STRING MODEL OF CHEMICAL REACTION COORDINATE

Akitomo TACHIBANA

Department of Hydrocarbon Chemistry and Division of Molecular Engineering, Faculty of Engineering, Kyoto University, Kyoto 606, Japan

Abstract

A geometrical model for estimating the effects of external fields upon a reaction path is proposed. The reaction path is defined as the intrinsic reaction coordinate (IRC) which is treated as a "string". The IRC frame is introduced in order to uniquely determine the attitude of the string with respect to the reaction medium. The string is thrown in the external fields of the reaction medium, and slides or rotates, and is deformed. The cell structure attached to the string is also deformed. A perturbational approach to the reaction rate formula is presented.

1. Introduction

External fields to chemical reaction systems have influence on the dynamics of the chemical reaction. We shall introduce a new concept of the "string model" in order to treat this kind of problem. Preliminary numerical results have been published elsewhere [1,2]. Much of the basic idea has been formulated in terms of differential geometry [3].

If we are treating the dynamics of the isolated molecular system, then we have the complete molecular Hamiltonian in terms of differential geometry, thereby introducing the concept of "molecular gauge potential" for the treatment of the vibration−rotation coupling [4(a)]. The fibre bundle theory of differential geometry has clarified complexities in the traditional approaches of nonrigid molecular dynamics [5] and Wilson's G matrix theory for semirigid molecular dynamics [6].

In the isolated reaction system, the Eckart frame for the treatment of the rigid to semirigid molecular vibrational problems is immaterial because it is not uniquely determined [4]. However, in the string model, in what follows in this paper, a moving frame attached to the string has significant meaning because we should determine the "attitude" of the reaction system with respect to the reaction medium. For this purpose, the concept of the "IRC" (intrinsic reaction coordinate) introduced by Fukui [7] is very helpful because along the IRC, the moving frame is defined uniquely. This is because the IRC satisfies a first-order differential equation, called the IRC equation [8]. The IRC passes through the *TS* (transition state) connecting *R* (reactant) and *P* (product) configuration using the boundary condition at the *TS*. The IRC equation utilizes the gradient vector of the Born−Oppenheimer adiabatic

potential energy of the reaction system. For isolated systems equipped with only internal forces, the IRC equation is nothing but the steepest-descent path in the mass-weighted coordinate system. The IRC then satisfies the coordinate-free characterization of the translation-free and rotation-free reaction path. We may call the moving frame associated with the IRC the IRC-driven moving frame, or the IRC frame for short. The IRC frame determines uniquely the attitude of the string with respect to the reaction medium.

From its definition, the IRC carries the potential energy characterization of the configurations of the reactant, the transition state, and the product: the "cell" structure partitioning of the configuration space of the reaction system [9]. We also note the catchment region concept for the characterization of the Born–Oppenheimer adiabatic potential energy surface [10]. The cell structure allows the picture of the local vibrational mode orthogonal to the IRC, defined by using the extended Hessian matrix [11] along the IRC. The concept of the local vibrational mode further allows the picture of the local characteristics of the reaction dynamics.

In the string model, the local vibrational motions attached to the IRC are all determined uniquely in the reaction medium using the IRC frame as the unique moving frame. Variational principles of the IRC have also been studied in this connection [3, 12].

2.   String model

We would like to apply our theoretical model to estimate the effects of the external fields upon a given reaction path [3]. First, consider a chemical reaction system A. Calculate a reaction path and the reaction rate. Second, let the system be embedded in a reaction medium M. The schematic view is shown in fig. 1.
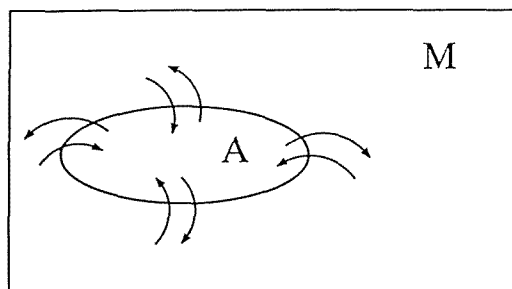
Reaction System A and Reaction Medium M

Fig. 1. Interaction of a chemical reaction
system A and the reaction medium M.

The interaction between A and M affects the original reaction path and the original reaction rate. For example, let A be a gas phase reaction system. Then, M

is a solvent, water, for example, or a surface of a catalyst. Our approach here is that, for any complex situation, we first consider an isolated system *A* and, second, consider a reaction medium *M*, and then introduce the interaction. If the interaction is mainly due to small intermolecular forces, then we may appeal to perturbation theory. In general, however, if the interaction is very large then, for example, the exchange of heat and vibrational energies and moreover of electrons should also be taken into account. Furthermore, the solvent molecule may intervene in the reaction system. For example, consider a proton transfer system for *A*. If the solvent can form a hydrogen bond to the system and make a hydrogen relay system, then we observe a strong deformation of the original reaction path, namely, a bifurcation of the original reaction path may be brought about. For all these situations, we shall stick to the simple model "*A* and *M* associated with the mutual interaction" [3].

In order to proceed in a well-defined manner, we may first want to systematically settle the system *A* distinguished from *M*. For this purpose, it may be convenient to treat the system *A* as a huge molecule as a whole, a supermolecule. The translational motion and the rotational motion of the system *A* can then be treated as those of this supermolecule. The vibrational motions are now to be separated from these collective translational and rotational motions. The reaction path for *A* is then identified with one of the large-amplitude vibrational motions. For this purpose, the IRC (intrinsic reaction coordinate) proposed by Fukui [7] is suitable because along the IRC, the translation and rotation as a whole does not occur. We shall then formulate the properties of the IRC as follows.

The IRC is defined by a differential equation: the IRC equation using the potential energy U_A of the reaction system *A* – the adiabatic potential based on the Born–Oppenheimer approximation. We represent the nuclear configuration of a chemical reaction system composed of *N* nuclei by a point in $3N$-dimensional space-fixed Cartesian configuration space with coordinates X_α, Y_α, and Z_α ($\alpha = 1, 2, \ldots, N$). The potential energy U_A is a function of these coordinates.

The Lagrange equations of motion for the nuclei are given as

$$(\mathrm{d}/\mathrm{d}t)[M_\alpha \dot{X}_\alpha] = -\partial U_A / \partial X_\alpha,$$

$$(\mathrm{d}/\mathrm{d}t)[M_\alpha \dot{Y}_\alpha] = -\partial U_A / \partial Y_\alpha,$$

$$(\mathrm{d}/\mathrm{d}t)[M_\alpha \dot{Z}_\alpha] = -\partial U_A / \partial Z_\alpha; \qquad \alpha = 1, 2, \ldots, N, \qquad (1)$$

where t and M_α denote the time and the mass of the αth nucleus, respectively. Consider an infinitesimal velocity at every instance, which gives

$$M_\alpha \dot{X}_\alpha = -(\partial U_A / \partial X_\alpha)\Delta t,$$

$$M_\alpha \dot{Y}_\alpha = -(\partial U_A / \partial Y_\alpha)\Delta t,$$

$$M_\alpha \dot{Z}_\alpha = -(\partial U_A / \partial Z_\alpha)\Delta t; \qquad \alpha = 1, 2, \ldots, N, \qquad (2)$$

for an infinitesimal time interval Δt. Here, the concept of the "intrinsic motion" is introduced. In this way, we finally obtain the simultaneous equations, the IRC equation:

$$M_\alpha dX_\alpha /(\partial U_A /\partial X_\alpha) = M_\alpha dY_\alpha /(\partial U_A /\partial Y_\alpha)$$

$$= M_\alpha dZ_\alpha /(\partial U_A /\partial Z_\alpha) = \text{const}; \quad \alpha = 1, 2, \ldots, N. \quad (3)$$

The IRC is the particular solution of the IRC equation using the boundary condition at the *TS* in such a way that the displacement vector for nuclei to move from the *TS* should be that of the unstable vibrational mode uniquely defined at the *TS*. The meta-IRC is a general solution of the IRC equation which is suitable for excited state chemical reactions [8]. Because we consider only internal forces for the potential U_A, the intrinsic motions satisfy the Eckart conditions [1]:

$$\sum_{\alpha=1}^{N} M_\alpha dX_\alpha = \sum_{\alpha=1}^{N} M_\alpha dY_\alpha = \sum_{\alpha=1}^{N} M_\alpha dZ_\alpha = 0 \quad \text{(zero total linear momentum)}, \quad (4)$$

$$\sum_{\alpha=1}^{N} M_\alpha(X_\alpha dY_\alpha - Y_\alpha dX_\alpha) = \sum_{\alpha=1}^{N} M_\alpha(Y_\alpha dZ_\alpha - Z_\alpha dY_\alpha)$$

$$= \sum_{\alpha=1}^{N} M_\alpha(Z_\alpha dX_\alpha - X_\alpha dZ_\alpha) = 0$$

$$\text{(zero total angular momentum)}. \quad (5)$$

If a reaction medium M is applied to the reaction system A, such as a solvent or a catalyst, then the perturbation potential is introduced. The perturbation potential depends on the configuration of the system A for any configuration of the medium M. The interaction forces should obviously include nonlinear contributions.

We shall then appeal to the method of differential geometry in order to treat the system A embedded in the reaction medium M [4]. Since the translational motion of the system A can be separated out [4], we have the center-of-mass system X_A for molecular configuration in the system A as

$$X_A = \left\{ x \in X_0 \,\middle|\, \sum_{\alpha=1}^{N} M_\alpha x_\alpha = 0 \right\}, \quad (6)$$

where X_0 is a set of all n-ples $x = (x_1, \ldots, x_N)$, with $x_\alpha \in \mathbb{R}^3$ and $x_\alpha \neq x_\beta$ if $\alpha \neq \beta$. In this space X_A, we let the group $G = SO(3)$ of rotations act:

$$gx = (gx_1, \ldots, gx_N); \quad g \in G, \quad x \in X_A. \tag{7}$$

Then, an individual molecular configuration corresponds to a point in the quotient space

$$M_A = X_A/G. \tag{8}$$

In differential geometry, X_A is treated as a principal fiber bundle over the base manifold M_A with structure group $G = SO(3)$, and the Lie algebra of $SO(3)$ is naturally identified with $\mathbb{R}^3$. This abstract manifold M_A is referred to as the internal space of the system A. In M_A, the translation and rotation motions as a whole can be eliminated in the sense of differential geometry, and we can introduce a $(3N - 6)$-dimensional local coordinate system in M_A [4]. It should be noted that, in the center-of-mass system X_A, the rotational motion cannot be eliminated. This means that the Eckart frame for the reaction system A is not uniquely determined [4]. A small fluctuation in the vibrational motion may bring about the rotation of the whole system. This may be called the reaction holonomy. This situation is illustrated in fig. 2. Then, we shall introduce a moving frame, called the IRC frame, for the string in such a way that the moving frame is attached to the IRC excluding any such kinds of fluctuations.
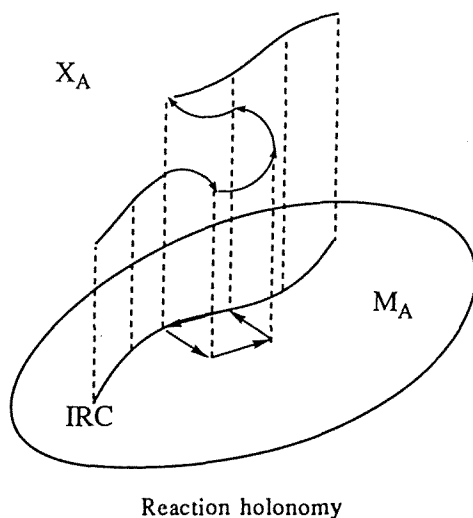

Reaction holonomy

Fig. 2. Reaction holonomy demonstrates that the Eckart frame of the reaction system A is not uniquely determined.

In the internal space M_A, the cell structure [9] of the chemical reaction system A plays an important role. The well-defined concept of the cell structure of the reaction system A may be illustrated as in fig. 3. As shown in fig. 3, meta-IRCs in a cell converge to a stable equilibrium point, the center of the cell. As a special
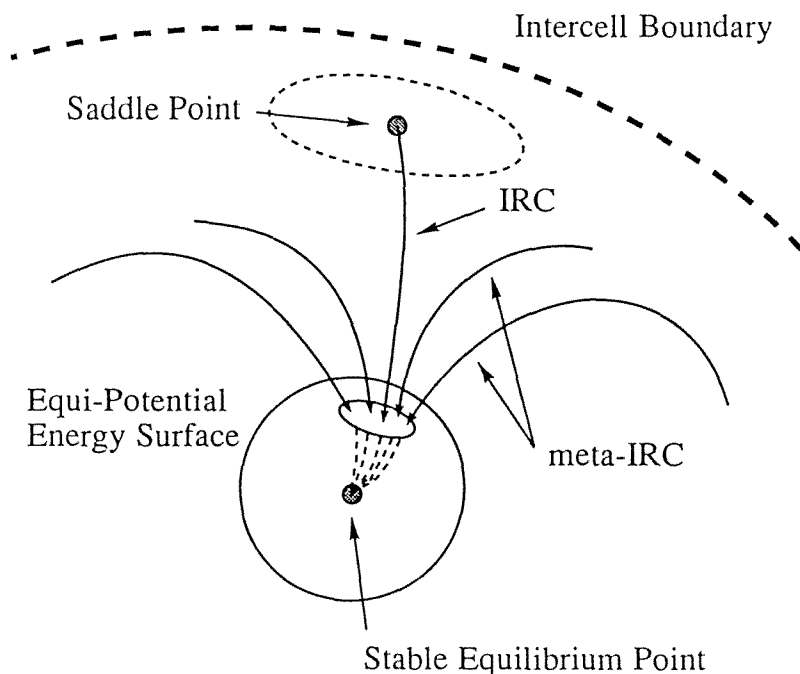
Cell Structure

Fig. 3. Cell structure associated with the IRC.

meta-IRC, only the IRC can go out of the cell through the saddle point. A schematic view of the cell structure and the potential energy surface associated with the cell structure are shown in fig. 4. This is a model of the isomerization reaction. In the figure, the local structure of the potential energy surface is described by the harmonic oscillators.

Now we are ready to introduce the concept of the string. The IRC and the associated local harmonic oscillators are combined to define a "string" in the internal space M_A. This is illustrated in fig. 5. In the following process, in which we embed the string in X_A, we must fix the moving frame attached to the string. According to the IRC frame, we suppose that we fix the frame for the configuration for *TS*, the center of the string, and then we can embed the string in X_A. For the isomerization reaction, the string is closed. For the fragmentation reaction, the string should be open. Successive reactions may be described by fusion of strings. In this sense, the string shown in fig. 5 is an elementary one. These geometrical characteristics of the reaction mechanisms have been described by pattern recognition of chemical reactions and the basic operations allowed for the fundamental patterns [8]. It should be noted here that the concepts of string and the fusion of strings are different but also show
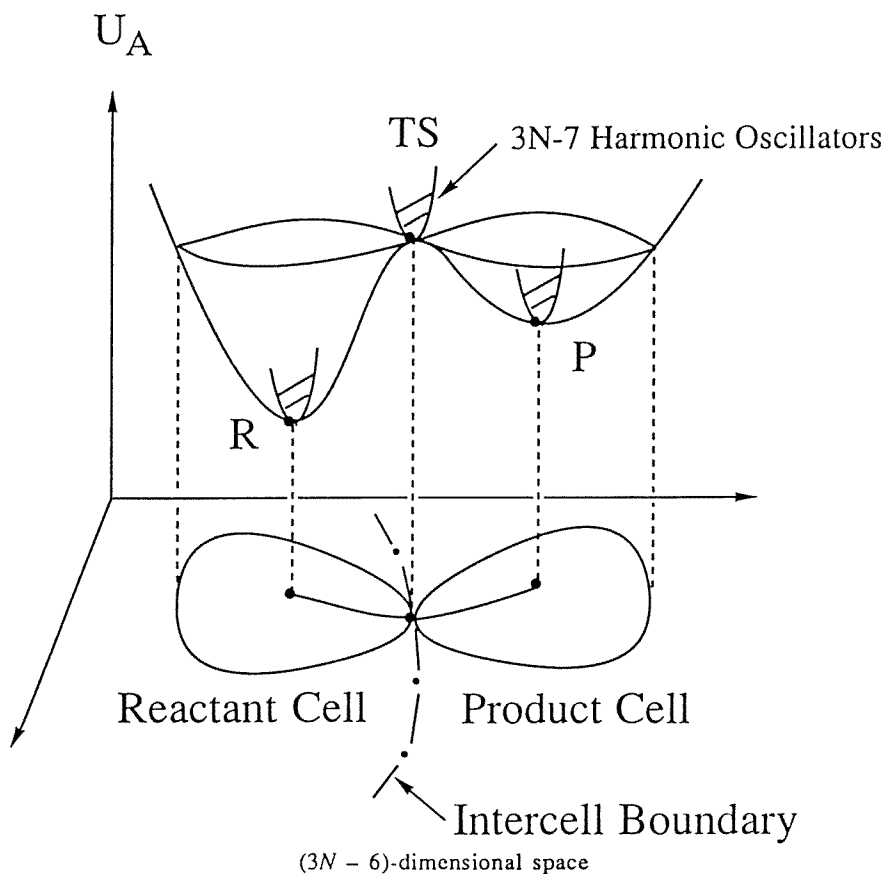
Fig. 4. Local vibrational motions attached to the IRC are represented by $3N-7$ harmonic oscillators.
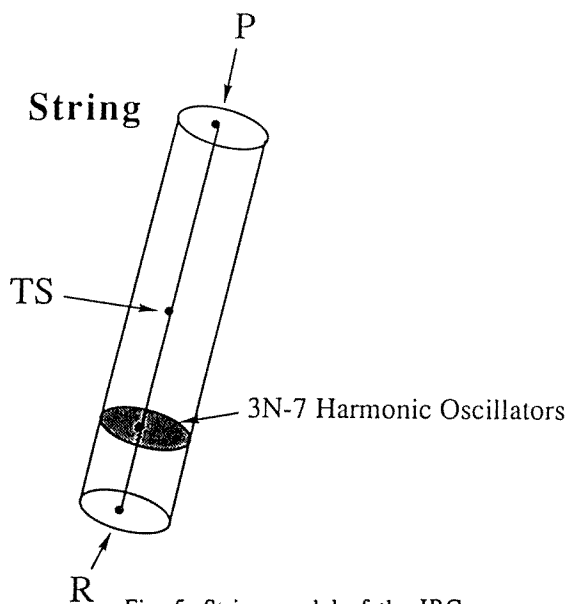

Fig. 5. String model of the IRC.

similarities to the homotopy classes and the product of such classes in the fundamental group of reaction mechanisms [10].

The next step is the embedding problem of the string of A in X_{A+M}; namely, we consider the perturbation by the medion M. The perturbed potential U may then be represented as [3]:

$$U = U_A + U_{AM} + U_M. \tag{9}$$

The interaction between A and M affects the original reaction path and the original reaction rate. The string may slide and rotate, and may be deformed as shown in fig. 6. The interaction potentials U_M and U_{AM} may be time dependent or temperature dependent in general.
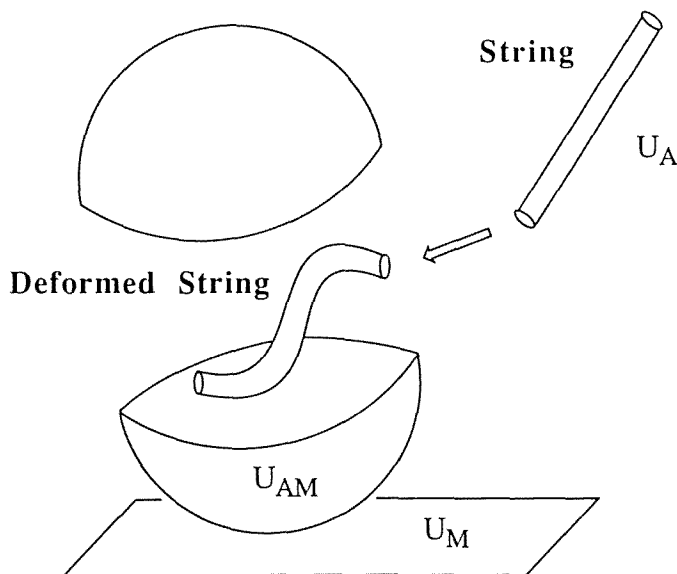

Fig. 6. A string thrown into the external fields
slides and rotates, and moreover is deformed.

The deformation of the string may be calculated by perturbation theory. First, the interaction energy itself changes the potential energy of the string at each point along the IRC. Second, the force exerted on the string shifts the equilibrium point of the string, as shown in fig. 7. The shift is calculated at each point on the IRC. In fig. 7, the IRC deformation is shown in terms of the shift of the equilibrium point of the harmonic oscillator orthogonal to the IRC. Q denotes the loc·l normal coordinate. It should be noted that the deformation of the string brings aoout *stabilization* of energy associated with the string. This stabilization is in contrast to the *destabilization* which is brought about at the *TS* along the IRC, as shown in fig. 8. The *TS* is shifted
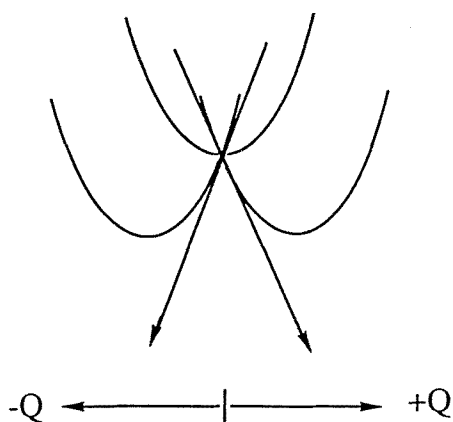
Fig. 7. The stable equilibrium point
is stabilized by the external forces.
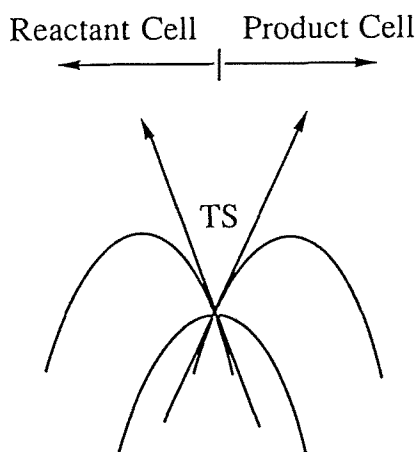
Reactant Cell   Product Cell

TS

Fig. 8. The unstable equilibrium point, the
TS, is destabilized by the external forces.

along the IRC. Accordingly, the cell structure is expanded or compressed, and the associated energy should be positive; destabilization of energy is observed, as shown in fig. 8. This is in marked contrast to the stabilization in the direction orthogonal to the string.

In general, the reaction rate should be obtained by the convolution of these mutually independent dynamics, which may be performed in a statistical manner.

3.   Perturbation theory of strings

3.1.   POTENTIAL ENERGY SURFACE

The adiabatic potential energy U_A for a reaction system composed of N nuclei is obtained as a function over $3N$-dimensional configuration space with space-fixed $3N$ Cartesian coordinates. The IRC equation is then represented as follows:

$$dx_i/ds = (\partial U_A/\partial x_i)/(dU_A/ds); \qquad i = 1, 2, \ldots, 3N, \tag{10}$$

where x_i and s denote "mass-weighted" Cartesian coordinates and the IRC, respectively. On the IRC, the configuration of the reaction system is represented as

$$x_i^{\text{IRC}} = x_i^{\text{IRC}}(s); \qquad i = 1, 2, \ldots, 3N. \tag{11}$$

Without the reaction medium M, the potential energy surface U_A along the reaction coordinate s can be approximated using the normal coordinate Q_i orthogonal to the IRC as follows:

$$U_A(s) = U^{(0)}(s) + \text{ higher order terms}, \tag{12a}$$

$$U^{(0)}(s) = U_{\text{IRC}}^{(0)}(s) + \sum_{i=1}^{3N-7} U_i^{(0)}(s), \tag{12b}$$

$$U_i^{(0)}(s) = (1/2)a_i^{(0)}(s)Q_i(s)^2, \tag{12c}$$

where $U_{\text{IRC}}^{(0)}$, $U_i^{(0)}$ and $a_i^{(0)}$ denote the adiabatic potential energy along the IRC, the potential energy in the direction of the ith normal coordinate, and the force constant for $U_i^{(0)}$, respectively. In the neighborhood of the IRC along the IRC, the configuration of the reaction system is then represented as

$$x_i = x_i(s, Q_i(s)); \qquad i = 1, 2, \ldots, 3N. \tag{13}$$

The IRC is then the center line, defined as

$$x_i^{\text{IRC}} = x_i(s, 0); \qquad i = 1, 2, \ldots, 3N. \tag{14}$$

The effect of the reaction medium upon the reaction system proceeding along the reaction path is now considered. If the medium gives only a weak intermolecular force not involving the formation of a chemical bond, the addition of the medium may be treated as a small perturbation. The reaction medium does not break the reaction system itself, but intervenes in the reaction system as an external force

field. When the reaction medium interacts with the reaction system, a perturbation energy U_{AM} appears. The U_{AM} may be approximated as follows:

$$U_{AM}(s) = U_{IRC}^{(1)}(s) + \sum_{i=1}^{3N-7} U_i^{(1)}(s), \tag{15a}$$

$$U_i^{(1)}(s) = -F_i(s)Q_i(s), \tag{15b}$$

where $U_{IRC}^{(1)}$, $U_i^{(1)}$ and F_i denote the static energy change brought about by association of the medium, the perturbation due to the external force field, and the strength of the force of the medium affecting the ith normal coordinate, respectively. In the nonadiabatic regime, the medium is fixed in the course of the chemical reaction. Hence, the additional perturbation potential U_M is zero by definition.

For the sake of convenience, we have neglected the higher-order perturbation terms and U_M. The energy for the perturbed system then becomes:

$$U = U_A + U_{AM} = U_{IRC}(s) + \sum_{i=1}^{3N-7} U_i(s) + \text{higher order terms}, \tag{16a}$$

$$U_{IRC}(s) = U_{IRC}^{(0)}(s) + U_{IRC}^{(1)}(s), \tag{16b}$$

$$U_i(s) = U_i^{(0)}(s) + U_i^{(1)}(s). \tag{16c}$$

Using eqs. (12c) and (15b), the potential energy for the ith mode may be represented as

$$U_i(s) = (1/2)a_i^{(0)}(s)Q_i(s)^2 - F_i(s)Q_i(s)$$

$$= (1/2)a_i^{(0)}(s)(Q_i(s) - \Delta Q_i(s))^2 + \Delta U_i(s). \tag{17}$$

The effect of the external field upon $U_i(s)$ emerges as a deviation,

$$\Delta Q_i(s) = F_i(s)/a_i^{(0)}(s), \tag{18}$$

of the reaction path in the direction of $Q_i(s)$. This demonstrates the min–max relationship that the smaller the magnitude of the force constant of the normal mode orthogonal to the string, the larger the deformation of the string in the direction of the normal mode. Moreover, we obtain the energy difference,

$$\Delta U_i(s) = -F_i(s)^2/2a_i^{(0)}(s), \tag{19}$$

of the reaction path. For stable vibrational modes, the $a_i^{(0)}(s)$ are all positive, and a stabilization of energy is obtained: $\Delta U_i(s) < 0$. On the other hand, for unstable vibrational modes including the mode of the IRC, a destablization of energy is obtained: $\Delta U_i(s) > 0$.

It should be noted that the "translation–rotation–vibration" perturbation and the deformation of the string should be defined in the IRC frame in order to uniquely define the "attitude" or "configuration" of the string with respect to the reaction medium. It should also be noted that if, as shown in fig. 6, the external interaction is strong, then the deformation of the string should moreover be represented as the rotation and mixing of the normal modes $Q_i(s)$ orthogonal to the IRC. Furthermore, the originally "free" translational and rotational motions of the string in terms of the IRC frame may turn out to be fixed, in the sense that the string is "caught" in the reaction medium, whereby the originally free translational and rotational motions of the reaction system A may reduce to the local "vibrational motion" of the string with respect to the reaction medium M. The latter effect should also contribute to the reaction rate formula.

3.2.   RATE CONSTANT

In this subsection, the reaction rate constants are discussed within the RRKM theory [2, 13]. The standard expression for the unimolecular rate constant of an isolated molecule with total energy E is

$$k(E) = N(E)/2\pi\hbar N_0'(E), \tag{20}$$

where $N(E)$ and $N_0(E)$ are the integral density of states for the transition state and for the reactant molecule, respectively:

$$N_0(E) = \sum_n h(E - e_n), \tag{21a}$$

$$N(E) = \sum_n h(E - V_0 - e_n^{\neq}), \tag{21b}$$

where $h(x)$ is a step function, and e_n and $e_n^{\neq}$ are the vibrational energy levels of R and TS, respectively, and where V_0 is the activation energy. Within the separable approximation of the vibrational states, the tunneling effect is accounted for by replacing $N(E)$ in eq. (22) by $N_{QM}(E)$ as [14, 15]

$$N_{QM}(E) = \sum_n P(E - V_0 - e_n^{\neq}). \tag{21c}$$

If the reaction system is perturbed by the reaction medium, the vibrational energies in eq. (21) are expressed using the perturbation theory:

$$e_n = e_n^{(0)} + e_n^{(1)} + e_n^{(2)} + \dots , \tag{22a}$$

$$e_n^{\neq} = e_n^{\neq(0)} + e_n^{\neq(1)} + e_n^{\neq(2)} + \dots . \tag{22b}$$

For the unperturbed system, we have

$$e_n^{(0)} = \sum_{i=1}^{f} \hbar w_i^{(0)}(n_i + (1/2)), \tag{23a}$$

$$e_n^{\neq(0)} = \sum_{i=1}^{f-1} \hbar w_i^{\neq(0)}(n_i + (1/2)), \tag{23b}$$

where f is the number of vibrational degrees of freedom of the stable molecule, $f = 3N - 6$, $w_i^{(0)}$ and $w_i^{\neq(0)}$ are the normal mode frequencies of the R and the TS, respectively. The standard expressions for $N_0^{(0)}$ and $N^{(0)}$ are given as

$$N_0^{(0)}(E) = E^f/f! \prod_{i=1}^{f} (\hbar w_i^{(0)}), \tag{24a}$$

$$N^{(0)}(E) = (E - V_0^{(0)})^{f-1}/(f-1)! \prod_{i=1}^{f-1} (\hbar w_i^{\neq(0)}). \tag{24b}$$

The next step is to include the higher-order perturbations. The second-order perturbation represents the change of force constant. Moreover, it has an effect on the gradient direction used in defining the force constant projector. Therefore, the second-order perturbation is very important.

4. Application

We have reported a preliminary study of the string model for the rate constant of nonadiabatic solvation in the hydration reaction of carbon dioxide [2]. An external point charge, proton, has been used to express a model of the enzymic catalysis of the hydration of CO_2. This reaction is of vital interest in biological processes [16].

The reaction system now considered is shown in fig. 9. From left to right, R, TS, and P mean the configurations of the reactant, the transition state, and the product, respectively. These configurations are all coplanar except for one hydrogen atom H6 at the TS configuration. The activation energy is 48.98 kcal/mol (HF/3-21G), and the reaction is exothermic by 3.65 kcal/mol (HF/3-21G) [2].

As an application of the present treatment, an external water molecule is now situated as shown in fig. 10. Here, we consider two schemes of interaction, M1 and M2, of the external water molecule. Throughout the reaction, we fix the coplanarity
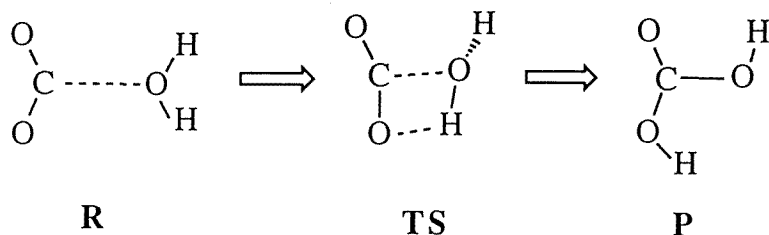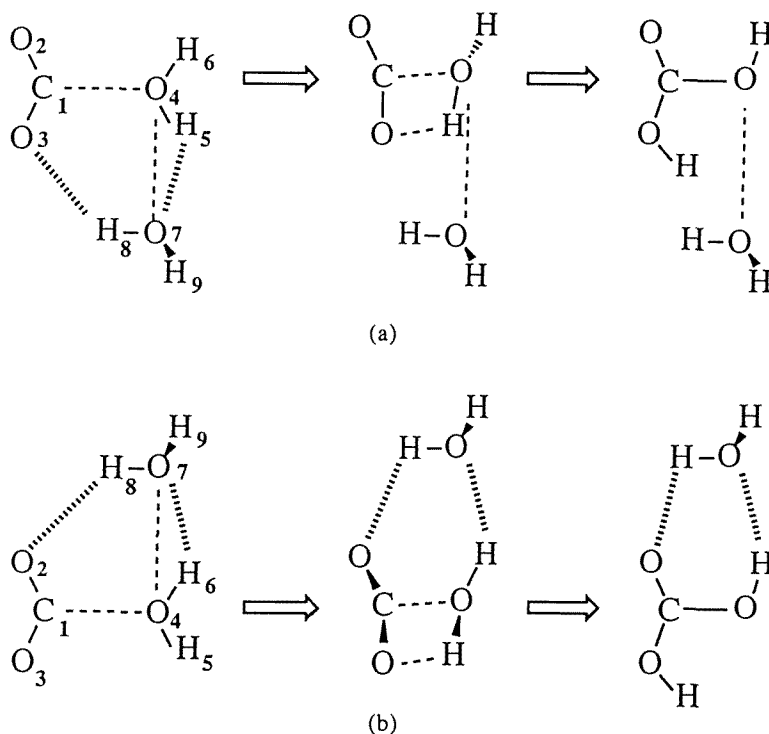
Fig. 9. Reaction pathway for the hydration of CO_2 in vacuum.

(a)

(b)

Fig. 10. Scheme of interaction of the external water molecule. (a) Scheme M1, and (b) scheme M2.

of the O7–H8 bond with respect to the reaction system except for the *TS* configuration, and the dihedral angle $\Phi_{9784} = 120°$. For both schemes M1 and M2, the external molecule is weakly interacting with the system *A*. First, for the adduct of CO_2 and H_2O in the *R* configuration, a pair of weak hydrogen bonds are observed. Here, we set the O7–H8 bond to be parallel to the C1–O4 bond, where the O4–O7 direction is perpendicular to the C1–O4 bond with the O4–O7 distance being 3 Å. Next, in the *TS* configuration, hydrogen migration occurs in a mutually different manner for

the schemes M1 and M2. In scheme M1, the hydrogen migration occurs in the front of the external water molecule. Then the hydrogen bonds are broken, which event occurs also for the *P* configuration. Throughout in scheme M1, the external water is situated in the same manner as in the *R* configuration.

In scheme M2, on the other hand, hydrogen migration occurs in the back of the external water molecule. For the *TS* configuration as well as for the *P* configuration, here we maintain the situation in such a way that the coplanarity of the O7−H8 bond is fixed with respect to the O4−H6−O2 plane and the angle Φ_{678} is fixed to be the same as for the *R* configuration.
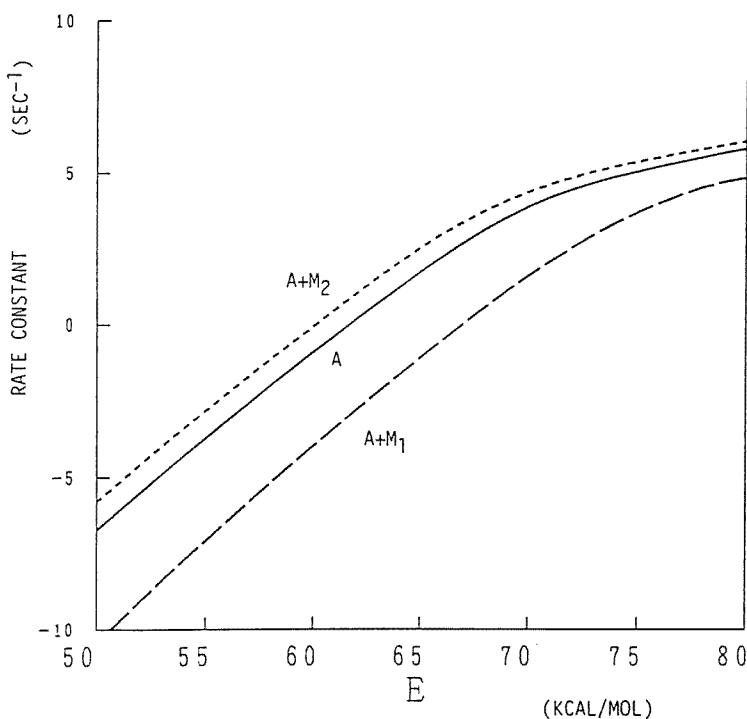

Fig. 11. Reaction rates.

Using the method presented in section 3.1, the perturbation energies to the string are calculated. As a result, the activation energy increases in scheme M1 by 4.63 kcal/mol, while it decreases in scheme M2 by 1.35 kcal/mol. Next, the reaction rate is calculated using the method presented in section 3.2 and the result is shown in fig. 11 [2]. A distinct acceleration effect is demonstrated in scheme M2, in contrast to deceleration in scheme M1.

Acknowledgements

References

[1] A. Tachibana, M. Koizumi, M. Murashima and T. Yamabe, Theor. Chim. Acta (Berlin) 75(1989)401.
[2] A. Tachibana, H. Fueno, E. Tanaka, M. Murashima, M. Koizumi and T. Yamabe, Int. J. Quant. Chem., in press; A. Tachibana et al., to be published.
[3] A. Tachibana and K. Fukui, Theor. Chim. Acta (Berlin) 51(1979)275.
[4] (a) A. Tachibana and T. Iwai, Phys. Rev. A33(1986)2262.
     (b) J.D. Louck and H. Galbraith, Rev. Mod. Phys. 48(1976)69.
[5] J.O. Hirschfelder, Ann. Rev. Phys. Chem. 34(1983)1, and references cited therein.
[6] E.B. Wilson, J.C. Decius and P.C. Cross, Molecular Vibrations (McGraw–Hill, New York, 1955).
[7] K. Fukui, J. Phys. Chem. 74(1970)4161.
[8] A. Tachibana and K. Fukui, Theor. Chim. Acta (Berlin) 49(1978)321.
[9] A. Tachibana and K. Fukui, Theor. Chim. Acta (Berlin) 51(1979)189.
[10] P.G. Mezey, Potential Energy Hypersurfaces (Elsevier, Amsterdam, 1987).
[11] A. Tachibana, Theor. Chim. Acta (Berlin) 58(1981)301.
[12] A. Tachibana and K. Fukui, Theor. Chim. Acta (Berlin) 57(1980)81.
[13] P.J. Robinson and K.A. Holbrook, Unimolecular Reactions (Wiley, New York, 1972);
     W. Forst, Theory of Unimolecular Reactions (Academic Press, New York, 1973).
[14] W.H. Miller, J. Amer. Chem. Soc. 101(1979)6810.
[15] B.C. Garrett and D.G. Truhlar, J. Phys. Chem. 83(1979)1079.
[16] J.-Y. Liang and W.N. Lipscomb, Int. J. Quant. Chem. 36(1989)299, and references cited therein.