Collective coordinates and the mechanism for conformational transitions of complex molecules

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Reduction of dimensionality is crucial for the deeper understanding of the mechanism for large-amplitude conformational transitions of complex molecules. By taking up a six-atom cluster as an illustrative example, we present a general methodology to understand conformational transitions of molecules in terms of the low-dimensional dynamics of molecular gyration radii. The dynamics of gyration radii is generally governed by the interplay between the ordinary potential force and a dynamical force called the internal centrifugal force. We show that the internal centrifugal force can be more important than the original potential barrier and gives rise to a new dynamical barrier that truly dominates the conformational transitions of the system. This kind of dynamical effect should be crucially important in a wide class of molecular reaction dynamics.

1 Introduction

Conformational transitions of polyatomic molecules, clusters, and biopolymers are a typical large-amplitude collective motion that involves a large number of degrees of freedom in a coherent manner. Understanding the mechanism for such collective motions is a very important challenge in current molecular science. To achieve this goal, it is crucial to reduce the dimensionality of the dynamics of molecules by extracting small number of collective variables that essentially dominate the dynamics of the whole system. In this paper, we present a general method to understand large-amplitude conformational transitions of molecules in terms of the low-dimensional dynamics of a particular type of collective variables.

As an illustrative example, we focus on the conformational transition dynamics of the six-atom Morse cluster, whose reaction scheme is summarized in Fig. 1 (a). This cluster has two geometrically distinct isomers: One is called OCT (octahedron) and the other is called CTBP (capped trigonal bipyramid). The OCT is highly symmetric and has a deep potential well compared to the CTBP. While the OCT has a spherical mass distribution, the CTBP has an elongated mass distribution. When the total internal energy of the cluster is higher than the saddle point energy, conformational transition (isomerization) is energetically possible. A striking fact is that the cluster prefers to stay in the CTBP at sufficiently high internal energy, even though the potential energy is much lower in the OCT than in the CTBP. Our goal here is to understand effectively the mechanism that makes the system prefer the CTBP at high internal energy by reducing the dimension of the dynamics.

2 Collective coordinates and dynamical reaction barrier

Our approach to systematic reduction of dimension is based on the framework of geometric mechanics [1, 2] and hyperspherical coordinates [3]. In the hyperspherical coordinates, one can express the internal motions of an n-atom system in terms of the three gyration radii and the $(3n - 9)$ hyperangular variables. The three gyration radii, a_1, a_2, and a_3, represent mass distribution along the three instantaneous principal axes of the system. The three gyration radii generally serve as predominant collective variables that essentially dominate large-amplitude motions of the system, while the hyperangular variables act as "bath" modes. This separation of variables into the collective and "bath" modes is based mainly on the following two facts: First, the gyration radii change slowly compared to the hyperangular variables (time scale separation) [4]. Second, the gyration radii need to acquire much more kinetic energy than the hyperangular modes in order for the system to undergo large-amplitude conformational transitions. Thus, as shown in Fig. 1 (b), it is reasonable to focus on the low-dimensional dynamics of gyration radii as an essential part of the high-dimensional dynamics of the whole system.

The equations of motion for the three gyration radii reveal that these collective variables are subject to two different kinds of forces: One is the ordinary potential force and the other is a dynamical force called the internal centrifugal force. The potential force generally works to keep the mass distribution of the system compact and symmetric (symmetry restoring), while the internal centrifugal force works to distort and elongate it (symmetry breaking). Fig. 2 (a) shows the averaged field of the potential force along a reaction path in the three-dimensional space of gyration radii, which is obtained by averaging many reactive trajectories as in Fig. 1 (b). We see that the averaged field of potential force is roughly directed to the regions that correspond to the two minima of the potential energy. Fig. 2 (b) shows the averaged field of the internal centrifugal force

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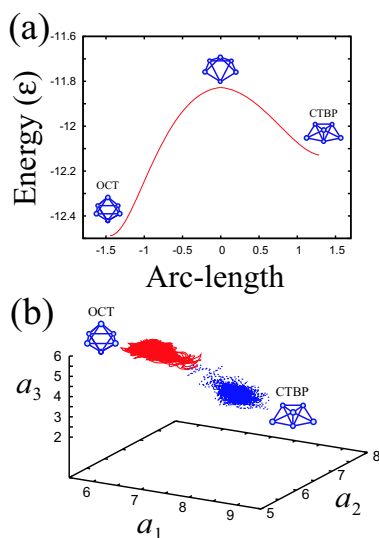
Fig. 1 (a) Potential energy curve of the six-atom Morse cluster along the steepest descent path. The cluster has two geometrically distinct isomers called OCT and CTBP. (b) A typical trajectory projected onto the space of gyration radii. The two trapping regions correspond to the OCT (solid line) and the CTBP (broken line).
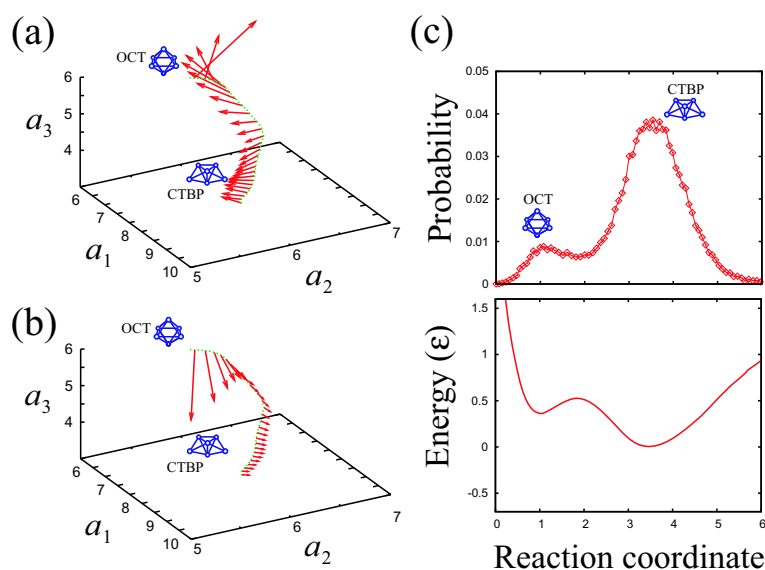

Fig. 2 Averaged field of the potential force [Panel (a)] and that of the internal centrifugal force [Panel (b)] along the reaction path. The upper panel of (c) shows the probability distribution of the system along the reaction path at high energy. The lower panel of (c) represents the corresponding effective energy along the reaction path, which is defined as the line integral of the sum of the averaged force fields in (a) and (b).

along the same reaction path as in Fig. 2 (a). As opposed to the potential force, the internal centrifugal force is strongly unidirectional from the OCT region to the CTBP region in the space of gyration radii. Thus, the internal centrifugal force acts as the critical driving force for the reaction from OCT to CTBP, and as a dynamical barrier for the reaction from CTBP to OCT.

In order to quantify the interplay between the potential force and internal centrifugal force, we computed the line integral of the sum of the averaged fields of these two forces along the path. This integral, which we call effective energy, characterizes actual energetic barrier for the conformation transition. The solid curve in the lower panel of Fig. 2 (c) shows this effective energy at high total energy. We see that even though the OCT has a deep potential well (see Fig. 1 (a)), the OCT is dynamically not very stable, having a shallow well of the effective energy compared to the CTBP. This effective energy explains the fact that the system prefers to be in the CTBP conformation at high energy as mentioned earlier (see the probability distribution in the upper figure of Fig. 2 (c)).

In summary, by focusing on the low-dimensional dynamics of gyration radii, we have clarified the mechanism that governs the large-amplitude conformational transitions of clusters in terms of the interplay between the potential force and the internal centrifugal force. Since the internal centrifugal force is a dynamical force, the effect of this force generally becomes more significant in a higher-energy (or higher-temperature) range. We expect that the competition scheme between the two forces is ubiquitous in a wide class of conformational transitions of molecules including the folding/unfolding transition of biopolymers: In a low energy (or temperature) range, potential forces are generally predominant and molecules tend to be confined to compact and symmetric conformations such as the OCT in our example. On the other hand, in a high energy (or temperature) range, the effect of the internal centrifugal force becomes dominant, and elongated and asymmetric conformations such as the CTBP in our example are generally preferred. The conventional reaction-rate theories heavily rely on the potential energy topography. However, as we have shown here, vibration of molecules itself can induce dynamical forces such as the internal centrifugal force, which can often overshadow the original potential energy topography significantly. Evaluation of this kind of dynamical effect should be crucial for a deeper understanding of the rate processes in molecular reactions.

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