Response to "Comment on 'Analyses of bifurcation of reaction pathways on a global reaction route map: A case study of gold cluster Au$_5$'" [J. Chem. Phys. 143, 177101 (2015)]

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Response to "Comment on 'Analyses of bifurcation of reaction pathways on a global reaction route map: A case study of gold cluster Au₅'" [J. Chem. Phys. 143, 177101 (2015)]

Yu Harabuchi,[1,2] Yuriko Ono,[1] Satoshi Maeda,[1,2] and Tetsuya Taketsugu[1,2,a]
[1]*Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060-0810, Japan*
[2]*CREST, Japan Science and Technology Agency, Tokyo 102-8666, Japan*

Bifurcation is a concept widely used in various fields of science. In chemical kinetics and reaction dynamics, *bifurcation* indicates a phenomena that there are two distinguishable dynamical motions of nuclei, going over a single transition state (TS) on a potential energy surface (PES). In this context, molecular dynamics (MD) is an effective approach to examine dynamical aspect of bifurcating reactions. An occurrence of bifurcation could be confirmed by a detection of branching of trajectories that start from TS to a product-side. The dynamical nature of bifurcation and a branching ratio of the products have been investigated for several chemical reactions by *ab initio* MD simulations.[1–5] Recently, bifurcation becomes one of the interesting topics in organic chemistry;[6,7] it was shown by experiments and MD simulations that a branching ratio in Beckmann rearrangement/fragmentation could be tuned through a modification of the bifurcating pathways by utilizing substitution effects.[8]

In quantum chemistry, the concept of bifurcation of chemical reactions was originally discussed based on potential curvatures in directions orthogonal to the reaction pathway such as intrinsic reaction coordinate (IRC). In the early stage, it was pointed out that geometric feature of the potential could change from a bottom of valley to a top of ridge along the IRC,[9] and the effect of unstable region of the reaction paths was discussed based on model potential surfaces.[10] The concept, *valley-ridge inflection* (VRI), was introduced to represent such a feature of the potential for actual reactions.[11] Quapp introduced a more general definition of the VRI point in multidimensional coordinate space; in this definition, VRI is not necessarily located on the IRC.[12,13] The change of geometric feature from valley to ridge on the IRC was also discussed from a viewpoint of the symmetry of transverse vibrational modes, i.e., non-totally symmetric and totally symmetric modes.[14,15] Because there is no curvature coupling between non-totally symmetric modes and the reaction coordinate, only the totally symmetric modes are affected by a projection procedure of the Hessian matrix.[16] Then, to represent a valley-ridge change in a direction of the totally symmetric vibrational coordinate orthogonal to the IRC, a new concept, *VRT*, was introduced.[17] The difference between VRI and VRT is discussed in a recent review on the IRC.[18]

In our recent paper, we generated a global reaction route map for Au₅ cluster and located all VRT points along the IRCs to understand the reaction path network including bifurcating pathways.[19] To understand the relation of VRT and bifurcation of an ensemble of trajectories, MD simulations are performed with a 2-dimensional Neria, Foscher, Karplus (NFK) potential defined as[20]

$$V(x,y) = C(x^2 + y^2)^2 + xy - 9\exp\left(-(x-3)^2 - y^2\right) - 9\exp\left(-(x+3)^2 - y^2\right), \quad (1)$$

where a parameter C is set to 0.015 (referred to as NFK($C = 0.015$)). Fig. 1(a) shows traces of 100 trajectories starting from a TS region with a constant energy, ΔE, to a product-side ($x \sim 2.5$). As shown in Fig. 1(a), NFK($C = 0.015$) accompanies two minima, referred to as MIN1 (upper one) and MIN2 (below one), and the IRC from TS is connected to MIN1, as indicated by a green arrow. There is a VRT point along the IRC that is verified from potential contour lines. Trajectories clearly show a bifurcating nature that one group goes to MIN1 (in red) while the other goes to MIN2 (in blue). In the comment,[21] Quapp introduced a NFK potential with $C = 0.03$ where MIN2 of NFK($C = 0.015$) changes its nature from minimum to quasi-shoulder (QS) that is located around $(x,y) = (2,-2)$ (Fig. 1(b)); it was claimed that there is a VRT along the IRC but no VRI point in this coordinate space, indicating that there occurs no bifurcation. Then, we performed MD simulations using this NFK($C = 0.03$) potential. The results are shown in Fig. 1(b) where traces of trajectories indicate a branching nature to MIN1 (in red) and to QS (in blue). Actually, all trajectories should lead to MIN1 at the end, but traces of the respective groups show clearly different mechanisms (direct reaching and indirect reaching) from a viewpoint of dynamics, even though there is no VRI point in this 2-dimensional space. In this sense, branching of trajectories could be understood as the occurrence of bifurcation, which can be predicted by appearance of VRT along the IRC. Note that the branching nature of trajectories appears mainly at the diagonal side of the PES wall as mentioned in the previous dynamics study.[22]

Analyzing a finite number of trajectories calculated from a TS to a product-side is one of the useful approaches to

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[a]Author to whom correspondence should be addressed. Electronic mail: take@sci.hokudai.ac.jp
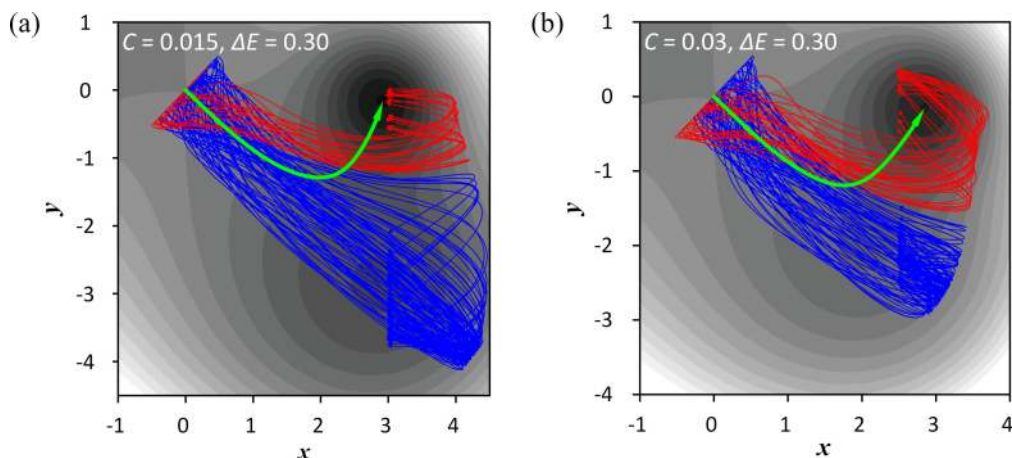
FIG. 1. Traces of 100 trajectories (blue and red) and IRC (green) calculated on (a) NFK($C = 0.015$) and (b) NFK($C = 0.03$) potentials.

examine a bifurcating mechanism of chemical reactions from a dynamical viewpoint. However, the MD simulation requires pre-determination of the initial and terminating conditions of trajectory calculations for individual reactions. On the other hand, location of VRT points along the IRC can be uniquely determined, using a projection technique for Hessian matrices,[16,23] and appearances of VRT points provide information on possible bifurcation of the reaction pathways. Therefore, finding VRT along the IRC is the method of choice to notice the indication of bifurcation in the actual chemical reactions from static analyses of the PES.

[1]T. Taketsugu, T. Yanai, K. Hirao, and M. S. Gordon, J. Mol. Struct.: THEOCHEM **451**, 163 (1998).
[2]H. Yamataka, M. Aida, and M. Dupuis, Chem. Phys. Lett. **300**, 583 (1999).
[3]T. Taketsugu and Y. Kumeda, J. Chem. Phys. **114**, 6973 (2001).
[4]D. A. Singleton, C. Hang, M. J. Szymanski, and E. E. Greenwald, J. Am. Chem. Soc. **125**, 1176 (2003).
[5]J. Li, X. S. Li, S. Shaik, and H. B. Schlegel, J. Phys. Chem. A **108**, 8526 (2004).
[6]D. A. Singleton, C. Hang, M. J. Szymanski, M. P. Meyer, A. G. Leach *et al.*, J. Am. Chem. Soc. **125**, 1319 (2003).
[7]D. H. Ess, S. E. Wheeler, R. G. Iafe, L. Xu, N. Celebi-Olcum *et al.*, Angew. Chem., Int. Ed. **47**, 7592 (2008).
[8]H. Yamataka, M. Sato, H. Hasegawa, and S. C. Ammal, Faraday Discuss. **145**, 327 (2010).
[9]H. Metiu, J. Ross, R. Silbey, and T. F. George, J. Chem. Phys. **61**, 3200 (1974).
[10]P. G. Mezey, Theor. Chim. Acta **54**, 95 (1980).
[11]P. Valtazanos and K. Ruedenberg, Theor. Chim. Acta **69**, 281 (1986).
[12]W. Quapp, J. Mol. Struct. **695**, 95 (2004).
[13]M. Hirsch and W. Quapp, J. Math. Chem. **36**, 307 (2004).
[14]T. Taketsugu and T. Hirano, J. Chem. Phys. **99**, 9806 (1993).
[15]T. Taketsugu and K. Hirao, in *The Transition State: A Theoretical Approach*, edited by T. Fueno (Kodansha-Gordon and Breach Science Publishers, 1999), Sec. 3, p. 45.
[16]Y. Harabuchi and T. Taketsugu, Theor. Chem. Acc. **130**, 305 (2011).
[17]J. M. Bofill and W. Quapp, J. Math. Chem. **51**, 1099 (2013).
[18]S. Maeda, Y. Harabuchi, Y. Ono, T. Taketsugu, and K. Morokuma, Int. J. Quantum Chem. **115**, 258 (2015).
[19]Y. Harabuchi, Y. Ono, S. Maeda, and T. Taketsugu, J. Chem. Phys. **143**, 014301 (2015).
[20]E. Neria, S. Fischer, and M. Karplus, J. Chem. Phys. **105**, 1902 (1996).
[21]W. Quapp, J. Chem. Phys. **143**, 177101 (2015).
[22]P. Collins, B. K. Carpenter, G. S. Ezra, and S. Wiggins, J. Chem. Phys. **139**, 154108 (2013).
[23]J. Baker and P. M. W. Gill, J. Comput. Chem. **9**, 465 (1988).