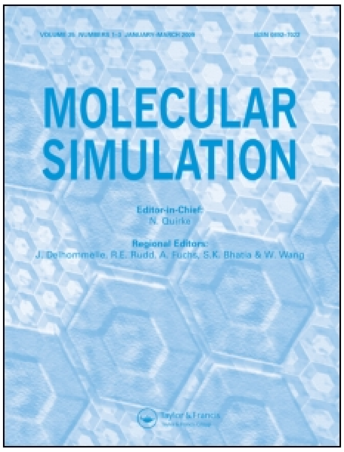

**Molecular Simulation**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

# A Quantum Dynamics Simulation of Molecular Vibrations by the Pechukas Method

Susumu Okazaki[a]
[a] Department of Electronic Chemistry, Tokyo Institute of Technology, Yokohama, Japan

**To cite this Article** Okazaki, Susumu(1996) 'A Quantum Dynamics Simulation of Molecular Vibrations by the Pechukas Method', Molecular Simulation, 16: 1, 107 — 117
**To link to this Article: DOI:** 10.1080/08927029608024065
**URL:** http://dx.doi.org/10.1080/08927029608024065

*Molecular Simulation*, 1996, Vol. 16, pp. 107–117
Reprints available directly from the publisher
Photocopying permitted by license only

# A QUANTUM DYNAMICS SIMULATION OF MOLECULAR VIBRATIONS BY THE PECHUKAS METHOD

SUSUMU OKAZAKI

*Department of Electronic Chemistry, Tokyo*
*Institute of Technology, 4259 Nagatsuta,*
*Midori-ku, Yokohama 226, Japan*

*(Received February 1995, accepted April 1995)*

A quantum dynamics simulation of vibrations of molecules including transition from state to state is demonstrated based upon the Pechukas method. The method has been examined to clarify characteristics in relation to the simulation. It may present a lot of useful information of the vibrational relaxation and thermal excitation of the molecule.

KEY WORDS: Quantum dynamics, simulation, vibration, pechukas method.

## 1 INTRODUCTION

The vibrational dynamics of molecules and ions in liquids has been one of the most interesting areas of physical chemistry, since thermal excitation and relaxation phenomena are closely related to chemical reactions. For example, recent development of ultrafast time resolved spectroscopy has stated to give various information on vibrational relaxation in liquids [1,2]. In spite of this, however, little is known about the molecular based microscopic picture of the dynamics.

With regard to computer simulation study on the vibration, the classical equation of motion has been adopted to simulate ground state dynamics [3]–[9]. However, this is no more than a rough approximation since the motion of atoms is no doubt quantized. In particular, the transition of quantum state, *i.e.* thermal exitation and vibrational energy transfer cannot be investigated by conventional classical simulation techniques. Vibration of molecules in liquids is, in principle, a problem of the quantum dynamics of many-particle system. It is hopelessly difficult to solve the time-dependent Schrödinger equation for the whole system rigorously at least at present.

Recently, we have obtained a numerical solution of time-dependent Schrödinger equation for the vibration of an ion in a liquid based upon time-dependent one-particle potential with respect to an intramolecular degree of freedom [10]. The vibrational potential was evaluated by *ab initio* calculation assuming a frozen-field local-mode approximation for the oscillator based upon actual trajectories of structure of the liquid obtained by classical MD calculation [9, 11]. The resultant time evolution of expansion coefficient of state vector of vibration by its eigen state could show pure dephasing as well as a possibility of thermal excitation. However, this model does not include explicitly a coupling of vibration with environment in the equation of motion. It is taken into account just through the one-particle potential. That is, ideally smooth and rapid energy flow was assumed instead of the vibrational-rotational (V-R) and vibrational-translational (V-T) energy transfer through the actual motion of environmental molecules. Motion of the oscillator as well as the environmental degrees of freedom must be coupled with each other. If the real time coupling is neglected in the calculation, it may be misleading for the dynamics of the system of interest.

In the present study, Pechukas method was adopted to obtain a rough understanding for the vibrational energy transfer in liquid, *i.e.* thermal excitation and radiationless relaxation. The method may reproduce V-R and V-T transfer by just solving an equation of motion with quantum force originally proposed by Pechukas [12] and applied, for the first time, to simulate hydrated electron by Rossky's group [13, 14]. However, the method has two large assumptions. One is that time step $\Delta t$ used in the simulation is long enough for the quantum system to lose the coherence with either its initial state and the classical system. Another is that the path integral to describe the propagation of the system can be represented by just single stationary phase path near the classical path without quantum degree of freedom. Rigorously speaking, it might be hard to guarantee these two assumptions since little has been known about this kind of quantities. In spite of the ambiguity above, we believe that the Pechukas method is still powerful to describe the equation of motion of classical degrees of freedom coupled with a quantum system.

In this paper, a calculation of vibrational energy transfer between $N_2$-like molecule in liquid Ar is reported. After describing equation of motion specialized for the vibration in Sec. 2, fundamental properties concerning the method and the resultant motion of the classical system on the transition of vibrational state will be discussed.

## 2 CALCULATION

According to Pechukas [12], quantum mechanical force $\mathbf{f}(\mathbf{r}(t))$ on classical degree of freedom $\mathbf{r}(t)$ at $t = t$ in contact with quantum system may be calculated as

$$\mathbf{f}(\mathbf{r}(t)) = \mathrm{Re}\frac{\left\langle \beta(t) \left| -\frac{\partial H}{\partial \mathbf{r}} \right| \alpha(t) \right\rangle}{\langle \beta(t) | \alpha(t) \rangle} \tag{1}$$

where $|\alpha(t_i)>$ and $|\beta(t_f)>$ are initial and final quantum system states of interest, respectively, and $H$ the total hamiltonian. $|\alpha(t)>$ and $|\beta(t)>$ must satisfy forward and backward time-dependent Schrödinger equation with hamiltonian $H(t)$ $(= H(\mathbf{r}(t)))$ starting from $|\alpha(t_i)>$ and $|\beta(t_f)>$, respectively.

(12–6) Lennard-Jones potential was assumed for Ar–Ar and N–N interatomic interaction. For the former, $\varepsilon/k = 119.8$ K and $\sigma = 3.405$ Å and, for the latter,

$\varepsilon/k = 35.3$ K and $\sigma = 3.314$ Å, Lorentz-Beltherot rule being assumed for the cross term. Harmonic oscillator is also assumed for the intramolecular N–N interaction.

$$v_{\text{intra}}(x) = \frac{1}{2}\mu\omega_0^2(x - x_0)^2 \tag{2}$$

where $\omega_0 = 50$ cm$^{-1}$ instead of experimental 2,300 cm$^{-1}$ was adopted to increase transition probability artificially; the experimental population decay time may be greater than ns [2], which is too long to simulate. The value of equilibrium bond length in vacuum $x_0$ was 1.101 Å. Thus, the present oscillator is not $N_2$ but $I_2$-like $N_2$. Reduced hamiltonian for the quantum system $h$ is

$$h = \frac{p^2}{2\mu} + \frac{1}{2}\mu\omega_0^2(x - x_0)^2 + \sum_i \{v_{\text{N-Ar}}(r_{1-i}) + v_{\text{N-Ar}}(r_{2-i})\} \tag{3}$$

where subscripts 1 and 2 of $r$ represent atom 1 and 2 of $N_2$, respectively, and $i$ the $i$-th Ar molecule. Now, we can approximately rewrite the above hamiltonian as time-dependent hamiltonian at $t = t$ of the form

$$h(t) = \frac{p^2}{2\mu} + \frac{1}{2}\mu\omega_{\mathbf{r}}(t)\{x - x_{\mathbf{r}}(t)\}^2 + e_{\mathbf{r}}(t) \tag{4}$$

where subscript **r** implies that the relevant potential parameters are function of the trajectory of the classical degree of freedom, in other words instantaneous solvation structure. Schrödinger equation was solved for this time dependent hamiltonian to obtain $|\alpha(t)>$ and $|\beta(t)>$. Since instantaneous energy eigen state vector $|n(t)\rangle$ is obtainable at every $t$ algebraically, the equation may be solved almost rigorously just assuming a little slow change of hamiltonian $h(t)$. This can be done, for example, for the state vector $|\alpha(t)>$ by solving a coupled differential equation

$$\dot{a}_k(t) = \sum_{n \neq k} \frac{a_n(t)}{E_k(t) - E_n(t)} \langle k(t) \left| \frac{\partial H}{\partial t} \right| n(t)\rangle \times \exp\left[ -\frac{1}{i\hbar} \int_{t_0}^{t} \{E_k(t') - E_n(t')\} dt' \right] \tag{5}$$

where $a_n(t)$ is an expansion coefficient of $|\alpha(t)>$ with respect to its eigen vector $|n(t)\rangle$

$$|\alpha(t)> = \sum_n a_n(t)|n(t)\rangle \exp\left[ -\frac{1}{i\hbar} \int_{t_0}^{t} E_n(t')dt' \right] \tag{6}$$

In the case of harmonic oscillator system, this differential equation may be simplified to the form

$$\begin{aligned}\dot{\mathbf{a}}(t) = [&f(t)\exp\{-i\phi(t)\}\mathbf{F} - f(t)\exp\{i\phi(t)\}\mathbf{F}' \\ &- g(t)\exp\{-2i\phi(t)\}\mathbf{G} + g(t)\exp\{2i\phi(t)\}\mathbf{G}']\mathbf{a}(t) \end{aligned} \tag{7}$$

where

$$\mathbf{a}(t) = \begin{pmatrix} a_0(t) \\ a_1(t) \\ a_2(t) \\ \cdot \\ \cdot \end{pmatrix} \tag{8}$$

$$f(t) = \sqrt{\frac{\mu\omega(t)}{2\hbar}}\left\{\frac{2\dot{\omega}(t)a(t)}{\omega(t)} + \dot{a}(t)\right\} \tag{9}$$

$$g(t) = \frac{\dot{\omega}(t)}{4\omega(t)} \tag{10}$$

$$\phi(t) = \int_0^t \omega(t')dt' \tag{11}$$

$$F = \begin{pmatrix} 0 & 1 & & & & & \\ & 0 & \sqrt{2} & & & & \\ & & 0 & \sqrt{3} & & & \\ & & & 0 & & & \\ & & & & \cdot & & \\ & & & & & \cdot & \\ & & & & & & \cdot \end{pmatrix} \tag{12}$$

and

$$G = \begin{pmatrix} 0 & 0 & \sqrt{2} & & & & \\ & 0 & 0 & \sqrt{6} & & & \\ & & 0 & 0 & 2\sqrt{3} & & \\ & & & 0 & 0 & & \\ & & & & 0 & & \\ & & & & & \cdot & \\ & & & & & & \cdot \end{pmatrix} \tag{13}$$

In the numerical calculation, excited states up to the $n = 10$ were taken into account. Since instantaneous eigen functions were not obtained algebraically in the case of the hydrated electron, Rossky's group approximated the integral of operator over time by a scalar integration to get a time evolution operator. This might cause some error. Concerning the forward and backward time evolution of the state vectors, the present calculation is rigorous within a time step of Pechukas method, being free from such approximation.

Since the quantum force of Eq. (1) depends upon future system state, trajectory of the classical degrees of freedom was solved selfconsistently by iteration starting from the trajectory based upon the rigid rotor model for the oscillator. Time step $\Delta t$ of 130 fs was adopted, during which time-dependent Schrödinger equation and conventional classical equation of motion were solved by Runge-Kutta method and predictor corrector method in NEV ensemble, respectively, with a time step $\delta t = 0.1$ fs and number of particles $N = 216$. The resultant temperature was about 95 K.

We assumed that the oscillator was initially in the first excited state $n = 1$. Trajectories of classical degrees of freedom were calculated for three cases: (i) at a certain time, the system was further exited thermally to the second excited state ($n = 1 \rightarrow 2$), (ii) it stayed at the first excited state throughout the time (transitionless process), and (iii) the system state fell down to the ground state ($n = 1 \rightarrow 0$). Several trajectories on the transitions above have been calculated starting with different initial liquid structures.

## 3 RESULTS AND DISCUSSION

An example of convergence of one of cartesian coordinates $y$ of center of mass of the oscillator, which corresponds to a classical degree of freedom, is shown in Figure 1

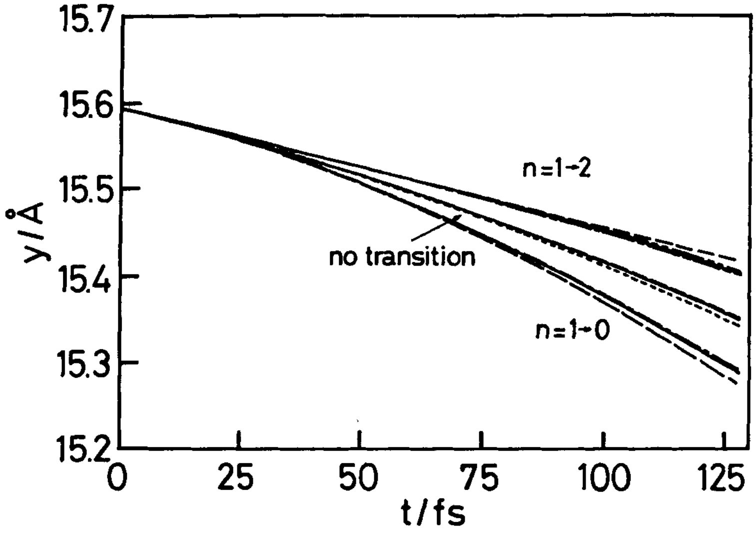

**Figure 1** Convergence of coordinate $y$ of the oscillator. Time step was 130 fs. - - - - - : initial path; – – – : the first iteration; — - —: the second iteration; – - - –: the third iteration; ———: the fourth iteration.

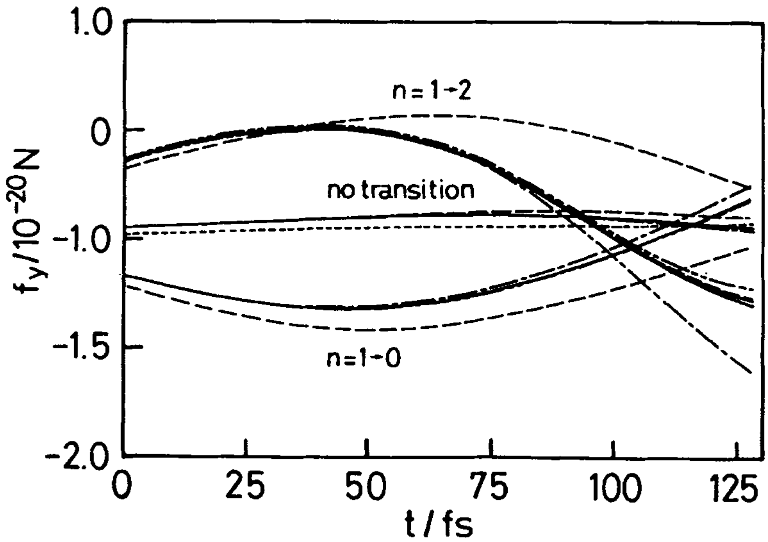

**Figure 2** Convergence of force $f_y$ on the oscillator. Time step was 130 fs. - - - - - : initial path; – – – : the first iteration; — - —: the second iteration; - - - -: the third iteration; ——: the fourth iteration. The lines are repeated in the same order for the fifth iteration, the sixth iteration, etc.

for $n = 1 \rightarrow 2$, transitionless, and $n = 1 \rightarrow 0$ processes. Averaged increment $\Delta y$ over the path was $\sim 10^{-4}$ Å for the third iteration of the $n = 1 \rightarrow 0$ case and it converged to $\sim 10^{-6}$ Å for the sixth iteration. The convergence was more rapid for the transitionless process than this. Compared with the actual translation of the molecule in this time step $\sim 10^{-1}$ Å, the convergence is excellent. Force $f_y$ on the oscillator in Eq. (1) is presented in Figure 2 for the same period. The convergence of the force is good, too, although the dispersion is greater than that of the position coordinate. It is also clear that when transitions occur, in other words, when the energy transfer is large, the convergence becomes considerably slow. In this figure, it is interesting that the direction of the quantum force is opposite to each other between energy absorbing and releasing processes. On the transition, variation of total energy was at most about 2 J mol$^{-1}$, which is very small compared with the total energy of about 4,400 J mol$^{-1}$. Energy conservation in the simulation is thus satisfactory. Trajectories of the position and the force for the transitionless process in Figure 1 and Figure 2, respectively, are slightly different from those of the rigid rotor, *i.e.* the initial path. This clearly means that vibration of molecule has a coupling with translation and rotation, although the influence on the trajectory is very small.

Time evolution of squared absolute values of expansion coefficients $|a_0|^2, |a_1|^2$, and $|a_2|^2$ are presented in Figure 3 for the forward propagation of $|\alpha(t)>$ over the same period as in Figures 1 and 2. Each value represents the probability that the system is found in the relevant eigen state at $t = t$. As clearly seen in the figure, the plot shows plateaus; $|a_1|^2$ was almost unity for the first 40 fs, then it became to decrease, and after about 60 fs of interaction time it seems to reach a stationary value. The plots of $|a_0|^2$ and $|a_2|^2$ show the same character except that they started from zero probability and reached non zero stationary values. Considering the

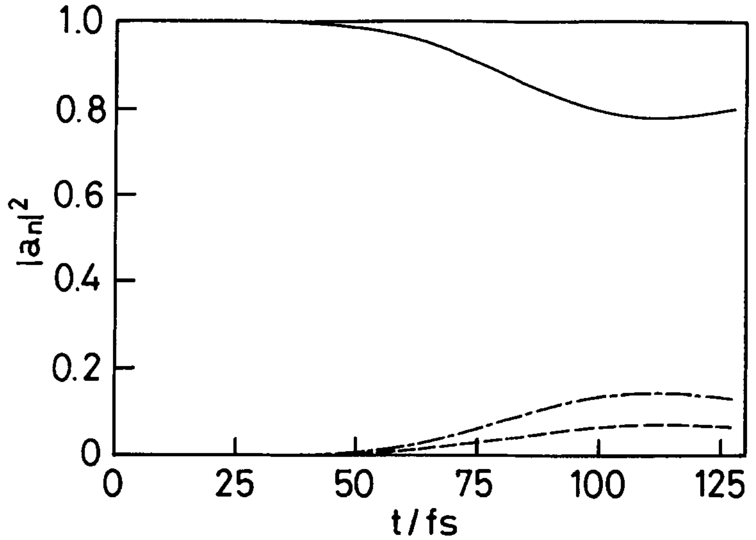

**Figure 3** Time evolution of probability that the system is found in the eigen states. The system was initially in the first excited state $n = 1$. – – – : $n = 0$; ——— : $n = 1$; — - - : $n = 2$.

rather small transition frequency of the oscillator in the present study, the time step $\Delta t = 130$ fs might be too short for the system to lose coherence with its initial state and with the classical system. However, it is interesting to see that the probabilities seem to reach the stationary values in this time step, although the decoherence between the quantum system and classical system is still unknown.

A long time trajectory of the classical degree of freedom $y$ is presented in Figure 4 for the transitionless process and the $n = 1 \rightarrow 0$ one. Trajectory assuming a rigid rotor for $N_2$ is also plotted in the figure. The system was set to make a transition $n = 1 \rightarrow 0$ from $t = 1.34$ ps to 1.47 ps. First, the trajectory of $y$ for the transitionless process is almost the same as that of the rigid rotor within the simulation period. This means that the translational degree of freedom does not depend much upon the vibrational degree of freedom. However, a small difference is certainly found. This may be related to an isotope effect on the structure of liquid in the meaning that the translation has a small but non zero correlation with the vibration which posseses a large isotope effect. Second, when the oscillator fell down to the ground state, a dissipation of quantum energy to the classical system was observed. The coordinate shows different trajectory from that of the transitionless process; the system escaped from a local potential well in a few periods of the libration after it gained the energy from the quantum system, transferring to other quenched structure of the liquid.

One of the rotational degree of freedom of the oscillator, *i.e.* one of the quaternion, is plotted in Figure 5. Fundamental features stated above are clearly found in this figure, too. The influence of the energy transfer is greater in the rotation than in the translation.

The energy transfer may be examined by kinetic energy of the classical degree of freedom better than by the relevant coordinate. The kinetic energy with respect to

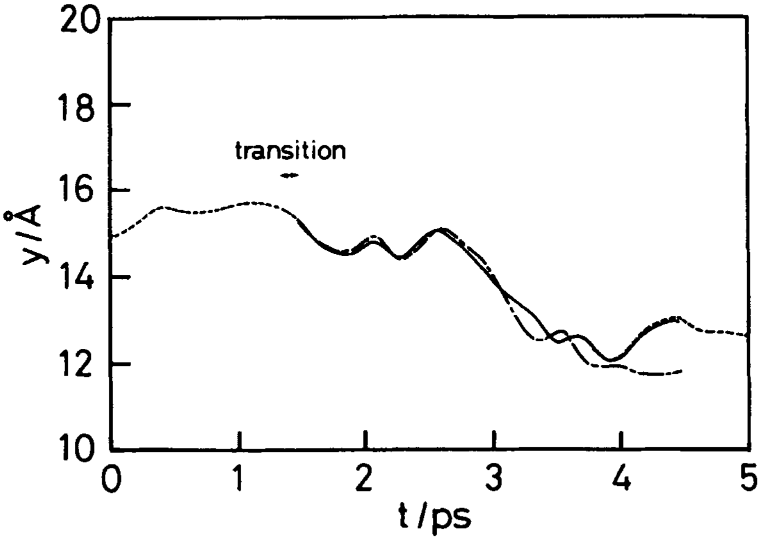

**Figure 4** Long time trajectory of position coordinate $y$ of the oscillator. The system was set to make a transition from $t = 1.34$ ps to 1.47 ps. - - - - - : rigid rotor; ——— : no transition; — - — : $n = 1 \rightarrow 0$.

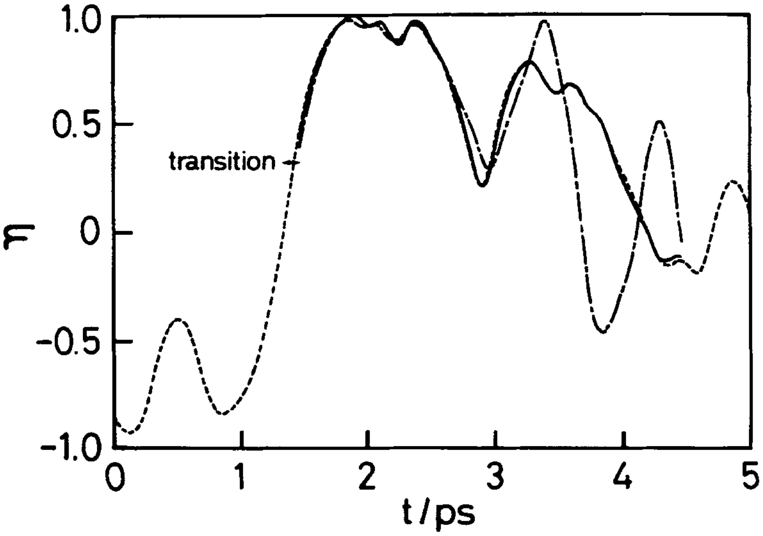

**Figure 5** Long time trajectory of one of the quaternion of the oscillator. The system was set to make a transition from $t = 1.34$ ps to 1.47 ps. - - - - - : rigid rotor; ——— : no transition; — - — : $n = 1 \rightarrow 0$.

translation and rotation are plotted in Figure 6 and Figure 7, respectively. Figure 8 also presents the potential energy of the oscillator. Although the amount of energy transferred from the vibration to the classical system was as small as about 600 J mol$^{-1}$, the dissipation to the surrounding solvents are clearly found. Amplitude of

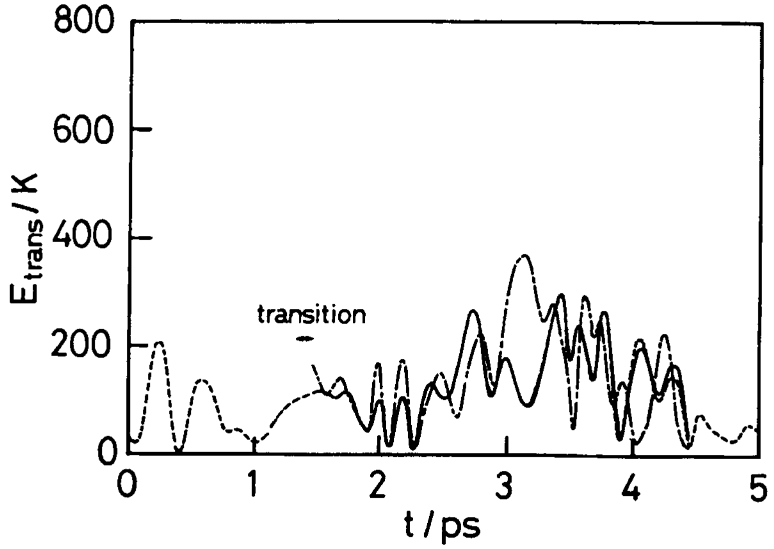

Figure 6 Kinetic energy of translation of the oscillator in K. The system was set to make a transition from $t = 1.34$ ps to 1.47 ps. - - - - -: rigid rotor; ———: no transition; — - —: $n = 1 \rightarrow 0$.

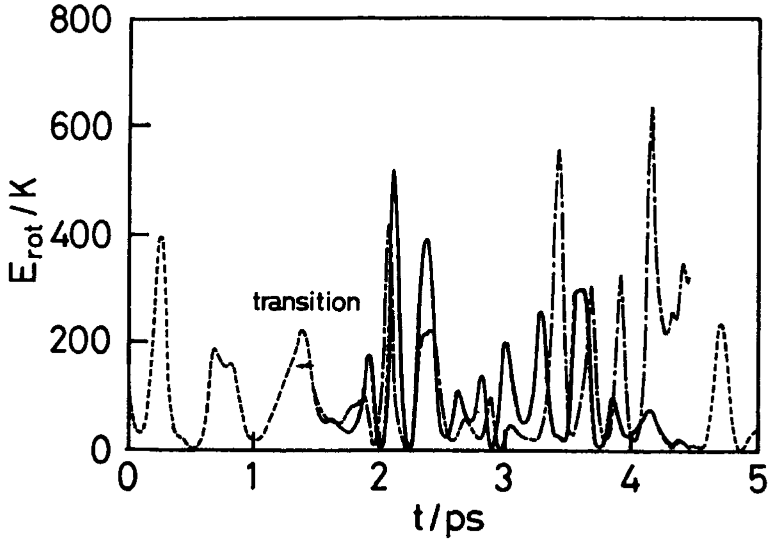

Figure 7 Kinetic energy of rotation of the oscillator in K. The system was set to make a transition from $t = 1.34$ ps to 1.47 ps. - - - - -: rigid rotor; ———: no transition; — - —: $n = 1 \rightarrow 0$.

oscillation of the kinetic energy caused by the libration became considerably greater after the transition than the case of the transitionless process. The phases of the oscillation of the kinetic energies deviate from those of the transitionless process about 0.5 ps after the transition. Furthermore, it is interesting that the potential or solvation energy of the oscillator increased just after the transition and merged into the trajectory of the transitionless process.

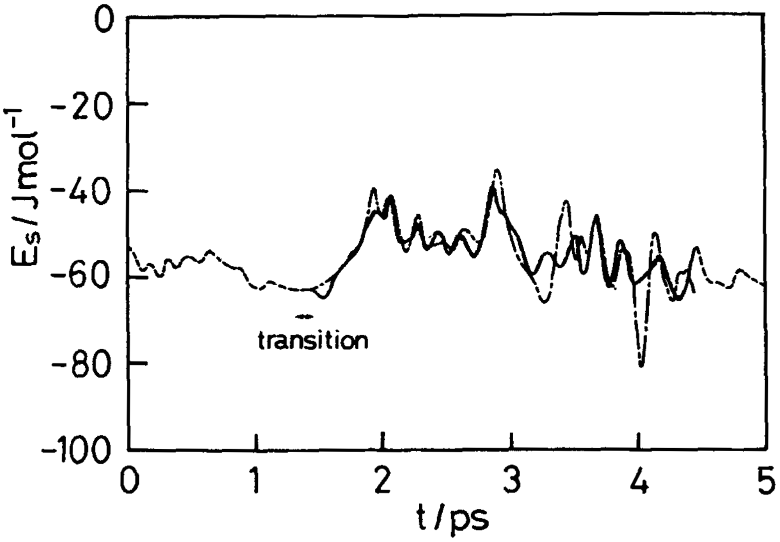

**Figure 8** Solvation energy of the oscillator. The system was set to make a transition from $t = 1.34$ ps to 1.47 ps. - - - - - : rigid rotor; ———— : no transition; — - — : $n = 1 \rightarrow 0$.

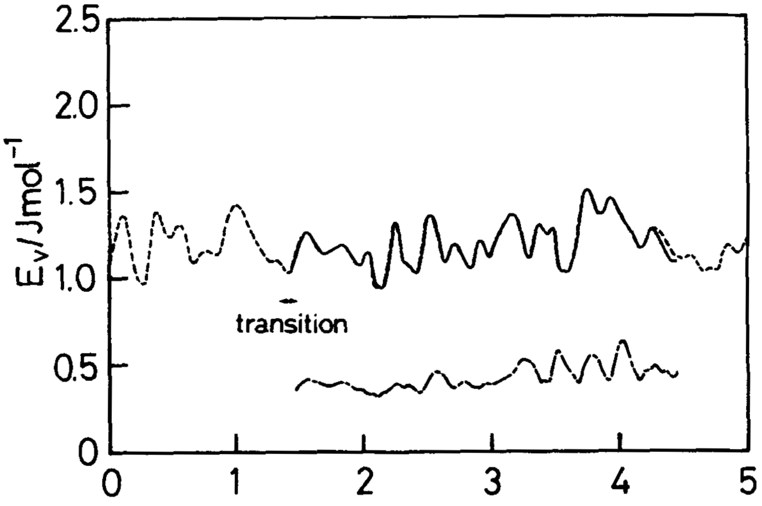

**Figure 9** Vibrational energy of the oscillator. The value was estimated for the rigid rotor, too, in the same way as the other two assuming a harmonic oscillator. The system was set to make a transition from $t = 1.34$ ps to 1.47 ps. - - - - - : rigid rotor; ———— : no transition; — - — : $n = 1 \rightarrow 0$.

Figure 9 shows vibrational energy of the oscillator. After the $n = 1 \rightarrow 0$ transition, the value becomes small as expected. It is interesting, however, that the fluctuation of the energy looks smaller for the ground state than for the first excited state even if the fact that the energy of the first excited state is three times as sensitive to the fluctuation of potential parameter as the ground state is taken into account. This kind of fluctuation is one of the origin of broadening of vibrational spectrum in liquids. The difference in the magnitude of the fluctuation might result in a difference of band width between, for example, $n = 0 \rightarrow 1$ transition and $n = 1 \rightarrow 2$ transition.

## 4 CONCLUSION

A quantum dynamic simulation of vibration of molecules including transitions has been demonstrated based upon Pechukas method. It may present various useful information of the vibrational relaxation and thermal excitation of the molecule in liquid. Application of the method to more realistic systems is straightforward.

### *Acknowledgements*

The author thanks the computer centers of the Institute for Molecular Science and the High Energy Physics Institute for the use of the computers. He gratefully acknowledge financial support of this work by a Grant-in Aid for Scientific Research on Priority Areas "Supercritical Fluid" and "Many-body Chemistry" from the Ministry of Education, Science, and Culture, Japan.

### *References*

[1] S. Mukamel, "Femtosecond optical spectroscopy: A direct look at elementary chemical events," *Annu. Rev. Phys. Chem.*, **41**, 647 (1990).

[2] J. Chesnoy and G. M. Gale, "Vibrational relaxation in condensed phases," *Adv. Chem. Phys.*, **70**, 297 (1988).

[3] A. Rahman, F. H. Stillinger, and H. L. Lemberg, "Study of a central force model for liquid water by molecular dynamics," *J. Chem. Phys.*, **63**, 5223 (1975).

[4] G. Jansco and P. Bopp, "The dependence of the internal vibrational frequencies of liquid water on central force potentials," *Z. Naturforsch.*, **38a**, 206 (1983).

[5] R. Bansil, T. Berger, K. Toukan, M. A. Ricci, and S. H. Chen, "A molecular dynamics study of the OH stretching vibrational spectrum of liquid water," *Chem. Phys. Lett.*, **132**, 165 (1986).

[6] O. Teleman, B. Jönsson, and S. Engström, "A molecular dynamics simulation of a water model with intramolecular degree of freedom," *Mol. Phys.*, **60**, 193 (1987).

[7] J. Anderson, J. J. Ullo, and S. Yip, "Molecular dynamics simulation of hydrocarbon molecules in condensed phase. II. Benzene," *J. Chem. Phys.*, **86**, 4078 (1987).

[8] T. Kato, K. Machida, M. Oobatake, and S. Hayashi, "Vibrational dephasing in computer simulated molten $LiNO_3$," *J. Chem. Phys.*, **93**, 3970 (1990).

[9] S. Okazaki and I. Okada, "A simulation approach to vibrational dynamics of the $OH^-$ ion in molten LiOH," *J. Chem. Phys.*, **98**, 607 (1993).

[10] S. Okazaki, "A quantum simulation of vibrational dynamics of an ion based upon time-dependent one-particle potential," to be published.

[11] S. Okazaki, N. Ohtori, and I. Okada, "Molecular dynamics studies on molten hydroxides. II. Rotational and translational motions of ions in molten LiOH," *J. Chem. Phys.*, **93**, 5954 (1990).

[12] P. Pechukas, "Time-dependent semiclassical scattering theory. II. Atomic collisions," *Phys. Rev.*, **181**, 174 (1969).

[13] F. S. Webster, J. Schnitker, M. S. Friedrichs, R. A. Friesner, and P. J. Rossky, "Solvation dynamics of the hydrated electron: A nonadiabatic quantum simulation," *Phys. Rev.*, **66**, 3172 (1991).

[14] F. Webster, P. J. Rossky, and R. A. Friesner, "Nonadiabatic processes in condensed matter: Semiclassical theory and implementation," *Comp. Phys. Commun.*, **63**, 494 (1991).