Chemical Education Journal (CEJ), Vol. 13, No. 1 /Registration No. 13-2/Received July 29, 2009.
URL = http://chem.sci.utsunomiya-u.ac.jp/cejrnlE.html

# Calculation of potential energy in the reaction of "I + $H_2$ → HI + H" and its visualization

IKUO Akira*, NAGASHIMA Hiroshi, YOSHINAGA Yusuke, and OGAWA Haruo

*Department of Chemistry, Tokyo Gakugei University, Tokyo 184-8501, Japan*
*Author for correspondence e-mail: ikuo@u-gakugei.ac.jp

***Keywords:*** Calculation, potential energy, visualization

**Abstract**
Geometries and potential energies (PE) for intermediates of "I-H-H" around the transition state in the reaction of "I + $H_2$ → HI + H" were calculated, and computer graphics (CGs) of PE in two-dimension (2-D) and PE surface in three-dimension (3-D), ball-and-stick model, electrostatic potential on electron density (EPED) of intermediate on the way of the reaction, and the reaction profile were produced. CG animation composed of four CGs was proposed in order to express images of the reaction.

## 1. Introduction

The reaction of simple molecule such as hydrogen halide and related compounds plays a fundamental role in the development of chemical kinetics and theoretical chemistry [1]. Generally, reaction profile is used to represent relationship between potential energies (PE) and reaction coordinate. The profile is often used in high school chemistry textbooks [2]. It is sometimes difficult for learner to realize the meaning of reaction coordinate. Visualization of computer graphics (CG) gives us great help to realize not only images of molecules but also images for dynamical reaction mechanism. Visualization of PE surface in 3-D could clearly provide images of reaction coordinate from the standpoint of subject on energy. A diagram of PE surface in 2-D is often used, and limited number of analogues in 3-D is used in physical chemistry textbook of university [3]. It is our aim to produce computer programs, which provide realizable images of chemical reactions. Recently, the CG animation of esterification of acetic acid and ethyl alcohol based on quantum chemical calculations has been reported [4]. The animation could demonstrate the reaction profile and structural change of the molecules with ball-and–stick model on screen.

The reaction of "I + $H_2$ → HI + H" is often used for explanation of reaction rate and chemical equilibrium in Japanese high school [2d], but the reaction path and the change of PE during reaction are explained by ambiguous expression based on old model [5]. Mechanism of the reaction has been reported that HI formation progressed as following elementary reactions [6].

$$I_2 \rightarrow 2I \qquad \text{(Eq. 1)}$$

$$I + H_2 \rightarrow HI + H \qquad \text{(Eq. 2)}$$

$$H + I \rightarrow HI \qquad \text{(Eq. 3)}$$

We developed the program of the rearrangement of diatomic molecule and one atom by collision. The program provides information concerning changes of PE and realistic image of intermediate in the Eq. 2, which leads to better understanding of reaction profile.

## 2. Procedure

### 2.1 Calculation based on quantum chemistry

The semi-empirical molecular orbital calculation software MOPAC in the CAChe Work System for Windows ver. 6.01 (Fujitsu, Inc.) with PM3 Hamiltonian was used in all of calculations for optimization of geometry by the Eigenvector Following method, for search of potential energies of various geometries of intermediates by use of the program with Optimized map, for search of the reaction path from the reactants to the products via the transition state by calculation of the intrinsic reaction coordinate (IRC) [7]. The electrostatic potential on electron density (EPED) was calculated based on structures from the results of the IRC calculation.

### 2.2 Production of potential surface

Data of potential energies and geometries of intermediates were extracted from the "energy.map" file from the calculation of Optimized map, and these were pasted on the worksheet of Excel 2007 (Microsoft). Potential energy surface in 3-D was drawn by the Excel.

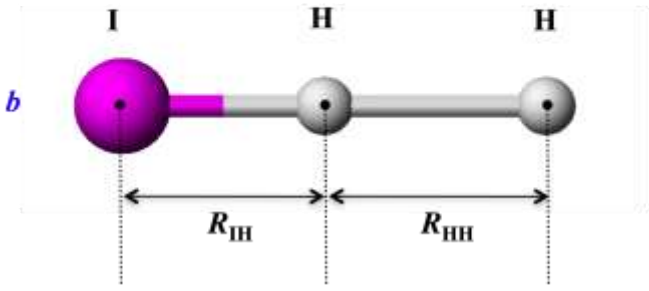
### 2.3 Production of CG software

CG was drawn by the CAChe (Fujitsu, Inc.) and Power point 2007 (Microsoft), and CG animation was produced by the Flash 8 software (Macromedia, Inc.).

## 3. Results and discussion

### 3.1 Potential energy (PE) surface

*a* $\mathrm{I + H_2 \longrightarrow HI + H}$




Scheme 1 Reaction of a) "$\mathrm{I + H_2}$" and
b) image of inter-atomic distance

The reaction images of an attack of iodine atom I to $H_2$ molecule is shown in scheme 1. Bond angle of I-H-H was adjusted to 180 °. Intermediates of I-H-H on the way of the reaction were set for calculation of PEs as follows. Inter-atomic distance of I-H ($R_{IH}$) was changed from 0.50 to 4.00 Å at intervals of 0.05 Å, and that of H-H ($R_{HH}$) was changed from 0.10 to 3.00 Å at intervals of 0.05 Å. PE of each intermediate on the way of the reaction was calculated by MOPAC with PM3 Hamiltonians [8]. PE in two-dimension (2-D) is shown in Figure 1 along with figure legend of color boundaries. Inter-atomic distance of I-H ($R_{IH}$) is drawn as a horizontal axis and that of H-H ($R_{HH}$) is as a vertical axis. The lowest value of PE is there around 4.0 Å of $R_{IH}$ and 0.7 Å of $R_{HH}$, and the secondarily lowest PE is around 1.6 Å of $R_{IH}$ and 3.0 Å of $R_{HH}$. The transition state is located near the point of 1.6 Å of $R_{IH}$ and 1.8 Å of $R_{HH}$. The vibrational analysis of the intermediate was performed by use of the program FORCE in MOPAC. A single absorption peak in the negative region was found at *ca*. -762.34 $cm^{-1}$. The result indicates vibrational mode due to the decrease of potential energy for the direction of only one path *via* a true transition state at the saddle point. The reaction path from the reactants to the products *via* the transition state was searched by the intrinsic reaction coordinate (IRC) calculation [7] in MOPAC. After the calculation, each reaction path from the transition state to the state of the reactants or reaction path from the transition state to the state of the products was searched. Total number of 75 steps means the same number of geometries of intermediates on allover the reaction path were obtained.

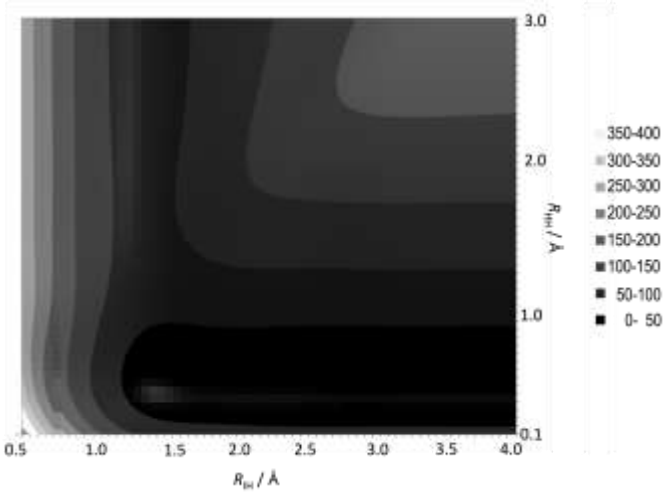



Figure 1 Potential Energy in 2-D

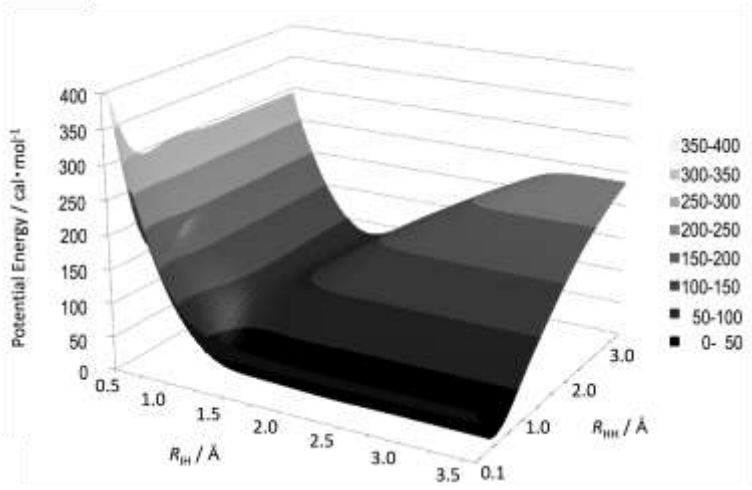



Figure 2 Potential Energy Surface in 3-D

Figure 2 clearly shows these changes of PEs with display on PE surface in 3-D, which offers a bird-eye view of the reaction profile. Two Valleys of lower energies and hilltop on the

transition state at the saddle point can be recognized boldly. Possible pathways of the reaction from the reactants of I and $H_2$ to the products of HI via the transition state at saddle point can be readily traced.

### 3.2 Electrostatic potential in the transition state

The electrostatic potential [9] was calculated based on the coordinates of atoms from the IRC calculation and superimposed on to the iso-surface of the electron density at the value of 0.01 e $Å^{-3}$ as shown in Figure 3. The values of electrostatic potentials were represented in different color on the model of intermediate in the transition state, and figure legend of color boundaries for electrostatic potential was also listed. Distribution of the electrostatic potential among the intermediate can be seen by the colors. For example, both ends of $H_2$ molecule are positively charged with relative value of +0.09 based on evaluation of energy of interactions of prove proton to the charge of iso-surface. The model by EPED provides information about electrostatic distribution of the intermediate with realistic shape on the way of the reaction.

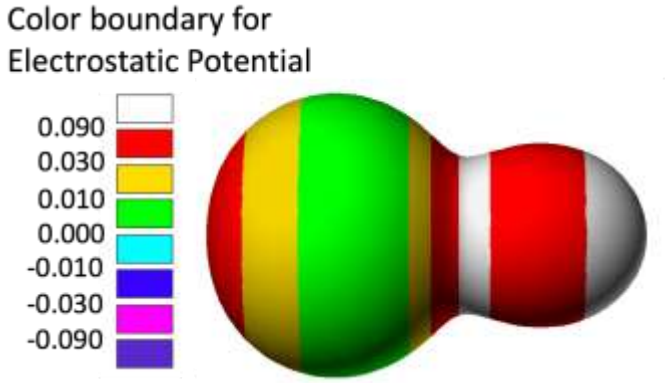



Figure 3 Electrostatic potential on electron density (EPED) of the intermediate

### 3.3 Visualization with CG animation

Four CGs of the PE in 2-D and PE surface in 3-D, ball-and-stick model, electrostatic potential on electron density (EPED) of intermediate, and reaction profile were made and combined in Figure 4. The ball-and-stick model and EPED show skeletal structure of the intermediate and electrostatic potential, correspondingly. The reaction profile demonstrates the degree of the reaction progress by the ball indicating PE *vs.* reaction coordinate. This combined CG is able to provide information about characteristics of intermediate of molecule in a certain state on the progress of reaction simultaneously. The combined CG leads up to pertinent acquisition of dynamical images of the chemical reaction.

CG animation was created by use of combination CGs. The animation demonstrates the changes of electrostatic potential and realistic shape of the intermediate of the reaction on the reaction profile in all stages at the same time. The ball on the reaction profile can move by users' choice of the way of automatic movement or manual movement along the reaction coordinate, which indicates the most probable pathway of chemical reaction according to the IRC theory [7]. The CG animation synchronized with the movement of the ball on the reaction profile by use of the Quick Time control bar so that the degree of the reaction progress and

structural change of the molecules of all stages could be demonstrated simultaneously. The animation provides details of the chemical reaction mechanism dynamically.

The animation could be used in the high school, of course in the university, as a supplement to the figure of reaction profile often found in the subject of "structure and the chemical equilibrium of the material" in the high school chemistry textbook [2] and also in the university textbook [3].

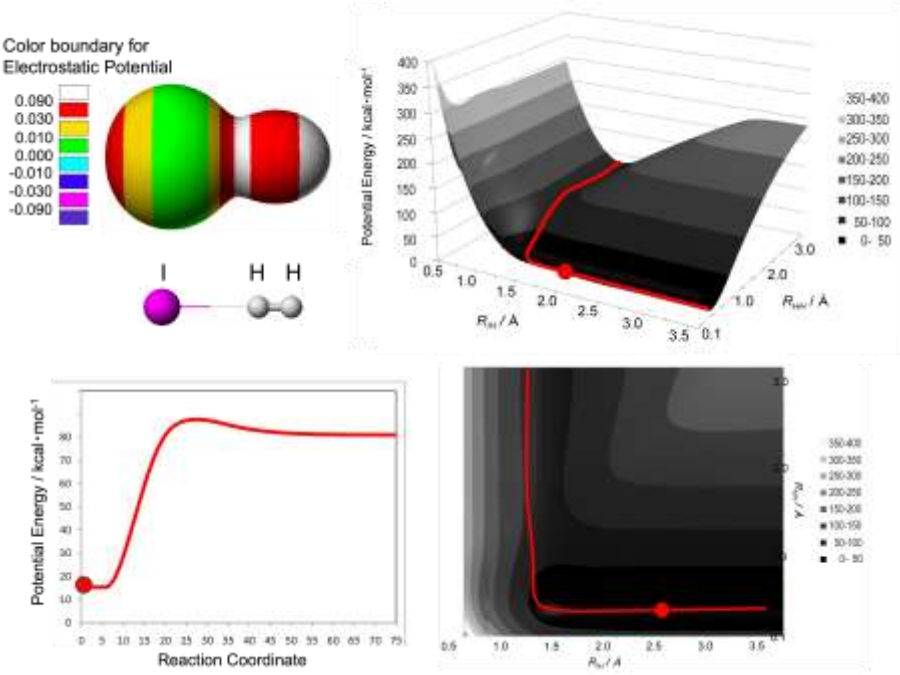



Figure 4　Combination CG

## 4. Conclusion

Geometries and PE for intermediates of "I-H-H" around the transition state in the reaction of "$I + H_2 \rightarrow HI + H$" were calculated. The intermediate on the transition state was formed at the point of $R_{HI}$ of 1.651 Å and $R_{HH}$ of 1.866 Å. This intermediate was supported by the method of IRC. CGs of the PE in 2-D and PE surface in 3-D, ball-and-stick model, electrostatic potential on electron density (EPED) of intermediate, and reaction profile were made and combined. CG animation composed of four CGs was made in order to express images of the reaction. The animation demonstrates the changes of PE and skeletal structure and electrostatic potential of the intermediate on the reaction profile in all stages, simultaneously.

**Reference**

[1] Eyring, H., Polanyi, M., Z. Phys. Chem., **B12**, 279 (1913); Sullivan, J. H., J. Chem. Phys., **46(1)** 73-78 (1967)

[2] Textbooks of "Chemistry II" in Japanese high school: a) Daiichigakusyusya (2004); b) Jikkyosyuppan (2004); c) Keirinkan (2003); d) Sanseido (2004); e) Tokyosyoseki (2004)(all in Japanese) Textbooks were listed in alphabetical order.

[3] For example: Atkins, P, Paula, Y.: ATKINS Physical Chemistry 7th. Ed., pp.966-969, OXFORD UNIVERSITY PRESS (2002); Moor, W. J.: PHYSICAL CHEMISTRY, 4th. Ed., pp. 382-387, Tokyo Kagakudojin (1982) (in Japanese)
[4] Ikuo, A., Ikarashi, Y., Shishido, T. and Ogawa, H., Journal of Science Education in Japan, **30** (4), 210-215 (2006)
[5] M. Bodenstein, Ber., **26**, 2603 (1893).
[6] Sullivan, J. H., J. Chem. Phys., 46 (1) 73-78 (1967)
[7] Fukui, K., J. Phys. Chem., **74**, 4161-4163 (1970)
[8] Stewart, J. J. P., J Comp. Chem., **10**, 209–220 (1989); Stewart, J. J. P., J. Comp. Chem., **10**, 221–264 (1989); Stewart, J. J. P., J. Comp. Chem., **12**, 320–341 (1991)
[9] Kahn, S. D., Pau, C. F., Overman, L. E. and Hehre, W. J., J. Am. Chem. Soc., **108**, 7381-7396 (1986).