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Mass-Related Dynamical Barriers in Triatomic Reactions*

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Abstract. A methodology is given to determine the effect of different mass distributions for triatomic reactions using the geometry of shape space. Atomic masses are incorporated into the non-Euclidean shape space metric after the separation of rotations. Using the equations of motion in this non-Euclidean shape space, an averaged field of velocity-dependent fictitious forces is determined. This force field, as opposed to the force arising from the potential, dominates branching ratios of isomerization dynamics of a triatomic molecule. This methodology may be useful for qualitative prediction of branching ratios in general triatomic reactions.

1 Introduction

The roles played by atomic masses are of great interest in current chemical physics. Atomic-mass effects will be the most prominent in isotopic reactions such as the breakup dynamics of the triatomic hydrogen ion H_3^+ and its isotopomers, D_2H^+, H_2D^+, and D_3^+ [1]. The anomalous isotope effect in ozone O_3 [2, 3] also provides intriguing problems that are related to the influence of atomic masses. Therefore, a general framework to describe the effect of atomic masses in triatomic reactions should serve many purposes.

Atomic masses are incorporated into the metric tensor of shape space on the basis of reduction theory [4] and gauge theory [5–7] that is used for the separation of rotational degrees of freedom. The metric tensor after reduction is generally non-Euclidean for three- and more-atom systems. As a result, the dynamical effects that have their origin in the non-Euclidean nature of the metric of shape space,

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should be important for understanding the effect of the masses. It should be noted that while the Born-Oppenheimer potential energy surface changes depending on the system, the geometry of shape space is rather intrinsic and independent of the system. Therefore, it is important to study the geometry of shape space of many-body systems.

Its non-Euclidean nature suggests that trajectories in shape space possess a certain directionality, even without the influence of the potential energy surface. This directionality is of importance in branching processes in multi-channel reactions. The behavior of geodesics signals this ''preference'' of motion in shape space. In this article, using suitable coordinates, an averaged field of ''fictitious forces'' is found that accounts for the directionality of geodesics. It is shown that this force field does, in fact, dominate mass-influenced branching ratios of isomerization dynamics of a triatomic molecule.

A prototypical model to study mass-related branching ratios of isomerization reactions is presented in Sect. 2, and Sect. 3 gives a theoretical explanation for the branching ratios via the geometry of shape space.

2 Model Reactions and Branching Ratios

This section investigates the isomerization dynamics of a molecular cluster composed of three atoms with different masses $(m_1, m_2, m_3) = (1, 1, 0.1)$ with the aim of determining the effects of the values of the masses. The total angular momentum of the system is taken to be zero for simplicity. The three atoms interact equally through a pairwise Morse potential. Because of the mass difference, this system is called a ''modified'' M_3 cluster. The dimensionless Hamiltonian of the system is given by

$$\frac{\mathcal{H}}{\varepsilon} = \frac{1}{2}m_1\dot{\boldsymbol{r}}_1^2 + \frac{1}{2}m_2\dot{\boldsymbol{r}}_2^2 + \frac{1}{2}m_3\dot{\boldsymbol{r}}_3^2 + \sum_{i<j}\{\exp[-2(d_{ij}-6)] - 2\exp[-(d_{ij}-6)]\}, \quad (1)$$

where $\boldsymbol{r}_i = (r_{ix}, r_{iy}, r_{iz})^T (i = 1, 2, 3)$ is the three-dimensional position vector of each atom. Here, ε represents the depth of the Morse potential and d_{ij} is the inter-particle distance between the i-th and j-th atoms. In what follows, our numerical results are presented in absolute units.

As shown in Fig. 1a, this cluster has two local equilibrium structures (isomers) whose potential energy is $V = -3.00\varepsilon$. These are equilateral triangle and permutationally distinct since motion of the system is confined to a plane because of the assumption of zero total angular momentum. The system has three saddle points with potential energy $V \approx -2.005\varepsilon$, which correspond to collinear configurations. They are also permutationally distinct. Channels 1 and 2 are essentially equivalent and only Channel 3 is different from the other two. The potential-barrier heights for these three channels are exactly the same since the three particles interact equally through the pairwise Morse potential. The difference lies in the effect that different masses have on the dynamics of the isomerization reactions.

Fig. 1b shows the energy dependence of the relative reaction frequencies for the respective channels. In this numerical experiment, the frequencies of reactions

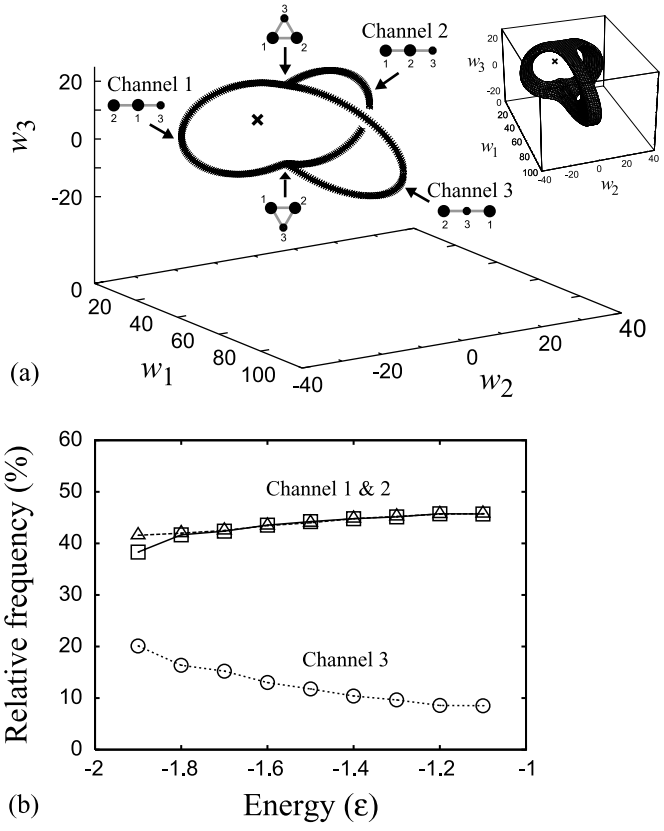


Fig. 1. a: Two equilibrium configurations and three saddle configurations of the modified M_3 cluster. The curves are the steepest descent paths of the potential energy. The two equilibrium points are located at $(w_1, w_2, w_3) = (15.429, 0, \pm 13.607)$. The saddle point for Channel 1 is at (10.277, −23.548, 0) while that for Channel 2 is located at (10.277, 23.548, 0). The saddle point for Channel 3 is at (71.939, 0, 0). Inset is the equi-potential surface at $V = -1.4\varepsilon$. **b**: Energy dependence of the relative reaction frequency for each channel

through respective channels are counted and normalized to 100. To avoid overcounting reactions due to recrossing, only the event in which the system leaves the vicinity of one of the equilibrium points and arrives at the vicinity of the other equilibrium point is counted. It is evident from Fig. 1b that the reaction through Channel 3 is much less frequent than those through Channels 1 and 2. In other words, the system prefers the reaction through heavy-heavy-light configurations rather than heavy-light-heavy configurations. Furthermore, this tendency is observed to become more prominent as the energy of the system increases. The bias in the reaction frequency in Fig. 1b cannot be explained simply by the potential energy barrier height since the barrier heights for the three channels are the same. Instead, the bias must be related to the mass. In the next section, a possible explanation for this mass effect is given.

3 Geometry of Shape Space and Dynamical Barriers

A useful coordinate system for characterization of mass effect in triatomic reactions is the so-called "symmetrical coordinates" [6, 7], which is defined as follows. First, the mass-weighted Jacobi vectors are defined as

$$\boldsymbol{\rho}_1 = \sqrt{\mu_1}(\boldsymbol{r}_1 - \boldsymbol{r}_2), \qquad \boldsymbol{\rho}_2 = \sqrt{\mu_2}\left(\frac{m_1\boldsymbol{r}_1 + m_2\boldsymbol{r}_2}{m_1 + m_2} - \boldsymbol{r}_3\right), \tag{2}$$

where $\mu_1 = m_1 m_2/(m_1 + m_2)$ and $\mu_2 = (m_1 + m_2)m_3/(m_1 + m_2 + m_3)$ are the reduced masses. Then the shape (internal) coordinates are defined as,

$$w_1 = |\boldsymbol{\rho}_1|^2 - |\boldsymbol{\rho}_2|^2, \qquad w_2 = 2\boldsymbol{\rho}_1 \cdot \boldsymbol{\rho}_2, \qquad w_3 = 2\boldsymbol{\rho}_1 \times \boldsymbol{\rho}_2, \tag{3}$$

where the sign of w_3 specifies the permutational isomers of the modified M_3 cluster. Fig. 1a shows the steepest descent paths of the potential energy connecting the two equilibrium points via the three saddle points. The inset shows the equi-potential surface of the modified M_3 cluster at $V = -1.4\varepsilon$. The interior region of the equi-potential surface is called "Hill's region" in analogy with usage in astrophysics. The structures in Fig. 1a have reflection symmetry with respect to the w_1-w_2 plane and the w_1-w_3 plane.

The intrinsic metric tensor of shape space for the coordinates (w_1, w_2, w_3) is known to be diagonal [6, 7] with $g_{11} = g_{22} = g_{33} = 1/4w$, where $w = \sqrt{w_1^2 + w_2^2 + w_3^2}$ and $g_{ij} = 0$ (for $i \neq j$). Therefore the Lagrangian for the triatomic system with zero-angular momentum is

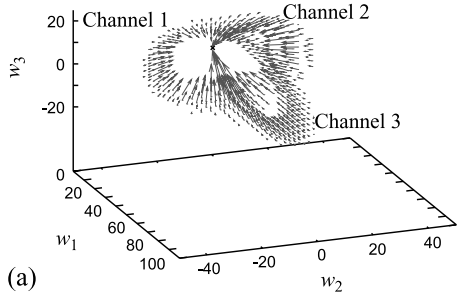
$$\mathcal{L} = \frac{1}{2}\left(\frac{1}{4w}\right)\dot{w}_1^2 + \frac{1}{2}\left(\frac{1}{4w}\right)\dot{w}_2^2 + \frac{1}{2}\left(\frac{1}{4w}\right)\dot{w}_3^2 - V(w_1, w_2, w_3). \tag{4}$$

Then the classical equations of motion derived from this Lagrangian are

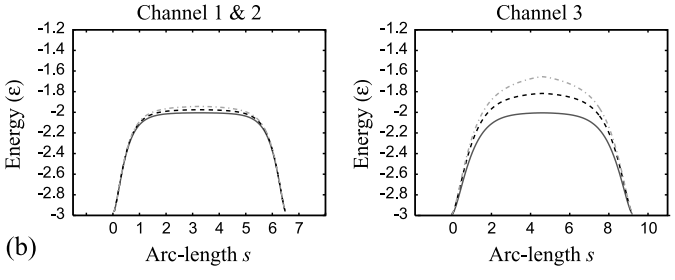
$$\frac{1}{4w}\ddot{w}_1 - \frac{w_1}{8w^3}\dot{w}_1^2 + \frac{w_1}{8w^3}\dot{w}_2^2 + \frac{w_1}{8w^3}\dot{w}_3^2 - \frac{w_2}{4w^3}\dot{w}_1\dot{w}_2 - \frac{w_3}{4w^3}\dot{w}_1\dot{w}_3 = -\frac{\partial V}{\partial w_1}, \tag{5}$$

$$\frac{1}{4w}\ddot{w}_2 + \frac{w_2}{8w^3}\dot{w}_1^2 - \frac{w_2}{8w^3}\dot{w}_2^2 + \frac{w_2}{8w^3}\dot{w}_3^2 - \frac{w_1}{4w^3}\dot{w}_2\dot{w}_1 - \frac{w_3}{4w^3}\dot{w}_2\dot{w}_3 = -\frac{\partial V}{\partial w_2}, \tag{6}$$

$$\frac{1}{4w}\ddot{w}_3 + \frac{w_3}{8w^3}\dot{w}_1^2 + \frac{w_3}{8w^3}\dot{w}_2^2 - \frac{w_3}{8w^3}\dot{w}_3^2 - \frac{w_2}{4w^3}\dot{w}_3\dot{w}_2 - \frac{w_1}{4w^3}\dot{w}_3\dot{w}_1 = -\frac{\partial V}{\partial w_3}. \tag{7}$$



(a)



(b)

Fig. 2. **a**: Field of the averaged fictitious force in Hill's region at $E = -1.4\varepsilon$. **b**: Solid lines are the original potential for respective reaction channels. The broken lines and the dotted lines are the reaction-path potential at total energy $E = -1.8\varepsilon$ and $E = -1.4\varepsilon$, respectively

The terms from the 2nd to the 6th on the left-hand sides of these equations are quadratic in the velocity components $\dot{w}_i$. These terms are originated from the non-Euclidean metric of shape space and can be regarded as velocity-dependent ''fictitious forces'' in the coordinate chart depicted in Fig. 1. These terms characterize the behavior of geodesics.

To extract the essential property of these velocity-dependent force terms, their averages are considered. This is reasonable since these velocity-dependent terms (forces) usually fluctuate rapidly in the chaotic dynamics of the system. If the distribution of velocity vectors in the tangent space at each point is sufficiently stochastic, then the equipartition law holds for the kinetic energy terms in Eq. (4). As a result, one obtains, for the averages of the diagonal quadratic terms, $\langle \dot{w}_1^2 \rangle = \langle \dot{w}_2^2 \rangle = \langle \dot{w}_3^2 \rangle = 8wK/3$, where $K = E - V(w_1, w_2, w_3)$ is the kinetic energy at each point in the shape space. As for the cross terms, one gets $\langle \dot{w}_i \dot{w}_j \rangle = 0$ (for $i \neq j$), since one can assume $\dot{w}_i$ and $\dot{w}_j$ are independent in a stochastic system. Applying these averages to the velocity-dependent terms in Eqs. (5)–(7), an averaged force field is finally obtained as

$$\left(-\frac{Kw_1}{3w^2}, -\frac{Kw_2}{3w^2}, -\frac{Kw_3}{3w^2} \right). \tag{8}$$

This force field should be working effectively in the dynamics of the cluster.

Fig. 2a shows the field of Eq. (8) in the Hill's region at $E = -1.4\varepsilon$. Observe that the averaged force works to block trajectories to get into the reaction pathway of Channel 3 at the vicinity of the two equilibrium points. This is the mass-related dynamical barrier originated from the geometry of shape space. To quantify the effects of the averaged force, a ''reaction-path potential'' is introduced, which is defined as the sum of the original potential and the line-integral of the averaged force along a path. For simplicity, the steepest descent paths are chosen in Fig. 1a as the reaction paths. Fig. 2b shows the original potential and the reaction-path potential as a function of arc-length of the path for respective channels. The height of the original potential barrier is the same for all the channels. The barrier of the reaction-path potential becomes higher and higher as the energy increases in Channel 3, while the energy dependence of the reaction-path potential is very weak for Channels 1 and 2. This explains why the isomerization reaction through Channel 3 becomes much less frequent as the energy increases.

In conclusion, a concise method to characterize the effect of different masses for triatomic reactions has been proposed. An averaged force field has been deduced using the non-Euclidean metric of shape space. This force field is shown to play a crucial role in determining the mass-related branching ratios of isomerization of the triatomic cluster. Since the geometry of shape space is independent of the system, the proposed methodology should be useful for varieties of triatomic reactions.

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