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A string model for the chemical reaction coordinate in static external fields

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A theoretical method for estimating the effects of a static external field upon a reaction path is proposed. The reaction path is defined as the intrinsic reaction coordinate (IRC) which is treated as a "string". The string is deformed by the external static force field. We project the external force onto the normal modes orthogonal and parallel to the string. The string is dragged along each direction of the normal mode. The cell structure [10b] attached to the string is also deformed; the transition state (TS) is shifted, and the internal structure of the reaction system is expanded or compressed in configuration space. A min-max relationship of the external effect on the string is found: 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. As an example, the effects of one water molecule for hydrogen-migrating isomerization of formaldehyde and fluoroformaldehyde are considered.

Key words: String model — Reaction coordinate — Static external force field

1. Introduction

In the field of theoretical chemistry, one of the topics attracting much attention now is how to describe solution reactions or catalytic reactions [1–8]. Because of the development of quantum chemical calculational techniques, the description of fairly large reaction systems becomes possible at the molecular level, and we can get microscopic information and descriptions which could not be obtained by experimental work. Nevertheless, with respect to condensed phase reactions, there are some difficulties in interpreting the behavior of reacting molecules theoretically, because they have complicated interactions with the reaction medium, solvent or catalyst. The main questions are; (1) Is the reaction path in the condensed phase essentially different from that in the gas phase? (2) If it is different, what effect does the reaction medium have on the reaction path? The focus of attention is on the interaction between the reaction path and the external force field.

The chemical reaction path is a concept which has a foundation in empirical observations. The problem of how to connect this empirical concept of a reaction path to a model amenable to theoretical treatment is a matter of deep concern in chemistry. Here, the discussion is focussed on the "intrinsic reaction coordinate" or "IRC" approach [9-11].

In the present paper, we treat the microscopic electronic interaction between a chemical reaction system and its environment on an infinitely small time scale along the IRC, and calculate a potential energy surface of the chemical reaction system under the influence of the environment. We propose a model for such an interaction energy. We are not in a position, therefore, to give a statistical mechanical interpretation of coarse-grained feature of dynamical processes. Interaction energy between the chemical reaction systen and environment is considered to be static, excluding nuclear kinetic energy under the Born-Opphenheimer adiabatic approximation. Intra-and inter-molecular electron correlation energies are incorporated into the potential energy surface (although this is not demonstrated here in actual numerical calculation) which should be important for more sophisticated accurate development of theory.

We treat the IRC as a "string" thrown in the static external field and analyze the effects of the static external field on the string. We find the deformation of the string and the cell structure [10b] attached to the string. A method of estimating the external effect is proposed. We treat the static effects of one water molecule for hydrogen-migrating isomerizations of formaldehyde and fluoroformaldehyde as examples. This paper refers only to irreversible processes which occur under a static external field. Extensions of the present treatment to processes which proceed under time-dependent forces or thermodynamical forces are not discussed here.

2. Theory

2.1. *Definition of reaction path*

The *ab initio* quantum-chemical method is capable of calculating the total energy of a molecular system with a fixed nuclear arrangement - the adiabatic potential, U - based on the Born-Oppenheimer approximation. We represent the nuclear configuration of a chemically reacting 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 function, U, is a function of X_α, Y_α, and Z_α.

The classical equations of motion for the nuclei are

$$\frac{d}{dt}(M_\alpha \dot{X}_\alpha) = -\frac{\partial U}{\partial X_\alpha}, \qquad \frac{d}{dt}(M_\alpha \dot{Y}_\alpha) = -\frac{\partial U}{\partial Y_\alpha},$$
$$\frac{d}{dt}(M_\alpha \dot{Z}_\alpha) = -\frac{\partial U}{\partial Z_\alpha}; \qquad \alpha = 1, 2, \ldots, N, \tag{1}$$

where t and M_α denote the time, and the mass of the αth nucleus respectively. Consider a movement of the nucleus from a given point with an *infinitesimal* velocity. The velocities of the nuclei are given by

$$M_\alpha \dot{X}_\alpha = -\frac{\partial U}{\partial X_\alpha}\Delta t, \qquad M_\alpha \dot{Y}_\alpha = -\frac{\partial U}{\partial Y_\alpha}\Delta t,$$
$$M_\alpha \dot{Z}_\alpha = -\frac{\partial U}{\partial Z_\alpha}\Delta t; \qquad \alpha = 1, 2, \ldots, N, \tag{2}$$

for a small time interval Δt. Since, by assumption, the nuclei start to move with an infinitesimal velocity, i.e. $\dot{X}_\alpha = \dot{Y}_\alpha = \dot{Z}_\alpha = 0$ ($\alpha = 1, 2, \ldots, N$) at $t = 0$, the integration constants should be zero. This nuclear change introduces the concept of "intrinsic motion".

In this way, we obtain the simultaneous equations [9]

$$\frac{M_\alpha dX_\alpha}{\partial U/\partial X_\alpha} = \frac{M_\alpha dY_\alpha}{\partial U/\partial Y_\alpha} = \frac{M_\alpha dZ_\alpha}{\partial U/\partial Z_\alpha} = \text{const}; \qquad \alpha = 1, 2, \ldots, N. \tag{3}$$

The Eckart conditions to fix the translation and rotation of the whole system [12] are automatically satisfied:

$$\sum_\alpha M_\alpha \, dX_\alpha = \sum_\alpha M_\alpha \, dY_\alpha = \sum_\alpha M_\alpha \, dZ_\alpha = 0 \tag{4a}$$

and

$$\sum_\alpha M_\alpha (X_\alpha \, dY_\alpha - Y_\alpha \, dX_\alpha) = \sum_\alpha M_\alpha (Y_\alpha \, dZ_\alpha - Z_\alpha \, dY_\alpha)$$
$$= \sum_\alpha M_\alpha (Z_\alpha \, dX_\alpha - X_\alpha \, dZ_\alpha) = 0. \tag{4b}$$

If we adopt the "mass-weighted" cartesian coordinates x_i ($i = 1, 2, \ldots, 3N$) in which

$$M_\alpha^{1/2} X_\alpha = x_{3\alpha-2}, \qquad M_\alpha^{1/2} Y_\alpha = x_{3\alpha-1}, \qquad M_\alpha^{1/2} Z_\alpha = x_{3\alpha};$$
$$\alpha = 1, 2, \ldots, N, \tag{5}$$

then Eq. (3) becomes

$$\frac{dx_1}{\partial U/\partial x_1} = \frac{dx_2}{\partial U/\partial x_2} = \cdots = \frac{dx_{3N}}{\partial U/\partial x_{3N}}. \tag{6}$$

The basic idea of this formalism has been proposed by many workers [9]. The solution of this equation which reaches a transition-state (TS) point from a stable equilibrium point was named "intrinsic reaction coordinate" (IRC) by Fukui; Eqs. (3) and (6) may be called the "IRC equations". These equations are regarded as the fundamental ones that determine the "center line" of the bundle of reactive trajectories when inertial effects arising from curvature of the reaction path are not too large. We note that the IRC equation also has an infinite number of solutions in addition to the IRC, which are generally called "meta-IRCs" [10b]. The IRC will be denoted as s in the present paper; the origin of s corresponds to the TS and the $s > 0$ or $s < 0$ regions correspond to the product cell (P cell) and reactant cell (R cell) [10b], respectively. The deviation of reactive trajectories from the IRC is represented by the local normal coordinates ξ_i ($i = 1, 2, \ldots, f$; $f = 3N-7$). Each ξ_i is orthogonal to the IRC and is regarded as a heat bath for the IRC [9–11].

We treat the IRC as a "string" in configuration space, the ends of which are denoted as R and P, and with the TS located in between the R and P; the geometry of the string is then characterized by the cell structure [10b] attached to it. Vibration of the string is represented by the local normal modes that are orthogonal to it.

2.2. *Effects of static external field upon the string*

Now, let us consider the effects of the static external field upon the reaction system proceeding along the reaction path: R cell → TS → P cell. The potential energy of the reaction system along the string is then given as

$$U(s) = U^{(0)}(s) + U^{(1)}(s), \tag{7}$$

where $U^{(0)}(s)$ and $U^{(1)}(s)$ denote the unperturbed potential energy and the pertubation energy, respectively.

The unperturbed potential energy may be represented approximately by using the local normal coordinate ξ_i as follows:

$$U^{(0)}(s) = U^{(0)}_{IRC}(s) + \sum_{i=1}^{f} U^{(0)}_i(s), \tag{8a}$$

$$U^{(0)}_i(s) = \tfrac{1}{2}a_i(s)\xi_i(s)^2, \tag{8b}$$

where $U^{(0)}_{IRC}(s)$, $U^{(0)}_i(s)$, and $a_i(s)$ denote the potential energy on the string, the potential energy on the ith normal mode, and the force constant of the ith normal mode, respectively. Note that the normal mode is supposed to be "stable" in the present paper, that is $a_i > 0$; the critical case of an unstable normal mode is studied elsewhere [13].

The perturbation energy of the static external field may be represented by

$$U^{(1)}(s) = U^{(1)}_{IRC}(s) + \sum_{i=1}^{f} U^{(1)}_i(s), \tag{9a}$$

$$U^{(1)}_i(s) = -F_i(s)\xi_i(s), \tag{9b}$$

where $U^{(1)}_{IRC}(s)$, $U^{(1)}_i(s)$, and $F_i(s)$ denote the perturbation energy term on the string, the perturbation potential on the ith normal mode, and the strength of the external force affecting the ith normal mode, respectively. F_i is obtained by projecting the external force f from outside the reaction system onto each normal mode:

$$F_i(s)=\sum_{\alpha=1}^{N}\sum_{j=1}^{3}\nu^i_{\alpha j}(s)f_{\alpha j}(s), \tag{10a}$$

where $\nu^i_{\alpha j}$ is the expansion coefficient of the ith normal coordinate ξ_i in the jth Cartesian coordinate of the atom α:

$$\nu^i_{\alpha j}=\frac{\partial x_{3(\alpha-1)+j}}{\partial \xi_i} \qquad (\alpha=1,2,\ldots,N;j=1,2,3), \tag{10b}$$

and where the $f_{\alpha j}$ is the component of the external force in the direction of the jth Cartesian coordinate of the atom α. Using Eqs. (7)-(9), we obtain the decomposition scheme of the potential energy as follows:

$$U(s)=U_{IRC}(s)+\sum_{i=1}^{f}U_i(s), \tag{11a}$$

where the perturbation expansion is given as

$$U_{IRC}(s)=U^{(0)}_{IRC}(s)+U^{(1)}_{IRC}(s), \tag{11b}$$

$$\begin{aligned} U_i(s)&=U^{(0)}_i(s)+U^{(1)}_i(s)\\ &=\tfrac{1}{2}a_i(s)\left(\xi_i(s)-\frac{F_i(s)}{a_i(s)}\right)^2-\frac{1}{2}\frac{F_i(s)^2}{a_i(s)}. \end{aligned} \tag{11c}$$

The effects of the static external force are classified into two typical modes of interaction as follows.

(I) At each point along the string, the external effect upon $U_i(s)$ emerges as the deviation $F_i(s)/a_i(s)$ of the origin in the positive direction of ξ_i, and as the energy difference $-F^2_i(s)/2a_i(s)$. It follows that, (a) when $F_i>0$, the $+\xi_i$ region expands, and (b) when $F_i<0$, the $-\xi_i$ region expands.

In both of these cases, the external force drags and deforms the string, as shown in Fig. 1. The energy corresponding to the deformation of the string is $-F^2_i/2a_i$, which is always negative, and acts as a stabilization energy. Here, it is clear that

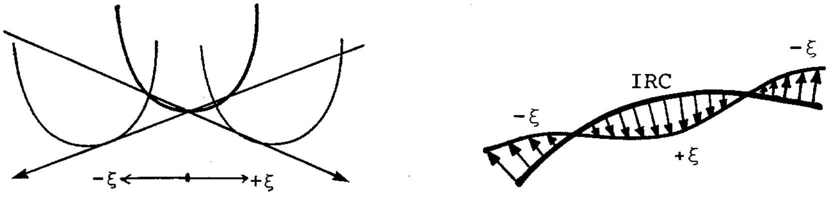


Fig. 1. Schematic representation of the way the external force can drag and deform the string

the larger the projected force F_i is, the larger the deviation F_i/a_i is; this is also true for the magnitude of the stabilization energy. Moreover, it is improtant to note that the smaller the force constant a_i is, the larger the deviation F_i/a_i. This is a min-max relationship of the external effect on the chemical reaction path, and it also applies to the magnitude of the stabilization energy.

(II) In particular, in the neighborhood of the TS we have

$$U_{IRC}^{(0)}(s)=\tfrac{1}{2}a_{IRC}(0)s^2; \qquad a_{IRC}(0)<0, \tag{12a}$$

$$U_{IRC}^{(1)}(s)=U_{IRC}^{(1)}(0)-F_{IRC}(0)s, \tag{12b}$$

so that Eq. (11b) is reduced to

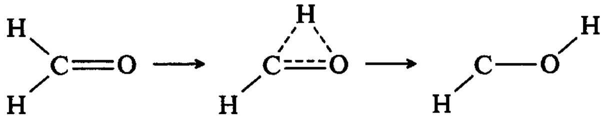
$$U_{IRC}(s)=U_{IRC}^{(1)}(0)+\tfrac{1}{2}a_{IRC}(0)\left(s-\frac{F_{IRC}(0)}{a_{IRC}(0)}\right)^2-\frac{1}{2}\frac{F_{IRC}(0)^2}{a_{IRC}(0)}. \tag{12c}$$

It follows that (a) when $F_{IRC}(0)>0$, the potential barrier shifts to the $-s$ region, that is to the R cell, and the P cell expands, and (b) when $F_{IRC}(0)<0$, the potential barrier shifts to the $+s$ region, that is to the P cell, and the R cell expands. In both of these cases, the external force compresses the string, as shown in Fig. 2. The energy of compression is $-F_{IRC}^2(0)/2a_{IRC}(0)$, which is always positive, and hence is a destabilizing influence.

3. Model system calculation

3.1. Selection of the model reaction system

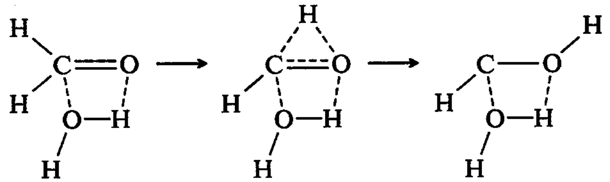
As an illustrative example, we treat the static effects of a water molecule upon the isomerization reaction of formaldehyde:



1 (R) 2 (TS) 3 (P)

In this scheme, R, TS and P mean reactant, transition state and product, respectively. Many *ab initio* MO calculations have been performed on this 1,2-H migration of formaldehyde. It is an isomerization which proceeds in a molecular plane with an activation energy, $E_a \sim 90$ kcal/mol [14].

We treated the following interaction between the reaction system and a static water molecule:



4 5 6

In this model reaction system, the water molecule plays the role of a static external field. The orientation of the addition is shown in Fig. 3, where w denotes the

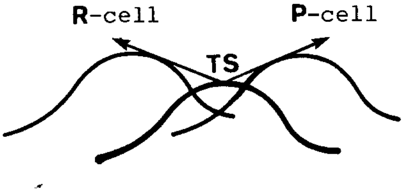
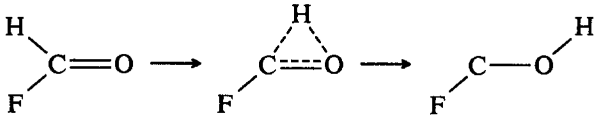


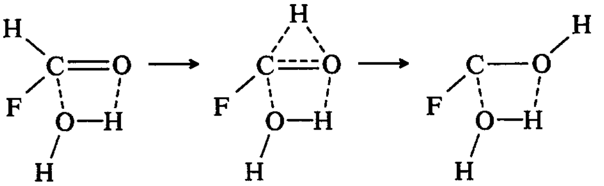
Fig. 2. Schematic representation of the way the external force can compress the string

atoms which belong to the water. The H_2O molecule was set on a plane including the CO bond, and normal to the molecular plane of formaldehyde.

In order to estimate the effect of a substituent, we compared this reaction with the following isomerization of fluorine-substituted formaldehyde:



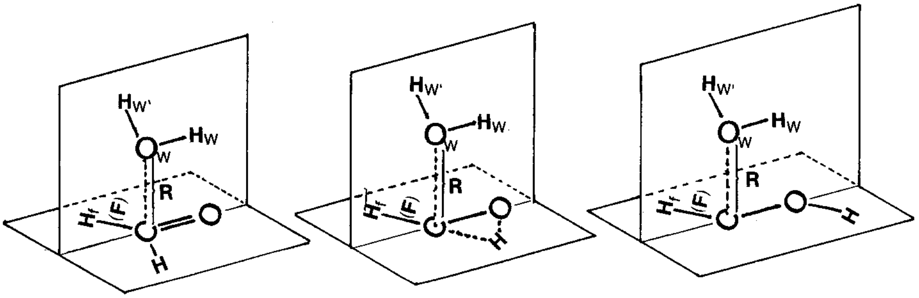
7 (R) **8** (TS) **9** (P)



10 **11** **12**

3.2. *Method of calculation*

The *ab initio* MO calculations were carried out at the RHF/4-31G level [15], with the GAUSSIAN 82 program package [16]. Evaluation of the energy gradient and the optimization of the geometry was performed by using analytical first



4 (10) 5(11) 6(12)

Fig. 3. The orientation of addition of a water molecule to the reactant species. H_f denotes the hydrogen atom which is fixed in formaldehyde (**4**–**6**), or is being fluoro-substituted in fluoroformaldehyde (**10**–**12**). w denotes the atoms belonging to water. For these adducts, **4**, **5**, **6**, **10**, **11**, and **12**, we use a fixed $R = 2.5$ Å as the association distance, where the water molecule can produce only a weak molecular interaction

derivatives [17]; for the vibrational analyses, we made use of analytical second derivatives [18]. We analyzed the effect of the water with the RHF/4-31G optimized geometry upon the equilibrium points, **1**, **2**, **3**, **7**, **8**, and **9**, whose geometries were also fixed at the optimized configuration determined from RHF/4-31G calculations.

4. Results and discussion

Figure 4 shows the vectors of $6(=3N-6)$ vibrational modes at the equilibrium points **1**, **2**, **3**, **7**, **8**, and **9**. In the two TS s **2**, and **8** in Fig. 4b, e, v_1 has an imaginary frequency which corresponds to the direction of the IRC at the TS. Figure 5 shows the force vectors $\boldsymbol{f}$ exerted on the reaction system by the water molecule in complexes **4**, **5**, **6**, **10**, **11**, and **12**; the $\boldsymbol{f}$'s were projected on the vibrational modes shown in Fig. 4 according to Eq. (10a), and are shown in Table 1. The deformation of the string and the energy changes according to Eqs. (11) and (12) are also listed in Table 1. We compared the effects of the water molecule on the reaction path of the H_2CO system and the HFCO system.

4.1. *Effects upon the R cell*

Table 1a shows the projected force F_i at the center of the R cell, that is, the stable equilibrium point of $H_2C{=}O$, for which $H_2C{=}O$ has the C_{2v} carbonyl double-bond form. The force induced by H_2O is projected onto the four symmetric vibrational modes of $H_2C{=}O$, because the asymmetric modes do not interact with the H_2O at this configuration. The largest projection is 0.552×10^{-4} (hartree/bohr) on the symmetric CH stretching mode (v_5; 3191 cm^{-1}), and the second largest projection is 0.456×10^{-4} on the symmetric deformation mode (v_3; 1680 cm^{-1}). On the other hand, the largest deviation F_i/a_i is 0.182×10^{-1} ($\text{amu}^{1/2}$bohr) in v_3, while the second is 0.881×10^{-2} in the symmetric CH stretching mode (v_4; 1924 cm^{-1}), and the third is -0.765×10^{-2} in the out-of-plane vibrational mode (v_1; 1332 cm^{-1}). This verifies the min-max relationship of the external effect presented in Sect. 2.2: even a small projected force can make the string slide considerably in the direction of a normal mode provided that the mode has a small frequency. In this case, v_3 has a smaller frequency than v_5, so in the direction of v_3 the string can be deformed more easily and by a lesser force. The v_3 and v_5 modes correspond to the lengthening of the CO bond length and the compressing of the ∠HCH, respectively. The out-of-plane mode v_1 corresponds to the carbon atom C of the formaldehyde approaching the oxygen atom O_w of the water, while the oxygen atom O of formaldehyde separates from the hydrogen atom H_w of water.

On the other hand, the interaction between fluoroformaldehyde $HFC{=}O$ and water (Table 1d) shows that the largest projected force is -0.737×10^{-4} on the CO stretching mode (v_5; 1996 cm^{-1}), followed by -0.663×10^{-4} on the CH stretching mode (v_6; 3394 cm^{-1}), and the third, -0.504×10^{-4} on the out-of-plane mode (v_2; 1146 cm^{-1}). The ordering of the deviation is as follows: first, -0.433×10^{-1} in v_2, second, -0.209×10^{-1} in v_5, third, -0.171×10^{-1} in the CF stretching

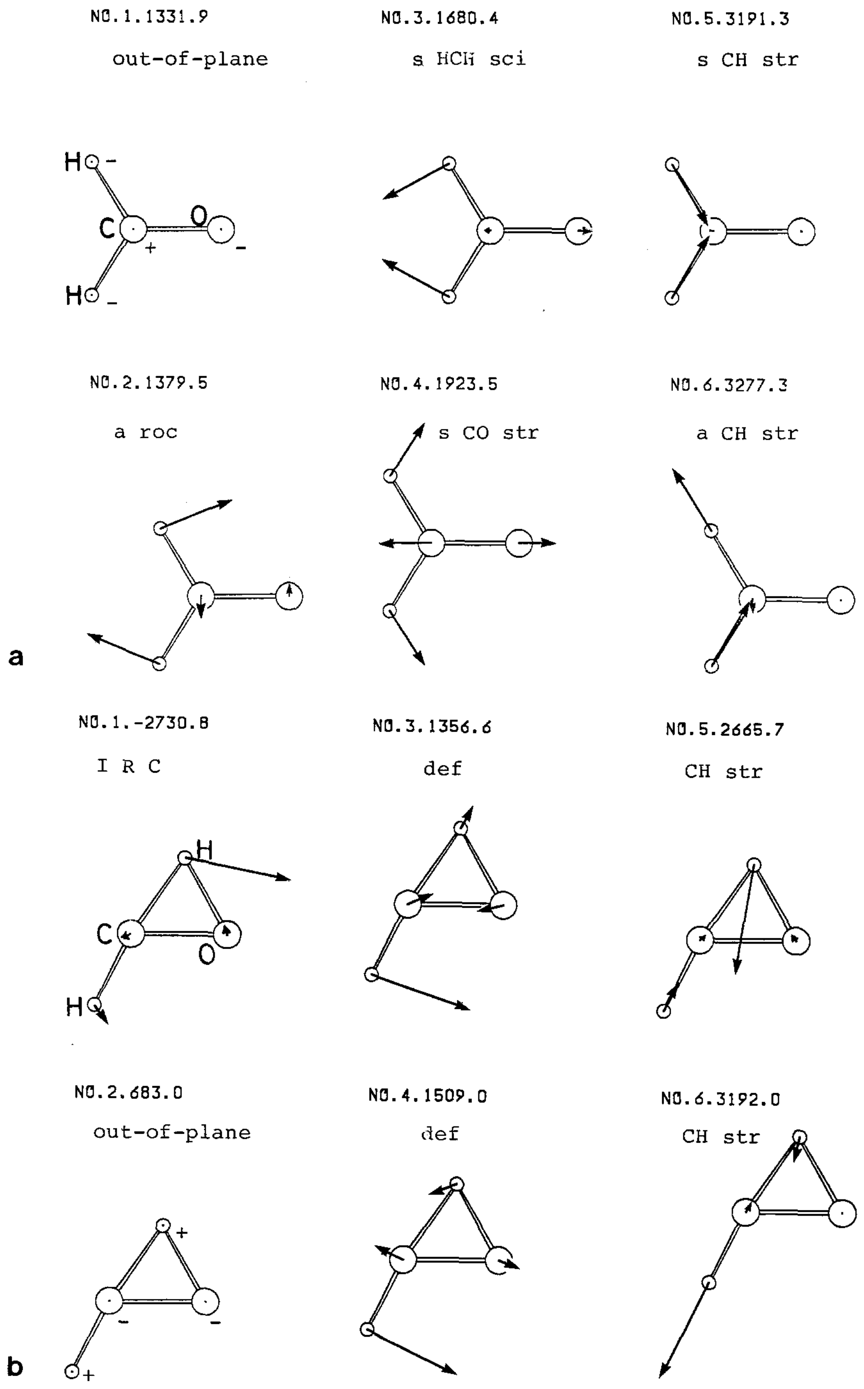


Fig. 4a–f. The vectors of $6(=3N-6)$ vibrational modes on the equilibrium points **1**, **2**, **3**, **7**, **8**, and **9** which are shown in **a–f**, respectively. Note that we look up at the molecular plane in Fig. 3

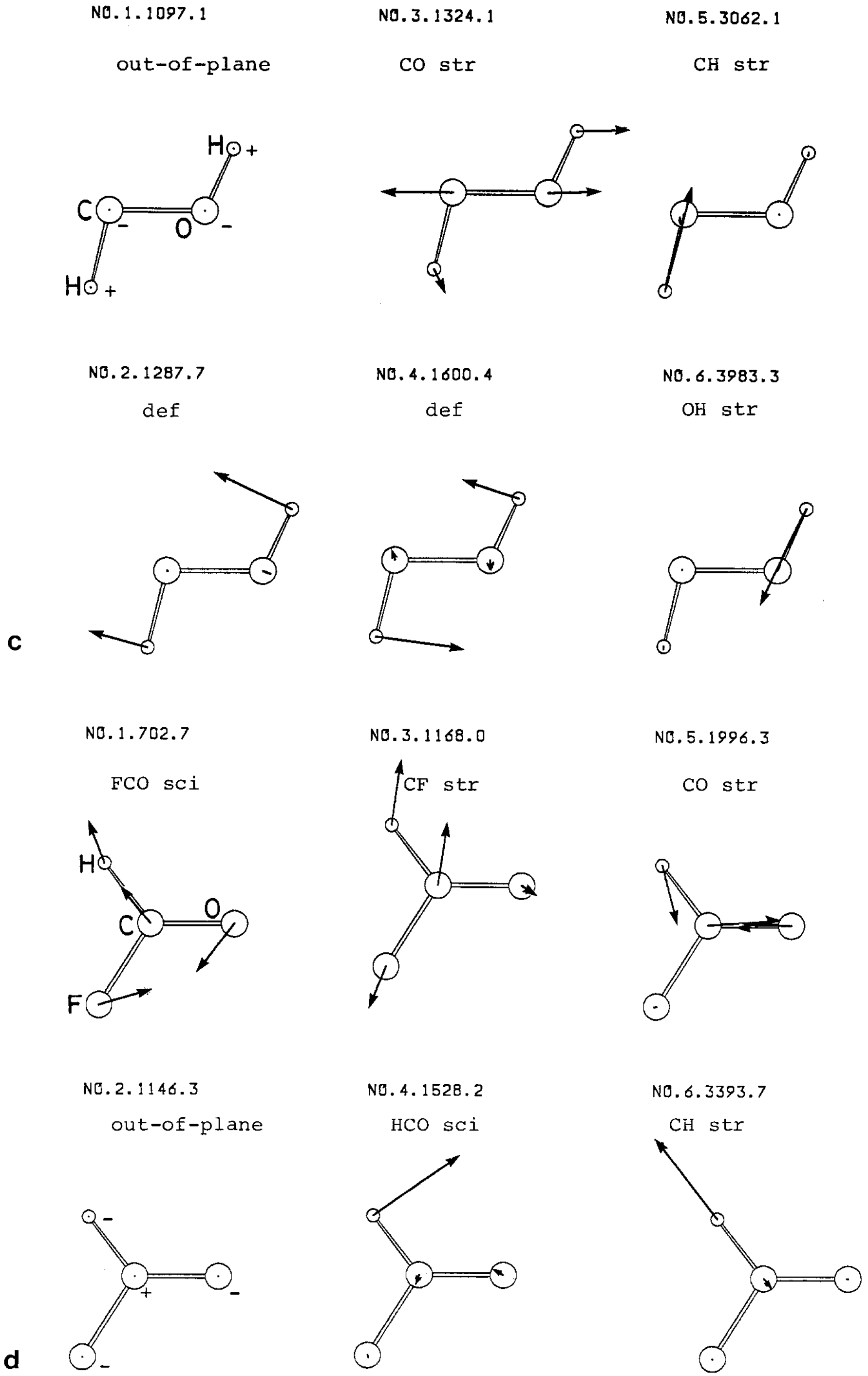


Fig. 4—continued

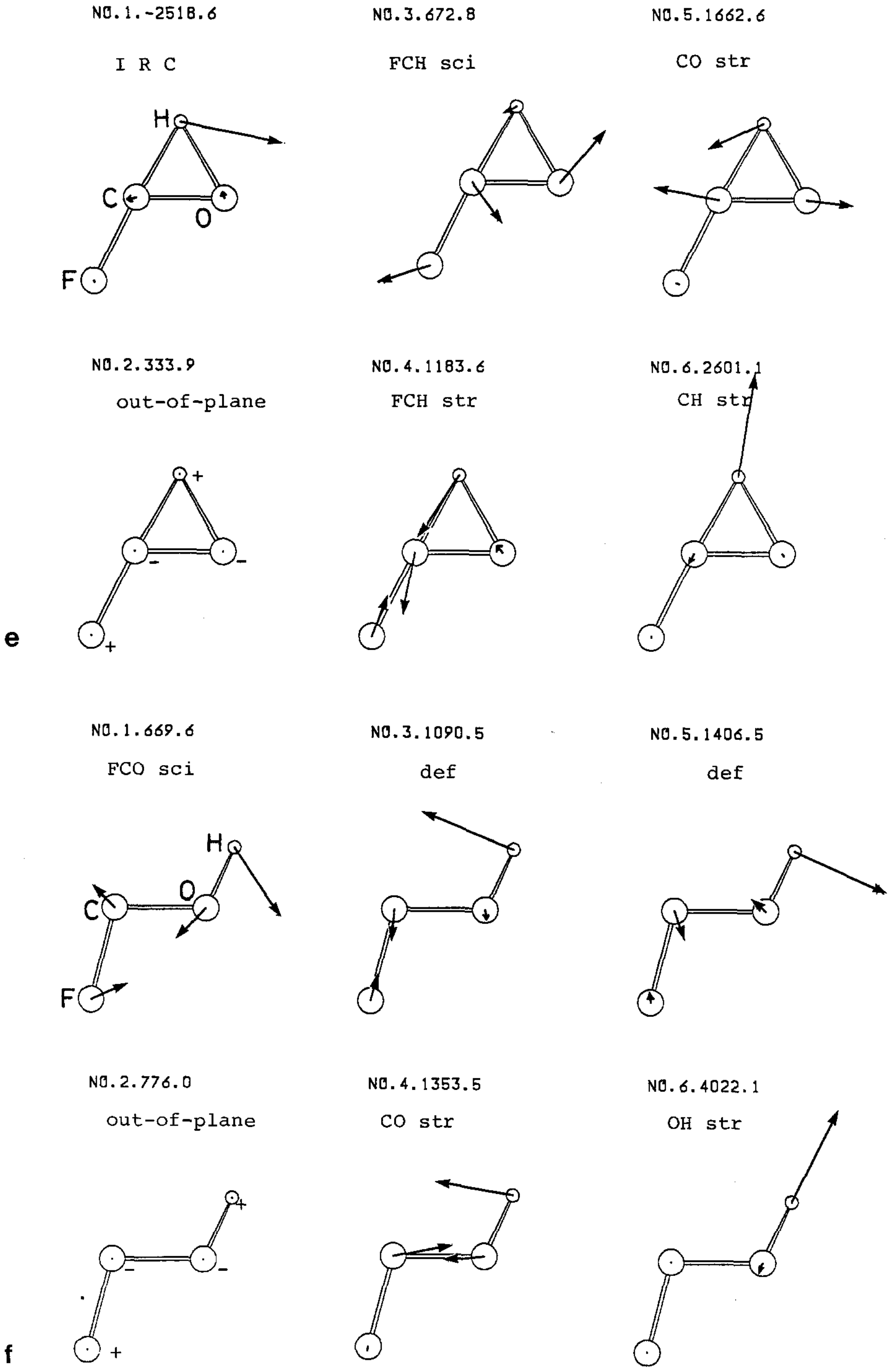


Fig. 4—continued

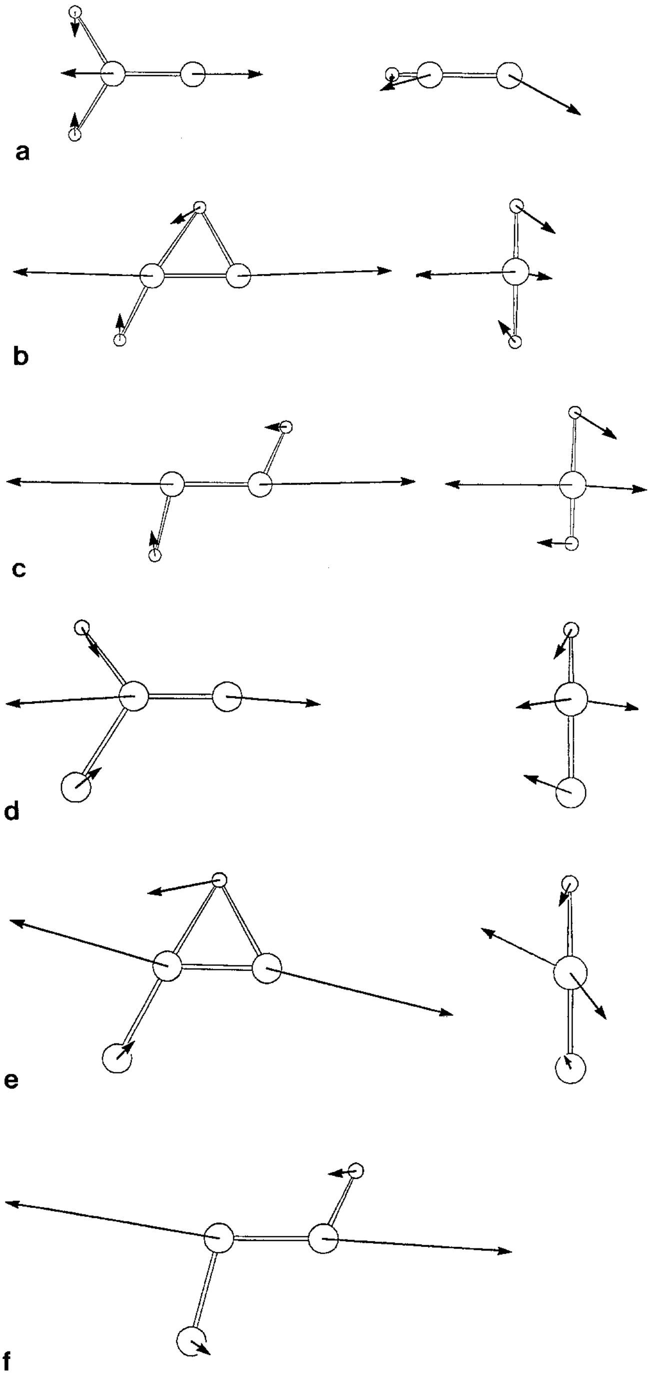


Fig. 5a–f. The forces **f** exerted on the reaction system by a water molecule in the complexes **4(a)**, **5(b)**, **6(c)**, **10(d)**, **11(e)**, and **12(f)**. Water molecules are not drawn. *Left-hand figures* are front views, *right-hand ones* are side views. **f** does not have a side view. For side views, we look at carbon in **b** and **c** and oxygen in **d** and **e**, and set water on their right

Table 1. Static effects of one water molecule upon isomerization reactions of (a–c) H_2CO and (d–f) FHCO. Projected force F_i, deviation F_i/a_i and energy difference $\Delta E_i = -F_i^2/2a_i$ are all found in text. R, TS and P denote reactant, transition state and product for the reaction, respectively. Last digits are rounded

Species	Vibrational mode				F_i/a_i ($\sqrt{\text{amu}}\cdot$bohr)	ΔE_i (kcal/mol)
	i	Classification	v_i (cm^{-1})	F_i (au)		
(a) **4**	1	out-of-plane	1332	−0.00001	−0.01	−0.001
R($H_2C{=}O$)+H_2O	2	a roc	1380	0.0	0.0	−0.0
	3	s HCH sci	1680	0.00005	0.02	−0.011
	4	s CO str	1924	0.00003	0.01	−0.003
	5	s CH str	3191	0.00006	0.01	−0.005
	6	a CH str	3277	0.0	0.0	−0.0
						Total $\Sigma_i \Delta E_i = -0.020$
(b) **5**	1	IRC	2731i	−0.00004	0.01	0.004
TS(HCHO)+H_2O	2	out-of-plane	683	−0.00006	−0.16	−0.135
	3	def	1357	−0.00011	−0.07	−0.104
	4	def	1509	0.00009	0.04	−0.049
	5	CH str	2666	0.00004	0.01	−0.003
	6	CH str	3192	−0.00005	−0.01	−0.004
						Total $\Sigma_i \Delta E_i = -0.295$
(c) **6**	1	out-of-plane	1097	0.00000	0.00	−0.000
P(HCOH)+H_2O	2	def	1288	0.00006	0.04	−0.035
	3	CO str	1324	0.00013	0.09	−0.151
	4	def	1600	0.00002	0.01	−0.002
	5	CH str	3062	0.00006	0.01	−0.005
	6	OH str	3983	0.00003	0.00	−0.001
						Total $\Sigma_i \Delta E_i = -0.194$
(d) **10**	1	FCO sci	703	0.00000	0.01	−0.000
R(FHC=O)+H_2O	2	out-of-plane	1146	−0.00005	−0.04	−0.029
	3	CF str	1168	−0.00002	−0.02	−0.005
	4	HCO sci	1528	−0.00001	−0.00	−0.001
	5	CO str	1996	−0.00007	−0.02	−0.021
	6	CH str	3394	−0.00007	−0.01	−0.006
						Total $\Sigma_i \Delta E_i = -0.061$
(e) **11**	1	IRC	2519i	−0.00012	0.02	0.032
TS(FCHO)+H_2O	2	out-of-plane	334	−0.00001	−0.09	−0.010
	3	FCH sci	673	−0.00000	−0.00	−0.000
	4	FCH str	1184	0.00002	0.01	−0.004
	5	CO str	1663	0.00016	0.06	−0.138
	6	CH str	2601	−0.00004	−0.01	−0.003
						Total $\Sigma_i \Delta E_i = -0.155$
(f) **12**	1	FCO sci	670	−0.00000	−0.00	−0.000
P(FCOH)+H_2O	2	out-of-plane	776	0.00007	0.13	−0.114
	3	def	1091	0.00003	0.02	−0.008
	4	CO str	1354	−0.00013	−0.08	−0.131
	5	def	1407	−0.00010	−0.05	−0.069
	6	OH str	4022	−0.00004	−0.00	−0.002
						Total $\Sigma_i \Delta E_i = -0.325$

mode (v_3; 1168 cm^{-1}). The deviation is the largest in the v_2 out-of-plane mode, which again verifies the min-max relationship presented in Sect. 2.2. This largest out-of-plane motion means that, as with $H_2C{=}O$, the C and O_w come together although this is emphasized in the HFC=O case. The movement in the molecular plane shortens both the CH and CF lengths, which is also similar to the formaldehyde case. Considering the energy change in a whole molecule, the HFC=O is affected about 4 times more than $H_2C{=}O$.

4.2. Effects upon the TS

The effects of the external force from the water upon the TS of HCHO are shown in Table 1b. The projection of the force on the normal mode is listed in order of decreasing magnitude as: -0.113×10^{-3} on the deformation mode (v_3; 1357 cm^{-1}) $>0.859\times10^{-4}$ on the deformation mode (v_4; 1509 cm^{-1}) $>$ -0.645×10^{-4} on the out-of-plane mode (v_2; 683 cm^{-1}). The deviation in the normal mode is listed in decreasing order: -0.156 in $v_2 > -0.690\times10^{-1}$ in $v_3 >$ -0.426×10^{-1} in v_4. In the out-of-plane mode, v_2, the deviation is the largest, which again verifies the min-max relationship presented in Sect. 2.2; however contrary to the R cell behaviour, here v_2 mode separates C from the O_w and thereby inhibits the formation of a new CO_w bond. The other effects are similar to that upon the R cell: the stretching of the CO length and the decreasing of the ∠HfCO are enhanced. Finally, the v_1 mode corresponds to the reaction coordinate, and the deviation in the v_1 mode is negative, -0.646×10^{-2}; consequently the P cell is compressed, which means that the external force expands the R cell. In other words, the solvent attracts the reaction system into the R cell. Table 1e shows the effects upon the TS of FCHO. The projection of the force has the largest value 0.159×10^{-3} for the in-plane CO stretching mode (v_5; 1663 cm^{-1}) and the deviation in the normal mode is largest -0.879×10^{-1} in the out-of-plane mode (v_2; 334 cm^{-1}). These effects are quite similar to those for the HCHO case, obeying the min-max relationship presented in Sect. 2.2, although the deviation is larger for HCHO than it is for FCHO. The character of the shift of potential barrier is also similar to the HCHO case, with the P cell being compressed and the R cell expanded, although in this case the magnitude of the deviation is larger for FCHO than for HCHO. The energy change is also larger in FCHO than in HCHO: it is 4 times as large in the R cell, but only twice as large in the TS.

4.3. Effects upon the P *cell*

The product carbenes X-C-O-H (X = H or F) are affected by the solvent water, as shown in Tables 1c and f. On HCOH, the projection of the force is listed in order of decreasing magnitude: 0.132×10^{-3} on the CO stretching mode (v_3; 1324 cm^{-1}) $>0.622\times10^{-4}$ on the deformation mode (v_2; 1288 cm^{-1}) $>0.568\times10^{-4}$ on the CH stretching mode (v_5; 3062 cm^{-1}). It should be noted that the projection of force on the out-of-plane mode is negligible. The deviation in the normal mode is also listed in decreasing order: 0.851×10^{-1} along $v_3 > 0.423\times10^{-1}$ along $v_2 > 0.714\times10^{-2}$ along the deformation mode (v_4; 1600 cm^{-1}) $\fallingdotseq 0.683\times10^{-2}$ along

v_5. Both the projected force and the deviation are large in the molecular plane, and are negligible in the out-of-plane mode. The min-max relationship is also applicable in this case, although the projected force itself is nearly zero and hence the deviation in the out-of-plane mode becomes zero; this is a feature which is not found in the R cell or the TS of H_2CO and HFCO. Among the in-plane modes, the deviation is especially large in the v_2 which, having the smallest frequency of the in-plane modes, is considered to be the IRC mode [10b]. This deviation attracts the reactant into the R cell.

As for FCOH, the magnitude of the projection of the force decreases in the order: -0.126×10^{-3} on the CO stretching mode (v_4; 1354 cm^{-1}) $> -0.953 \times 10^{-4}$ on the deformation mode (v_5; 1407 cm^{-1}) $> 0.675 \times 10^{-4}$ on the out-of-plane mode (v_2; 776 cm^{-1}). The corresponding ordering for the deviation in the normal mode is: 0.126 in $v_2 > -0.776 \times 10^{-1}$ in $v_4 > -0.544 \times 10^{-1}$ in v_5. Note that the largest deviation is observed in the out-of-plane mode, in accord with the min-max relationship presented in Sect. 2.2. This means that the C atom and the O atom approach close to the O_w and the H_w atom, respectively. This is attributed to the fact that the charge of the C atom becomes more positive after the substitution of the H atom by the more electronegative F atom, so that the increasing interaction brings about an attractive force between the C atom and the O_w atom. For the R cell and TS, however, the neighbouring H atoms soften the positive charge of the C atom in both $H_2C{=}O$ and $HFC{=}O$, and the interaction between the C atom and the O_w atom is not so large. In the P cell, the C atom becomes more positive, and this charge increase has a large effect upon the force. Among the in-plane modes, the v_1 mode has the lowest frequency, 670 cm^{-1}, and hence is the IRC mode [10b]. The effect of water upon this mode is smaller than for the other five normal modes of FCOH, which is not observed in the case of HCOH. The energy change is very large for FCOH, being about 6 times larger than the HCOH case on the average.

5. Conclusion

The effects of a static external field on the chemical reaction cooordinate have been studied in terms of the string model in which the deformation of the string and the associated deformation of the cell structure are controlled by the external force. Local normal mode analysis characterizes the underlying mechanism of the string deformation. In the model reaction system, the predominant interaction with a water molecule is observed in the C-O_w interaction, with the string being deformed along the C-O_w bond. This deformation for the formation of a new C-O_w bond is shown in both the R cell and the P cell, but not in the TS. The TS itself is shifted towards the P cell. Then we can say that the water molecule attracts the transition state into the P cell: the water has the effect of expanding the R cell for this H-migrating process. Moreover, for fluoroformaldehyde, the force of the water molecule correlates very well with the out-of-plane vibration mode and contributes to the stabilization of the P cell. This may finally bring about the formation of a "new reaction path", in other words, bifurcation or formation of a new string.

As the external field is static, the string model thus presented can be said to provide a perturbation theoretical approach for the reaction coordinate theory in the particular case discussed. The extension to processes involving thermodynamical effects [8i] should be fruitful.

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