Rotational energy analysis for rotating–vibrating linear molecules in classical trajectory simulation

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(Received 24 July 1997; accepted 10 September 1997)

A method has been developed to evaluate the rotational energy of a rotating–vibrating linear molecule in classical trajectory simulation. The method is based on our finding that the component of the angular momentum perpendicular to the figure axis which closely approximates the pure rotational angular momentum is a fairly good constant of motion. Classical kinetic energy of the system has been reorganized to separate the rotational and vibrational parts according to the above concept. Time evolution of the rotational energy thus evaluated shows much less irregular behavior than the ones evaluated with the previous methods over a wide range of rotational and vibrational energies. Combined with the method for mode-specific vibrational energy analysis reported previously, the present method allows a reliable separation of the total energy into each degree of freedom. In particular, the accuracy of the present method seems to be good enough for the rotational energy determination at an instantaneous configuration point along a trajectory, enabling the classical study of real time dynamics. © 1997 American Institute of Physics.

I. INTRODUCTION

Even though quantum mechanical approach1–4 would be inherently more appropriate than a classical one to handle chemical reaction dynamics,5 the latter has been widely adopted in such investigations. This is because the quantum mechanical study of reaction dynamics is a formidable task even for a simple system.

To study the energy partitioning in the reaction products by classical trajectory calculation,6 one wishes to carry out mode-specific energy analysis at the end of each trajectory run. Evaluation of the translational energy7 for relative motion of products is straightforward because the translation is clearly separable from rotation and vibration. It is well-known, however, that the separation of rotation and vibration is not clear-cut.8–10 As the zeroth order approximation, one may ignore the rotation–vibration interaction as in the rigid rotor-harmonic oscillator model. This model fails as soon as a molecule begins to rotate and vibrate as is evident from the results of high resolution spectroscopic studies. The traditional approach11–24 to handle the rotation–vibration problem is to set up a moving coordinate system or an Eckart frame by imposing Sayvetz conditions.9,25 The zeroth order term in the rotation–vibration interaction vanishes in that case, and the remainder is called the Coriolis energy.

In our previous investigation,26 the mode-specific analysis of product energy in classical trajectory simulation, the above traditional approach was taken. Focus of the study was on the reliable evaluation of the energy in each normal mode of vibration of a polyatomic product, which was achieved by using internal coordinate system together with some method for anharmonicity correction. Not much attention was paid to the rotational part mainly because its evaluation was based on the well-known separation scheme dictated by Sayvetz conditions. However, continuing studies on the time evolution of the rotational energy along a trajectory revealed some irregularities in the case of linear molecules. For example, sum of the rotational and Coriolis energies evaluated by the above scheme became negative for some trajectories with very small rotational energy. Excessive fluctuation of the rotational energy in some trajectories was another disturbing observation.

In this work, results from our recent investigation on the rotational energy evaluation for rotating–vibrating linear molecules along classical trajectories are presented. An effort has been made to devise a physically meaningful method with sufficient accuracy to handle the classical trajectory results because a rigorous separation of the rotational and vibrational parts is not possible. The method is based on our finding in this work that the pure rotational angular momentum of rotating–vibrating linear molecule is a fairly good constant of motion. This also allows us to specify the rotational energy at the initial point of a trajectory run, which is of an invaluable help in judging the reliability of various approaches attempted.

II. THEORETICAL OUTLINE

Let us first review briefly the approach taken in our previous work26 to separate the rotational and vibrational parts of the kinetic energy at an instantaneous location along a classical trajectory. Taking $\mathbf{x}_o(\alpha = 1, 2, \ldots, N)$ as the mass-weighted Cartesian coordinate vector of the $\alpha$th atom with respect to the center-of-mass of a molecule, the rotational inertia tensor $(\mathbf{I})$ and the total angular velocity $^7,27,28 \; (\mathbf{o})$ were given by
\[
I = \sum_{\alpha} \left[ I \left( \mathbf{x}_{\alpha} \cdot \mathbf{x}_{\alpha} \right) - \mathbf{x}_{\alpha} \mathbf{x}_{\alpha} \cdot \right]
\]  

(1)

and

\[
\mathbf{\omega} = I^{-1} \cdot \sum_{\alpha} \mathbf{x}_{\alpha} \times \mathbf{x}_{\alpha}.
\]  

(2)

The pure rotational angular velocity\(^9\) \(\mathbf{\omega}_r\) was evaluated from the instantaneous atomic positions and momenta as the angular velocity of the equilibrium configuration \(\{\mathbf{a}_\alpha\}\) which satisfies the Eckart condition\(^29,30\)

\[
\sum_{\alpha} \mathbf{a}_\alpha \times (\mathbf{x}_{\alpha} - \mathbf{a}_\alpha) = 0.
\]  

(3)

Then, the difference between \(\mathbf{\omega}\) and \(\mathbf{\omega}_r\) was related to the angular motion of molecular vibration. Defining \(\mathbf{u}_\alpha\) as the atomic velocity for such a motion,

\[
\mathbf{u}_\alpha = (\mathbf{\omega} - \mathbf{\omega}_r) \times \mathbf{x}_{\alpha},
\]  

(4)

the overall velocity of the \(\alpha\)th particle became

\[
\dot{\mathbf{x}}_{\alpha} = \mathbf{v}_{\alpha} + \mathbf{u}_\alpha + \mathbf{\omega}_r \times \mathbf{x}_{\alpha}.
\]  

(5)

Here, \(\mathbf{v}_{\alpha}\) is the velocity related to the angular motion free part of vibration. Equation (5) led to the following expression for the kinetic energy of the molecule:

\[
T = \frac{1}{2} \sum_{\alpha} \mathbf{v}_{\alpha} \cdot \mathbf{v}_{\alpha} + \frac{1}{2} \sum_{\alpha} \mathbf{u}_\alpha \cdot \mathbf{u}_\alpha + \frac{1}{2} \mathbf{\omega}_r \cdot I \cdot \mathbf{\omega}_r
+ \sum_{\alpha} \mathbf{u}_\alpha \cdot (\mathbf{\omega}_r \times \mathbf{x}_{\alpha}).
\]  

(6)

Equation (6) is identical with the expression for the kinetic energy derived with Sayvetz conditions.\(^9,25\) Sum of the first two terms is usually called the pure vibrational part, the third term the pure rotational part, and the last term the Coriolis energy. In our previous work, we calculated the pure rotational energy and the Coriolis energy accordingly, which displayed some irregularities mentioned in the previous section. Upon closer inspection of Eq. (6), one realizes that the above designation for the pure vibrational and rotational parts is valid only in the limit of negligible Coriolis interaction. Namely, rigorous separation of the pure vibrational and rotational parts under Sayvetz conditions is possible only in the limit of small vibrations.\(^29\) Specifically, the third term which incorporates the angular velocity of the moving frame and the moment of inertia at an instantaneous configuration cannot be considered as the pure rotational energy of a molecule undergoing large-amplitude vibration.\(^29\) Hence, adoption of the above scheme would lead to intermixing of the vibrational and rotational parts for vigorously rotating and vibrating systems.

For a rigid linear molecule undergoing rotation, the pure rotational angular momentum is directed perpendicular to the figure axis, the axis formed by connecting nuclei. Excitation of the bending vibration(s) results in the vibrational angular momentum\(^10\) along the figure axis. In addition, Coriolis interaction between the rotational and vibrational motions induces small vibrational angular momentum directed opposite to the pure rotational angular momentum.\(^10\) Sum of all these angular momenta results in the total angular momentum which is a constant of motion for a rotating–vibrating linear molecule. Namely, the pure rotational angular momentum is not a constant of motion and will be affected by the molecular vibration. The approach taken in this work to evaluate the rotational energy is, however, based on the assumption that the pure rotational angular momentum can be regarded as a fairly good constant of motion. This is likely because the vibrational angular momentum originating from Coriolis interaction is known to be small and the influence of the small angular momentum of bending vibrations directed perpendicular to the rotational one would not be important. This hypothesis will be tested numerically in a following section. Assumption of the constant pure rotational angular momentum directed perpendicular to the figure axis suggests that the pure rotational energy can be evaluated from this component as far as a very high energy resolution is not pursued as in high resolution spectroscopy. The first step in this direction is to set up three rotational axes for an instantaneous configuration of a rotating–vibrating linear molecule. From numerical point of view, the principal axis frame and the Eckart frame\(^29,30\) are convenient to use. In both of these frames, the component of the total angular momentum perpendicular to the figure axis is a fairly good constant of motion even though the former is more convenient than the latter in the evaluation of the rotational energy, as will be seen later. Let us designate \(A, B\), and \(C\) as the three rotational axes with the axis \(A\) corresponding to the figure axis at the equilibrium geometry. Then, the approximate rotational angular momentum \((\mathbf{J}^{2D})\) is given by the sum of the \(B\) and \(C\) components \((\mathbf{J}_B\) and \(\mathbf{J}_C)\) of the total angular momentum \((\mathbf{J})\),

\[
\mathbf{J}^{2D} = \mathbf{J}_B + \mathbf{J}_C = \mathbf{J} - \mathbf{J}_A.
\]  

(7)

Then, the 2-dimensional angular velocity \((\mathbf{\omega}^{2D})\) given below becomes a good approximation for the pure rotational angular velocity,

\[
\mathbf{\omega}^{2D} = I^{-1} \cdot \mathbf{J}^{2D}.
\]  

(8)

To develop an algorithm to separate rotation and vibration in a linear molecule, let us manipulate the expression of the kinetic energy as follows:

\[
T = \frac{1}{2} \sum_a \dot{\mathbf{x}}_a^2
= \frac{1}{2} \sum_a \left[ (\dot{\mathbf{x}}_a - \mathbf{\omega} \times \mathbf{x}_a)^2 + \mathbf{\omega} \times \mathbf{x}_a \right]^2
= \frac{1}{2} \sum_a (\dot{\mathbf{x}}_a - \mathbf{\omega} \times \mathbf{x}_a)^2 + \frac{1}{2} \sum_a (\mathbf{\omega} \times \mathbf{x}_a)^2
+ \sum_a (\dot{\mathbf{x}}_a - \mathbf{\omega} \times \mathbf{x}_a) \cdot (\mathbf{\omega} \times \mathbf{x}_a).
\]  

(9)

This equation is a general expression which holds for any choice of angular velocity. For example, taking \(\mathbf{\omega}_r\), satisfying the second Sayvetz condition as \(\mathbf{\omega}\), Eq. (9) becomes identical.
to Eq. (6). To evaluate the rotational energy using the 2-
dimensional angular frequency, one may substitute $\omega^{2D}$ in
Eq. (9),

$$T = \frac{1}{2} \sum \alpha (\dot{x}_\alpha - \omega^{2D} \times x_\alpha)^2 + \frac{1}{2} \sum \alpha (\omega^{2D} \times x_\alpha)^2$$

$$+ \sum \alpha (\dot{x}_\alpha - \omega^{2D} \times x_\alpha) \cdot (\omega^{2D} \times x_\alpha). \tag{10}$$

The first, second, and third terms correspond to the vibra-
tional, rotational, and Coriolis parts, respectively. Use of
Eqs. (1) and (2) and some vector algebra converts the first
part of the last term, $\sum \alpha (\omega^{2D} \times x_\alpha)$, into $\omega^{2D} \cdot I \cdot \omega$. Similarly, the second part is converted to $\omega^{2D} \cdot I \cdot \omega^{2D}$. Hence,

Coriolis energy $= \omega^{2D} \cdot I \cdot \omega - \omega^{2D} \cdot I \cdot \omega^{2D}$

$$= \omega^{2D} \cdot I \cdot \omega_\lambda. \tag{11}$$

When the principal axis frame is used, the instantaneous
moment of inertia tensor is diagonal and the following relations
hold between components of $\omega$ and $J$:

$$\omega_A = I_A^{-1} J_A,$$

$$\omega_B = I_B^{-1} J_B,$$

$$\omega_C = I_C^{-1} J_C. \tag{12}$$

The fact that the moment of inertia is diagonal in the prin-
cipal axis frame is especially useful because the Coriolis term
[Eq. (11)] vanishes in this case. Since the second term in Eq.
(10) is equivalent to $\omega^{2D} \cdot I \cdot \omega^{2D}$, the rotational energy under
the assumption of a constant $J^{2D}$ can be written as follows
when the principal axis frame is used:

$$E_{rot} = \frac{1}{2} \omega^{2D} \cdot I \cdot \omega^{2D}. \tag{13}$$

Vanishing of the Coriolis term does not occur when the Eck-
art frame is used to evaluate $J^{2D}$. In this case, sum of
the rotational and Coriolis parts becomes

$$E_{rot} + E_{Corr} = \frac{1}{2} \omega^{2D} \cdot I \cdot \omega^{2D} + \omega^{2D} \cdot I \cdot \omega_\lambda$$

$$= \frac{1}{2} \omega^{2D} \cdot I \cdot (\omega + \omega_\lambda). \tag{14}$$

III. COMPUTATIONAL

The methods described in the previous section have been
tested for several nonreacting linear triatomic and tetratomic
systems such as HCN, CHO⁺, CO₂, CO₂⁺, and C₂H₂. Since
the results obtained from all these systems are comparable,
only those from HCN and C₂H₂ will be presented here. In
addition, calculation has been performed for the triatomic
product of the reaction

$$\text{CH}_2\text{OH} \rightarrow \text{CHO}^+ + \text{H}_2. \tag{15}$$

investigated previously to demonstrate the advantage of the
present approach.

Potential energy surfaces (PESs) of these systems were
constructed using the interpolation algorithm\textsuperscript{31} reported
previously. Briefly, the potential energy and its derivatives (gra-
dient and hessian) were calculated at a number of data points
with \textit{ab initio} quantum chemical methods. The overall PES
was expressed as a weighted sum of the local harmonic sur-
faced obtained as Taylor expansions. The number of configu-
rations points used in the construction of PES for each non-
acting system was 100 and 340 points were used for
reaction (15). Quantum chemical calculations were per-
formed on MP2-RHF/6-31G(d,p) level for HCN and CHO⁺
and on RHF/6-31G(d,p) level for others using GAMESS\textsuperscript{35}
package. It is to be pointed out that the accuracy of PESs is
not critical for the present purpose.

Instead of the usual random sampling,\textsuperscript{36–38} a mode-
specific sampling\textsuperscript{39,40} was used to select the initial phase
space point of a classical trajectory run for the nonreacting
cases. This was to study the influence of each vibrational
mode on the rotational angular momentum and energy. Ex-
citation of a single vibrational mode was done by momentum
sampling at the equilibrium geometry. This is particularly
useful because the vibrational angular momentum vanishes
at the equilibrium geometry. Then, the angular momentum
added in a direction perpendicular to the figure axis specifies
the initial pure rotational angular momentum of a trajectory
run. Ability to specify the initial values of the rotational an-
gular momentum and energy is of great help in judging the
reliability of various schemes to evaluate the rotational en-
ergy along a classical trajectory. For the test of the present
methods, it was also useful to excite degenerate bending modes
simultaneously such that a nonvanishing vibrational angular
momentum was present at the trajectory initial point.
Obviously, this cannot be achieved by the momentum sam-
ping at the equilibrium geometry. For simultaneous excita-
tion of degenerate bending modes with finite phase differ-
ence, half of the intended vibrational energy was assigned to
one of the degenerate bending modes as the kinetic energy
and the other half to the other mode as the potential energy.
Since the method adopted was not ideal for simultaneous
excitation of degenerate bending modes, a small angular mom-
entum component appeared perpendicular to the figure axis
in addition to the main one along the figure axis. The former
was subtracted and the intended rotational angular momentum
was added perpendicular to the figure axis. Phase differ-
ence close to 90° was achieved in this way even though the
vibrational energy after the angular momentum manipulation
became a little bit less than originally added. C₂H₂ contains
two sets of degenerate bending modes and 6 combinations of
excitation scheme are possible, all of which were investi-
gated. Up to 2 eV was added as the vibrational energy and
the rotational energy corresponding to kT at 30, 300, or 3000
K (0.0026, 0.026, or 0.26 eV, respectively) was added. For
reaction (15), momentum sampling at the transition state was
done as was described in a previous work.\textsuperscript{26,31,32}

To calculate a classical trajectory, Hamilton’s equations of
motion\textsuperscript{62} were integrated using Gear’s variable-order and
variable-step algorithm.\textsuperscript{41} For nonreacting systems, time ev-
olutions of angular momentum, rotational energy, and mode-
specific vibrational energy were evaluated at every femtosec-
ond for a period long enough for one full rotation. Mode-
specific vibrational energy analysis\textsuperscript{26} was performed in the
internal coordinate\textsuperscript{8} system as described in the previous
work. The only difference from the previous approach was to eliminate the contribution from the second term in Eq. (6) which is not needed in the present method.

Rotational angular momentum, namely the component of the total angular momentum perpendicular to the figure axis, was calculated using the principal axis and Eckart frames. Rotational and Coriolis energies were calculated with five different schemes. In Scheme I, rotational energy was calculated with the 3-dimensional total angular momentum, which has been widely used until recently.27,28 Scheme II calculated the rotational energy under the Sayvetz conditions,25 namely the third term in Eq. (6). Sum of the rotational and Coriolis energies under these conditions, namely the sum of the third and fourth terms in Eq. (6), was calculated in Scheme III. Schemes IV and V utilized the 2-dimensional angular velocities as developed in this work. The main difference between these two is in the evaluation of 2-dimensional angular velocities, the principal axis frame being used in the former and the Eckart frame in the latter. In addition, Eq. (13) was used in the former while Eq. (14) was used in the latter.

For reaction (15), the mode-specific energy analysis was performed at the reaction end point which was taken to be located at the product separation of 4.5 Å. Also calculated was the time average over 18 fs after the system reached the reaction end point, which corresponds to one vibrational period of the bending motion. Total of 3000 trajectories were calculated of which 1296 trajectories were reactive.

IV. RESULTS AND DISCUSSION

A. Constancy of the rotational angular momentum

Vibrational normal modes of a linear triatomic molecule are usually designated as \(v_1\), \(v_2\), and \(v_3\), representing symmetric stretching, bending, and asymmetric stretching vibrations,10 respectively. The \(v_2\) modes can be differentiated in the present study based on the orientation of the angular momentum vector with respect to the bending plane. The bending mode whose plane of motion contains the angular momentum vector with respect to the bending plane. When both of the bending modes are excited with a phase difference close to 90°, the situation will be called \(v_2 + v_2^*\) excitation. Acetylene10,42 has three stretching modes, \(v_1\) (symmetric CH), \(v_2\) (CC), and \(v_3\) (asymmetric CH) vibrations. Two sets of bending modes, \(v_4\) ("trans" bending) and \(v_5\) ("cis" bending), will be differentiated as \(v_4\) and \(v_4^*\) and \(v_5\) and \(v_5^*\) as for the triatomic molecules.

Figure 1 shows the time evolutions of the axial (\(J_A\)) and perpendicular (\(J^{2D}\)) components of the total angular momentum of HCN at the initial vibrational energy of 1 eV and the rotational energy corresponding to 300 K. The components of the angular momentum were analyzed in the principal axis frame. The results obtained with the Eckart frame are essentially the same except that the vibrational modulation (to be explained) is a little bit less. When the vibrational energy was deposited initially in \(v_1\), \(v_2\) \& \(v_3\), and \(v_3\) modes, there was no angular momentum along the figure axis and \(J^{2D}\) was a constant of motion as can be seen in Figs. 1(a), 1(d), and 1(b), respectively. The same pattern was observed at higher rotational and vibrational energies investigated and for acetylene also. With \(v_2\) excitation [Fig. 1(c)], \(J_A\) fluctuates around zero with the frequency of the bending mode. This fluctuation seems to occur due to the fact that the coordinate system used for the angular momentum analysis is not perfect for nonrigid rotor. Use of the Eckart frame to separate \(J\) reduces the amplitude of this fluctuation to less than half. Similar fluctuation is observed in \(v_2 + v_2^*\) excitation [Fig. 1(e)]. A large vibrational angular momentum in this case leads to observable fluctuation in \(J^{2D}\). Regardless of this fluctuation, however, it is clear from the figures that \(J^{2D}\) can be regarded as a fairly good constant of motion. Figure 2 shows similar data obtained at the rotational energy corresponding to 300 K with \(v_2\) and \(v_2 + v_2^*\) excitations by 1 eV. In addition to the modulation with the bending frequency, \(J_A\) displays another long-term modulation as is seen in Fig. 2(a). Calculation of the time evolution of only the angular momentum but also the mode-specific vibrational energies for a period
of 10 ps revealed that oscillatory energy exchange between \( \nu_2 \) and \( \nu_2' + \nu_2 \) was the main cause for the long-term modulation. However, the reason for the oscillatory energy exchange is not known at the moment. Time evolutions after \( \nu_2 \) and \( \nu_2' + \nu_2 \) excitations by 2 eV at 3000 K rotational energy are shown in Fig. 3. The overall trend is the same as before except that the long term modulation of \( J_{2D} \) becomes more significant. Regardless, near constancy of \( J_{2D} \) is obvious in this case of rather extreme rotational and vibrational excitation.

As was mentioned earlier, excitation of stretching vibrations of \( \text{C}_2\text{H}_2 \) did not affect \( J_A \) and \( J_{2D} \) over an extended period of time. The same was true for the excitation of the cis bending modes (\( \nu_4 \) and \( \nu_4' \)) and the out-of-plane trans bending mode (\( \nu_4 \)). Only when the in-plane trans bending mode (\( \nu_4 \)) was excited either alone or together with other modes, fluctuation of \( J_{2D} \) was observed. Time evolutions of \( J_A \) and \( J_{2D} \) at some combinations of the rotational and vibrational energies are shown in Fig. 4. The trend here is the same as for the excitation of \( \nu_2 \) mode of HCN. Hence, one can conclude that \( J_{2D} \) of a linear molecule is a virtual constant of motion even when the molecule is rotationally and vibrationally excited extensively.

**B. Evaluation of the rotational energy**

Time evolutions of the rotational and Coriolis energies of HCN and \( \text{C}_2\text{H}_2 \) were calculated at various combinations of initial rotational and vibrational energies according to Schemes I–V described in the previous section. Even though Coriolis energy was added to the rotational one in Schemes III and V, the sum will be loosely called the rotational energy. Coriolis term vanishes in Schemes I and IV. Discussion will be focused mainly on the results from Schemes I–IV. Features in the results from Scheme V will be explained at the end.

Figure 5 shows the time evolutions of the rotational energies of HCN which was excited initially to 1 eV in vibrational energy and 1 ev and 300 K (0.0026 eV) in rotational energy. Under the \( \nu_1 \) excitation [Fig. 5(a)], time evolutions evaluated with Schemes I–IV were essentially identical. Sinusoidal oscillation of the rotational energy is due to the oscillatory change in the moment of inertia due to the stretching vibration. Oscillatory behavior under the \( \nu_3 \) excitation [Fig. 5(b)] is more complicated. A Fourier transformation (not shown) of the figure displayed \( \nu_3 \) frequency component in addition to the expected \( \nu_3 \) component. This arose because initial
State sampling was done at the equilibrium geometry of the nonrotating molecule. Namely, the rotational excitation at the equilibrium geometry induced vibrational excitation due to centrifugal distortion.24 In particular, a slight excitation of the $v_1$ mode resulted in noticeable fluctuation which can be seen when Fig. 5 is magnified. It is important to note that the rotational energy oscillates around the initial value of 0.0026 eV ($\sim 30$ K) regardless of the schemes when the vibrational energy is deposited in the stretching modes. The same trend was observed at higher rotational and vibrational energies of HCN and for C$_2$H$_2$ also. The results from the stretching mode excitation will not be discussed further in the rest of the paper. Dramatic differences among the different schemes appear with the excitation of the degenerate bending modes [Figs. 5(c)–5(e)]. With the $v_2$ excitation, the rotational energy under Scheme I displays periodic spikes separated by half bending period. As was reported in the previous work, these spikes occur near the linear configuration of the molecule which corresponds to a singular point in the three dimensional treatment of a linear molecule. Rotational energies evaluated with Schemes II and III also display irregular behaviors, sometimes going negative as was pointed out earlier. Such irregular behaviors are absent with Scheme IV. In particular, the rotational energy with this scheme oscillates around the initial value. Irregular behaviors with Schemes I–III are also observed under the $v_2$ and $v_2 + v_2'$ excitations [Figs. 5(d) and 5(e)]. In all these cases, the rotational energy with Scheme IV oscillates around the initial value. Difficulty with Scheme I persists at other rotational and vibrational energies. The results from Schemes II and III, especially the latter, converge to the results from Scheme IV as the rotational energies increase, even though a concomitant increase in the vibrational energy reduces the reliability of Schemes II and III. Some representative results are shown in Fig. 6. It is to be mentioned that the results obtained for other linear triatomic molecules such as HCO$^+$,
CO$_2$ and CO$_2^+$ are essentially identical to the above and will not be explained in details. Figure 7 shows some representative results of the rotational energy evolution after the initial $v_4$ (in-plane trans bending) excitation of C$_2$H$_2$. The trend observed here is essentially identical to that for the $v_2$ excitation of linear triatomic molecules. It is obvious from all these calculated results that the 2-dimensional method developed in this work allows reliable evaluation of the rotational energy from the classical trajectory results. The method based on the Sayvetz conditions, Scheme III, proposed previously is also expected to provide a good estimate especially when the average over many trajectory results is taken. However, significant errors in the low rotational energy region seem to be unavoidable.

It was mentioned earlier that use of the Eckart frame in the separation of the total angular momentum into $J_A$ and $J_D$ resulted in less fluctuation than use of the principal axis frame. Then, one may expect that the former be superior, even though slightly, to the latter in the evaluation of the rotational energy also. Figure 8 compares the time evolutions of the rotational energies evaluated by Schemes IV and V of HCN with initial rotational energy of 300 K (0.026 eV) and the $v_2 + v_{2r}$ excitation of 1 eV. The rotational energy calculated by Scheme V fluctuates significantly around the initial value while the fluctuation is much less with Scheme IV. Time averaged rotational energies in these two cases are essentially the same. Hence, it is clear that the principal axis frame can be more advantageous than the Eckart frame in the evaluation of the rotational energy.

### C. Rotational energy evaluation for reaction products

In the evaluation of the rotational energy distribution of a reaction product from classical trajectory results, it is usual to average the rotational energy over a vibrational period along each trajectory. This is to reduce the fluctuation arising from the vibrational motion. Averaging over a period time, however, means that an instantaneous rotational energy cannot be evaluated. This can be troublesome when one attempts to study the time evolution of product states in real time. In this regard, it is useful to note that averaging over many instantaneous trajectory results can have the effect of vibrational phase averaging. The fact that the rotational energy evaluated with the present method displays much less fluctuation than in the results from other methods indicates that averaging the present rotational energies over a limited number of trajectories can replace the time averaging. Figure 9 compares the rotational energy distributions for reaction (15) obtained from 50 reactive trajectories with and without time averaging. The two results are essentially identical. This means that the rotational energy distribution at a certain location in the configuration space such as at a specified position along the intrinsic reaction path can be determined reliably with the present method.

### V. CONCLUSION

A reliable method to evaluate the rotational energy of a linear product in classical trajectory simulation has been developed. The method is based on the fact that the component of the angular momentum of a linear molecule perpendicular to the figure axis, which is essentially the rotational angular
momentum, is a fairly good constant of motion. Expression for the total kinetic energy of a molecule could be reorganized according to the above concept. When the principal axis frame was used to separate the total angular momentum into components, the Coriolis term vanished, obviating the difficulty in the treatment and assignment of this term. Reduced fluctuation and good accuracy of the rotational energy thus evaluated may allow the investigation of real time dynamics by averaging over limited number of trajectories. The method developed here removes the complication involved in the rotational energy evaluation from classical trajectory results of linear products which arises from the presence of vibrational angular momentum and Coriolis effect. Negligible vibrational angular momentum originating from Coriolis interaction in an asymmetric top molecule means that the rotational energy can be evaluated with the total angular momentum in this case. On the other hand, Coriolis effect is known to be important for symmetric and spherical top molecules, more so than for linear one. Reliable evaluation of the classical rotational energy of these molecules is still an outstanding problem.

ACKNOWLEDGMENTS

This work was supported by the Ministry of Education, Republic of Korea, and by the Korea Science and Engineering Foundation (KOSEF) through the Center for Molecular Catalysis at Seoul National University. Computations in the present work were carried out by using the CRAY C90 of the Systems Engineering Research Institute (SERI) supercomputer center through Grant No. D2117, which is gratefully acknowledged. We are also grateful to the Educational and Research Computing Center at Seoul National University for access to an IBM SP2 computer. The publication cost was supported in part by the Research Institute of Molecular Science.