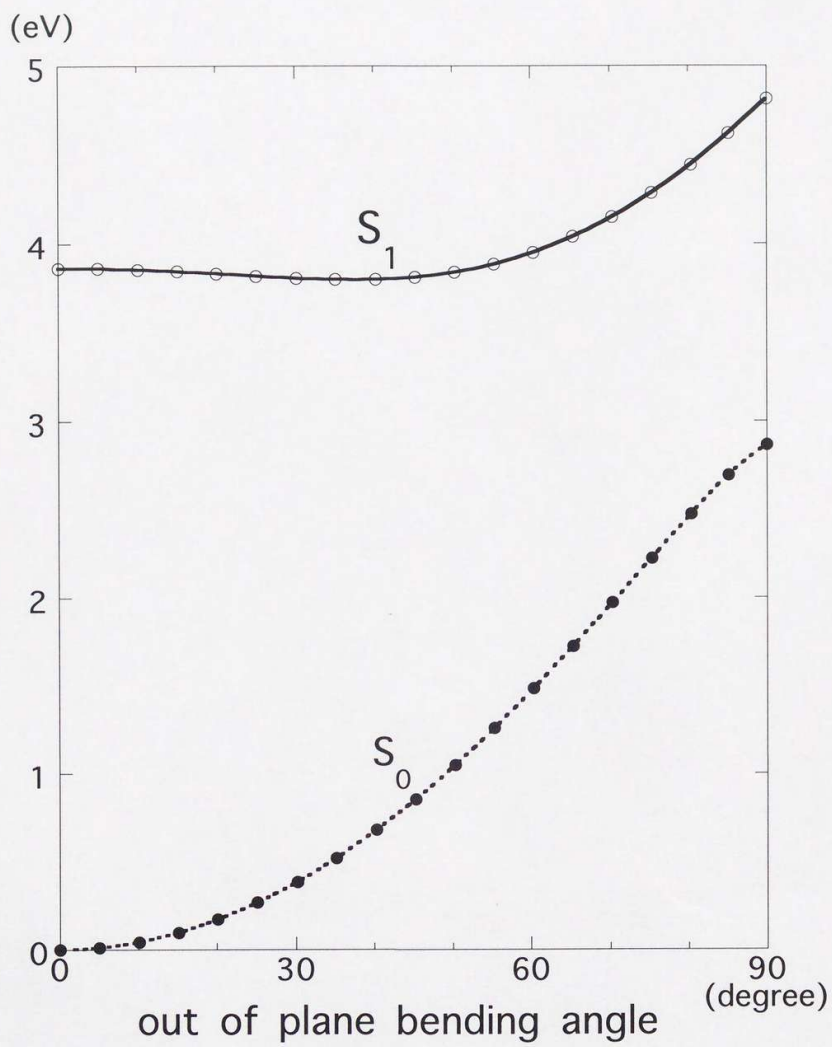


Fig. 2

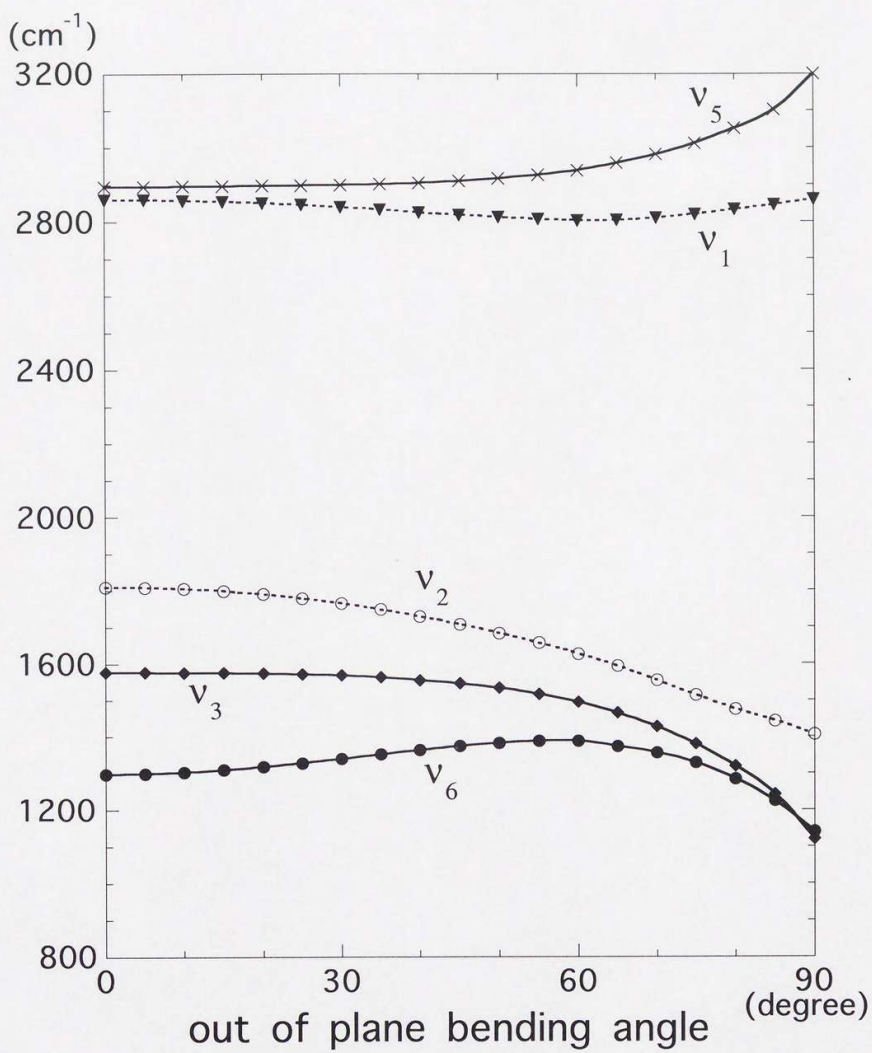


Fig. 3(a)

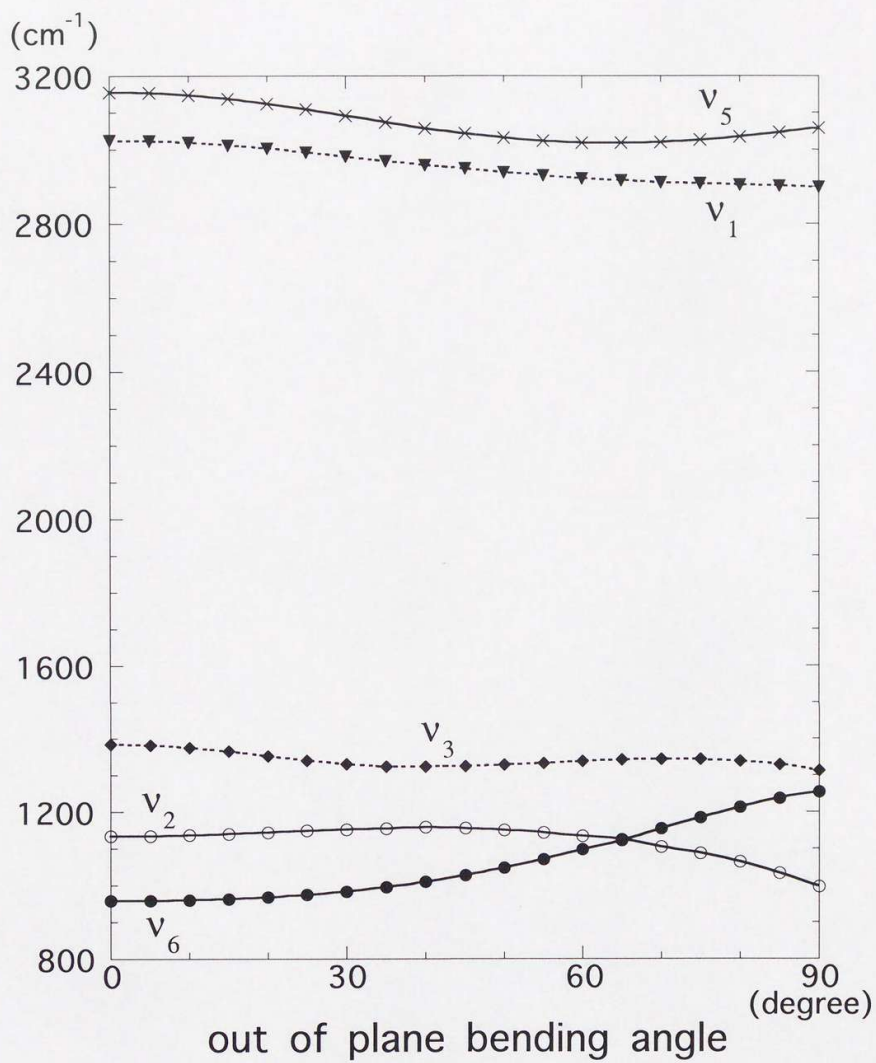


Fig. 3(b)

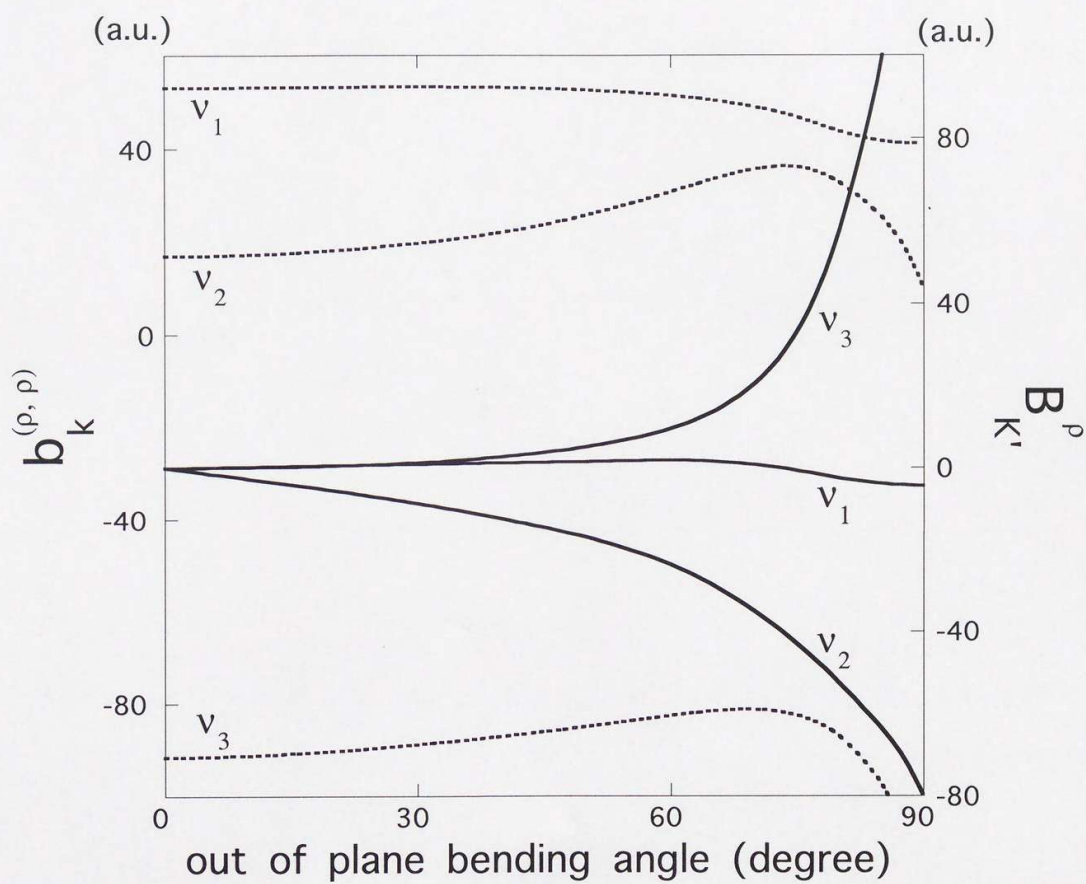


Fig. 4

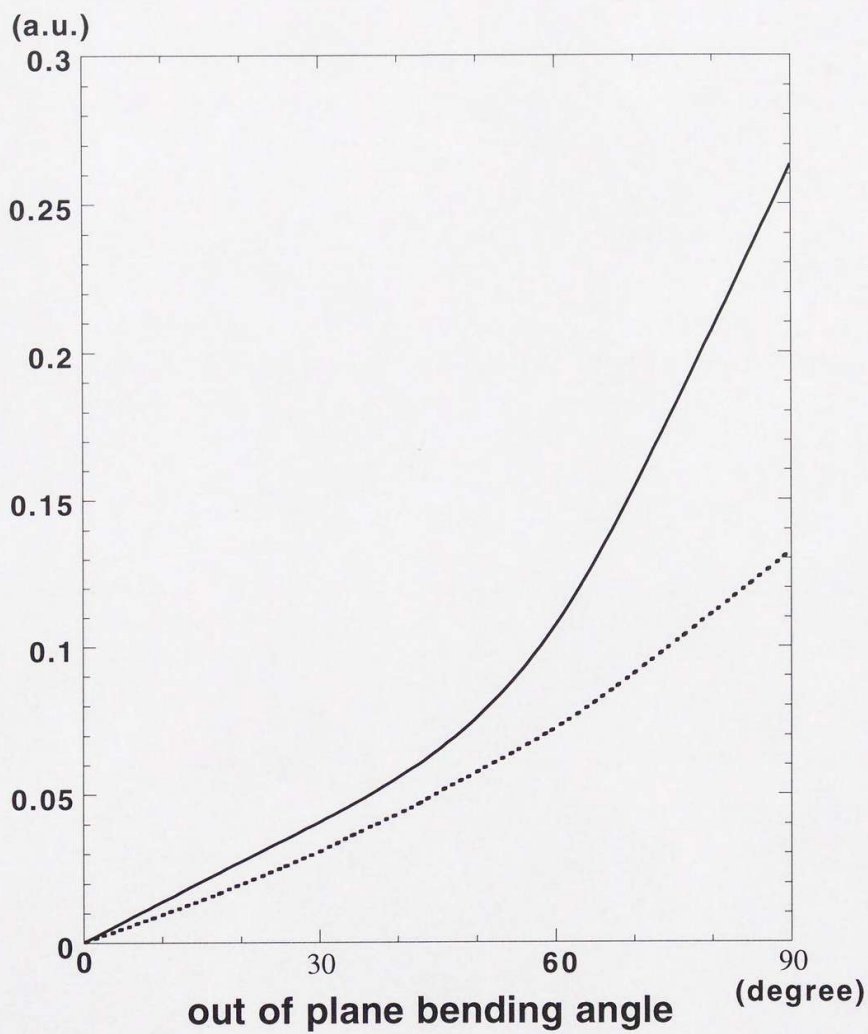


Fig. 5

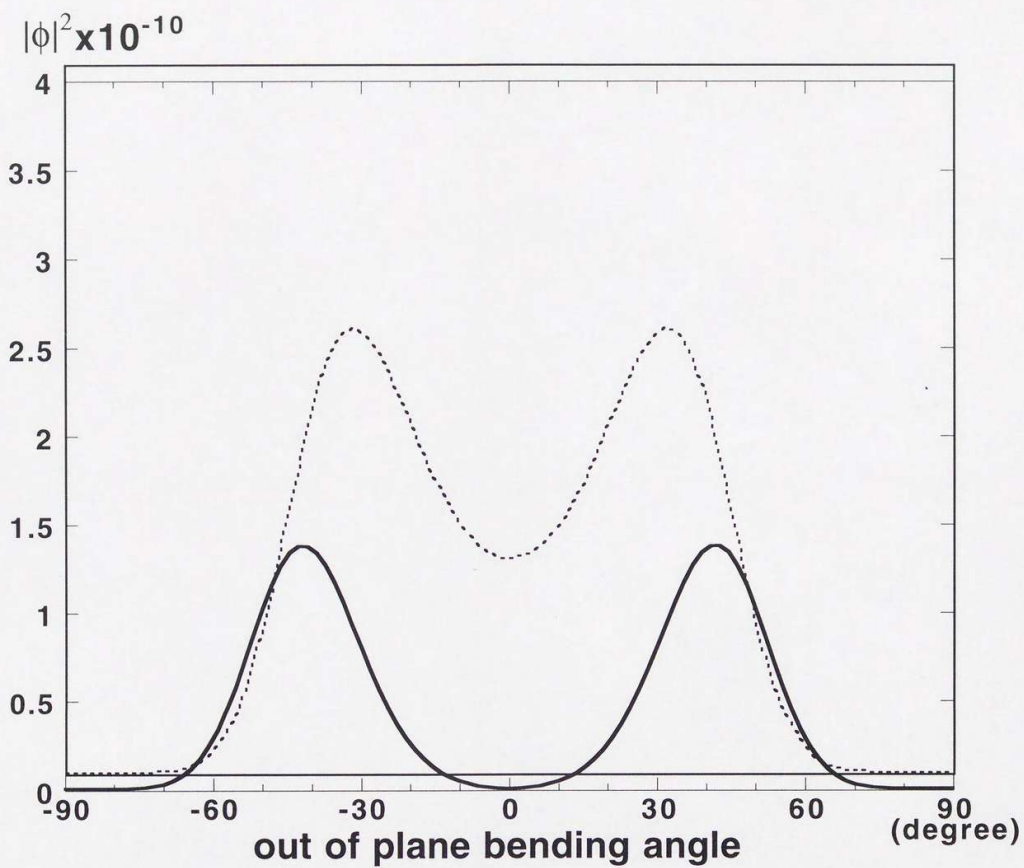


Fig. 6(a)

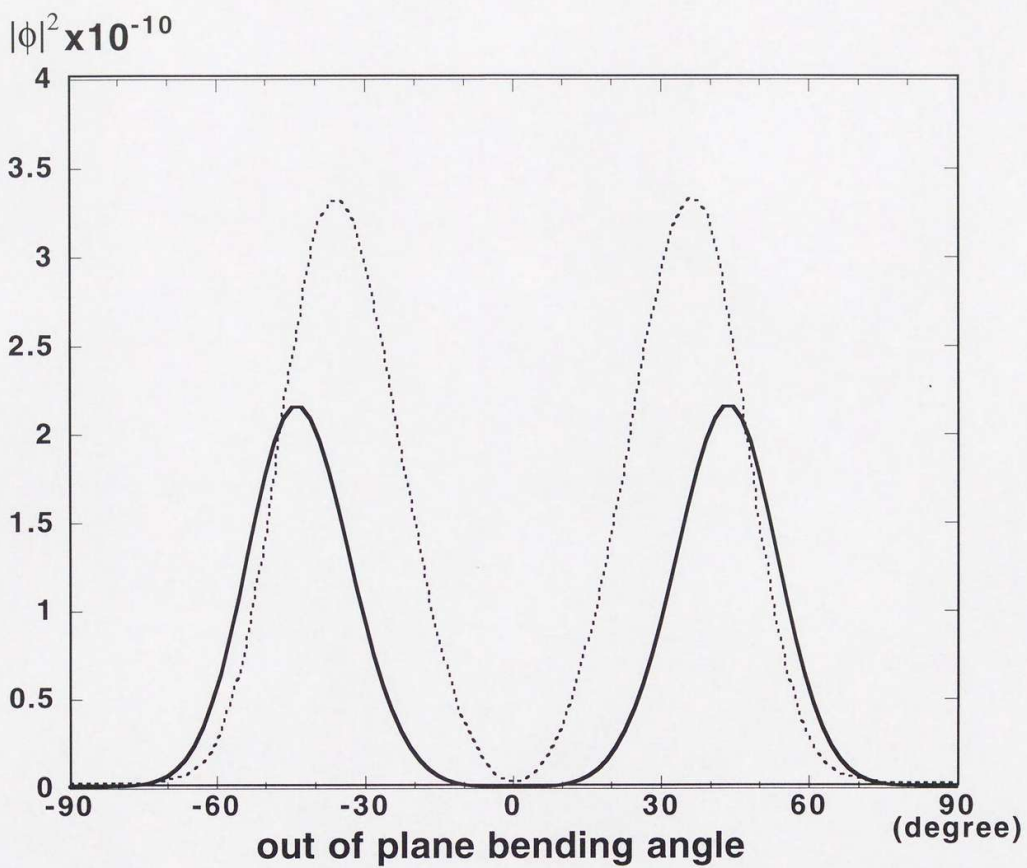


Fig. 6(b)

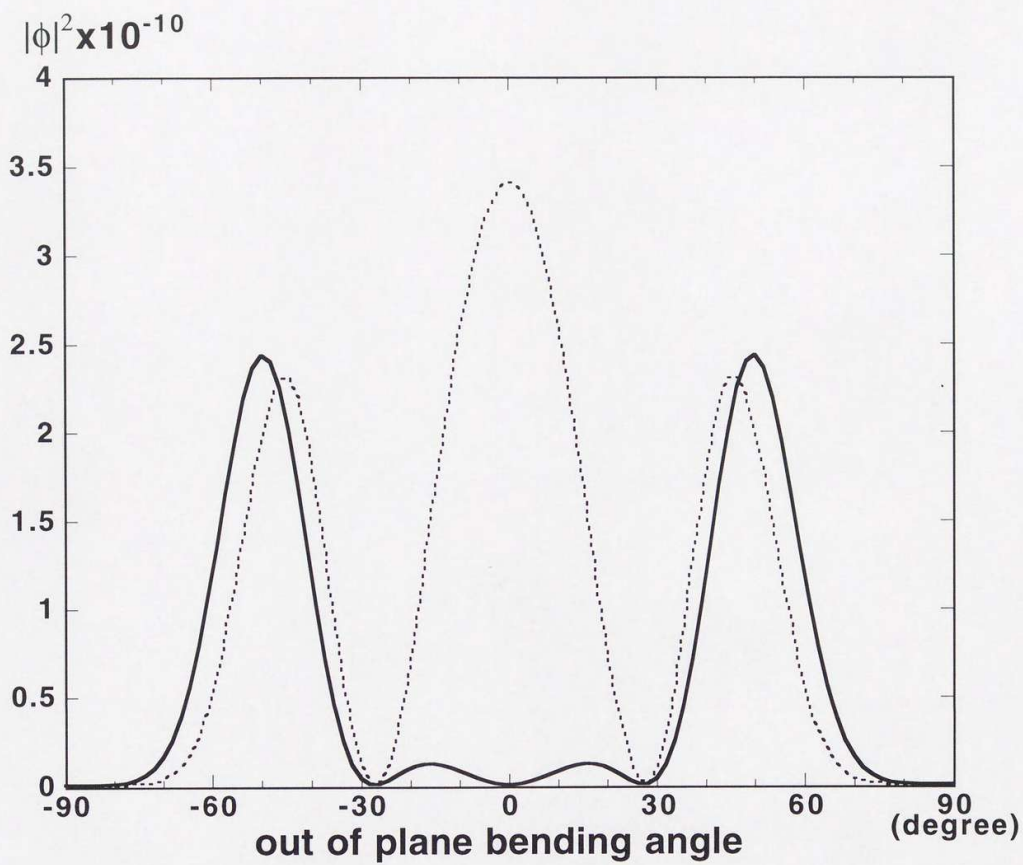


Fig. 6(c)

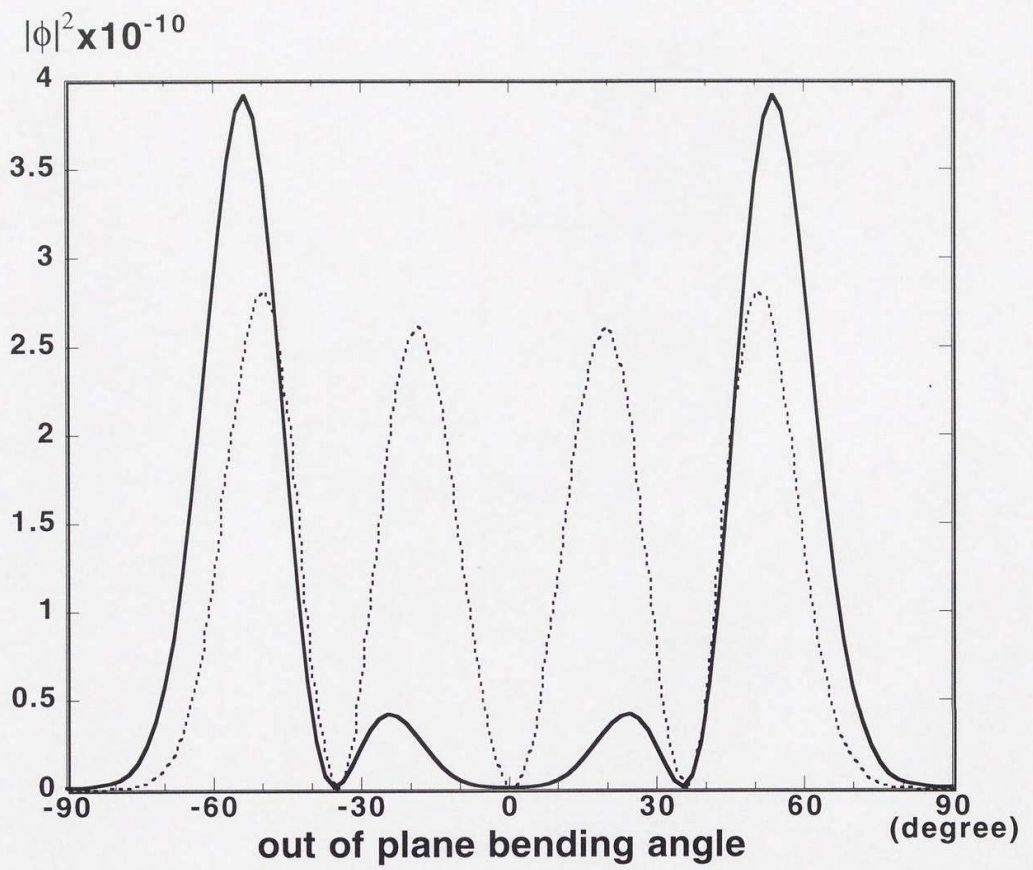


Fig. 6(d)

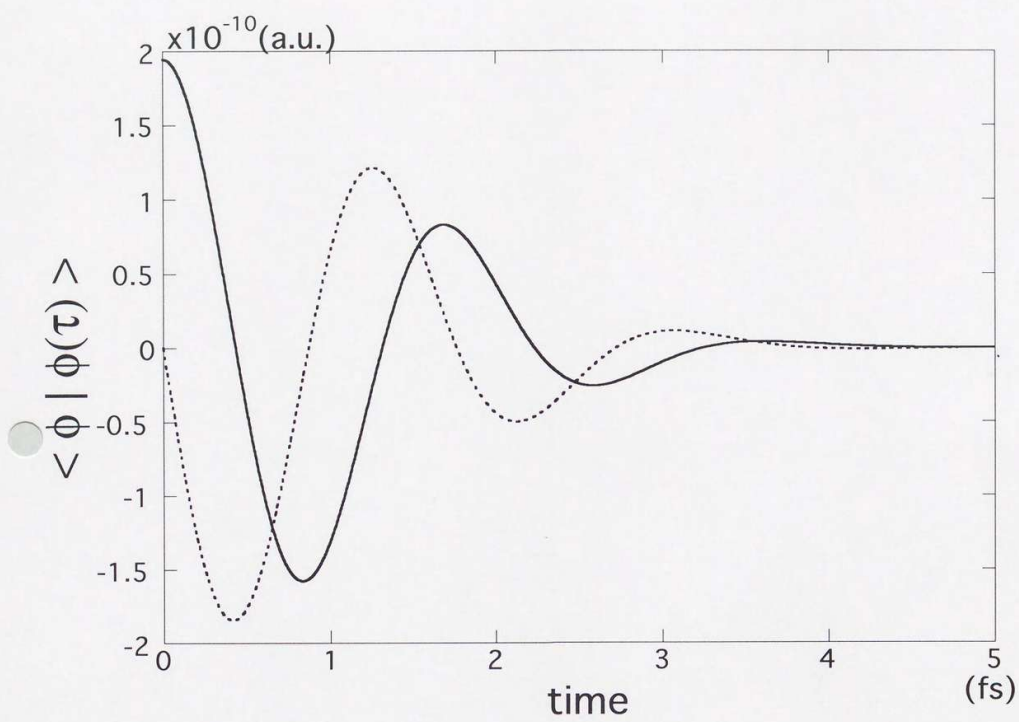


Fig. 7

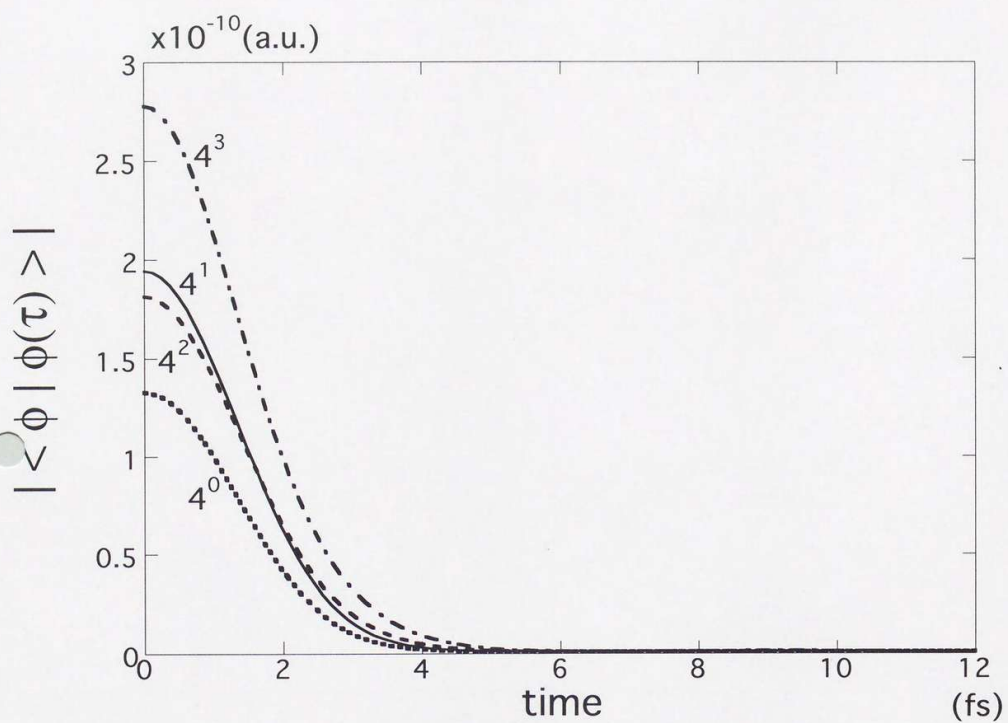


Fig. 8

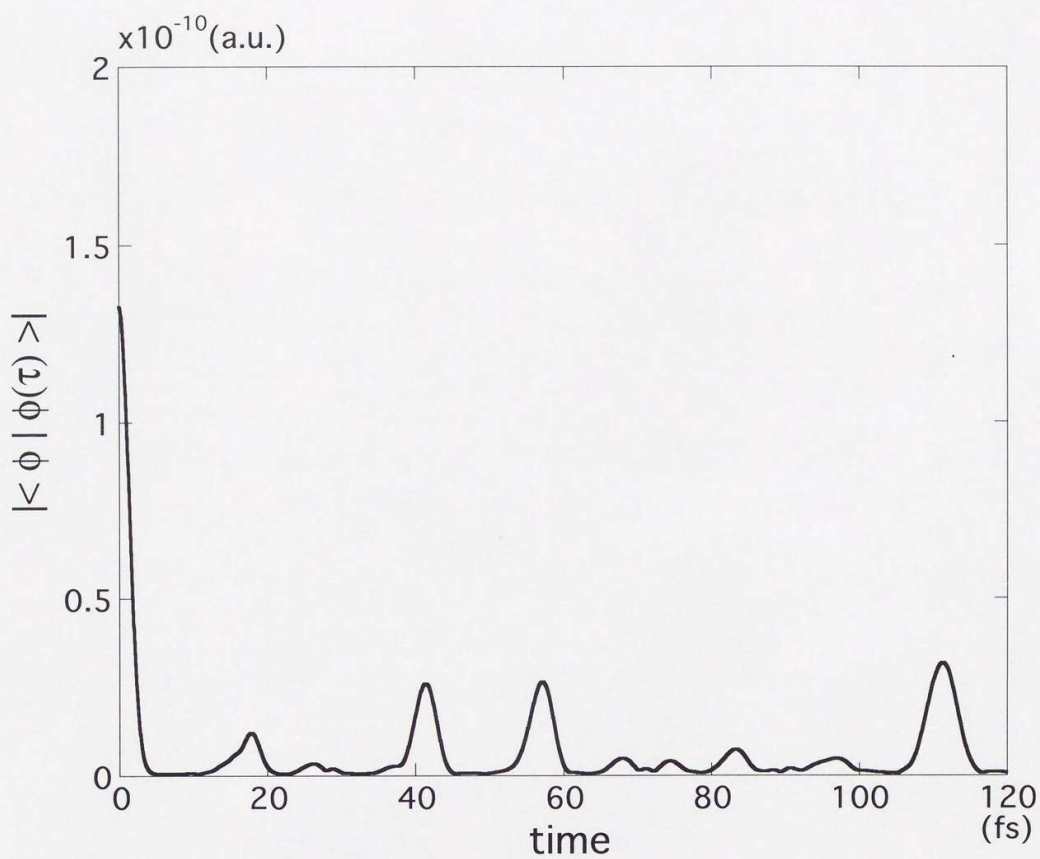


Fig. 9(a)

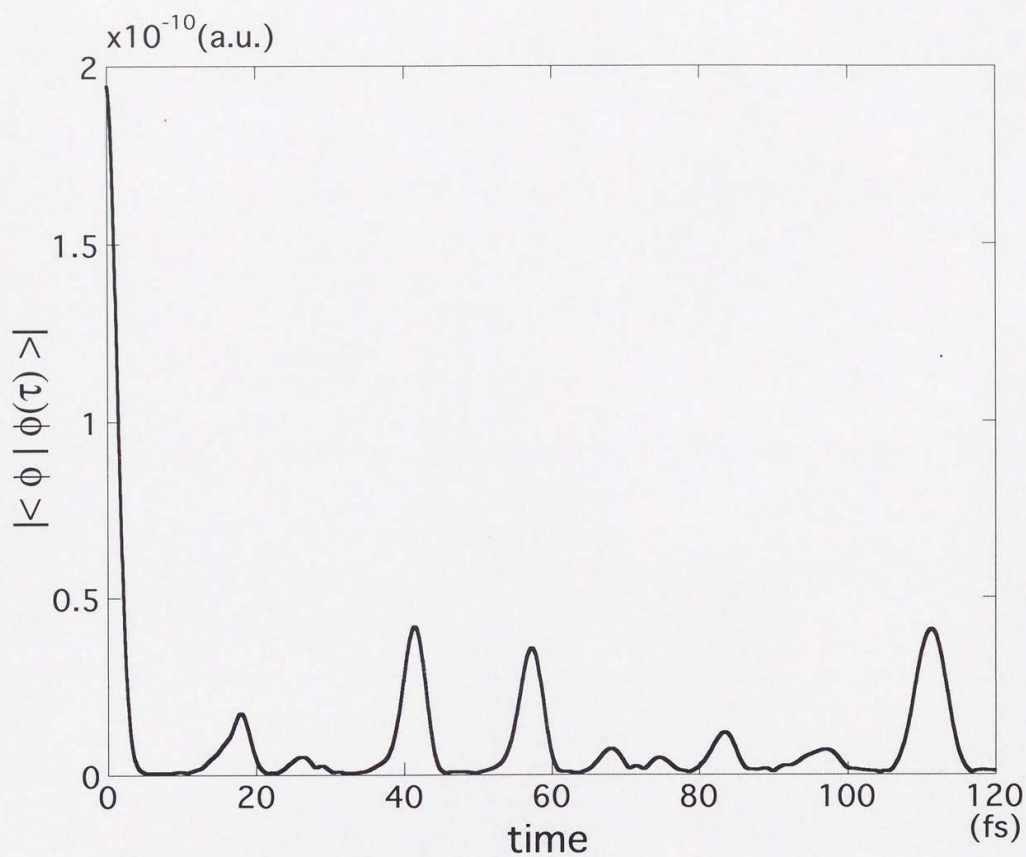


Fig. 9(b)

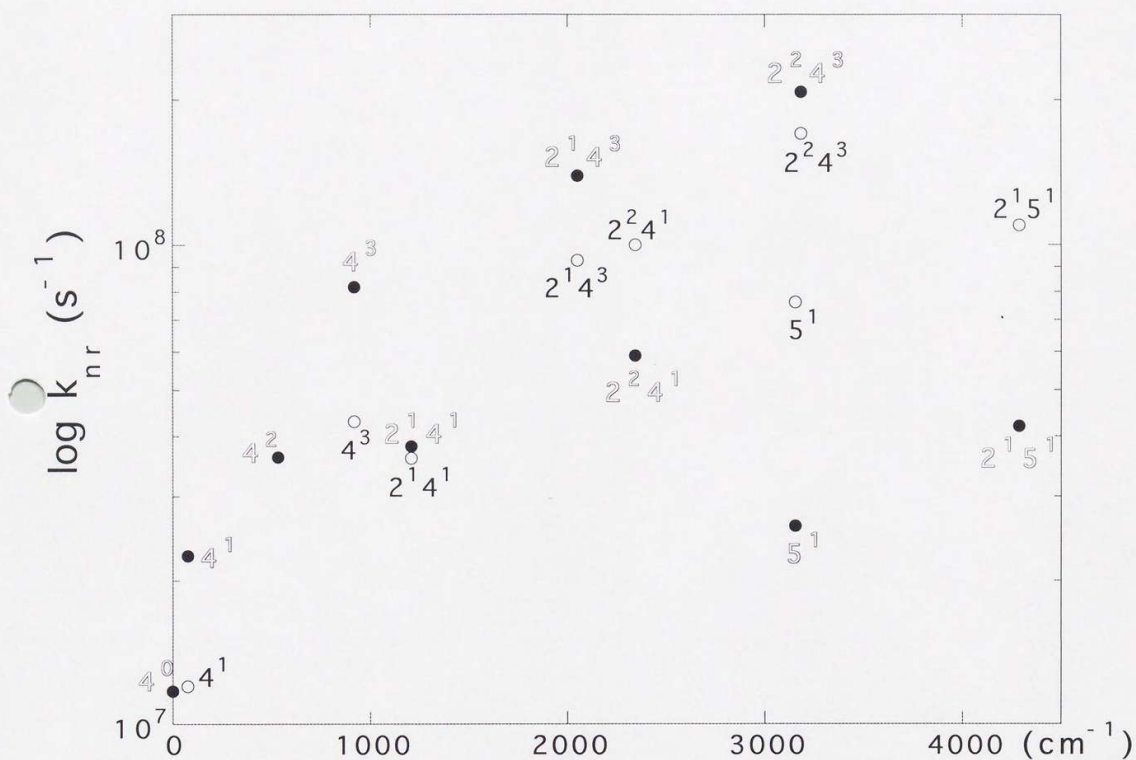


Fig. 10

Table 1: Vibrational frequencies of $H_2CO(S_0$ and S_1)

mode	assignment	S_0		S_1	
		calc.	expl. ^{a)}	calc.	expl. ^{a)}
ν_1	sym C-H stret.	2858	2782	2962	2847
ν_2	C=O stret.	1811	1746	1142	1173
ν_3	sym H-C-H bend	1578	1500	1370	1290
ν_4	out of plane bend	1214	1167	-	-
ν_5	asym C-H stret.	2889	2843	3060	2968
ν_6	asym H-C-H bend	1299	1249	987	898

a) the experimental values taken from C. M. Hadad et al.

(J. Phys. Chem. **97** (1993) 4293).

Table 2: Rate constants of $H_2CO(S_1 \rightarrow S_0)$

S_1 state	Rate constants	
	calc. (s^{-1})	exp. (s^{-1}) ^{a)}
4^0	1.17×10^7	-
4^1	2.25×10^7	1.2×10^7
4^2	3.62×10^7	-
4^3	8.18×10^7	4.3×10^7
$2^1 4^1$	3.81×10^7	3.6×10^7
$2^1 4^3$	1.39×10^8	9.3×10^7
$2^2 4^1$	5.89×10^7	1.0×10^8
$2^2 4^3$	2.07×10^8	1.7×10^8
5^1	2.60×10^7	7.6×10^7
$2^1 5^1$	4.20×10^7	1.1×10^8

a) the experimental values taken from

Miller and Lee (J. Chem. Phys. **68** (1978) 4448).

(Figure Caption for Fig. 1)

The reference positions of C, O , and two H atoms in the molecule-fixed coordinate system. The out-of-plane angle ρ is chosen as the reaction path and 2α is equal to HCH angle. In this configuration, C and O atoms are on the yz -plane, two H atoms are located to be C_s symmetry with respect to the yz -plane, the center of mass is the origin, and ε is chosen in such a way that the angular momentum equals to be zero in this coordinate system.

(Figure Caption for Fig. 2)

Potential energy surfaces along the out-of-plane bending angle (the reaction path denoted by ρ in Fig. 1) of formaldehyde. The dashed curve is the S_0 potential energy surface and the solid curve is the S_1 potential energy surface, respectively.

(Figure Caption for Fig. 3)

Changes of the frequencies for (a) the S_0 state and (b) the S_1 state along the out-of-plane bending angle (the reaction path denoted by ρ in Fig. 1) of H_2CO . ν_1 : symmetric C-H stretching mode. ν_2 : C-O stretching mode. ν_3 : symmetric H-C-H bending mode. ν_5 : asymmetric C-H stretching mode. ν_6 : asymmetric H-C-H bending mode.

(Figure Caption for Fig. 4)

Variations of $b_k^{(\rho, \rho)}$ and $B_{k'}^\rho$ along the out-of-plane bending angle (the reaction path denoted by ρ in Fig. 1) as representative elements of the reaction path Hamiltonian of H_2CO . The dashed curve is for $b_k^{(\rho, \rho)}$ and the solid curve is for $B_{k'}^\rho$, respectively. ν_1, ν_2 , and ν_3 are correspond to the vibrational modes shown in Fig. 3 and Table 1.

(Figure Caption for Fig. 5)

Absolute values of the electronic matrix elements of nonadiabatic coupling, calculated by state-averaged CASSCF method, along the out-of-plane bending angle (the reaction path denoted by ρ in Fig. 1) of formaldehyde. The dashed curve is for the asymmetric C-H stretch and the solid curve is for the asymmetric H-C-H bend, respectively.

(Figure Caption for Fig. 6)

The dashed curves are for squares of the initial wave functions, $\langle \psi_i | \psi_i \rangle$, obtained by the Fourier grid Hamiltonian method using the vibrational adiabatic Hamiltonian in arbitrary units. The solid curves are for squares of the initial wave packet, $\langle \phi(0) | \phi(0) \rangle$, affected by the nonadiabatic coupling along the out-of-plane bending angle (the reaction path denoted by ρ in Fig. 1) of H_2CO . For (a) 4^0 ; (b) 4^1 ; (c) 4^2 ; (d) 4^3 state of S_1 .

(Figure Caption for Fig. 7)

Time dependence of auto-correlation function, $\langle \phi(0) | \phi(t) \rangle$, for 4^1 state of S_1 . The solid line denotes the real part of auto-correlation function and the dashed line the imaginary part of auto-correlation function.

(Figure Caption for Fig. 8)

Time dependence of absolute values of auto-correlation functions, $|\langle \phi(0) | \phi(t) \rangle|$, for 4^0 , 4^1 , 4^2 , and 4^3 state of S_1 .

(Figure Caption for Fig. 9)

Time dependence of absolute values of auto-correlation functions, $|\langle \phi(0) | \phi(t) \rangle|$, calculated with the vibrational adiabatic approximation; (a) for 4^0 state and (b) for 4^1 state.

(Figure Caption for Fig. 10)

Calculated nonradiative transition rate constants ($\bullet$) for the single vibronic levels of H_2CO along with the experimental values ($\circ$). The initial levels are labeled by the vibrational mode, corresponding to that shown in Fig. 3 and Table 1, with the superscript representing the number of quanta in its mode of S_1 state.

Chapter 4

Conclusion

In the present thesis, the author has proposed a time-dependent method to estimate non-radiative transition rate constants theoretically and applied it to the problem of internal conversion from S_1 to S_0 state in formaldehyde.

In the Chapter 2, another derivation of coupled perturbed state-averaged (CPSA) CASSCF equations has been presented. Under the Born-Oppenheimer approximation usually used in ab initio MO methods, the nonadiabatic coupling is the origin of the nonadiabatic transition between the electronic states. The state-averaged CASSCF wave function has the desirable features for the evaluation of nonadiabatic coupling as (1) molecular orbitals are optimized for both the considering electronic states with arbitrary weights and (2) the orthogonality is satisfied between these electronic states. Though the matrix elements of electronic nonadiabatic coupling is indispensable to estimate the nonadiabatic transition rates, there are no studies in which these matrix elements were calculated analytically with the state-averaged CASSCF wave functions because the CPSACASSCF equations is need to be solved. Using the derivatives of CI and MO coefficients evaluated from these equations, it is also possible to calculate the energy gradients in the plural electronic states simultaneously with the state-averaged CASSCF wave function analytically and we expect to obtain the information on the region of the avoided crossing in detail.

In the Chapter 3, the nonradiative transition rates from the single vibronic levels of S_1 to S_0 state were estimated using a new time-dependent method based on Fermi's Golden rule. In the present method, the initial wave packets are prepared on the basis functions of S_0 state with the use of nonadiabatic coupling matrix elements calculated by ab initio molecular orbital method. The basis functions are composed of the DVR basis functions for the large amplitude motion and the harmonic functions for the small amplitude motion.

The wave packet dynamics calculations are carried out using the reaction path Hamiltonian. The vibrational relaxation on the S_0 surface is treated by introducing the effective Hamiltonian. The parameters required to construct these Hamiltonians are obtained with the CASSCF wave functions and the electronic matrix elements of nonadiabatic coupling between the S_0 and S_1 states are calculated with the state-averaged CASSCF wave function analytically using the CPSACASSCF equations, described in the Chapter 2.

The advantages of the present method are summarized as follows; (1) introducing the basis set consisted of the DVR basis functions and the harmonic functions and employing the wave packet dynamics calculations with the Fermi's Golden rule transformed to the time-dependent form, it is not necessary to determine the highly vibrational excited states characterized by the chaotic motion, (2) the Hamiltonian matrix used in the time propagation is efficiently reduced by introducing the effective Hamiltonian and the vibrational relaxation can be easily treated in the dynamics calculations, and (3) the nonradiative transition rates are expected to obtain due to the adoption of the realistic matrix elements of nonadiabatic coupling.

The estimations of nonradiative transition rates in formaldehyde indicate that the propagation time needed in the present dynamics calculation method is considerably short because the auto-correlation functions decay rapidly due to the dephasing process of wave packets on the vibrational basis functions of S_0 . The calculated rate constants were in good agreement with the experimental ones.

The author believes that the present time-dependent approach proposed in the Chapter 3 is also applicable to the photodissociation reactions, in which the nonadiabatic transition plays an important role, and becomes an effective tool to elucidate the mechanism of electronic and vibrational relaxation.

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