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Determination of the Intrinsic Reaction Coordinate in the $2H+O(^1D)$ System Near the Equilibrium H_2O

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Synopsis. A normal coordinate analysis was applied to the $2H+O(^1D)$ three atomic system, using the Schinke-Lester analytic expression for the adiabatic potential energy. Defining the reaction coordinates as the "infinitely slow motion trajectories," the reaction coordinate of the heavy oxygen atom was calculated easily, while that of the light hydrogen atom was obtained with some difficulty. Several repeated corrections were needed to converge the reaction coordinates to the "intrinsic" reaction coordinate. The intrinsic reaction coordinate of a hydogen atom to the uphill side of H_2O was found to be very difficult to follow. This fact might help to explain the low frequency factor of the decomposition reaction of H_2O.

A chemical reaction arises from a relative motion of nuclei in a system composed of atoms. When the adiabatic potential energy surface of the system is extensively calculated by quantum mechanics, determination of the reaction coordinates turn into a problem of classical mechanics. In a preceding paper,[1] we have defined the reaction coordinates as the infinitely slow motion trajectory,[2] and proved the reaction coordinates to coincide with the normal coordinates.[3] The HNC-to-HCN isomerization reaction was treated by normal coordinate analysis using the STO-3G potential surface, and the intrinsic reaction coordinate[4] was easily calculated. As might be expected, the extension of this work to the reaction of H_2CO was not so easy as the case of HNC. In this paper we treat the $2H+O(^1D)$ three atomic system. For this system contour maps of the potential energy surface could be drawn and the reaction coordinates could be shown explicitly. Schinke and Lester[5] fitted the extensive first-order configuration interaction energies of Howard et al.[6] with an analytic expression, and carried out trajectory calculations.

At first we briefly review the normal coordinate analysis of reaction coordinates. The potential energy V of a system can be expanded in a Taylor series in terms of the normal coordinates Q_i,

$$V = V_0 + \sum_i g_i Q_i + \frac{1}{2}\sum_i \lambda_i Q_i^2, \tag{1}$$

where the expansion is truncated to the second-order. The Lagrange equations of motion are set up and solved by assuming the infinitely slow motions of nuclei. The solutions are given by

$$Q_i = -\tau^2 g_i/(1+\tau^2\lambda_i), \quad (i = 1, 2, \cdots, f) \tag{2}$$

where τ^2 is a constant. Equations 2 imply that the nuclei move along Q_i infinitely slowly, vibrating simple-harmonically along the same Q_i. The magnitude of Q_i is greater the greater the absolute value of g_i and the smaller the absolute value of λ_i. In an equilibrium state the first-order gradients g_i and the reaction coordinates Q_i are all vanishing. The first-order gradients are, however, not always vanishing in any non-equilibrium states and a few or several reaction coordinates are possible. If one of the non-zero reaction coordinates is chosen to be the "intrinsic," the other reaction coordinates should be corrected to zero. The corrections can be easily calculated to

$$d_i = -g_i/\lambda_i, \quad (i = 1, 2, \cdots, f) \tag{3}$$

Equations 3 are consequences of Eq. 1. Once the corrections are made by Eqs. 3, the intrinsic reaction coordinate can be followed step by step uphill or downhill by taking care of the sign of the gradient along the intrinsic reaction coordinate.

If $O(^1D)$ aproaches the H_2 molecule colinearly, a small barrier of about 1 kcal mol^{-1} (1 cal=4.184 J) is found at O-H distance about 1.8 Å, as described by Schinke and Lester.[5] Passing through the barrier, the H-H distance increases rapidly and an equilibrium state is attained. In the equilibrium state, the geometry of R(OH)=0.99 Å and R(HH)=2.86 Å is calculated. The Van der Waals complex has three vibrational modes. ν_1=206 cm^{-1} (doubly degenerate), ν_2=396 cm^{-1}, and ν_3=3737 cm^{-1} (the vibrational modes are numbered in an increasing order of wavenumber for convenience sake.) We decided to set up this state as a starting point.

The ν_3 mode is the OH stretching, and the ν_2 mode is an H $\cdots$ HO vibration. The motion along Q_2 leads to a further separation of H $\cdots$ H or backwards to the H_2+O state. The lowest wavenumber mode is a bending one, along which one is led to a saddle point and further to the equilibrium state of H_2O. The normal coordinate Q_1 is then chosen as the "intrinsic" reaction coordinate of this system. To ascend the potential energy valley to the saddle point, a constant step width (0.05 Å) was used in spite of Eqs. 2. Corrections expressed by Eqs. 3 were made at each step. These movements are illustrated graphically in Fig. 1 and Fig. 2. Figure 1 shows the motion of the oxygen nucleus along the "intrinsic" reaction coordinate, which is plotted in a potential energy contour map. One of the hydrogen atoms is fixed at the origin and the other is floating on the left side of the abscissa. The oxygen atom goes round the hydrogen atom at the origin and no irregularities occur. The saddle point is located at R(OH)=0.99 Å, R(OH′)=3.22 Å, and ∠HOH′=50.0°, and the energy is 1.8 kcal mol^{-1} above the H $\cdots$ HO or 112.0 kcal mol^{-1} above the H_2O states. The valley of the potential energy surface is well-defined in Fig. 1.

On the other hand, Fig. 2 shows the motion of one hydrogen nucleus plotted in a contour map, in which the oxygen atom is fixed at the origin and the second hydrogen atom is slightly floating on the right side of

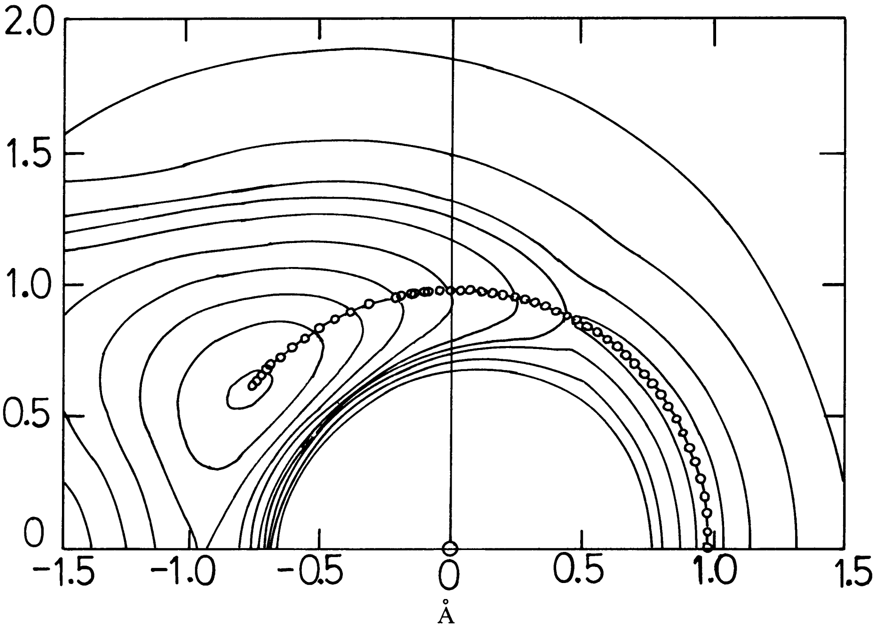

Fig. 1. Contour map of O-motion in the 2H+O(^{1}D) system near the equilibrium H_2O, using the Schinke-Lester analytical expression of energy. One hydrogen atom is located at the origin and the other is floating on the left side of the abscissa. The energies are 2, 20, 40, 60, 80, 100, 112, 120, 140, and 160 kcal mol^{-1} above the equilibrium H_2O. The points denoted by —O— are the calculated intrinsic reaction trajectories of the oxygen atom.

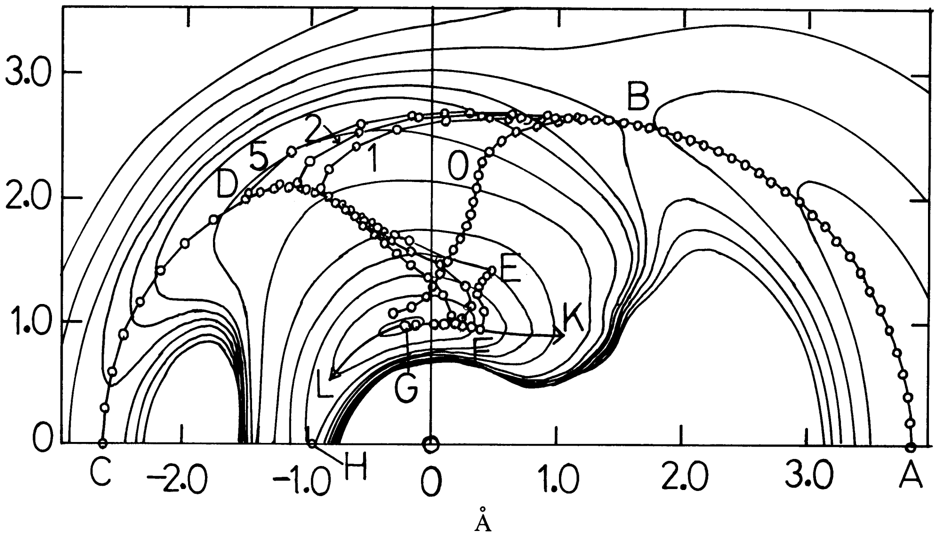

Fig. 2. Contour map of H-motion in the 2H+O(^{1}D) system near the equilibrium H_2O, using the Schinke-Lester analytical expression of energy. The oxygen atom is fixed at the origin and the second hydrogen atom is slightly floating on the right side of the abscissa. The energies are 2, 20, 40, 60, 80, 100, 107, 110, 111, 112, 113, 114, and 115 kcal mol^{-1} above the equilibrium H_2O. The points denoted by —O— are the calculated reaction trajectories of the hydrogen atom.

the abscissa. The intrinsic reaction trajectory of the hydrogen atom is well-defined from the H···HO equilibrium state (denoted by A in the figure) to the saddle point (denoted by B). Passing through the saddle point, the points become scattered. This results from the fact that the corrections given by Eqs. 3 become large and several repeated applications of Eqs. 3 are required. A few of these calculations are also plotted in Fig. 2. The points denoted by 0 describe the calculations with no correction, the points denoted by 1 the calculations with up to one correction at each cycle, and so on. The curve 0 means a "least-motion"

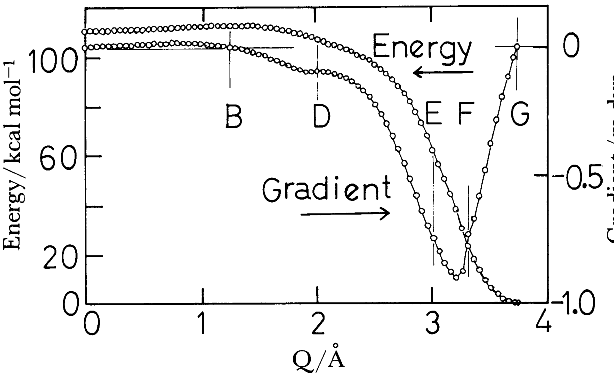

Fig. 3. Variations of the potential energy and the gradient along the intrinsic reaction coordinate of the 2H+O(^{1}D) system near the equilibrium H_2O. The point where the gradient is vanishing corresponds to the saddle point.

reaction coordinate. It closely resembles to the "steepest-descent" reaction coordinate, as can be seen from the figure. Once corrections are made, the curves are remote from the "least-motion" reaction coordinate. With up to fivefold correction iteration, the curves converge to the "intrinsic" reaction coordinate. The points C to D denote the descending pathway from a saddle point expressed as H ··· O-H (the point C in Fig. 2). The intrinsic reaction coordinate merges in the descending pathway at the point D. Descending the potential energy valley, the curve turns at E and F. The curve F-G is along the bending mode of the vibrations of the equilibrium H_2O.

The reason for this complicated behavior of the hydrogen atom is not yet clear. It is difficult to reverse the intrinsic reaction coordinate from the equilibrium H_2O to the H ··· H-O state. The equilibrium H_2O state is calculated to have three vibrational modes, a doubly degenerate bending (ν_1=1568 cm^{-1}), a symmetrical stretching (ν_2=3527 cm^{-1}),and an antisymmetric stretching (ν_3=4037 cm^{-1}) vibrations. If one follows the lowest wavenumber mode Q_1, it leads to the direction of K or L in Fig. 2, which results in the inversion of H_2O. The C_{2v} symmetry of equilibrium H_2O is retained in the inversion pathway. To ascend the "intrinsic" reaction coordinate, one should move along Q_3 (the antisymmetric stretching mode) at the point F. Then the path turns at the point E, and at the point D. Although the intrinsic reaction coordinate does not correspond to any actual trajectory, it is considered to give a path along which many actual trajectories, especially those of low energy, are likely to travel.[4] These facts might be helpful to explain the low frequency factor of the decomposition reaction of H_2O.

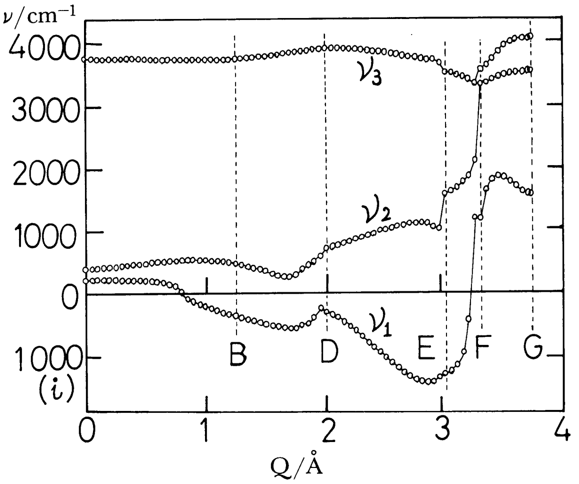

Fig. 4. Variations of the vibrational wavenumber along the intrinsic reaction coordinate of the 2H+O(^{1}D) system near the equilibrium H_2O. The points were calculated on the Schinke-Lester analytical expression of the potential energy surface.

Despite the complexity of the H-motion, energies and gradients along the intrinsic reaction coordinate vary smoothly, as is seen in Fig. 3. Variations of the vibratinal wavenumber along the pathway were, however, remarkable as is shown in Fig. 4. The saddle point was of little significance in this case. Discontinuous changes of wavenumber occur at points D,E, and F, where the hydrogen atom comes in another valley on the potential surface. Again, the wavenumbers along the reaction coordinate were imaginary over a wide range of the reaction process.

In conclusion, the determination of an intrinsic reaction coordinate was difficult, especially for the light hydrogen atom. Nevertheless it provides an insight into the detailed mechanism of the chemical reactions.

The whole calculations, including the contour mapping, were carried out with a NEC PC-9801 personal computer in our laboratory.

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