Dynamic Reaction Path Analysis Based on an Intrinsic Reaction Coordinate

Tetsuya Taketsugu
Iowa State University

Mark S. Gordon
Iowa State University, mgordon@iastate.edu

Follow this and additional works at: http://lib.dr.iastate.edu/chem_pubs

Part of the Chemistry Commons

The complete bibliographic information for this item can be found at http://lib.dr.iastate.edu/chem_pubs/300. For information on how to cite this item, please visit http://lib.dr.iastate.edu/howtocite.html.

This Article is brought to you for free and open access by the Chemistry at Iowa State University Digital Repository. It has been accepted for inclusion in Chemistry Publications by an authorized administrator of Iowa State University Digital Repository. For more information, please contact digirep@iastate.edu.
Dynamic Reaction Path Analysis Based on an Intrinsic Reaction Coordinate

Abstract
We propose two methods that may be used to describe the dynamic reaction path (DRP) based on an intrinsic reaction coordinate (IRC) or minimum energy path, to examine how the actual dynamics proceeds relative to the IRC path. In the first of these, any point on the DRP is expressed in terms of the IRC and the distance from the IRC path. In the second method, any DRP point is expressed in terms of the IRC, the curvature coordinate, and the distance from a two-dimensional “reaction plane” determined by the IRC path tangent and curvature vectors. The latter representation is based on the fact that the 3N−8 dimensional space orthogonal to the reaction plane is independent of an internal centrifugal force caused by the motion along the IRC path. To analyze the relation between geometrical features of the IRC path and the dynamics, we introduce a function that estimates the variation of the reaction plane along the IRC path. As demonstrations, the methods are applied to the dissociation reaction of thioformaldehyde (H₂CS→H₂+CS).

Keywords
Centrifugal force, Dissociation, Hydrogen reactions, Physics demonstrations

Disciplines
Chemistry

Comments

Rights
Copyright 1995 American Institute of Physics. This article may be downloaded for personal use only. Any other use requires prior permission of the author and the American Institute of Physics.
Dynamic reaction path analysis based on an intrinsic reaction coordinate
Tetsuya Taketsugu and Mark S. Gordon

Citation: The Journal of Chemical Physics 103, 10042 (1995); doi: 10.1063/1.470704
View online: http://dx.doi.org/10.1063/1.470704
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/103/23?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in
A quantum generalization of intrinsic reaction coordinate using path integral centroid coordinates

Nonlinear reaction coordinate analysis in the reweighted path ensemble

The reaction path intrinsic reaction coordinate method and the Hamilton–Jacobi theory

Reaction path Hamiltonian based on a reaction coordinate and a curvature coordinate

The definition of reaction coordinates for reaction-path dynamics
I. INTRODUCTION

Recent progress in quantum chemistry has made it possible to calculate a reliable potential energy surface to describe a chemical reaction. The starting point for studying a chemical reaction is to determine the location of the reactant, product, and transition state (TS) geometries on the potential energy surface. Once the TS geometry is obtained, an intrinsic reaction coordinate (IRC) analysis may be performed to follow the minimum energy path to reactants and products and verify that this TS does indeed connect the reactants and products of interest. The IRC path is defined as the steepest descent path in mass-weighted Cartesian coordinates. When the reaction system descends from the TS to the reactant or product on the potential energy surface with infinitesimal velocity (infinite damping), it should follow the IRC path.

In actual reaction dynamics, since the kinetic energy in the system will be nonzero, the molecular system should proceed with vibrational (as well as rotational and translational) motions relative to the IRC path. Based on a vibrationally adiabatic model, Miller et al. proposed a reaction path Hamiltonian (RPH), in which the reaction process is described in terms of the reaction coordinate and 3N−7 vibrational coordinates orthogonal to the reaction coordinate. In this scheme, 3N−7 vibrational modes are regarded as bath modes (i.e., the deviation from the IRC path is small throughout the reaction). A variational transition state theory developed by Truhlar et al. for dynamics calculations is also based on such a picture.

In reaction-path-based dynamics calculations, one should give care to the curvature of the reaction path. In general, a molecular system cannot change its direction rapidly due to its velocity. When the IRC curvature is small, a molecular system can remain on or close to the IRC path. On the other hand, in a region where the IRC path has a large curvature, the reaction system can deviate more strongly from the IRC path, resulting in energy transfer to vibrational modes which couple with the IRC (vibrational excitation). Kato and Morokuma proposed a mechanism of energy disposal along the IRC path by mapping the IRC curvature vector onto 3N−7 normal vibrational modes based on a RPH scheme. Truhlar and co-workers have extensively considered the effect of small and large path curvatures on reaction-path-based dynamics methods.

It is also important to consider the stability of a reaction path. In a RPH scheme, the reaction path is presumed to be a stable path; i.e., any point on this reference reaction path should be the bottom of a valley (local minimum) relative to all directions orthogonal to that of the reaction coordinate. This means that, after projecting out the direction of the reaction coordinate, the Hessian matrix at any point on the reference path should have only positive eigenvalues. If a Hessian eigenvalue changes its sign from positive to negative (valley—ridge) at some point along the IRC path, the reaction system is expected to leave the IRC path. Subsequently, the system may or may not return to the vicinity of this reference path.

Very recently, an ab initio classical trajectory method, the dynamic reaction path (DRP) method based on ab initio molecular orbital (MO) calculations, has been implemented into the electronic structure program package, GAMESS. The DRP method determines atomic accelerations, velocities, and positions using the energy gradient, and does not require prior knowledge of the potential energy surface. In addition, all degrees of freedom are automatically taken into account. Recently, Taketsugu et al. examined intramolecular vibrational mixing in H2O by mapping the DRP onto normal modes used as basis vectors. This method was extended to treat chemical reactions and applied to the dynamical process of the attack of H+ on SiH4. The DRP’s were then analyzed in terms of normal modes of both reactant and product. This analysis successfully demonstrated the nature of the intramolecular vibrational energy transfer.

In this paper, we use the DRP method to examine how the actual dynamics proceeds relative to the IRC path. For this examination, one needs first to specify a reaction coordinate for a given DRP point. Truhlar and co-workers have noted that the choice of reaction coordinate for points off the IRC path is not so clearly defined and can influence the nature of harmonic reaction path frequencies. Since our pur...
pose here is to obtain a qualitative understanding of the dynamics relative to the IRC path, it is most convenient to determine the reaction coordinate of a point on the DRP simply by utilizing a least squares method in 3N mass-weighted Cartesian coordinates. Then, the DRP is expressed in terms of the reaction coordinate and the (3N−7 dimensional) displacement vector relative to a point on the IRC path. The magnitude of this displacement vector may be interpreted as the distance between the DRP point and the IRC path. The intrinsic reaction coordinate, the curvature coordinate, and the distance from the reaction plane is proposed based on the fact that the 3N−8 dimensional space orthogonal to the IRC and IRC curvature directions is independent of the energy disposal process along the IRC path.6

In order to demonstrate these methods, ab initio MO and DRP calculations are performed for the dissociation reaction of thioformaldehyde (H2CS→H2+CS). This reaction was reported to have a bifurcation along the 6-31G(d,p) IRC path calculated at the Hartree–Fock level of theory,11 and its bifurcation mechanism was explained in terms of the second-order Jahn–Teller effect.15 The existence of this bifurcation in the mass-weighted Cartesian coordinate system makes an interesting test of the new methods.

II. INTRINSIC REACTION COORDINATE SYSTEM

Consider a system containing N atoms in three-dimensional space. Such a system may be described in terms of N position vectors (r1,...,rN) or 3N Cartesian coordinates X = (X1,...,X3N) in 3N-dimensional space. Each point corresponds to some geometrical structure of the system and has an adiabatic potential energy V(X). This corresponds to a 3N-dimensional adiabatic potential energy surface. Reactant (XR) and product (XP) correspond to minima, while a transition state (XTS) corresponds to a first-order saddle point on the surface. The intrinsic reaction coordinate s, is defined as the arc length along the steepest descent path in mass-weighted Cartesian coordinates connecting reactant (sR<0), TS (s=0), and product (sP>0). In the following, we adopt the mass-weighted Cartesian coordinate representation for X.

A tangent unit vector on the IRC path is defined as

$$\mathbf{v}(s) = \frac{d \mathbf{X}_{IRC}(s)}{ds} = \begin{cases} \frac{-\nabla V(X)}{\nabla V(X)} & (s>0) \\ \nabla V(X) & (s<0) \end{cases},$$

where \(\mathbf{X}_{IRC}(s)\) denotes a set of 3N coordinates for the reaction system at a point s on the IRC path (sR≤s≤sP). Except for stationary points, \(\mathbf{v}(s)\) coincides with the positive (negative) of the normalized mass-weighted gradient of the potential for \(s<0\) (s>0). The vector \(\mathbf{v}(s)\) smoothly becomes one of the normal vibrational modes at the reactant and product minima and at the TS. A curvature vector \(\mathbf{v}^{(1)}(s)\) and scalar curvature \(\kappa(s)\) on the IRC path may be defined as

$$\mathbf{v}^{(1)}(s) = \frac{d \mathbf{v}(s)}{ds} = \frac{d^2 \mathbf{X}_{IRC}(s)}{ds^2},$$

$$\kappa(s) = |\mathbf{v}^{(1)}(s)|.$$  

(3)

Naturally, the vectors \(\mathbf{v}(s)\) and \(\mathbf{v}^{(1)}(s)\) are orthogonal to each other.

For any location X away from the IRC path, one can define a displacement vector, \(\mathbf{D}(X) = X - X_{IRC}(s(X))\), as well as a reaction coordinate, \(s(X)\), by mapping X onto the closest point on the IRC path (see Fig. 1). This is a least squares definition in 3N mass-weighted Cartesian coordinates. In the RPH scheme, \(\mathbf{D}(X)\) is expressed in terms of 3N−7 normal coordinates \([Q_1(X),...,Q_{3N-7}(X)]\) whose directions coincide with the eigenvectors of the projected Hessian matrix calculated at \(X_{IRC}(s(X))\), where \(s(X)\) refers to the closest point to X on the IRC path. Let \(d(X)\) denote the magnitude of \(\mathbf{D}(X)\), corresponding to the distance between X and the IRC path (see Fig. 1). Then \(d(X)\) consists of contributions from the 3N−7 transverse vibrations:

$$d(X) = \left\{ \sum_{i}^{3N} \{X_i - X_{IRC,i}\}^2 \right\}^{1/2},$$

$$= \left\{ \sum_{i}^{3N-7} Q_i(X)^2 \right\}^{1/2}.$$  

(4)

(5)

where \(X_i\) and \(X_{IRC,i}\) are the ith components of \(X\) and \(X_{IRC}(s(X))\), respectively. A representation \([s(X),d(X)]\), as well as a representation \([s(X),Q_1(X),...,Q_{3N-7}(X)]\) in the RPH, gives the location of X relative to the IRC path.

Dynamic calculations based on the RPH rely on the premise that the atoms explore only small amplitude deviations from the IRC path, i.e., \(d(X)\) remains small throughout the reaction. When large curvatures in the IRC path are encountered, however, one expects the system to deviate considerably from the minimum energy path. Based on the RPH scheme, Kato and Morokuma related the mechanism of energy disposal over the 3N−7 normal vibrational modes along the path to the magnitude of the projection of \(\mathbf{v}^{(1)}(s)\). Here, we propose an alternative approach: the reaction system proceeds on the two-dimensional reaction plane deter-

---

**FIG. 1.** Schematic illustration of X location relative to the IRC path, \(\mathbf{D}(X)\). XIRC(s(X)), s(X), d(X), v(s(X)), v1(s(X)), \(v^{(1)}(s)\), \(x(X)\), and \(d_s(X)\) are also illustrated.
mined by \( v(s) \) and \( v^{(1)}(s) \). Associated with this plane is a 3\( N - 8 \) dimensional vibrationally adiabatic space that extends from the reactant to the product region.\(^{22} \) These 3\( N - 8 \) transverse normal vibrational modes can be obtained as eigenvectors of the Hessian matrix after projecting out the \( v(s) \) and \( v^{(1)}(s) \) components. Since these normal modes are independent of the energy disposal process, they are true bath modes. If the curvature \( \kappa(s) \) remains small throughout the reaction, the deviation of the reaction system from the IRC path is expected to be small, and the reaction path Hamiltonian provides a reasonable description of the process.

It is important to consider the physical meaning of our scheme in comparison with the RPH scheme. A reaction system located at some point along the reaction path feels a force only in the direction of the reaction path due to the adiabatic potential energy gradient. From this point of view, the RPH separates the internal degrees of freedom into two parts: one dimension along the reaction path and 3\( N - 7 \) dimensions orthogonal to the reaction path. Since a vibrational motion occurs about the potential energy minimum (force = 0), internal motions in the 3\( N - 7 \) orthogonal dimensions can be regarded as vibrations. Next, consider the case where the system actually moves along the reaction path. Then, the system feels not only the force due to the adiabatic potential energy gradient, but also a centrifugal force due to the curve of the reaction path. Within the RPH framework, such a dynamic effect causes the origin of the vibrations to deviate from the reaction path (vibrational excitation) for all 3\( N - 7 \) vibrational modes. The centrifugal force is directed along the curvature vector, so the 3\( N - 8 \) dimensional space orthogonal to the two-dimensional plane defined by the reaction path and the curvature vector corresponds to a set of “dynamic” vibrational degrees of freedom. The system should not deviate from the path along these directions since the force is zero.

Based on the foregoing picture, we define the curvature coordinate \( \rho(X) \) and the displacement vector from the two-dimensional reaction plane \( D_p(X) \) as

\[
\rho(X) = -\left( \frac{v^{(1)}(s(X))}{\kappa(s(X))} \right)' \cdot D(X),
\]

\[
D_p(X) = D(X) - \rho(X) \cdot \left( -\frac{v^{(1)}(s(X))}{\kappa(s(X))} \right) \cdot D(X).
\]

\( D_p(X) \) can be expressed in terms of the 3\( N - 8 \) normal coordinates described earlier. Therefore, \( d_p(X) \), the magnitude of \( D_p(X) \), corresponding to the distance between \( X \) and the two-dimensional reaction plane (see Fig. 1), can be calculated as

\[
d_p(X) = \left[ d(X) - \rho(X) \cdot d_d(X) \right] \cdot D(X)
\]

So, \( d_p(X) \) consists of contributions from the 3\( N - 8 \) vibrational displacements from the IRC path. The location of any point \( X \) relative to the reaction plane is given by \( [s(X), \rho(X), d_p(X)] \).

The reaction plane determined by unit vectors \( v(s) \) and \( v^{(1)}(s)/\kappa(s) \) is a function of \( s \). In those regions where there are rapid changes in the plane, one expects that the reaction system will move away from this two-dimensional plane, in analogy with behavior expected in high curvature regions on a one-dimensional reaction path (IRC). The basis vectors of the two-dimensional reaction plane at \( s + \Delta s \) are \( v(s + \Delta s) \) and \( -v^{(1)}(s + \Delta s)/\kappa(s + \Delta s) \). When \( \Delta s \) is small, they can be expressed as

\[
v(s + \Delta s) = v(s) + v^{(1)}(s) \times \Delta s,
\]

\[
\frac{v^{(1)}(s + \Delta s)}{\kappa(s + \Delta s)} = \frac{v^{(1)}(s)}{\kappa(s)} - \left( \frac{v^{(2)}(s)}{\kappa(s)} \right) \frac{v^{(1)}(s)}{\kappa(s)^2} \times \Delta s,
\]

where

\[
v^{(2)}(s) = \frac{d^2 v(s)}{ds^2}.
\]

Since for small \( \Delta s \), \( v(s + \Delta s) \) stays on the reaction plane defined at \( s \) as shown in Eq. (9), a change in the reaction plane is determined by the second term in Eq. (10). Since this second term still has overlap with (i.e., is not orthogonal to) \( v(s) \), we define the vector \( w(s) \) as

\[
w(s) = \frac{v^{(2)}(s)}{\kappa(s)} - \left( \frac{v^{(1)}(s)}{\kappa(s)} \right)' \cdot \frac{v^{(2)}(s)}{\kappa(s)} \cdot v(s),
\]

in order to measure changes in the reaction plane. The larger \( |w(s)| \) becomes, the more rapidly the reaction plane changes.

III. METHODS OF CALCULATION

*Ab initio* 6-31G(d,p) MO calculations were performed for the reaction \( H_2CS\rightleftharpoons H_2S + CS \), using the restricted Hartree–Fock (RHF) method with GAMESS (Ref. 19) and GAUSSIAN92 (Ref. 23). In this study, the IRC path needs to be calculated as precisely as possible, since it is used as a reference path. Thus, the TS geometry was optimized so that the largest component of the (Cartesian) gradient is less than \( 10^{-7} \) hartree/bohr, and the IRC path was calculated by the Range–Kutta fourth order integration method\(^{24} \) with a step size of 0.004 bohr amu\(^{-2} \). The calculated points and corresponding tangent unit vectors were stored in \( X_{IRC}(s) \) and \( v(s) \), respectively. \( v^{(1)}(s) \) and \( v^{(2)}(s) \) along the IRC path were calculated by numerical differentiation, and \( \kappa(s) \) and \( w(s) \) were calculated according to Eqs. (3) and (12), respectively. Previous studies\(^{11,15} \) reported that the IRC path for the reaction of interest preserves \( C_s \) symmetry (within the \( A' \) irreducible representation) throughout the reaction, and has a bifurcation (in the direction of the out-of-plane \( A'' \) mode) that occurs between reactant and TS. To locate the bifurcation point, the eigenvalue of the out-of-plane mode was calculated along the IRC path.

DRP calculations were also performed with RHF/6-31G(d,p), using time steps of 0.1 fs with GAMESS. The calculated points on the DRP were stored in \( X_{DRP}(t) \). One trajectory was started from \( X_{TS} \) along the direction of the imaginary normal mode direction with 0.01 kcal/mol kinetic energy (KE). Therefore, this is a dynamic descent trajectory from TS, with \( C_s \) symmetry preserved. To examine the dy-
TABLE I. Geometrical parameters \( r \) (bond length), \( a \) (bond angle), and \( d \) (dihedral angle) of \( X_{TS}+Q_{06,0}^{TS} \). C and H1 and H2 correspond to those in Fig. 3. Bond length and angle are given in Å and degree, respectively.

<table>
<thead>
<tr>
<th></th>
<th>( r ) (CH(_1))</th>
<th>( r ) (CH(_2))</th>
<th>( a ) (SCH(_1))</th>
<th>( a ) (H(_1)CH(_2))</th>
<th>( d ) (H(_1)C(_2)H(_3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( r ) (CS)</td>
<td>1.405</td>
<td>1.199</td>
<td>98.7</td>
<td>41.9</td>
<td>-11.0</td>
</tr>
<tr>
<td>( r ) (CH(_1))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( r ) (CH(_2))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( a ) (SCH(_1))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( a ) (H(_1)CH(_2))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( d ) (H(_1)C(_2)H(_3))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

namical effect of the bifurcation, a trajectory was also initiated from \( X_{TS}+Q_{06,0}^{TS} \) in the \(-v(0)\) direction (i.e., toward the entrance channel) with a 0.61 kcal/mol KE. Here, \( L_{0}^{TS} \) is the out-of-plane mode at the transition state, and \( Q_{06,0}^{TS} \) is the coordinate corresponding to a classical turning point in the harmonic vibrational ground state: \( \lambda_{l}(Q_{06,0}^{TS})^{2}/2=h\nu_{l}/2 \), where \( h \) is Planck’s constant, and \( \lambda_{l} \) and \( \nu_{l} \) are harmonic force constant and frequency of \( L_{0}^{TS} \), respectively. \( Q_{06,0}^{TS} \) was calculated to be 0.367 bohr amu\(^{1/2}\). Table I gives the H\(_2\)CS geometry that corresponds to the structure at \( X_{TS}+Q_{06,0}^{TS} \). The trajectory calculations were terminated when \( s[X_{DRP}(t_{p})] \) left the region where \( s_{R} \leq s < s_{P} \).

IV. RESULTS AND DISCUSSION

A. IRC profile

As a result of the IRC calculation, 1876 points, including 875 points in the entrance channel (TS—reactant) and 1000 points in the product channel (TS—product), are stored in \( X_{IRC}(s) \) for \(-3.5 \leq s \leq 4.0\). Figure 2 shows the potential energy \( E \) and the eigenvalue (\( \lambda \)) corresponding to the out-of-plane mode as a function of the IRC (\( s \)). In Fig. 2 \( R \), BP1, BP2, and \( P \) denote reactant (H\(_1\)CS), the first bifurcation point, the second bifurcation point, and product (H\(_2\)+CS), respectively. Energy values are given relative to that of the reactant. The activation barrier is 107.9 kcal/mol, and the dissociation energy (H\(_2\)+CS) is 46.6 kcal/mol. The reactant (\( C_{s} \) symmetry), BP1 (\( s = -1.135 \)), BP2 (\( s = -0.660 \)), TS, and product geometries are shown in Fig. 3.

This \( C_{s} \) symmetry IRC path is stable relative to out-of-plane (\( C_{s} \rightarrow C_{1} \)) distortions from reactants \( R \) to BP1. At BP1, the force constant \( \lambda \) for the out-of-plane mode changes its sign from positive to negative, and the stable valley path becomes an unstable ridge path. Although the sign of \( \lambda \) again becomes positive at BP2, given sufficient kinetic energy, the reaction system is likely to depart from \( C_{s} \) symmetry in the region around BP1, resulting in vibrational excitation of the out-of-plane vibrational mode. After passing BP2, \( \lambda \) increases to about 0.5 mdyne/Å amu around TS (Fig. 2), and then decreases to zero at product. In the dissociation limit (H\(_2\)+CS), the out-of-plane mode becomes a rotational mode (\( \lambda = 0 \)) of the two fragments relative to each other. When the reaction system proceeds from product to reactant, BP2 is the initial bifurcation point.

Figure 4 shows changes in (a) \( \kappa(s) \) and (b) \( |w(s)| \) along the IRC path. \(^{25}\) Around the reactant region, the IRC path is sharply curved, and the reaction plane also changes sharply. As the reaction proceeds, \( \kappa(s) \) goes through three (sharply curved) maxima at \( s = -1.49, 0.18, \) and 2.11 bohr amu\(^{1/2}\), with an overall downward trend. The value of \( |w(s)| \) is large at the minima in \( \kappa(s) \), i.e., \( s = -0.48, 1.45, \) and 3.00 bohr amu\(^{1/2}\). Therefore, between two minima in \( \kappa(s) \) the reaction plane is stable (almost unchanged), while at a minimum in \( \kappa(s) \), the reaction plane undergoes rapid changes.

FIG. 2. Potential energy \( E \) (solid curve) and eigenvalue of out-of-plane mode \( \lambda \) (dashed curve) as a function of IRC’s, in which \( R \), BP1, BP2, and \( P \) denote reactant (H\(_1\)CS), the first bifurcation point (from \( R \) to TS), the second bifurcation point (from TS to \( R \)), and product (H\(_2\)+CS), respectively. Energy values are given relative to that of reactant.

FIG. 3. Molecular geometries of reactant, BP1, BP2, TS, and products. Bond lengths are in Å, angles in degrees.
This means that in regions of large curvature [corresponding to the peaks in $\kappa(s)$], the two-dimensional plane defined by $\kappa(s)$ and the IRC remains nearly constant.

At the reactant minimum ($s=s_R$), the IRC tangent vector $\mathbf{v}(s)$ converges to the antisymmetric SCH bending mode ($\mathbf{r}_{d}^R$), which has the smallest eigenvalue of the Hessian matrix. As is suggested by molecular structures of $R$ and BP1 in Fig. 3, the CH bond length is retained almost as a constant in many directions in which the energy gradient goes to zero. The fluctuations found in $|\mathbf{w}(s)|$ in the product region reflect the difficulty in locating the reaction path in the dissociation region because there are many directions in which the energy gradient goes to zero.

### B. DRP analysis

Figure 5 shows the changes in (a) the potential energy $E$ and (b) the coordinates $s$, $d$, $\rho$, and $d_d$ as a function of $t$, and (c) $d$, $\rho$, and $d_d$ as a function of $s$ along the DRP, starting from $X_{TS}$ in the $-\mathbf{v}(0)$ direction with KE=0.01 kcal/mol. Recall that $d$ and $d_d$ are the scalar distances from the IRC path and the two-dimensional plane, respectively. Since the trajectory conserves $C_s$ symmetry, it is unaffected by the instability in the out-of-plane ($A^2$) direction. In the first stage ($t<5$ fs), the reaction system stays almost at the TS ($s$ and $d$ are almost constant at 0) since the initial KE is small. Then, the IRC $s(t)$ and the potential energy $E(t)$ start to decrease. The distance from the IRC path, $d(t)$, remains at zero until about 15 fs. Thus, the reaction system proceeds along the IRC path from $t=5$ to 15 fs ($s=0$ to 1 bohr amu$^{1/2}$). The IRC $s(t)$ continues to decrease to $-3.5$ bohr amu$^{1/2}$ at $t=23.4$ fs. At the same time, $E(t)$ continues to decrease to 38.6 kcal mol$^{-1}$ at $t=20.2$ fs, whereupon it starts to increase.

Since the total energy is conserved in the trajectory, the reaction system acquires significant KE [$=E(0)-E(t)$] as the system descends into the reactant well, resulting in a rather energetic molecule.

Since $C_s$ symmetry is conserved, the reaction dynamics may be described in terms of a five-dimensional coordinate space. For instance, it can be analyzed in terms of five in-plane normal modes at the reactant,$^{18}$ or by the reaction coordinate and four in-plane normal modes defined at selected points along the reaction path.$^3$ In the spirit of the reaction path Hamiltonian approach, $d$ may be thought of as the sum of motions in the four bath modes throughout the trajectory.

In the representation of $\mathbf{v}(s)$, $-\mathbf{v}(s)/\kappa(s)$, and the remaining bath modes, $d(t)$ is replaced by $\rho(t)$ and $d_d(t)$. Although distances $d(t)$ and $d_d(t)$ are always positive, $\rho(t)$ may be positive or negative. When the reaction system proceeds along the IRC path, the centrifugal force pushes the system in the negative direction of the curvature vector, resulting in a positive $\rho(t)$. As shown in Fig. 5(c), $\rho(t)$ is almost the same magnitude as $d(t)$, while $d_d(t)$ remains small. Note that $\rho(t)$ is one-dimensional, while $d_d(t)$ results in a two-dimensional coordinate system.

![Figure 4](image-url)  
**FIG. 4.** Plots of (a) the scalar curvature $\kappa(s)$ and (b) the magnitude of $\mathbf{w}(s)$ along the IRC path.

![Figure 5](image-url)  
**FIG. 5.** Changes in (a) the potential energy $E$ and (b) the coordinates $s$, $d$, $\rho$, and $d_d$ as a function of $t$, and (c) $d$, $\rho$, and $d_d$ as a function of $s$ along the DRP, starting from $X_{TS}$ in the $-\mathbf{v}(0)$ direction with KE=0.01 kcal/mol.
from deviations from the path along three directions. While descending from transition state to reactant, the reaction plane changes rapidly at $s = -0.48 \, \text{bohr amu}^{1/2}$ [see Fig. 4(b)]. Until that point, the small initial velocity permits the reaction system to proceed along the IRC path in spite of the curvature. When the reaction system enters the region $s = -0.5 - 3.2 \, \text{bohr amu}^{1/2}$, the increasing velocity allows the system to deviate significantly from the IRC path in the direction of $-\mathbf{v}(1)(s)$. Near the reactant, $p(t)$ and $d_d(t)$ undergo rapid changes due to changes in the reaction plane as the system approaches a stationary point (minimum on the PES), and the path becomes coincident with the appropriate Hessian eigenvector.

Figure 6 shows changes in (a) the potential energy $E$ and (b) the coordinates $s$, $d$, $\rho$, and $d_d$ as a function of $t$, (c) $d$, $\rho$, and $d_d$ as a function of $s$, and (d) the out-of-plane coordinate $z$ of each atom as a function of $t$ along the DRP, starting from $X_{TS}^0 + Q_{6,0}^S$, in the $-\mathbf{v}(0)$ direction with KE=0.01 kcal/mol. Motion in the out-of-plane $z$ direction corresponds to deformation of the reaction system from $C_s$ to $C_1$ symmetry. The $E(t)$, $s(t)$, and $\rho(t)$ profiles are qualitatively similar to those in Fig. 5. The only difference is that they begin to decrease about 2 fs earlier, because of the initial force acting on the atoms in the out-of-plane direction. The distance from the IRC path, $d(t)$, is initially $0.367 \, \text{bohr amu}^{1/2}$ ($= Q_{6,0}^S$). This distance decreases almost to zero in the first 10 fs, so the reaction system returns to nearly $C_s$ symmetry and the IRC path. Of course, $d(t)$ has contributions from $A''$ and $A'$ (in plane) components. The $A''$ motion is shown for each atom in Fig. 6(d). At $t = 10$ fs, all atoms cross the symmetry plane. Note that $d(t)\approx d_d(t)$ [i.e., $p(t)\approx 0$] during this first 10 fs. At this stage, the reaction system remains near the transition state as noted above [$s = -0.30 \, \text{bohr amu}^{1/2}$, see Fig. 6(c)]. While all atoms move in the out-of-plane direction in the next 11 fs, the reaction system completes its descent to the reactant region $(s = s_\rho)$, and $d(t)$ smoothly increases to $1.2 \, \text{bohr amu}^{1/2}$. It may be seen by comparing the $d_d(t)$ profile in Fig. 6(c) with that in Fig. 5(c) that the difference between the two profiles is that the former contains contributions from the out-of-plane mode.

Although the reaction system can recognize the bifurcation and adjust to it in $C_1$ symmetry, it passes over the region between BP1 and BP2 within a very short time (~2 fs). Since the speed in the direction of the IRC is large in comparison with the out-of-plane vibrational motion, the bifurcation effect does not appear to be important in this case. Note that even a stiff vibrational mode has a period of more than 10 fs. If the instability region along the path were larger or the speed along the reaction path were smaller (e.g., if the barrier were small), the reaction system would be more likely to deviate from the path.

Figure 7 depicts changes in (a) the potential energy $E$ and (b) the coordinates $s$, $d$, $\rho$, and $d_d$ as a function of $t$, (c) $d$, $\rho$, and $d_d$ as a function of $s$ along the DRP, starting from $X_{TS}^0$ in the $+\mathbf{v}(0)$ direction with KE=0.01 kcal/mol. The dynamics proceeds in $C_s$ symmetry (in five-dimensional coordinate space), and the excess energy of 61.3 kcal/mol ($=107.9 - 46.6$) is distributed among the translational mode corresponding to the separation of the two fragments (reaction coordinate direction), the in-plane rotational mode and the vibrational mode of each fragment in the dissociation limit ($H_2 + CS$). The potential energy $E(t)$ decreases to 49.0 kcal/mol smoothly at $t = 24.0$ fs, and $s(t)$ continues its monotonic increase. Thus, most of the available energy goes into the relative translational energy of $H_2$ and $CS$.

In comparison with the trajectory from the transition state to reactant, the deviation from the path on the product side is small [compare Fig. 5(b) with Fig. 7(b)], since the IRC curvature is smaller on the product side [see Fig. 4(a)].
This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP:}

Figure 4(b) illustrates that as the system descends from TS to products it enters three distinct regions corresponding to $s = 0$–1.45, 1.45–3.00, and 3.00–4.00 bohr amu$^{1/2}$, respectively. In the first region, $\rho(t)$ continues to increase. Around the boundary between the first and second regions, $\rho(t)$ begins to decrease, and it reaches a minimum at about $s = 1.90$ bohr amu$^{1/2}$. Then, $\rho(t)$ again increases, and its increasing rate becomes large as the reaction proceeds. As the system enters the third region ($s = 3.00$ bohr amu$^{1/2}$), there is a shallow local maximum before $\rho(t)$ continues to increase. These results suggest that the centrifugal force in the $\rho(t)$ direction initially increases its rate of ascent (gradient) as the reaction system moves through one reaction region, and then slows as the boundary between regions is approached. When the system enters the next region, the gradient of $\rho(t)$ suddenly becomes negative because the direction of $\rho(t)$ ($-\mathbf{v}(s(t))$) also changes from the previous reaction region (rate of $\rho(t) = \text{projection of the velocity of the system onto } -\mathbf{v}(s(t))/\kappa(s(t))$). In the next region, the rate of ascent of $\rho(t)$ increases gradually. The $d_d(t)$ profile reflects the behavior of $\rho(t)$.

V. CONCLUSION

In this paper, we propose two methods to represent the DRP based on an IRC reference. In the first method, any point on the DRP is expressed in terms of the IRC and the distance from the IRC path. In the second approach, any DRP point is expressed in terms of the IRC, the curvature coordinate, and the distance from the reaction plane determined by the IRC and IRC curvature vectors. To examine changes in the reaction plane, the vector $\mathbf{w}(s)$ was introduced.

The method was applied to the dissociation reaction of thiophenol. The analysis of $\mathbf{w}(s)$ shows that this reaction path is characterized by four distinct reaction regions. Analyses of DRP’s based on the IRC reference suggest that the centrifugal force makes the reaction system deviate strongly from the IRC path in the direction of $\rho(t)$, with accompanying small deviations in bath vibrational modes while proceeding in one reaction region.

ACKNOWLEDGMENTS

T.T. thanks the Japanese Society for the Promotion of Science (JSPS) for postdoctoral fellowship support. This work was supported in part by grants from the National Science Foundation Grant No. CHE-9313717 and the Air Force Office of Scientific Research Grant No. F49620-95-1-0077. The calculations described here were performed on IBM RS 6000 work stations generously provided by Iowa State University and an IBM SP2 obtained from an NSF-ISU matching grant.

APPENDIX

Using representations based on the IRC reference, the DRP $\mathbf{X}_{DRP}(t)$ ($0 \leq t \leq t_{MAX}$) is expressed in terms of $[s(\mathbf{X}_{DRP}(t))], d(\mathbf{X}_{DRP}(t))$ or $[s(\mathbf{X}_{DRP}(t))], \rho(\mathbf{X}_{DRP}(t)), d_d(\mathbf{X}_{DRP}(t))$. To specify these coordinates for $\mathbf{X}_{DRP}(t)$, the two points that are closest to $\mathbf{X}_{DRP}(t_n)$ among previously evaluated points on the IRC path were first determined (denoted as $\mathbf{X}_{IRC}(s_j)$ and $\mathbf{X}_{IRC}(s_{j+1})$) by calculating distances between $\mathbf{X}_{DRP}(t_n)$ and the known points on the IRC path $[\mathbf{X}_{IRC}(s_i), s_R \leq s_i \leq s_P]$ in 3N-dimensional mass-weighted Cartesian coordinate space. By linear interpolation between $\mathbf{X}_{IRC}(s_j)$ and $\mathbf{X}_{IRC}(s_{j+1})$, the point closest to $\mathbf{X}_{DRP}(t_n)$ on the IRC path (i.e., $\mathbf{X}_{IRC} [s(\mathbf{X}_{DRP}(t_n))]$) can be expressed as

$$\mathbf{X}_{IRC} [s(\mathbf{X}_{DRP}(t_n))] = \frac{s_{j+1} - s(\mathbf{X}_{DRP}(t_n))}{s_{j+1} - s_j} \mathbf{X}_{IRC}(s_j) + \frac{s(\mathbf{X}_{DRP}(t_n)) - s_j}{s_{j+1} - s_j} \mathbf{X}_{IRC}(s_{j+1}) \text{.}$$

(A1)

Since $\mathbf{D} [\mathbf{X}_{DRP}(t_n)]$ and $\mathbf{v} [s(\mathbf{X}_{DRP}(t_n))]$ are orthogonal to each other,

$$\langle [\mathbf{X}_{DRP}(t_n) - \mathbf{X}_{IRC} [s(\mathbf{X}_{DRP}(t_n))] \rangle \cdot [\mathbf{X}_{IRC}(s_{j+1}) - \mathbf{X}_{IRC}(s_j)] \rangle = 0 \text{.}$$

(A2)

Substituting Eq. (A1) into Eq. (A2), $s(\mathbf{X}_{DRP}(t_n))$ can be determined as...
$s[X_{\text{DRP}}(t_n)] = \frac{1}{(s_{j+1}-s_j)^2} \sum_{j=1}^{3N} \left[ X_{\text{IRC}}(s_{j+1}) - X_{\text{IRC}}(s_j) \right]$

$\times \left[ (X_{\text{DRP}}(t_n) - X_{\text{IRC}}(s_j))s_j + (X_{\text{IRC}}(s_j) - X_{\text{DRP}}(t_n))s_j \right]. \quad (A3)$

Here, we used the relation, $s_{j+1} - s_j = [X_{\text{IRC}}(s_{j+1}) - X_{\text{IRC}}(s_j)]$. From Eqs. (4), (A1), and (A3), $X_{\text{IRC}}(s_j)$ and $d[X_{\text{DRP}}(t_n)]$ are determined. The curvature vector $v_{\text{IRC}}(s_j)$ can be determined by linear interpolation. Then, using Eqs. (3), (6), (7), and (8), $\beta[X_{\text{DRP}}(t_n)]$, $D_d[X_{\text{DRP}}(t_n)]$, and $d_d[X_{\text{DRP}}(t_n)]$ can be determined.


9. Truhlar and co-workers have discussed the dependence of harmonic reaction-path frequencies on coordinate choice. They showed that curvilinear valence coordinates often eliminate the imaginary frequency (leading to bifurcations) which appears in the Cartesian coordinates. G. A. Natanson, B. C. Garrett, T. N. Truong, T. Joseph, and D. G. Truhlar, J. Chem. Phys. 94, 7875 (1991); C. F. Jackels, Z. Gu, and D. G. Truhlar, ibid. 102, 3188 (1995).


21. It may happen that there are two points on the IRC path that are the same distance from X in high curvature regions. Thus, it is possible that the coordinate s(X) changes discontinuously in high curvature regions in a trajectory calculation. This definition loses its validity for large distances from the IRC path.

22. Miller et al. discussed intramolecular H atom transfer in malonaldehyde using a reaction surface Hamiltonian in which the reaction is described in terms of two reaction coordinate-like degrees of freedom that can undergo arbitrarily large amplitude motion (selected by chemical intuition) and 3N−8 degrees of freedom as bath modes; T. Carrington, Jr. and W. H. Miller, J. Chem. Phys. 81, 3942 (1984), 84, 4364 (1986).


24. The IRC path was initiated by displacing the TS geometry along the imaginary mode so that the energy is lowered by 10−6 hartree (resulting in 0.004 37 bohr amu1/2 displacement in both directions).

25. Some points near the TS should deviate from the path, and introduce an instability in $v_{\text{IRC}}(s)$ and $v_{\text{IRC}}(s)$ evaluated by numerical differentiation. Based on the preliminary calculations of the scalar curvature $s(s)$, six points near the TS have been removed.