Automated Exploration of Global Reaction Route Maps on the Potential Energy Surface

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I. Introduction

It has been believed that systematic exploration of the entire reaction channels on the potential energy surface (PES) is not possible except for very small systems, because uphill tracing along reaction pathways up to transition structures (TS) from an equilibrium structure (EQ) is difficult to be made without intuition [1].

An attempt to explore global reaction route maps in an automatic way has been made by an uphill tracing algorithm noting anharmonic downward distortion (ADD) of the PES [2-4]. The present talk shows how to make a global reaction route mapping on PES automatically and what could be explored by the ADD following, "a compass of the chemical world".

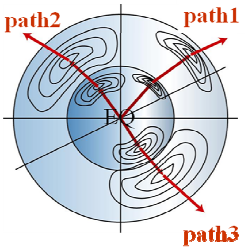

Fig.1 Uphill tracing by ADD following

II. Global reaction route mapping based on ADD following

As shown in Fig.1, use of *Scaled Normal Coordinate*, $q_i = \lambda_i^{1/2} Q_i$, leads to minima on hyperspheres around an EQ, since ADD along reaction pathways give the lower energies with respect to the reference harmonic energies which define isoenergy hypersphere surfaces. Uphill tracing along reaction pathways up to TS can thus become possible. After arriving at TS conventional IRC tracing reaches either another EQ or dissociation channel (DC). Subsequent hypersphere search yields further reaction pathways. Such procedures can be continued to search many EQ and TS one after another and finally to obtain the global reaction route map, as can be seen in Fig.2.

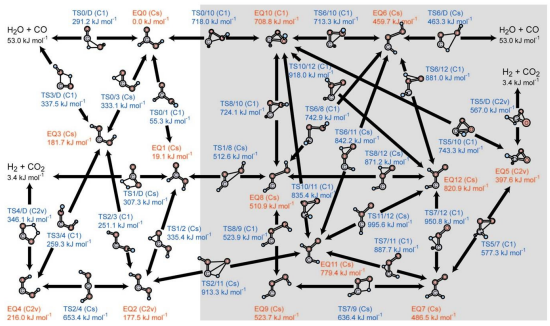
Fig.2 Global reaction route map for H_2CO_2.

III. Automated exploration of unknown chemistry

The ADD following procedures can be performed with no intuition. It follows that unknown chemistry can be discovered by the one-after-another search of the global reaction route map. Lower energy parts of reaction routes can be explored efficiently by a limited search, Automated data processing system further facilitates to analyze new chemistry discovered in the global reaction route map.

[1] Jensen, F. Introduction to Computational Chemistry, **1999** Wiley. [2] Ohno, K.; Maeda, S. *Chem. Phys. Lett.* **2004**, *384*, 277. [3] Maeda, S.; Ohno, K. *J. Phys. Chem. A* **2005**, *109*, 5742. [4] Ohno, K.; Maeda, S. *J. Phys. Chem. A* **2006**, *110*, 8933.