Intrinsic Reaction Coordinates for the Dissociation and the Isomerization Reactions of Formaldehyde

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Synopsis. Static and dynamic intrinsic reaction coordinates are defined by using the eigenvectors of the force constant matrix, and the simultaneous eigenvectors of the relative kinetic energy and the force constant matrix, respectively. The theory was applied to the dissociation and the isomerization reactions of the formaldehyde molecule. It is shown that the intrinsic reaction coordinate of the dissociation reaction of formaldehyde left from the normal coordinate of the equilibrium formaldehyde with the second lowest wavenumber, the rocking mode of vibration, while that of the isomerization reaction departed from the scissoring mode having the third lowest wavenumber.

The transition state is usually defined as a stationary point, that is, all the first-order differentials are vanishing, and the force constant matrix has only one negative eigenvalue.[1] A unit vector along the direction of the eigenvector with a negative eigenvalue is called the transition vector by McIver and Stanton.[2] Fukui[3] defined the intrinsic reaction coordinate (IRC) as a curve passing through the initial and the transition points and orthogonal to the energy equipotential contour surface. He also proved that at a stationary point, the IRC merges with one of the eigenvectors of the force constant matrix. From these considerations we might infer that the IRC is alternatively defined as a curve along one of the eigenvectors of the force constant matrix with a negative or a small positive eigenvalue, and all the first order differentials along the eigenvectors other than the IRC are null. This statement can also be applicable to the normal coordinate space,[4] where the eigenvectors of the force constant matrix should be replaced by the simultaneous eigenvectors of the relative kinetic energy and the force constant matrix.[5]

The IRC's in ordinary space and in the normal coordinate space may differ, since the transformation matrix is not unitary, nor orthogonal. The former is '*static*' as it lies on an adiabatic potential surface, while the latter is '*dynamic*' as the normal coordinates are the solutions of the classical equations of motion, despite of vibration or 'infinitely slow' motion.[5] However, actual calculations showed that the two IRC's are unexpectedly simillar to each other. This is partially because at each stage corrections were made so that the first order differentials along eigenvectors other than the IRC were zero. To follow the 'dynamic' IRC has some merit; it gives the vibrational mode of the initial state from which the reaction departs, and also the change of vibration wavenumbers during the course of the reaction.

The IRC's of the formaldehyde molecule were treated by normal coordinate analysis using the STO-3G potential surface. Although the potential surface of the formaldehyde molecule has been extensively investigated with the more extended basis sets,[6] we apted to choose the minimal basis set as a consideration of cost and quality.

Now we briefly review the procedure to determine the IRC. At first a normal coordinate analysis is applied to a transition state and the resulting normal coordinates are normalized, as the normal coordinates are usually not normalized. Choosing the transition vector as the IRC vector, we proceed downwards along the IRC at a constant stepwidth. At the next point we repeat the normal coordinate analysis and again normalize the resulting normal coordinates. From these normalized normal coordinates we choose a new IRC vector by calculating the overlaps between these and the IRC vector at the previous point. If necessary, the correction is made so that the first-order differentials along the normal coordinates other than the IRC vector are zero.[5] Thus the steepest-descent requirement of IRC[7] is automatically satisfied. These procedures are repeated until an equilibrium point is attained, where the first-order differential along the IRC vector is zero.

The program was implemented into HONDO76[8] and the calculations were carried out on the HITAC M-240H computer located at Gunma University.

The vibrational wavenumbers of the equilibrium state calculated on the STO-3G potential surface were in the correct order, although the calculated values were generally larger than the observed ones. The numbering of the normal coordinates is in an increasing order of wavenumber, and that of the eigenvectors of the force constant matrix is also in an increasing order of the magnitude of the eigenvalues. The Q_1

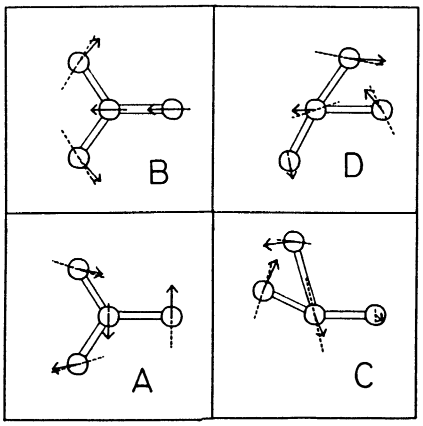

Fig. 1. Normalized normal coordinates and the nearest valleys on the formaldehyde STO-3G potential surface. (A) Q_2 and V_1; (B) Q_3 and V_2 at the equilibrium state; (C) Q_1 and V_1 at the dissociation transition state; (D) Q_1 and V_1 at the isomerization transition state (C_s symmetry).

normal coordinate is an out-of-plane wagging vibration and corresponds to the third eigenvector (V_3) of the force constant matrix, the third 'valley' of the potential energy surface. Q_1 is thus omitted from a candidate of IRC of the dissociation or the isomerization reaction. Q_2 and Q_3 might be chosen as IRC vectors, and are graphically shown in Fig. 1 with the nearest valleys. At this time it is difficult to decide, which normal coordinate, Q_2 or Q_3, lead to the dissociation reaction or the isomerization reaction of the formaldehyde molecule. The dissociation reaction IRC should pass the dissociation transition state,[9] and the isomerization IRC should go through the isomerization transition state.[9]

The transition vectors of the dissociation and the isomerization transition states are also shown in Fig. 1. (Actually using the geometry shown in Fig. 1-D, the formaldehyde molecule on the STO-3G potential surface has two imaginary wavenumbers and may be said to be on a '*hilltop*'. The lowest wavenumber vibration has C_s symmetry while the second one is in an out-of-plane mode. The more elaborate calculations[6] mentioned above gave C_s symmetry for the isomerization transition state of formaldehyde, so we ignored the second imaginary wavenumber vibration and adopted the C_s symmetry transition state.) The mode of the transition vector at the isomerization transition state (Fig. 1,D) is closely related to Q_3 of the equilibrium state (Fig. 1,B), while the correspondence between that of the dissociation transition state (Fig. 1,A) and Q_2 of the equilibrlum state (Fig. 1,C) is not clear.

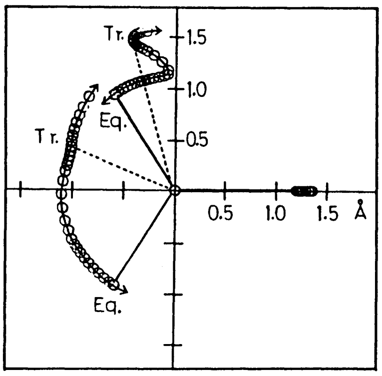

Fig. 2. Dissociation IRC of the formaldehyde on the STO-3G potential surface. The carbon atom is fixed at the origin and the oxygen atom is floating on the abscissa.

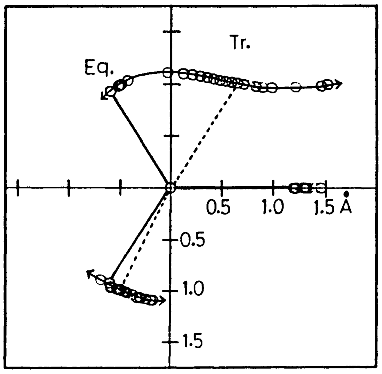

Fig. 3. Isomerization IRC of the formaldehyde on the STO-3G potential surface.

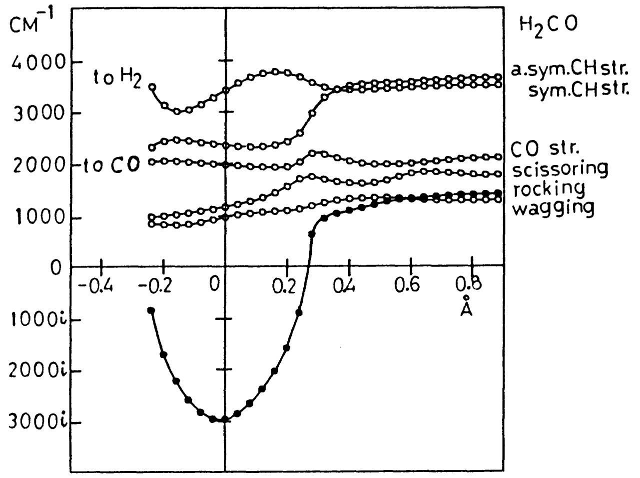

Fig. 4. Variations of vibrational wavenumbers in the course of the dissociation IRC of formaldehyde, calculated on the STO-3G potential surface.

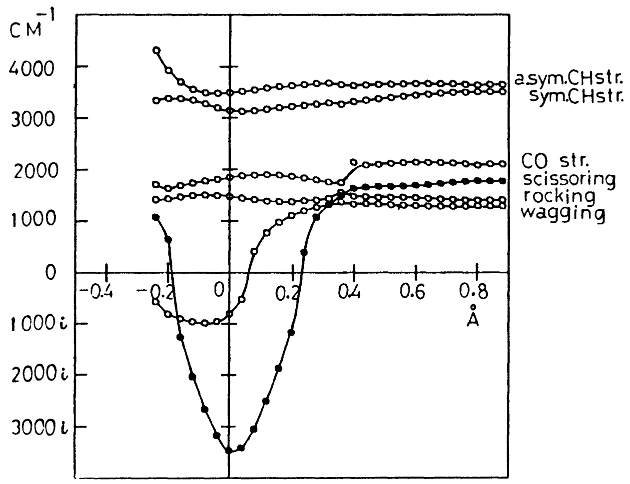

Fig. 5. Variations of vibrational wavenumbers in the course of the isomerization IRC of formaldehyde, calculated on the STO-3G potential surface.

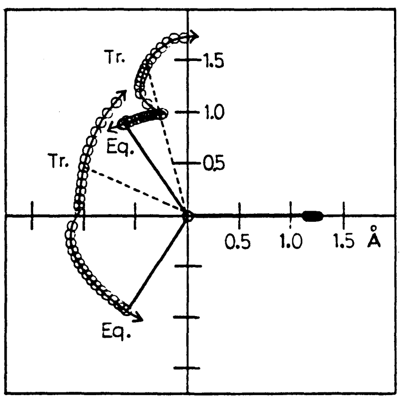

Fig. 6. '*Static*' IRC of the dissociation reaction of formaldehyde, calculated on the STO-3G potential surface.

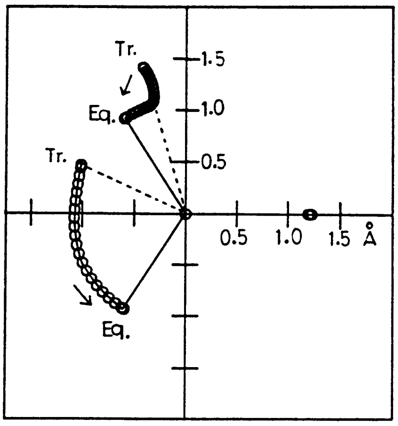

Fig. 7. *'Steepest descent'* IRC of the dissociation reaction of formaldehyde, calculated on the STO-3G potential surface, using the program GAMESS.[10]

The IRC's of the dissociation and the isomerization reactions of the formaldehyde molecule are shown in Figs. 2 and 3. The variations of the wavenumbers during the course of the IRC's are also shown in Figs. 4 and 5. From these figures it can be easily seen that the dissociation IRC and the isomerization IRC tend to the Q_2 (rocking) and the Q_3 (scissoring) mode of the equilibrium formaldehyde molecule, respectively. Finding these, we can follow the IRC's upwards to each transition state by leaving from Q_2 and Q_3, respectively.

The *'static'*, and the *'steepest descent'* IRC's calculated by GAMESS,[10] of the dissociation reaction of formaldehyde are shown in Figs. 6 and 7 for the comparison. Figure 6 resembles to the results by Cerjan and Miller[9] obtained on the adiabatic potential surface. On the other hand, the *'steepest descent'* IRC cannot reverse the direction, the uphill side from the equilibrium to the transition state.

In conclusion, the dissocation IRC of formaldehyde reaches the Q_2 normal coordinate (the rocking mode) at the equilibrium state, and the isomerization IRC leads to the Q_3 normal coordinate (the scissoring mode), respectlvely. The rocking and scissoring vibrations may be said to be 'key vibrations' of the dissociation and the isomerization reactions of equillbrium formaldehyde, in a sense recently described by Fuke et al.[11]

References

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