A Molecular Mechanical Calculation along the Intrinsic Reaction Coordinate

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Synopsis. A normal coordinate analysis was applied to nonequilibrium states composed of atoms. A normal coordinate, Q_k, can be the intrinsic reaction coordinate if, and only if, all the first-order differentials have vanished except the k-th one. The HNC-to-HCN isomerization reaction was treated with the *ab initio* STO-3G potential surface: we thus observed several interesting features.

Molecular mechanical calculations usually utilize empirical expressions of the potential energy, which approximate near the equilibrium state of atoms in the system. The adiabatic potential energy surface can now be calculated at the *ab initio* SCF or a more elaborate level over a wide range of nonequilibrium states. The extension of the molecular mechanical calculation to nonequilibrium states or to the "reaction coordinates" is desirable. This paper concerns this extension by means of *ab initio* STO-3G SCF calculations with standard parameters.[1]

The relative kinetic energy[2] of an N atomic system can be calculated from the total kinetic energy minus the translational energy of, and the rotational energy around, the center of gravity:

$$T = T^{\mathrm{tot}} - T^{\mathrm{trans}} - T^{\mathrm{rot}} = \frac{1}{2}\sum_{i,j=1}^{3N} T_{ij}\dot{q}_i\dot{q}_j, \tag{1}$$

and the potential energy is approximated by the Taylor expansion to the second order:

$$V = V_0 + \sum_{i=1}^{3N} d_i q_i + \frac{1}{2}\sum_{i,j=1}^{3N} F_{ij}q_iq_j, \tag{2}$$

$$d_i = \frac{\partial V}{\partial q_i}, \qquad F_{ij} = \frac{\partial^2 V}{\partial q_i \partial q_j}.$$

As is well-known, Eqs. 1 and 2 can be transformed simply, by the introduction of a normal coordinate,[3] Q, to:

$$T = \frac{1}{2}\sum_{i=1}^{f} \dot{Q}_i^2, \tag{3}$$

$$V = V_0 + \sum_{i=1}^{f} g_i q_i + \frac{1}{2}\sum_{i=1}^{f} \lambda_i Q_i^2, \tag{4}$$

so that the Lagrange equations of motion are given by:

$$\frac{d^2Q}{dt^2} + g_i + \lambda_i Q_i = 0, \quad i = 1,2,\cdots\cdots,f. \tag{5}$$

The ordinary solution of Eq. 5 involves the simple harmonic motion around the center, $-g_i/\lambda_i$, and ν_i, the frequency:

$$Q_i = A\sin(2\pi\nu_i t+\alpha) - g_i/\lambda_i, \quad \nu_i = \frac{1}{2\pi}\sqrt{\lambda_i}, \tag{6}$$

where A and α are determined from the initial conditions. The simple harmonic motion is generally thought to be a very fast motion of the nuclei. However, if we assume an infinitely slow motion[4] of the nuclei as the initial condition, the solutions are quite different from Eq. 6:

$$\frac{Q_i}{(g_i+\lambda_i Q_i)} = -\tau^2 = const.,$$

or:

$$Q_i = \frac{-\tau^2 g_i}{(1+\tau^2\lambda_i)}. \tag{7}$$

Thus, the normal coordinates are the solutions of the infinitely slow motion, *i.e.*, the "trajectories." If, and only if, all the gradients, g_i's, except one, say g_k, are zero, the nonvanishing trajectory is given by Q_k. This is the necessary and sufficient condition of the so-called "intrinsic reaction coordinate," previously defined by Fukui.[5]

The present normal coordinate analysis was applied to the HNC-to-HCN isomerization reaction using the *ab initio* STO-3G potential surface. The intrinsic reaction coordinate of this system was previously determined by Ishida *et al.*[6] by means of the gradient method: it was also treated by Cerjan and Miller[7] by making explicit use of the second-order derivatives of the potential energy surface. The equilibrium state of HNC has three vibrational modes, a NH-stretching vibration (4224 cm^{-1}), a CH-stretching vibration (2410 cm^{-1}), and a doubly-degenerate HNC bending vibration (758 cm^{-1}). All the reaction coordinates are, of course, zero. If the curvature of the potential energy surface is small enough for nuclei to reach far from the equilibrium position at a small excess vibrational energy, a chemical reaction will take place. Therefore, the initial step was taken along the lowest frequency vibration, the HNC bending. The step size was 0.2 Å. Departing from the equilibrium state, none of the gradients vanish, and no unique reaction coordinate is found. The distance to the bottom of a valley of the potential energy surface is found to be:

$$d_i = -g_i/\lambda_i, \tag{8}$$

d_3, corresponding to ν_3, being the largest in absolute value. Moving towards the bottom of valleys along ν_1 and ν_2, g_1 and g_2 become zero and the nonvanishing reaction coordinate remains Q_3.

The second step is to "walk uphill" along the reaction coordinate Q_3, taking care of the sign of the gradient. The process was repeated until the saddle point was reached, where the gradient along the reaction coordinate was zero. Then the reaction coordinate turned to "walk downhill" to the point of the HCN equilibrium. The whole process is

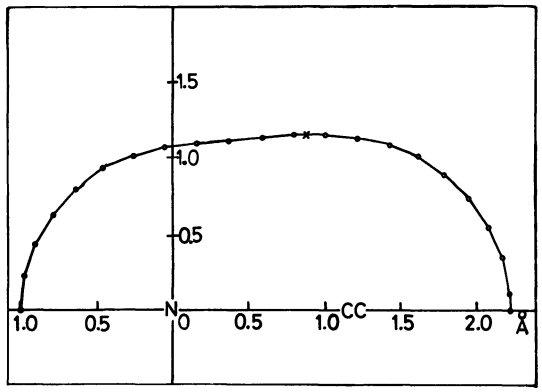

Fig. 1. The intrinsic reaction coordinate of H atom in the HNC-HCN isomerization reaction. The points denoted by —○— were calculated at the *ab initio* STO-3G potential surface and the solid lines connected these points. The symbol —⨯— is the saddle point. The N atom, denoted by N, is fixed at the origin and the C atom, denoted by C, moves slightly on the abscissa.

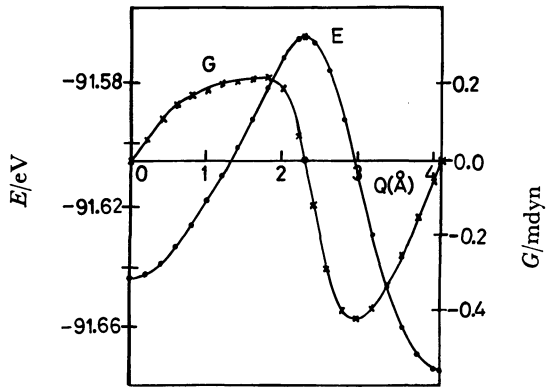

Fig. 2. The potential energy and the gradient curve along the intrinsic reaction coordinate of HNC-HCN reaction. The points denoted by —●— and —⨯— were calculated on the STO-3G potential surface. The point where the gradient is vanishing corresponds to the saddle point.

demonstrated graphically in Figs. 1 and 2, which completely reproduce those given by Ishida *et al.*[6]

More interesting features are seen in the variations of vibrational frequencies with the progress of the chemical reaction (Fig. 3). The frequency along the reaction coordinate is imaginary over a rather wide range. (The scattering of points is probably due to

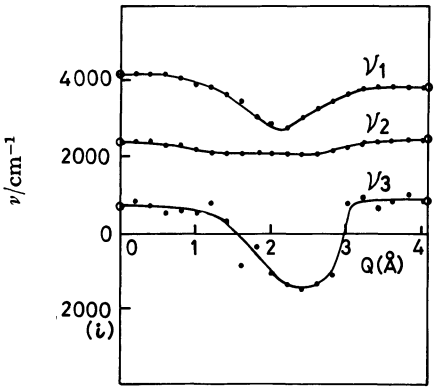

Fig. 3. The variation of the vibrational frequencies along the intrinsic reaction coordinate of HNC-HCN reaction. ν_1 corresponds to the NH or the CH stretching, ν_2 to the CN stretching, and ν_3 to the HNC bending vibrations. The points were calculated on the STO-3G potential surface.

errors in the numerical differentiation, as revealed by the lowest eigenvalue.) The CN stretching frequency is fairly constant throughout the whole process, while the NH stretching vibration transforms to the CH stretching vibration in the region of the transition state. These facts seem reasonable from the standpoint of chemistry.

The whole calculation, including the numerical differentiation to the second order, was carried out on the HITAC M-240H computer located at Gunma University. A more efficient program[8] and a more faster computer may facilitate the molecular mechanical analysis of chemical reactions.

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