40.2 kcal mol^{-1} and 0.82 eV, respectively, both corresponding to partial occupancy of the $7b_2$ LUMO. The lowest IE of cyclopentadienylidenecarbene is predicted to be greater than 8.85 eV, possibly although not conclusively as high as 9.28 eV (corresponding to the unassigned peak in the benzyne photoelectron spectrum).

This study is the highest level study performed on cyclopentadienylidenecarbene so far and clearly provides detail for both

further study and possibly experimental detection.

The Chemical Reaction Molecular Dynamics Method and the Dynamic Transition State: Proton Transfer Reaction in the Formamidine and Water Solvent System

Masataka Nagaoka,* **Yoshishige Okuno,**[†,‡] **and Tokio Yamabe**[†]

Contribution from the Institute for Fundamental Chemistry, 34-4, Takano-Nishihiraki-cho, Sakyo-ku, Kyoto 606, Japan. Received May 31, 1990

Abstract: The chemical reaction mechanism in solution is analyzed by using the chemical reaction molecular dynamics (CRMD) method where a solute molecule and a few solvent molecules are regarded as a supermolecule and the chemical reaction dynamics can be analyzed in a time-dependent way on the intrasupermolecular potential surface. We have examined a proton transfer reaction, the formamidine–water system, and focused on the dynamic effect in the chemical reaction after considering the static "electronic" solvent effect. Two schemes, the constant-temperature scheme (CTS) and the constant-energy scheme (CES), have been employed, and a new type of critical state, named the dynamic transition state (DTS), was found by the appearance of a cusp in the hydrogen-bonding correlation function (HBCF). The cusp is due to the stopping of change in the O–H bond length, which produces a water molecule in the product region. In the CES, alternately modulated oscillation appeared, which is a characteristic in triatomic systems and should play an important role in energy flow in solution. It is emphasized that chemical reaction dynamics should be studied in the phase space by taking the kinetic energy or momentum into consideration.

I. Introduction

The understanding of the molecular dynamics mechanism, i.e., how a chemical reaction in solution takes place, has been one of the most important themes for chemists for a long time. However, because of the complexity of real chemically reacting systems, many analytically unresolved problems still remain.[1-3] In recent years, the development of supercomputers has enabled some of those problems to be solved by numerical computation.[3-12] Previously, we have focused on the clarification of the static "electronic" solvent effect for chemical reactions by utilizing the supermolecule treatment with the intrinsic reaction coordinate (IRC) analysis,[4,5] where we have clarified that a special solvent water molecule should participate positively in the whole reaction in order to lower the net potential energy barrier by electron exchange between a solute and a solvent and have suggested that the intrasupermolecular hydrogen-rearrangement mechanism may serve as a fundamental model of double proton transfer mechanism in biochemical systems. Recently, Jorgensen's group regarded a chemical reaction in solution as a dynamical process on a free energy potential surface and developed its treatment for a typical S_N2 reaction in aqueous solution based on the potential of mean force that can be obtained from the radial distribution function by Monte Carlo calculations.[3,6,7] On the contrary, Benjamin et al. have concentrated on the role of energy fluctuation and transfer (i.e., heat wave) in thermally activated chemical reactions in solution and have examined the path of energy flow through the different modes of the solvent and the reagents for a model atom

exchange reaction in a rare gas solution.[11,12] However, in the former, the solvent effect was considered only statically by using the potential of mean force for a reactant species by summing up each of the intermolecular potential energies between the reactant and other solvent molecules and by averaging to obtain a radial distribution function.[1-3,6,7] It is also doubtful whether the intermolecular potential that is prepared between stable molecules is applicable to describe the chemical reaction dynamics in solution, which is, in fact, a common prescription used in most molecular dynamics (MD) studies[13-15] and might be justified if

* To whom correspondence should be addressed.
† Also associated with the Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Yoshida-moto-machi, Sakyo-ku, Kyoto 606 Japan.
‡ Permanent address: Daicel Chemical Industries, LTD, 1239, Shinzaike, Aboshi-ku, Himeji, Hyogo 671-12 Japan.

(1) Hynes, J. T. In *Theory of Chemical Reaction Dynamics*; Baer, M., Ed.; CRC Press: Boca Raton, FL, 1985; Vol. IV and references therein.
(2) Berne, B. J.; Borkovec, M.; Straub, J. E. *J. Phys. Chem.* **1988**, *92*, 3711.
(3) Jorgensen, W. L. *Adv. Chem. Phys.* **1988**, *70*, 469.
(4) Yamashita, K.; Kaminoyama, M.; Yamabe, T.; Fukui, K. *Theor. Chim. Acta* **1981**, *64*, 303.
(5) Yamabe, T.; Yamashita, K.; Kaminoyama, M.; Koizumi, M.; Tachibana, A.; Fukui, K. *J. Phys. Chem.* **1984**, *88*, 1459.
(6) Madura, J. D.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1986**, *108*, 2517.
(7) Jorgensen, W. L. *Acc. Chem. Res.* **1989**, *22*, 184.
(8) Ohmine, I. *J. Chem. Phys.* **1986**, *85*, 3342.
(9) Tanaka, H.; Ohmine, I. *J. Chem. Phys.* **1987**, *87*, 6128.
(10) Ohmine, I.; Tanaka, H.; Wolynes, P. G. *J. Chem. Phys.* **1988**, *89*, 5852.
(11) Benjamin, I.; Wilson, K. R. *J. Chem. Phys.* **1989**, *90*, 4176.
(12) Benjamin, I.; Gertner, B. J.; Tang, N. J.; Wilson, K. R. *J. Am. Chem. Soc.* **1990**, *112*, 524.
(13) Giccoti, G.; Hoover, W. G., Eds. *Molecular Dynamics Simulation of Statistical-Mechanical Systems*; North-Holland: Amsterdam, 1986.
(14) Giccoti, G.; Frenkel, D.; McDonald, I. D., Eds. *Simulation of Liquids and Solids. Molecular Dynamics and Monte Carlo Methods in Statistical Mechanics*; North-Holland: Amsterdam, 1987.
(15) Allen, M. P.; Tildesley, D. J. *Computer Simulation of Liquids*; Oxford University Press: New York, 1987.

one is interested in thermodynamic properties at equilibrium in solution.[13-15] In the latter theory, although the MD method has been utilized for the Cl + Cl$_2$ → Cl$_2$ + Cl reaction model in 100 Ar atoms,[12] the simplicity of the reaction itself and the electron exchange problem between solute and solvents are still remaining problems which must be solved in order to deal successfully with more realistic chemical reactions in solution.

In this article, on the basis of the previous understanding that only a few important solvent molecules should play a key role during the intermediate process of a chemical reaction where reactants convert their excess kinetic energy into potential energy as the barrier is surmounted,[4,5,16] a detailed investigation and analysis of the solution reaction dynamics are performed via an MD method in which a chemically reacting system is described by an intrasupermolecular potential function for a pair consisting of a solute molecule and a solvent molecule. As the previous studies have clarified,[8-10] it is true that water, the most common solvent, exhibits extremely large energy fluctuation as a whole and should yield a significant solvent effect.[8-10] In addition, in an actual reaction process in solvents, there exists necessarily an initial energy fluctuation involving the high translational excitation of a few solvents adjacent to the reactants followed by hard solvent–reactant collisions producing potential energy spikes. However, as this successive energy concentration to the reacting species occurs, it is plausible that there should also occur simultaneously energy stabilization due to the electron exchange between the solute and a few surrounding solvent molecules. Although this effect is usually neglected in those treatments via the MD methods, we have found that the effect must be taken into consideration,[4,5] and we insist presently that the molecular dynamic aspect should be discussed after the electronic solvent effect is included. The MD simulation should be executed on such a potential energy surface as is constructed by treating both electronically important solvent molecules, whose number must be small, and a solute molecule as a supermolecule. An above version of the MD method may be called the chemical reaction MD (CRMD) method in solution, and it makes possible the time-dependent analysis of a chemical reaction mechanism for a supermolecule, which surpasses the static IRC analysis. Naturally, the CRMD method can be applied to a chemical reaction in the gas phase.

As a model supermolecular reacting system, we have chosen here the following proton transfer reaction of formamidine (F) in water solvent (W) (the intrasupermolecular hydrogen-rearrangement process):

H$_2$N—CH≡NH + H$_2$O →

→ HN≡CH—NH$_2$ + H$_2$O
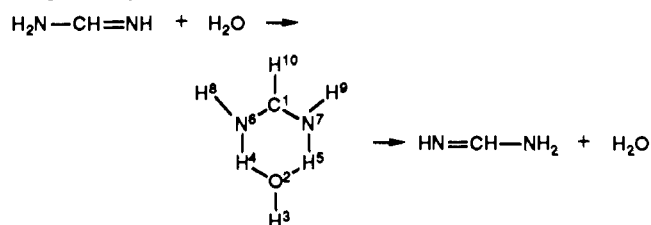
The potential energy barrier of the above process has been found to be 15.69 kcal/mol for the intrasupermolecular hydrogen-rearrangement process and is contrasted with 59.11 kcal/mol for the intramolecular hydrogen-rearrangement process.[5] Therefore, we have clarified the "dynamic" effect accompanying the potential barrier lowering induced by an electronically important solvent water molecule. The "dynamic" effect on the both kinetic and potential energy fluctuations emerges as time-dependent changes of both momenta and positions throughout the chemical reaction; they have been pursued for a few hundred or a few femtoseconds to a few picoseconds via the CRMD method, and the reaction mechanism has been analyzed using a subfemtosecond time step.

Regarding a formamidine and water molecule couple as a supermolecule, the optimization of equilibrium geometries, the tracing of IRC, and the additional optimization for a few thousand geometries selected randomly were performed with the STO-3G

basis set[17] by using the GAUSSIAN86 program[18] with the IRC algorithm.[19] The global potential function for the intrasupermolecular hydrogen-rearrangement process was fitted as a linear combination of 6–4–3–2–1 Lennard-Jones type analytical functions by a fitting algorithm that has been developed originally on the basis of the linear least-square method.[20] By using this analytical potential function, MD simulations were executed for a suitable set of initial conditions explained later, and thus we have obtained both dynamic and statistical information for the energy transfer mechanism between a formamidine and a water molecule.

In order to facilitate the MD simulation of the chemical reaction, the method of initiating trajectories at the barrier top has been often used.[21-23] Then, since the MD method is invariant under time inversion, it results that we see the reverse chemical reaction process. At the present system, the reactant and the product molecule are geometrically symmetric which means, therefore, that we observe the later half-reaction of the whole. The chemical reaction mechanism in an actual reaction can be investigated more clearly when such special trajectories are analyzed so that the time-reversed process of dissipation of energy occurs in sliding down the potential barrier. We have adopted the constant-temperature scheme (CTS) and the constant-energy scheme (CES) for the two different types of MD simulation. In the case of the CTS, we can regard a trajectory as an extended IRC because it starts with a finite velocity from the transition state (TS) to the stationary-state (SS) region. Although the CTS is far from a practically allowed chemical reaction scheme, we can obtain a useful perspective for the reaction ergodography in the neighborhood of IRC.[24-26] On the other hand, the CES dynamics, which can be called the microcanonical scheme, is executed also under the condition that initial velocities at the TS are selected to have a constant internal kinetic energy, i.e., the constant total energy. We can observe the "bobsleigh" effect,[27] more remarkably than in the pure IRC analysis,[26] and it brings about the potential energy fluctuation especially for the trajectories in CES calculations.

The CRMD treatment is unprecedented in the sense that the dynamic effect in a chemical reaction can be investigated at the atomic level in contrast with the usual MD method which usually simulates at the molecular level. In this article, we have paid attention to both kinetic energy fluctuations of constituent atoms and potential energy fluctuations between a couple of atoms for making clear the energy transfer mechanism of the proton transfer reaction in the formamidine–water system. Although the results obtained in this work are specific to this system, we can obtain some useful insights for understanding the other proton transfer reactions in aqueous solutions and can extend the CRMD strategy developed here to general chemical reactions both in the gas phase and in the condensed phase including biochemical systems.

The following section provides the methodology for the CRMD method and explains CTS and CES with definitions of the hydrogen-bonding correlation function and Fourier transforms of time-dependent potential energies and bond lengths. Results and Discussion are given in section III, followed in section IV by the Conclusion.

(16) Levine, R. D., private communication.

(17) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657.

(18) Frisch, M. J.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Melius, C. F.; Martin, R. L.; Stewart, J. J. P.; Bobrowicz, F. W.; Rohlfing, C. M.; Karn, L. R.; Defrees, D. J.; Seeger, R.; Whiteside, R. A.; Fox, D. J.; Fleuder, E. M.; Pople, J. A. *GAUSSIAN86*; Carnegie-Mellon Quantum Chemistry Publishing Unit: Pittsburgh, PA, 1984.

(19) Baker, J.; Gill, P. M. W. *J. Comput. Chem.* **1988**, *5*, 465.

(20) Nagaoka, M.; Okuno, Y.; Yamabe, T.; Fukui, K., to be published. Swaminathan, S.; Whitehead, R. J.; Guth, E.; Beveridge, D. L. *J. Am. Chem. Soc.* **1977**, *99*, 7817.

(21) Keck, J. C. *Discuss. Faraday Soc.* **1962**, *33*, 173.

(22) Bennet, C. H. In *Diffusion in Solids*; Burton, J. J., Ed.; Academic: New York, 1975; p 73.

(23) Anderson, J. B. *J. Chem. Phys.* **1973**, *58*, 4684; *Ibid.* **1975**, *62*, 2246.

(24) Fukui, K. *J. Phys. Chem.* **1970**, *74*, 4161.

(25) Fukui, K. *Acc. Chem. Res.* **1981**, *14*, 363.

(26) Kato, S.; Kato, H.; Fukui, K. *J. Am. Chem. Soc.* **1977**, *99*, 684.

(27) Levine, R. D.; Bernstein, R. B. *Molecular Reaction Dynamics and Chemical Reactivity*; Oxford University Press: New York, 1987.

Proton Transfer in Formamidine and Water
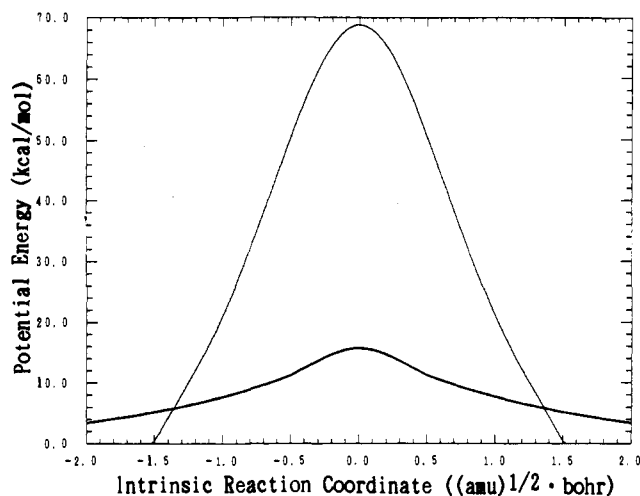
J. Am. Chem. Soc., Vol. 113, No. 3, 1991 771

Figure 1. Potential energy profile along the intrinsic reaction coordinate (IRC) for the proton transfer reaction of the formamidine system (solid line) and the formamidine–water system (bold line).

II. Methodology

A. Intrasupermolecular Potential Function for the CRMD Method. In our viewpoint of a chemical reaction in solution, some special solvents affect the reaction dynamic mechanism electronically after creation of a hot spot by cooperative motions of solvent molecules. Therefore, one can model a reacting system in solution as a supermolecule which consists of a solute system and a few solvent molecules. One question is how many solvents must be included although it should be dependent on the systems involved. It has been known in the present system that inclusion of only one water molecule reduces dramatically the potential barrier for the proton transfer reaction of formamidine[5] (i.e., Figure 1). Also, in a reaction in solution, it can be suggested that from the electron exchange point of view, the first special solvent molecule should have a definitely important role for the reaction accompanying an appropriate geometrical change.[16] The other solvent molecules may participate, more or less, in the reaction electronically but must show more statistical behavior.

Hence, in our CRMD method, the intrasupermolecular potential function must be obtained at first as an analytical function of Cartesian coordinates which represent geometrical configurations of the present 10-atomic supermolecular system in the laboratory system. For this, ab initio molecular orbital (MO) calculations[28] were executed to estimate potential energies for a few thousand configurations by using GAUSSIAN86[18] with the split-valence STO-3G basis set.[17] The configurations chosen include not only the SS and TS geometries but also 100 points on IRC which were obtained also by GAUSSIAN86 equipped with the IRC algorithm.[19] According to the fitting procedure,[20] a set of sample data base for fitting was prepared from the potential energy data thus obtained. Adopting the assumption of pairwise additivity, we assume that the total intrasupermolecular potential function $\Phi_{supermolecule}$ can be written as a sum of pairwise interaction energies between constituent atoms: a linear combination of 6-4-3-2-1 Lennard-Jones type analytical functions, $\phi(r_{ij})$.

$$\Phi_{supermolecule} = \sum_{i<j} \phi(r_{ij}) \tag{II.1}$$

$$\phi(r_{ij}) = \frac{a_{ij}}{r_{ij}} + \frac{b_{ij}}{r_{ij}^2} + \frac{c_{ij}}{r_{ij}^3} + \frac{d_{ij}}{r_{ij}^4} + \frac{e_{ij}}{r_{ij}^6} \tag{II.2}$$

where r_{ij} is the distance between atoms labeled i and j, and a_{ij}, b_{ij}, c_{ij}, d_{ij}, and e_{ij} are the parameters to be fitted.

B. The CRMD Simulation. The CRMD simulation is performed on the above analytical intrasupermolecular potential energy surface by using the following two sets of Hamilton's

equations of motion[29] for solute atoms and solvent atoms, respectively:

$$\dot{r}_{solute} = -\frac{\partial H}{\partial p_{solute}} \qquad \dot{p}_{solute} = \frac{\partial H}{\partial r_{solute}} \tag{II.3}$$

and

$$\dot{r}_{solvent} = -\frac{\partial H}{\partial p_{solvent}} \qquad \dot{p}_{solvent} = \frac{\partial H}{\partial r_{solvent}} \tag{II.4}$$

where r_{solute} and p_{solute} are the Cartesian coordinates for positions of solute atoms and their conjugate momenta, and $r_{solvent}$ and $p_{solvent}$ are those for solvent atoms. H is the Hamiltonian of the supermolecular system and is represented as follows:

$$H = K_{solute} + K_{solvent} + \Phi_{supermolecule} \tag{II.5}$$

where K's are the corresponding internal kinetic energies and $\Phi_{supermolecule}$ includes the nonseparable interaction terms originating from the electron exchange between the solute and the solvent. These sets of equations of motion are solved numerically by using the simple predictor–corrector algorithm.[15]

Each trajectory is initiated from the potential barrier top (i.e., TS) with initial velocities suitable for each problem. This technique has been developed by Keck,[21] Bennet,[22] and Anderson[23] and has often been utilized because it is practical and gives an efficient simulation. The initial internal velocities can be determined by a random number generator so as to reproduce the Maxwell–Boltzmann distribution at a given initial temperature T_0. In addition, the trajectory with the initial internal velocity vector along IRC (v_{IRC}) is examined and compared with the above trajectories.

C. The CES and CTS Schemes. Simulations are executed under two kinds of schemes, namely, the constant-energy scheme (CES) and the constant-temperature scheme (CTS). CES corresponds to the popular MD method where the total energy of a system is conserved. Although, at first sight, this scheme seems to be plausible considering the energy conservation law, it might not represent any true solution because the present model should be not an isolated system but a part of a real reacting system in solution essentially. In other words, there is no energy relaxation into the solvent environment in CES. On the contrary, CTS can be recognized to be the framework where each trajectory corresponds to an extended IRC and is allowed to keep a finite speed under the constraint that the system temperature is fixed to be a finite constant (T_0) throughout the reaction. This scheme can also be unrealistic, but its strong point is that the system is in contact with an ideal heat reservoir into which it can dissipate its internal energy in an ideally rapid and uniform manner. In order for this scheme to be realized numerically, the velocity rescaling method is employed, which makes it possible to keep the temperature at T_0 throughout the reaction by correcting the velocities at every moment:

$$\frac{1}{2}\sum_i m_i v_i(t)^2 = \frac{3}{2}Nk_B T_0 \tag{II.6}$$

where

$$v_i(t) = C_{cor} v_i^{uncorrected}(t) \tag{II.7}$$

and then

$$C_{cor} = \frac{\sum_i v_i(0)^2}{\sum_i v_i^{uncorrected}(t)^2} \tag{II.8}$$

In these expressions, $v_i(t)$, $v_i^{uncorrected}(t)$, and m_i are the corrected velocity at time t, the uncorrected velocity at time t, and the mass of the atom labeled i; N is the total number of atoms (10 in the present system) and k_B is the Boltzmann constant.

D. The Hydrogen-Bonding Correlation Function. We define the following hydrogen-bonding correlation function (HBCF) as

(28) Daudel, R.; Leroy, G.; Peeters, D.; Sana, M. *Quantum Chemistry*; Wiley: New York, 1983.

(29) Goldstein, H. *Classical Mechanics*, 2nd ed.; Addison-Wesley: Reading, MA, 1980.

a measure which probes the progress of the reaction:

$$D_{HB}(t) = \frac{2\Delta r_{24}(t)\Delta r_{25}(t)}{\Delta r_{24}(t)^2 + \Delta r_{25}(t)^2} \qquad (II.9)$$

where

$$\Delta r_{24}(t) = r_{24}(t + \Delta t) - r_{24}(t) \qquad (II.10)$$

i.e., Δ denotes the change of a quantity in a time interval Δt. If $D_{HB}(t)$ is less than zero, then asymmetric O–H motion occurs and it shows the tendency to move properly along IRC. On the contrary, if $D_{HB}(t)$ is greater than zero, it results in the symmetric deviation orthogonal to IRC. If $D_{HB}(t)$ is equal to zero, it suggests that at least one O–H bond motion has stopped.

In order to obtain not only statistical information but also some common features of these trajectories which appear from the specificity of the present reacting system, a number of trajectory calculations are executed.

E. Fourier Analysis. The following Fourier transforms are employed in CES to analyze how a proton transfer occurs at the local site of a parent molecule through the intermediation of a water molecule:

$$P(\omega) = \int_0^\tau p(t)e^{i\omega t}\,dt \qquad (II.11)$$

for the energy fluctuation and

$$L(\omega) = \int_0^\tau l(t)e^{i\omega t}\,dt \qquad (II.12)$$

for the bond-length fluctuation. In these formulas, $P(\omega)$ and $L(\omega)$ are the Fourier transforms of $p(t)$ and $l(t)$ which are, respectively, the total potential energy (PE) of the supermolecular system and length of the O–H bond at time t. The whole reaction time τ is 0.2 ps in CES, which results in the frequency resolution 166.8 cm^{-1}.

III. Results and Discussion

Both in the CTS simulation and in the CES simulation, a set of 11 trajectory calculations were each performed at the initial temperature T_0 equal to 1 K. One trajectory among each set was initiated with the velocity along the IRC direction. Each of the other 10 trajectories was started with 10 different initial velocities selected randomly to satisfy the condition that the internal kinetic energy corresponds to 1 K. We have calculated the CTS trajectories at every 0.01-fs interval and the CES ones every 0.001-fs interval, and recorded numerical data for the following physical quantities for 1 ps in every 1-fs interval in the CTS simulation and for 0.2 ps in every 0.1-fs interval in the CES one, respectively: kinetic energy (KE) for each atom, pairwise potential energy between two atoms selected arbitrarily, the total KE and PE, the bond lengths of O^2–H^4 and O^2–H^5, and HBCF. Although we observe the latter half-reaction (i.e., from TS to the product region) of the whole reaction (i.e., from the reactant region to the product region through TS), the former half-reaction can be observed also by tracing back the trajectory to the past because of the time-reversal invariance of the MD simulation and the geometrical symmetry of the reactant and the product.

A. The CTS Simulation and the Extended IRC. A trajectory which starts in CTS with initial velocity along the IRC direction can be regarded as an extended IRC. While IRC is defined by an infinitesimal motion without KE,[24,25] the extended IRC permits possession of a finite amount of KE along IRC; the rest, subtracted from the total KE (constant), is stored in the bath modes. The PE curve of this trajectory is compared with the PE one calculated by GAUSSIAN86 with the STO-3G basis set for the same geometries in Figure 2. The curve in the CTS simulation is very smooth from the TS to the SS region, and it was found to be very similar to the potential energy profile along the IRC for the form-amidine–water system (Figure 2). This fact shows that the present fitted potential surface represents the true surface quite well. It is true that the deviation between them is due to the still-remaining uncorrectness of the present analytical surface. However, potential energy surfaces calculated by ab initio MO methods with different
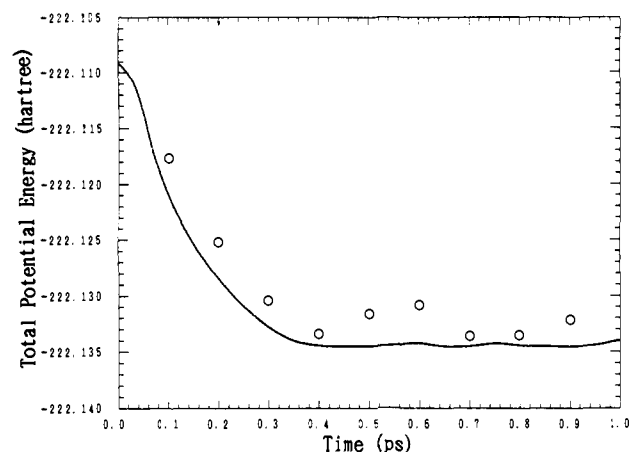
Figure 2. Total potential energy curve in the CTS with initial velocity along the IRC (—) and potential energy calculated by GAUSSIAN86 with STO-3G basis set for the same geometries (O). The corresponding coordinate is regarded as an extended IRC.
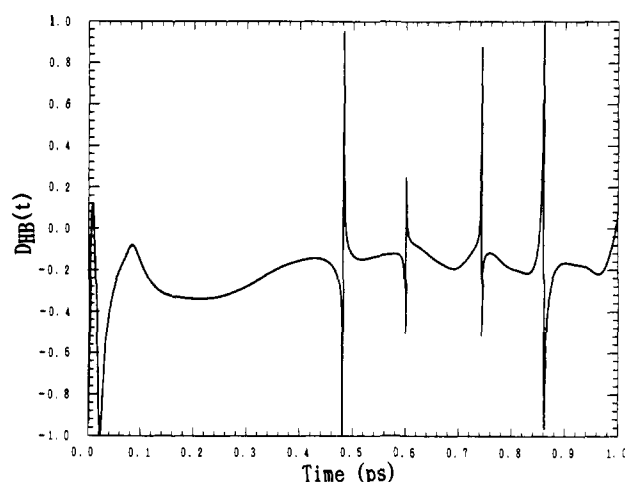
Figure 3. Correlation of hydrogen-bonding distances in the CTS with initial velocity along the IRC.

basis sets are different from each other[4,5] within the present energy deviation, and, therefore, it is concluded that the entire dynamics of the present system should be well-preserved.

We estimate the reaction time from the reactant region to the product region roughly as 0.8 ps which is twice as long as the time from the TS to the product region. In the SS region, slight oscillation of the PE is observed under the restriction of constant temperature (1 K). The HBCF (Figure 3) shows that the asymmetric O–H motion (i.e., the motion along IRC) continues monotonically except for the initial 0.02-ps period, which corresponds to wandering around the neighborhood of the TS until the entrance to the product region occurs. The rapid change of HBCF in the neighborhood of the TS indicates that the potential surface profile is so anharmonic as to permit easily energy interchange and suggests that the more the significant dynamic effect is brought about, the more kinetic energy the system obtains. In Figure 4, the time evolution of each constituent atom is shown in the CTS with initial velocity along the IRC. It is recognized also that the asymmetric motion is induced initially, which coincides with the IRC mode at the TS.

B. "Bobsleigh" Effect and the "Front and Rear" Effect. In the 10 trajectories with initial velocities selected randomly, after a short time of wandering around the TS, followed by slowly sliding down on the surface, the asymmetric O–H motion increases gradually, and ultimately the trajectory becomes close to the IRC (Figure 5). The PE profile shows a slight shoulder which indicates that it takes a little more time for the reacting system to reach the product region. Although reaction times from the reactant region to the product region depend on initial conditions (espe-
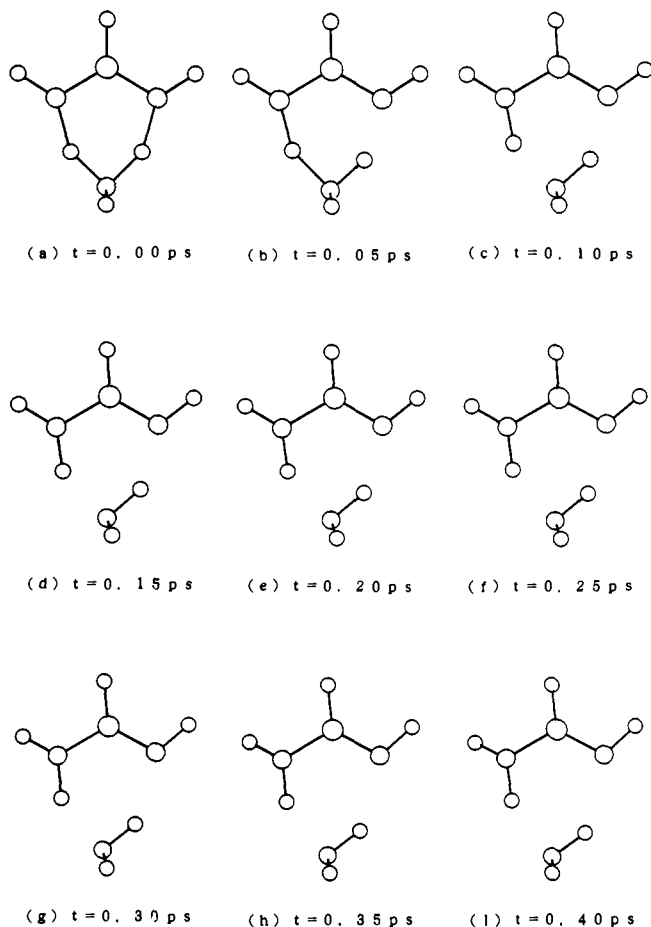
(a) t = 0. 0 0 p s　　(b) t = 0. 0 5 p s　　(c) t = 0. 1 0 p s

(d) t = 0. 1 5 p s　　(e) t = 0. 2 0 p s　　(f) t = 0. 2 5 p s

(g) t = 0. 3 0 p s　　(h) t = 0. 3 5 p s　　(l) t = 0. 4 0 p s

Figure 4. Time-dependent motion of each constituent atom in the CTS with initial velocity along the IRC.

cially, initial velocities), that are found to be almost 0.9 ps. It is interesting that, in spite of selecting initial velocities randomly, all trajectories are very similar to each other in comparison with the trajectory with the initial velocity along the IRC direction. These similarities are described as follows. Firstly, as soon as each trajectory starts from the TS, the large symmetric O–H motion (i.e., the motion away from the IRC) grows up in comparison with the trajectory with the initial velocity along the IRC direction which does not (Figure 6). This can induce the succeeding excitation of symmetric oscillations lasting for a longer time. Therefore, after wandering with the symmetric O–H motion which continues for a slightly longer period than in the trajectory with initial velocity along the IRC, those trajectories converge gradually to the direction along the IRC by way of various paths. Secondly, while a prominent "cusp" in the HBCF (shown as an arrow in each figure) is observed for all of those trajectories, this anomaly does not appear in the trajectory with initial velocity along the IRC direction. In Figure 7, the typical time evolution of each constituent atom is shown in the CTS with the initial velocity selected randomly. The symmetric motion is induced initially and is different from the IRC direction. Figure 7e ($t = 0.2$ ps) corresponds to the "cusp" geometry.

From time-dependent profiles of the O^2–H^4 bond and the O^2–H^5 bond (Figure 8), it has been clarified that the "cusp" is produced owing to the stopping of the length change in the $O–H_{water}$ bond which would become one O–H bond of the water molecule in an SS region. Taking into consideration the fact that the HBCFs for the above 10 trajectories are very similar, it may be insisted that the static IRC is rather special in the present system, and, furthermore, it can be postulated that reaction paths with the same finite temperature tend to pass through a certain characteristic region in phase space. Although the path connecting the TS and the corresponding singular point (i.e., "cusp") should be different in each trajectory, eventually, each experiences necessarily a
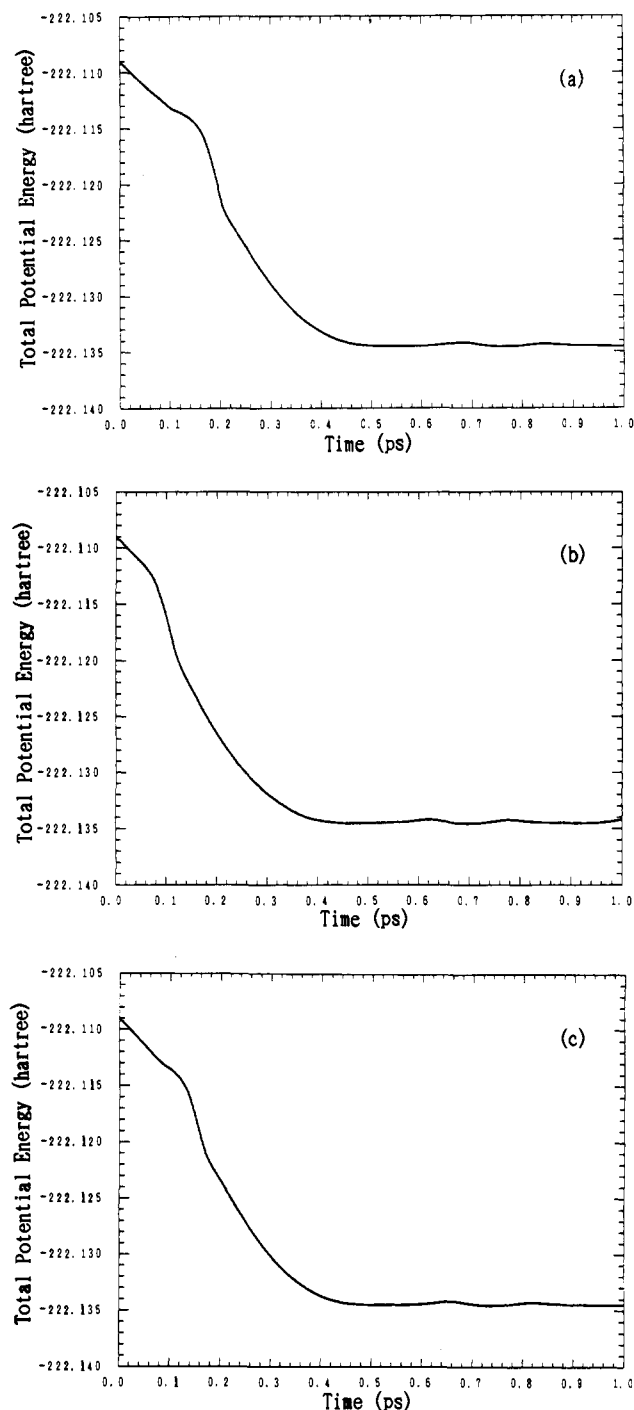

Figure 5. Total potential energy curves in the CTS with three initial velocities selected randomly. The corresponding reaction coordinate is each regarded also as an extended IRC.

"cusp". Therefore, it can be suggested that the phase space region which corresponds to the cusp is the rate-determining region in the sense that it is easy to reach the TS if a trajectory can go through the cusp point. By considering that the PE of the region between TS and the cusp is greater than the PE at the cusp, it can be stated that we cannot determine the rate-determining step by the static PE only. In the present system, it is possible to postulate that the cusp can correspond to the existence of a new transient region appearing if the dynamic effect is considered. It is true that our treatment, where the TS is the starting geometry for all simulations, is restricted because actual reacting species can vary their structures in the intermediate state near the TS, which may be similar to the TS geometry but different. However, the postulate states that it is possible that there is a new type of transient state in a thermal reaction, say, the "dynamic transition

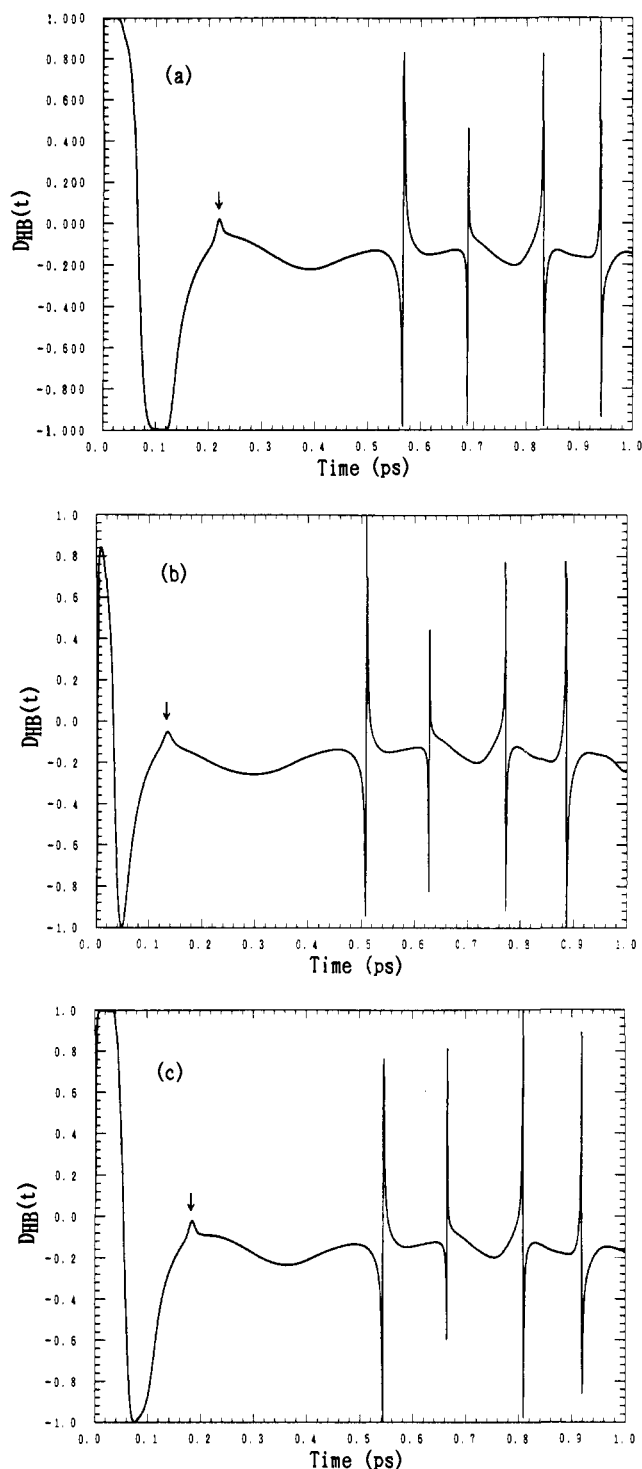774   *J. Am. Chem. Soc., Vol. 113, No. 3, 1991*

Nagaoka et al.

Figure 6. Correlation of hydrogen-bonding distances in the CTS with three initial velocities selected randomly. (a), (b), and (c) correspond to Figure 5, (a), (b), and (c), respectively. Each arrow indicates a cusp.
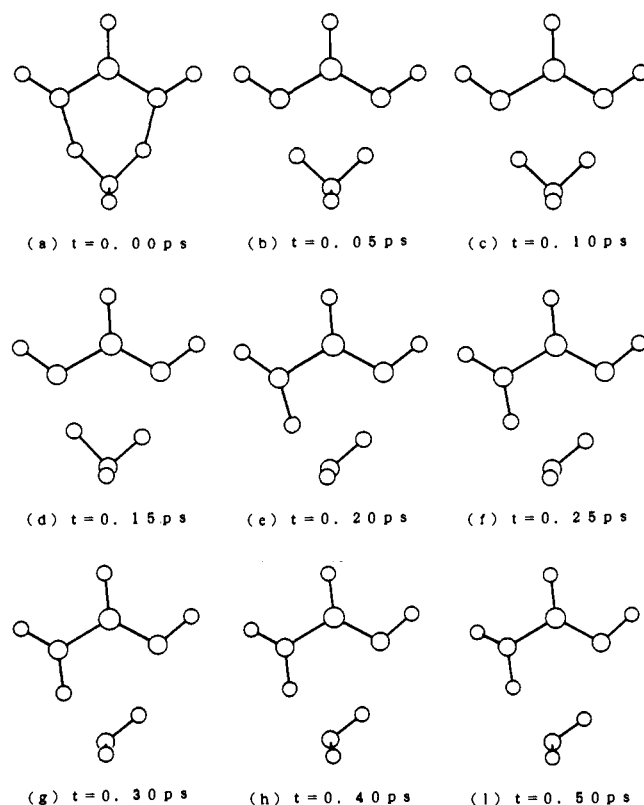

Figure 7. Time-dependent motion of each constituent atom in the CTS with initial velocity selected randomly. This motion corresponds to case a in both Figures 5 and 6.

state (DTS)", even if the present calculations were limited. In fact, one can regard this dynamic effect as the "front and rear" effect, which means that a characteristic region appears at a region shifted to the front or the rear of the TS. Therefore, it is conjectured also that there should exist complementarily the "transverse" effect in the more general CRMD treatment without restriction from the intermediate geometry.

Since the famous early work by Polanyi et al.,[30,31] chemical reactions have been discussed and analyzed by connecting their

dynamics with the shape of the potential energy surface. Nevertheless, the connection between them can be recognized still statically because the analysis is performed by loci of trajectories with respect to the restricted degrees of freedom. Therefore, we suggest that a more advanced treatment should be developed as a theoretical basis in phase space where explicit participation of momenta is possible (e.g., momentum correlation, etc.).

C. Remarkable Dynamic Effect in the CES Simulation. The CES simulations are also executed for the same two types of initial conditions as in the CTS simulations. The trajectory with initial velocity along the IRC direction shows that after sliding smoothly down from the TS for an initial 0.01 ps, the internal kinetic energy increases suddenly and it results in a strongly oscillating trajectory, inducing internal vibrations due to the curvature of the IRC (Figure 9). The strong oscillation of HBCF (Figure 10) and the appearance of the O^2-H^4 bond-length change (Figure 11) both stand for the induction of internal vibrations. The PE curve in the CES shows the "bobsleigh effect" more strikingly than in the pure IRC analysis due to inclusion of explicit time dependence, and it should be noted that any harmonic approximations for bath coordinates orthogonal to the IRC[32,33] cannot express this anharmonic PE profile successfully. This is related closely with the unavoidable anharmonicity in more realistic chemical reacting systems.

The PE curve shows also that there exists a turning point (t = 0.11 ps) when the high-frequency oscillation becomes more dominant than the low-frequency one. It is found that both the oscillation of the O^2-H^4 bond and the KE curve of the H^3 atom (Figure 12) also show a turning point at the same time, and then the mode switching by this energy flow within the water molecule is the origin of the turning point. This phenomenon indicates also that the solvent water molecule considered here should play a

(30) Polanyi, J. C.; Wong, W. H. *J. Chem. Phys.* **1969**, *51*, 1439.
(31) Polanyi, J. C. *Acc. Chem. Res.* **1972**, *5*, 161.

(32) Miller, W. H.; Handy, N. C.; Adams, J. E. *J. Chem. Phys.* **1980**, *72*, 99.

(33) Miller, W. H. In *New Theoretical Concepts for Understanding Organic Reactions*; Bertran, J., Csizmadia, I. G., Eds.; Kluwer Academic Publishers: Dordrecht, 1989; p 347 and references therein.
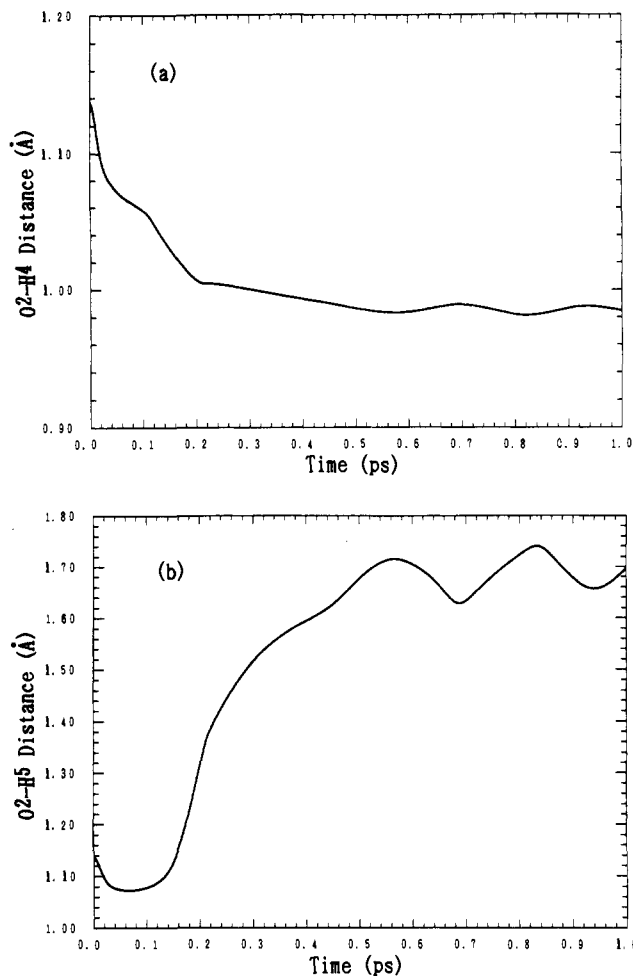
Proton Transfer in Formamidine and Water

J. Am. Chem. Soc., Vol. 113, No. 3, 1991 775

Figure 8. Time evolution of (a) the O^2-H^4 bond length and (b) the O^2-H^5 bond length.
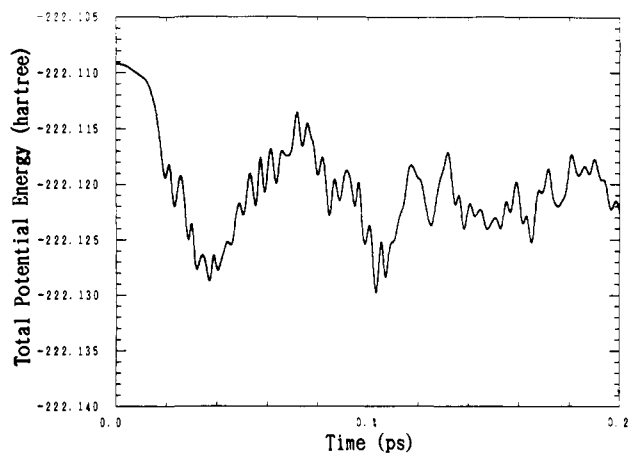
Figure 9. Total potential energy curve in the CES with initial velocity along the IRC.
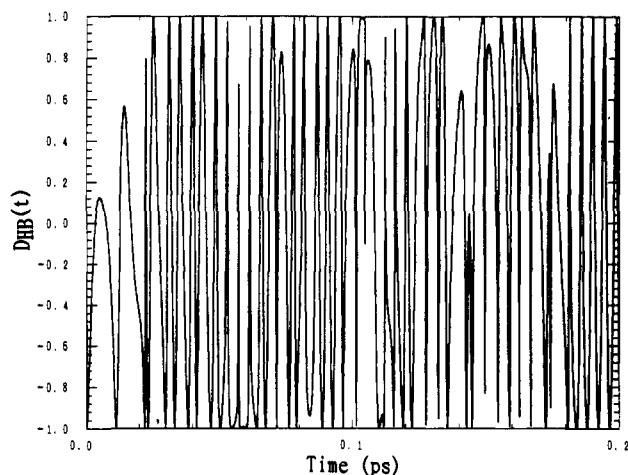

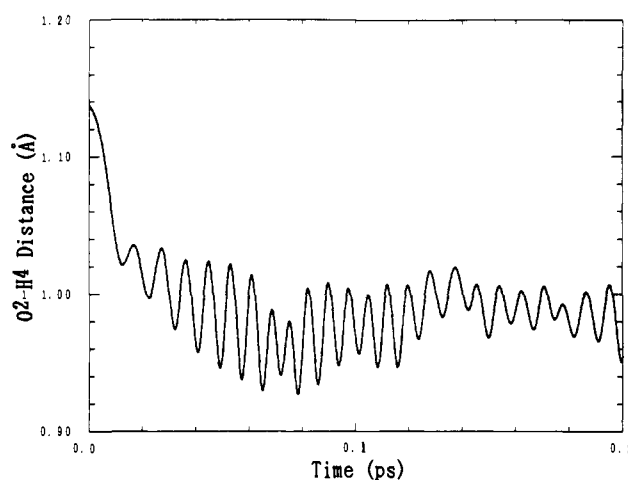**Figure 10.** Correlation of hydrogen-bonding distances in the CES with initial velocity along the IRC.

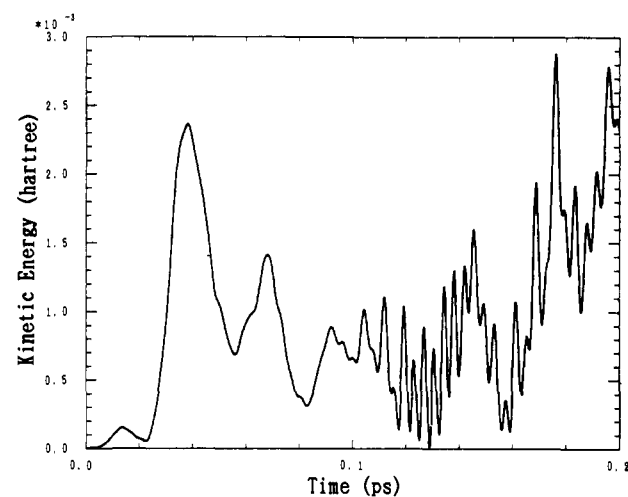**Figure 11.** Time evolution of the O^2-H^4 bond length.

Figure 12. Internal kinetic energy curve of the H^3 atom.

significant role not only in reducing the PE barrier for the proton transfer reaction of formamidine but also in relaxing the solute internal energy.

D. Alternately Modulated Oscillation in the CES Simulation. The trajectory with initial velocities selected randomly in the CES show that after each characteristic wandering time around the TS, during which it might sometimes climb up the hill again, it ultimately slides down followed by a sudden falling off to the product region accompanied by very strong oscillations (Figure 13). It is a very interesting feature that every PE has a very similar pattern, which can be called the "alternately modulated oscillation", in contrast with the trajectories with the initial velocity

along the IRC direction in the CES simulation. From the physical insight, it is recognized easily that this phenomenon is attributed to the triatomic motions in the system. The comparison between Figure 14 and Figure 15 indictes that almost the total KE concentrates only on the H^5 atom and then the alternately modulated oscillation of the PE curve is found to be due to the motion of H^5. For further investigation, pairwise PE profiles between the two bonds O^2-H^5 and H^5-N^7 (Figure 16) are plotted, and it is found that alternately modulated oscillation of the PE curve
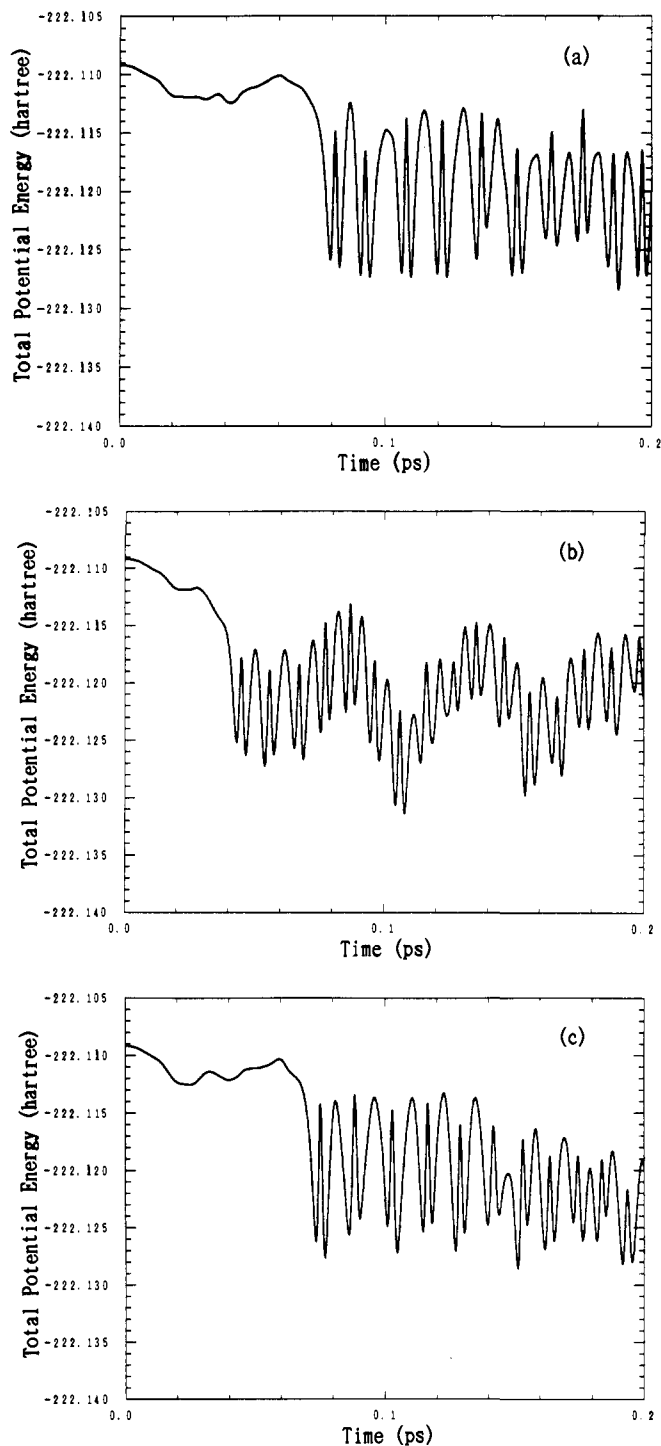
776   *J. Am. Chem. Soc., Vol. 113, No. 3, 1991*

Nagaoka et al.

Figure 13. Total potential energy curves in the CES with three initial velocities selected randomly.
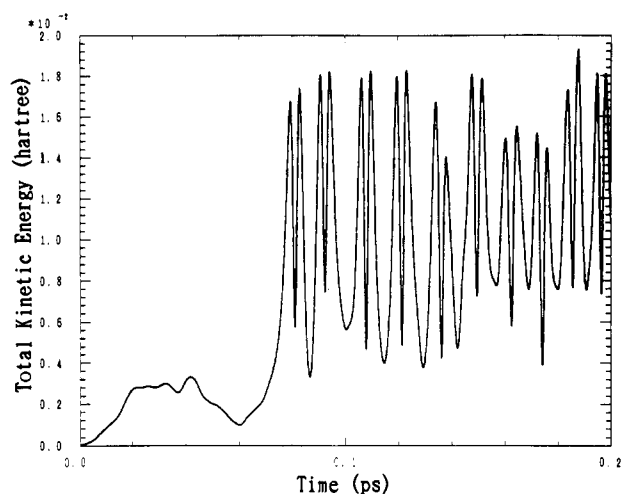

Figure 14. Total kinetic energy curve in the CES with initial velocity selected randomly. This curve corresponds to Figure 13a.
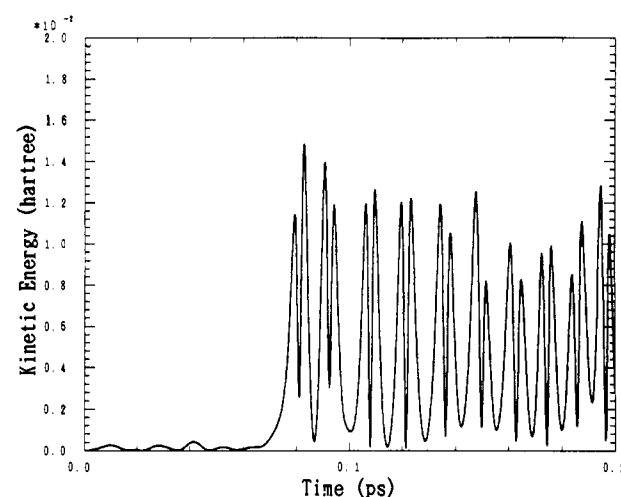

Figure 15. Internal kinetic energy curve of the H^5 atom in the CES with initial velocity selected randomly. This curve corresponds to Figure 14.

originates from both oscillations in the O^2-H^5 bond and the H^5-N^7 bond. That is, these three atoms bring about this remarkable alternately modulated oscillation in the total PE curve. It should be noted that this phenomenon can also be seen in the result of Benjamin et al.[12] and must be a general characteristic of triatomic systems. In every trajectory, most of the KE is possessed by the H^5 atom only in comparison with the case of the trajectory with the initial velocity along the IRC.

E. Fourier Analysis for Energy Fluctuations. In order to analyze the dynamic effect on this reaction system, Fourier analysis for PE fluctuations in the CES simulations were performed. The frequency resolution of the CES simulations is about 166.8 cm⁻¹, since the period of time in the CES simulation is 0.2 ps. The reason why this rather short time interval is adopted for obtaining

the Fourier spectrum is that we wanted to collect information over the period when the chemical reaction is in progress. We observe in Figure 17, which is calculated for the PE curve with initial velocity along the IRC, that the peak of 500 cm⁻¹ represents the mode along the IRC and other peaks stand for induction of other internal vibrations due to the mode couplings. In the spectrum calculated from the PE curve with initial velocity selected randomly, as shown in Figure 18, we can recognize two distinct differences from Figure 17. One is the shift of the greatest peak to the lower frequency, and the other is the growth of new peaks in the high-frequency region. The former indicates that those trajectories in the CES stay around the TS with the velocity component orthogonal to the IRC direction and are not affected directly by the imaginary frequency along IRC. The latter shows clearly the induction of internal vibrations compatible with the motion along the IRC.

In order to analyze the change of the hydrogen bond, Fourier analyses for the O–H bond distance in the CES simulations were also performed. The frequency resolution is also about 166.8 cm⁻¹. Fourier analysis of the O^2-H^4 bond distance with initial velocity along the IRC (Figure 19) shows the two peaks around 4300 cm⁻¹ which coincides with the existence of two different oscillations in the PE curve switched at the turning point ($t = 0.1$ ps) mentioned in section C. On the other hand, in the case of the initial velocity selected randomly (Figure 20), these two peaks decrease to one-half and one-tenth, respectively. This phenomenon originates from the delay of the induction of internal vibration. We notice also high intensity at the frequency near the origin; it can
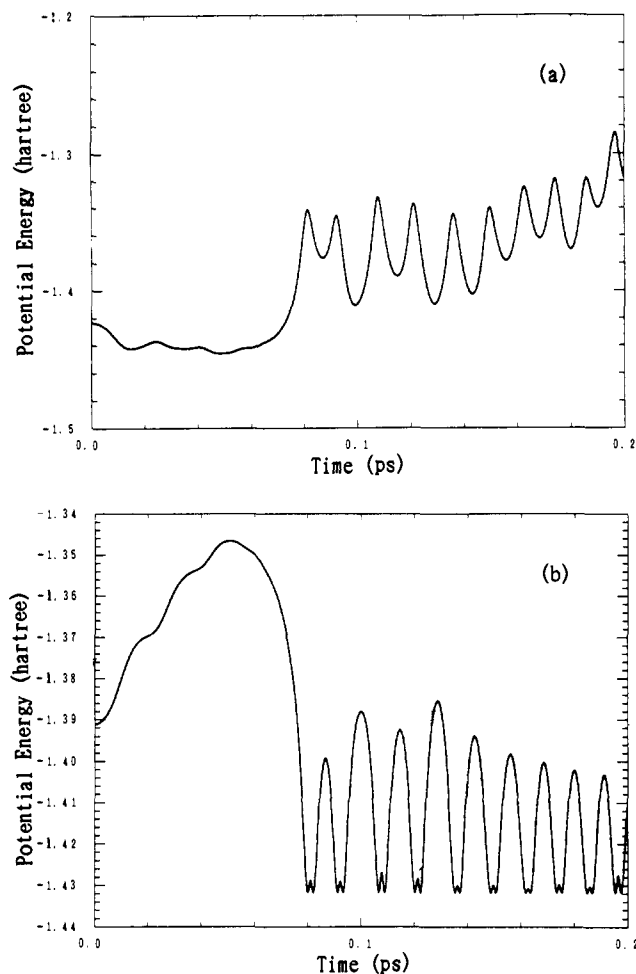
Figure 16. Potential energy curve of (a) the O^2-H^5 bond and (b) the H^5-N^7 bond in the CES with initial velocity selected randomly.
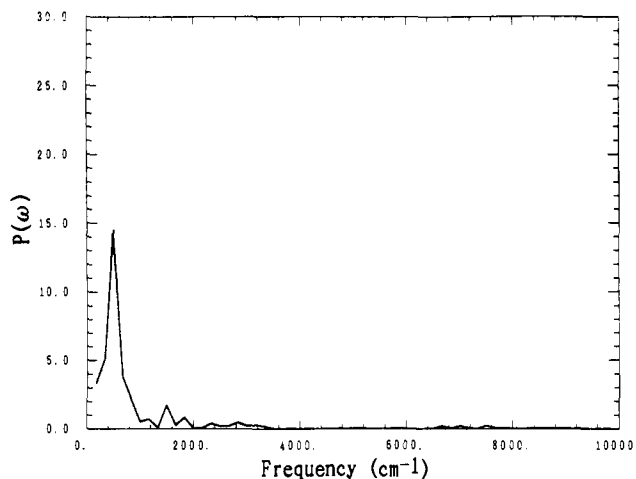

Figure 17. Fourier spectra of the total potential energy in the CES with initial velocity along the IRC.

Figure 18. Fourier spectra of the total potential energy in the CES with three initial velocities selected randomly. (a), (b), and (c) correspond to Figure 13, (a), (b), and (c), respectively.

be explained by the rather short period observed and the delay of relaxing. Hence, the CRMD method can facilitate a theoretical basis for studying the transition state spectroscopic experiments if any statistical averaging is taken.

IV. Conclusion

In this article, the CRMD method has been proposed for a chemical reaction in solution by assuming that the number of the most important solvent molecules should be small for lowering the potential barrier electronically, and the essential feature can be described by treating the solute and those solvent molecules
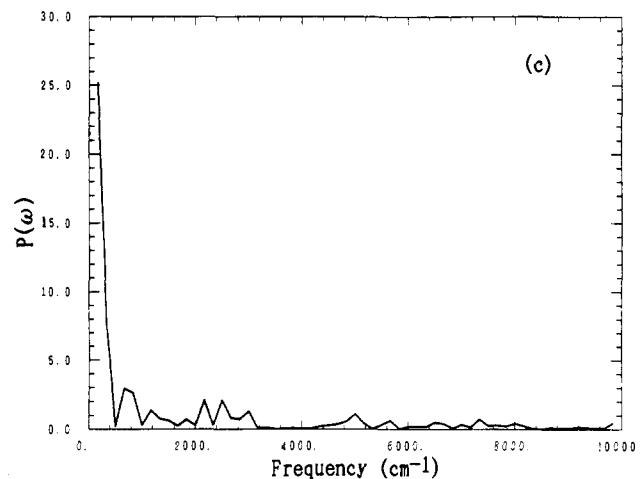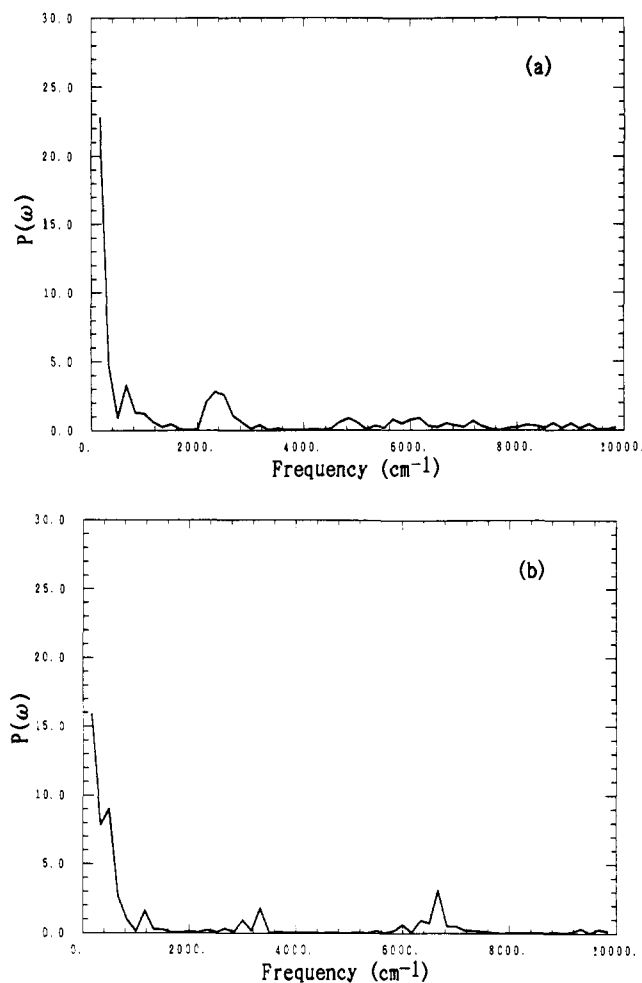
as a supermolecule. In particular, this picture is plausible for describing the barrier surmounting process at a hot spot to which energies of cooperative motions are concentrated from the surrounding solvents in solution. However, from the viewpoint of the dynamics, it is well known that the number of such molecules with excess energy is also a few and they appear near the reactants.[12] Thus, in this sense, it is also understood clearly that the CRMD method can deal justifiably with the chemical reaction dynamics in solution.

For a typical proton transfer reaction in the formamidine–water system, the CRMD method has been applied to investigate the reaction mechanism after energy concentration occurs for sur-
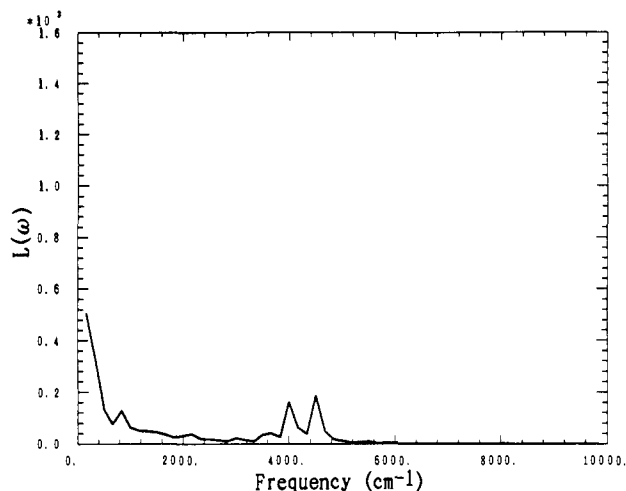
Figure 19. Fourier spectra of the O^2–H^4 bond distance in the CES with initial velocity along the IRC.
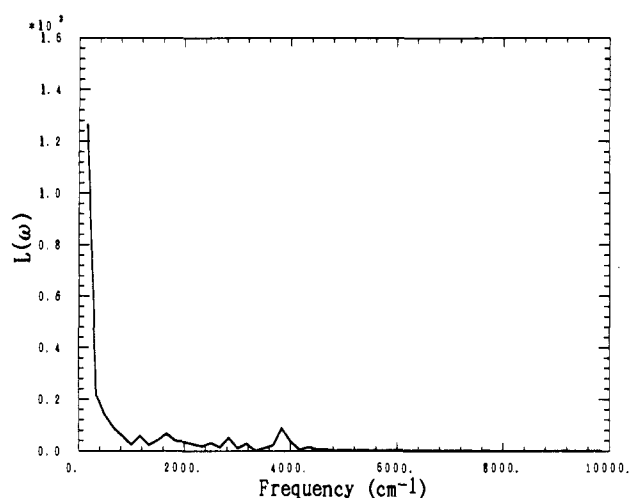

Figure 20. Fourier spectra of the O^2–H^4 bond distance in the CES with initial velocity selected randomly. This curve corresponds to Figure 13a.

mounting the barrier. In this system, it is enough to assume that there exists a solvent water molecule with an electronically important role for the potential barrier lowering; therefore, we have regarded the formamidine molecule and the water molecule as a supermolecule. We have employed two kinds of schemes, the constant-temperature scheme (CES) and the constant-energy scheme (CES), for each limit of ideal relaxation with a constant temperature or of no relaxation. In the CTS where a trajectory can be regarded as an extended IRC, it is understood that the trajectory with initial velocity along the IRC direction might play a central role but is rather special than other trajectories with different directional initial velocities. Furthermore, we have found a remarkable "cusp" in the hydrogen-bonding correlation function (HBCF), which has been recognized when the length of creating the O–H bond becomes constant and can suggest the existence of a new type of critical state, namely, the dynamic transition state (DTS). It is the kinetic energy, in other words, momentum, that brings about the DTS in the present chemical reaction dynamics. As is often mentioned, kinetic energy modes are important especially in solution chemistry for creating fluctuations which can induce the barrier surmounting process. In contrast to the common picture for chemical reactions using transition states defined statically in the configuration space, now is the time when a chemical reaction must be pictured in phase space in its own right. In the CES, the alternately modulated oscillations have been observed; this is considered as a characteristic in triatomic systems and has appeared in the previous study.[12] Clarification of the effect of other solvents in solution to the alternately modulated oscillation is another interesting problem in relating to excess kientic energy concentration. This problem can be analyzed by extending the present CRMD method to the general one rigged with the algorithm that can simulate also the dynamics of other solvent molecules. Finally, although we have dealt with a proton transfer reaction, the internal dynamics in the CRMD method would be more complicated if IRC had a more collective nature in general chemical reactions. Nevertheless, the CRMD treatment should be useful and is believed to be a powerful strategy in the clarification of chemical reactions in both the gas phase and condensed phase.

Registry No. Formamidine, 463-52-5.