

Mechanical Forces Alter Conical Intersections Topology

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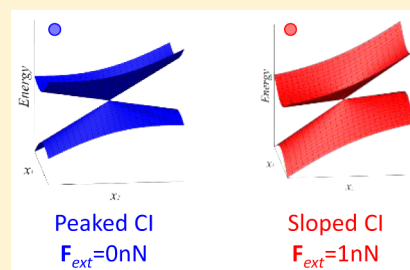
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Supporting Information

ABSTRACT: Photoreactivity can be influenced by mechanical forces acting over a reacting chromophore. Nevertheless, the specific effect of the external forces in the photoreaction mechanism remains essentially unknown. Conical intersections are key structures in photochemistry, as they constitute the funnels connecting excited and ground states. These crossing points are well known to provide valuable information on molecular photoreactivity, including crucial aspects as potential photoproducts which may be predicted by just inspection of the branching plane vectors. Here, we outline a general framework for understanding the effect of mechanical forces on conical intersections and their implications on photoreactivity. Benzene S_1/S_0 conical intersection topology can be dramatically altered by applying less than 1 nN force, making the peaked pattern of the intersection become a sloped one, also provoking the transition state in the excited state to disappear. Both effects can be related to an increase in the photostability as the conical intersection becomes more accessible, and its topology in this case favors the recovery of the initial reactant. The results indicate that the presence of external forces acting over a chromophore have to be considered as a potential method for photochemical reactivity control.



INTRODUCTION

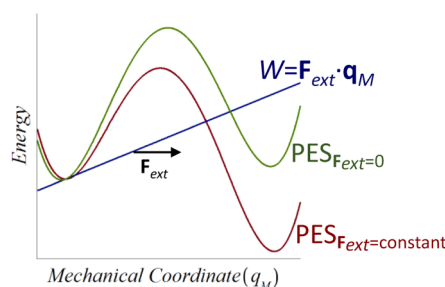
Mechanical stress has been proved to dramatically alter the chemical reactivity of molecular systems, defining the so-called field of covalent mechanochemistry.¹ Extensive work has been done in order to understand the interplay between mechanical forces and chemistry in the ground state, and many different examples are reported in the literature, ranging from mechanochemical catalysis activation,² cell adhesion,³ catch bonds in biological systems,⁴ and mechanoresponsive materials.⁵ Nevertheless, mechanochemistry of photoreactions involving excited states and surface crossings basically remains unexplored.

External forces can be introduced in a given mechanophore, i.e., a molecule activated by mechanical forces, using different strategies. The most common ways are AFM-derived techniques,⁶ sonication of a mechanophore anchored to bulky residues,⁷ and covalent attachment of a force probe to the mechanophore.⁸ Characteristic force magnitudes for these methods are in the range of picoNewtons to few nanoNewtons (nN), well below the typical C–C rupture forces of ca. 6.5–7 nN.⁹

Mechanical forces can affect the essential ground-state chemical properties of molecular systems such as thermodynamic stability or chemical kinetics.¹⁰ Different phenomenological models¹¹ and electronic structure approaches¹² have been proposed in order to understand mechanochemical phenomena in the ground state. It is worth noting that potential energy surfaces (PESs) play a crucial role as the inclusion of external forces in the Hamiltonian causes the PES

to be modified. In this way, the exerted force develops a work along its coordinate of application (i.e., mechanical coordinate); therefore, the PESs become altered as the mechanical work has to be added to the potential energy of the system. For instance, if the external force is constant, the work developed by the force is linearly dependent on the mechanical coordinate (see Scheme 1). This means that the inclusion of external forces changes the PES topology, not only by changing key structures as minima or transition states (TS) but also by changing the

Scheme 1. Effect of an External Force over the PES^a



^aEquilibrium and TS structures found at zero force ($PES_{F_{ext}=0}$) are displaced when the external force is exerted ($PES_{F_{ext}=constant}$), and the energy profile is shifted due to the inclusion of the work term (W), given by the straight blue line, in the Hamiltonian.

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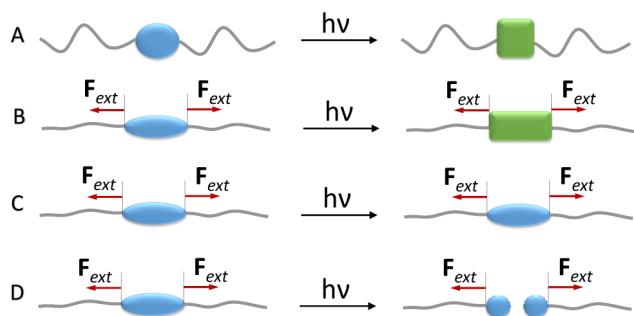
relative energy of different configurations due to the inclusion of the mechanical work term. An example of the effect of the exerted force on the topology of a simple one-dimensional PES is shown in Scheme 1. Moreover, the molecular environment of complex reacting systems can be understood in some cases as a collection of external forces, which may eventually alter the reactivity of the isolated system. In these cases, QM/MM schemes can be employed to simulate such an environment and therefore the external forces rather than mechanical forces.

Only in recent years, mainly due to the development of single-molecule manipulation techniques, sophisticated polymer synthesis and accurate computational methods, mechanocchemistry has experienced a significant advance, proving that mechanical forces are able to change the reactivity and chemical properties of molecular systems, guiding the design of mechanoresponsive systems.¹³

Few studies have been done concerning the effect of external forces on the chemical properties of molecular systems involving excited states.¹⁴ The absorption spectrum of different chromophores has been studied as a function of a variable external force, establishing a protocol to identify the optimal forces tuning the excitation energy¹⁵ or showing the sharp variation of the band shape and maxima of the bright states in a photoswitch.¹⁶ Force-induced chemiluminescence of the oxetane moiety inserted in a polymer chain proves that the population of excited states can also be promoted.¹⁷

Nevertheless, precedent work concerning the effect of external forces in photoreactivity is scarce and is mainly circumscribed to the photoisomerization of azobenzene-based systems under different induced stresses.¹⁸ As can be seen in Scheme 2, different effects of external forces on the

Scheme 2. Possible Effects of a Mechanical Force Exerted on a Given Chromophore Photoreaction (A)^b



^bThe photoreaction is not altered where the only effect of the forces is to strain the chromophore (B), the exerted force provides photostability by quenching the photoreaction and recovering the initial reactant (note that this could be a special case of quantum yield variation) (C), and alteration of the photoreactivity (D).

photoreactivity could be expected: (i) the photoreaction mechanism is not altered, and therefore, the only effect of the forces is to strain the molecule, (ii) photoreactivity is quenched providing photostability to the system, (iii) only quantum yield is affected (not shown in Scheme 2), or (iv) alteration of the photoreaction mechanism occurs (Scheme 2).

Conical intersections (CI) are crossings between electronic states, which provide highly efficient funnels for radiationless decay. CIs are essential to understand many molecular photoinduced processes¹⁹ as they constitute key features determining, to a large extent, the potential photoproducts.

PESs featuring this kind of crossing are double cone shaped in the vicinity of the crossing point, this topology being responsible for the term conical intersection. Such kinds of crossings are as relevant in photochemistry as TSs are for thermally activated processes (i.e., ground-state reactions). While the TS vector provides the minimum energy path direction from the TS, the so-called branching space, formed by the derivative coupling and gradient difference vectors, defines the two possible directions of evolution after the electronic hop (i.e., the photochemical reaction pathway).

RESULTS AND DISCUSSION

In this context, given two crossing electronic states with potential energy surfaces $E_1(\mathbf{q})$ and $E_2(\mathbf{q})$, and with ψ_1 and ψ_2 wave functions, if no mechanical energy is considered, the two intersecting PESs have in a first (linear) approximation a double cone shaped topology around the crossing point, where the nonadiabatic vectors, \mathbf{x}_1 and \mathbf{x}_2 , define the branching plane (i.e., the 2-dimensional subspace where the energy degeneracy is lifted). The vector $\mathbf{x}_1 = \nabla(E_2 - E_1)$, namely, the gradient difference vector, provides the largest variation of the energy difference in terms of internal coordinates, while $\mathbf{x}_2 = (E_2 - E_1)\langle\psi_1|\nabla\psi_2\rangle$, the energy difference times derivative coupling, provides the largest mixing of both electronic states. Additionally, the projection of the energy gradient addition vector $\mathbf{s} = ((1/2)\nabla(E_2 + E_1))$ onto the branching plane provides the CI tilt, determining whether the CI is, for instance, peaked or sloped.²⁰

If some mechanical forces are acting on a system, the crossing PES's topology is being changed because of the additional energy term related to the work developed by the force, which should be included in the Hamiltonian. For simplicity, we will consider in the following a constant external force defined by the force vector \mathbf{F}_{ext} . This vector can be decomposed into two components, one corresponding to the branching plane ($\mathbf{F}_{\text{ext}}^{\text{BP}}$) and the other to the intersection space ($\mathbf{F}_{\text{ext}}^{\text{IS}}$), that is $\mathbf{F}_{\text{ext}} = \mathbf{F}_{\text{ext}}^{\text{BP}} + \mathbf{F}_{\text{ext}}^{\text{IS}}$. Thus, if we focus on the topology of the double cone along the coordinates defined by \mathbf{x}_1 and \mathbf{x}_2 , when the energy term due to the mechanical work ($W = \mathbf{F}_{\text{ext}}^{\text{BS}} \cdot \delta\mathbf{q}$) is included in the Hamiltonian,²¹ the following CI topology for the adiabatic surfaces is obtained as a function of a displacement vector $\delta\mathbf{q}$ from the CI tip (see Supporting Information for details):

$$E_{\pm} = \mathbf{s} \cdot \delta\mathbf{q} - W \pm \frac{1}{2} \sqrt{(\mathbf{x}_1 \cdot \delta\mathbf{q})^2 + 4(\mathbf{x}_2 \cdot \delta\mathbf{q})^2}$$

Mechanical forces have no effect on the energy gradient difference (\mathbf{x}_1) since they equally affect both electronic states, nor do they change the derivative coupling vector (\mathbf{x}_2) as the wave function remains unaffected by the external force. Nevertheless, the tilt of the CI, originally defined by the \mathbf{s} vector projection in the branching plane, is now changed by adding the work term, giving rise to $\mathbf{s} - \mathbf{F}_{\text{ext}}^{\text{BP}}$ (see Figure 1).

The effect of the external force is not restricted to the CI double cone topology along the branching plane. The intersection space component of the external force vector, $\mathbf{F}_{\text{ext}}^{\text{IS}}$, may have a significant effect on the topology of the intersection space, as the new forces experienced by the chromophore are the sum of external plus internal forces. The most relevant change induced by $\mathbf{F}_{\text{ext}}^{\text{IS}}$ is the shift of the minimum energy CI structure, a crossing point especially relevant for understanding molecular photoreactivity. This kind of CI usually has the basic properties and features of the close

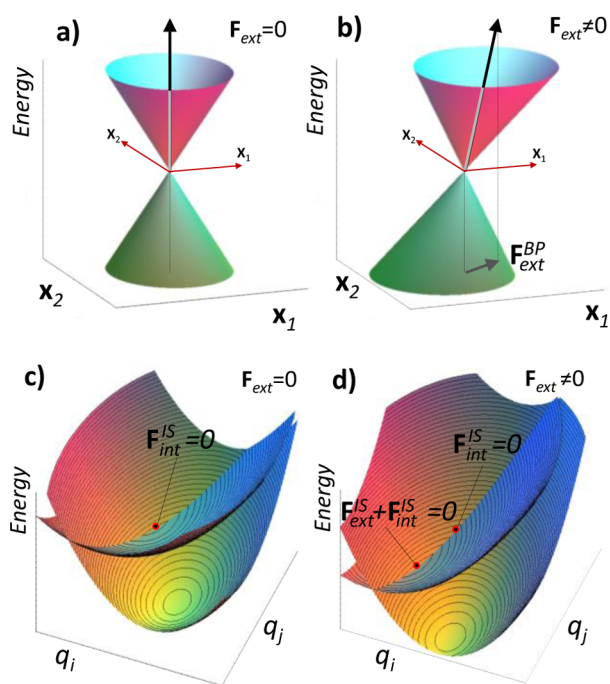


Figure 1. Double cone topology of crossing PES with (a) zero external force and (b) external force with a component along the branching plane ($F_{\text{ext}}^{\text{BP}}$). Effect on the intersection space topology of external forces: (c) with $F_{\text{ext}} = 0$, the minimum energy crossing point, is located where internal forces along the intersection space are vanishing (i.e., $F_{\text{int}}^{\text{IS}} = 0$). After the application of an external force with a component in the intersection space ($F_{\text{ext}}^{\text{IS}}$), the new minimum energy CI (d) is located where $F_{\text{ext}}^{\text{IS}} + F_{\text{int}}^{\text{IS}} = 0$.

surroundings seam found in the dynamical description of the system, and in some cases, it is very similar to the CI found along the minimum energy path. Therefore, the photochemical behavior predicted by the analysis of this CI may be representative of the surrounding crossing seam. If we consider a given external force F_{ext} applied along its corresponding mechanical coordinate q_M , with a component in the intersection space equal to $F_{\text{ext}}^{\text{IS}}$ the new minimal energy CI will correspond to the point in the intersection space where $F_{\text{ext}}^{\text{IS}}$ equals the internal molecular energy gradient, i.e., $F_{\text{ext}}^{\text{IS}} + F_{\text{int}}^{\text{IS}} = 0$ (see Figure 1c and d). Therefore, as a result of the exerted mechanical force, the minimum energy CI structure changes. These structural changes may have components in the whole set of internal coordinates of the chromophore, eventually making the nonadiabatic vectors to be also altered, not because of the direct effect of the external forces on these vectors but as the result of the change in the minimum energy CI structure. This change in the x_1 and x_2 vectors takes place because of the coupling between the branching plane coordinates and the mechanical coordinate along the intersection space. The measurement of this coupling is essential to understand the effect of external forces on the minimum energy CI topology. The main CI vectors x_1 , x_2 , and s can be therefore related to the mechanical coordinate by the following equation (see Supporting Information):

$$\mathbf{x}_1 = \mathbf{x}_{1,\text{opt}} + \left(\frac{\partial \mathbf{x}_1}{\partial q_\mu} \right)_{\text{CI}_{\text{opt}}} \delta q_\mu$$

where δq_μ indicates an arbitrary displacement along a coordinate parametrically dependent on q_M , the mechanical coordinate (see Supporting Information for details), and $\mathbf{x}_{1,\text{opt}}$ stands for the \mathbf{x}_1 vector determined for zero external force, minimum energy CI. The same relationship holds for x_2 and s . Here, the fundamental quantity $(\partial \mathbf{x}_1 / \partial q_\mu)_{\text{CI}_{\text{opt}}}$ provides the response of the \mathbf{x}_1 vector to the variation of the mechanical coordinate (with similar expressions for x_2 and s). These fundamental photomechanicochemical variables determine the response of the chromophore CI to the mechanical stimulus.

In order to analyze the effect of external forces on the CI topology, we chose the well-known S_1/S_0 CI of benzene²² as the case study. The external forces are applied on two added methyl carbon atoms in *meta* position providing a minimal model of a chain transmitting the effect of a mechanical force to the chromophore (see Figure 2). The distance between these

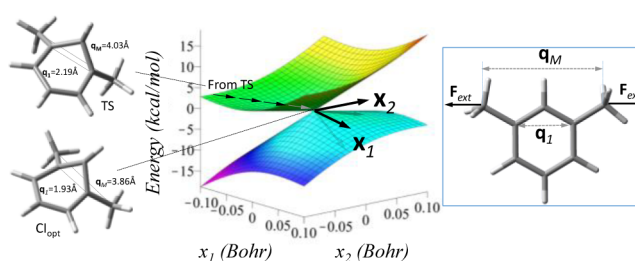


Figure 2. PESs around the minimum energy CI (CI_{opt}) as a function of the coordinates defined by x_1 and x_2 vectors. The CI is reached by overcoming a barrier (TS). The mechanical coordinate (q_M) and the photoreaction coordinate (q_1) are indicated.

two carbon atoms parametrically define the external force in equilibrium conditions, and it is therefore the mechanical coordinate q_M of this system. The inclusion of the external forces in the Hamiltonian was done with our own developed codes. All of the electronic structure calculations were done by using the complete active space method as implemented in the Gaussian suite of programs²³ (see Supporting Information for details).

The S_1/S_0 benzene CI is reached after overcoming an energy barrier on S_1 ,²⁴ where the TS vector mainly corresponds to the C–C σ bond formation defined by the q_1 coordinate (see Figure 2). The CI is therefore peaked, and the x_1 and x_2 vectors mainly correspond to the q_1 coordinate and π -electron coupling respectively (see Supporting Information for details).

The effect of the external force applied along the mechanical coordinate, q_M (i.e., the C–C methyl–methyl distance) provokes significant changes in the minimum energy CI. Considering a local quadratic expansion of the PES, the CI energy increases quadratically with the force magnitude (see Figure 3 and Supporting Information for details). On the one hand, the mechanical coordinate q_M varies linearly with the force magnitude as long as the harmonic oscillator regime is fulfilled, i.e., at ca. 1 nN. For higher force magnitudes, the variation is reduced due to the anharmonicity of the coordinate. On the other hand, the energy of the CI increases with the F_{ext} modulus, as is expected due to the stationary point character of the minimum energy CI in the intersection space with a force constant equal to $0.257 \text{ kcal} \cdot \text{mol}^{-1} \cdot \text{\AA}^{-1}$. Finally, the effect of the external force on the CI tilt can be analyzed by determining the component of the $s - F_{\text{ext}}^{\text{BP}}$ vector (see Figure 1) on the branching plane. The combined effect of CI structure change

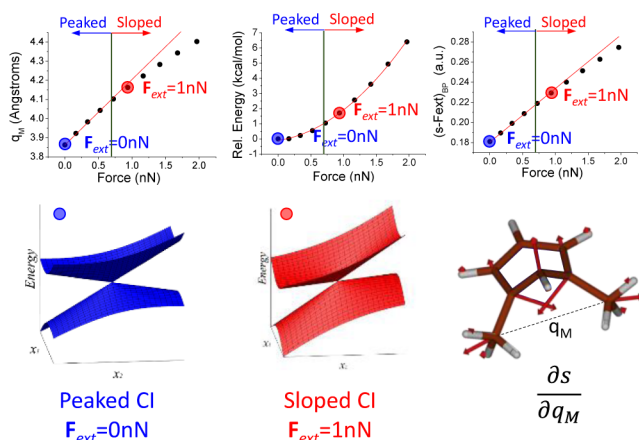


Figure 3. Variation of the mechanical coordinate (q_M) and the CI energy with the external force magnitude (top). The topology of the CI changes from peaked at zero forces to sloped at ca. 0.7 nN. The $\partial s / \partial q_M$ vector indicates the coupling between the mechanical coordinate q_M and the s vector.

due to the external force and the work exerted by the force itself makes the CI tilt vary by ca. 4.25 nN per 1 nN external force. The CI tilt variation rate with the external force is enough to transform the peaked CI pattern at zero forces to a sloped one at ca. 0.7 nN. At this external force, the \mathbf{x}_1 vector reaches the same but opposite value as the $\mathbf{s} - \mathbf{F}_{ext}^{BP}$ vector component on the branching plane, making the final slope along this branching plane direction zero. The component of the \mathbf{s} vector along the branching plane can be deduced from the $(\partial s / \partial q_M)_{CI_{opt}}$ vector, which is basically contained in the branching plane, concretely along the \mathbf{x}_1 vector, indicating that the variation of the mechanical coordinate (and consequently of the external force) mainly affects the CI topology along the gradient difference vector. Therefore, the exerted force pair in the methyl carbon atoms is mostly transferred in an amplified way to the branching plane, provoking a change in the tilt of the minimum energy CI (Figure 3).

The change from peaked to sloped CI topology results in a disappearance of the TS on S_1 . This result is coherent with the fact that the sloped CI induced by an external force is only compatible with (i) the TS disappearance or (ii) the appearance of a new minimum on S_1 . In order to get insight into the effect of the external forces on the PES topology, the ground and excited state PESs including the work term due to the external forces have been determined as a function of two main coordinates, the mechanical coordinate, q_M , and the q_1 coordinate (see Figure 4). It can be seen that external forces change the PES topology, causing the minimum energy CI as well as the TS to be strongly affected by the force. Specifically, the TS imaginary frequency progressively disappears with the external force (i.e., from ca. -348 cm^{-1} at zero forces, -235 cm^{-1} at 0.5 nN, or close to zero for 0.7 nN). This progressive flattening of the TS is correlated to the peaked to slope change in the CI topology. In fact, the sloped CI reached at ca. 0.7 nN external force can be related to an increase of the photostability of the system, as sloped CIs present parallel gradients on ground and excited states, conferring equivalent initial relaxation pathways for both states.

Nevertheless, the CI topology change is not the only factor favoring photostability. Additionally, the exerted external force develops a work along the mechanical coordinate, increasing

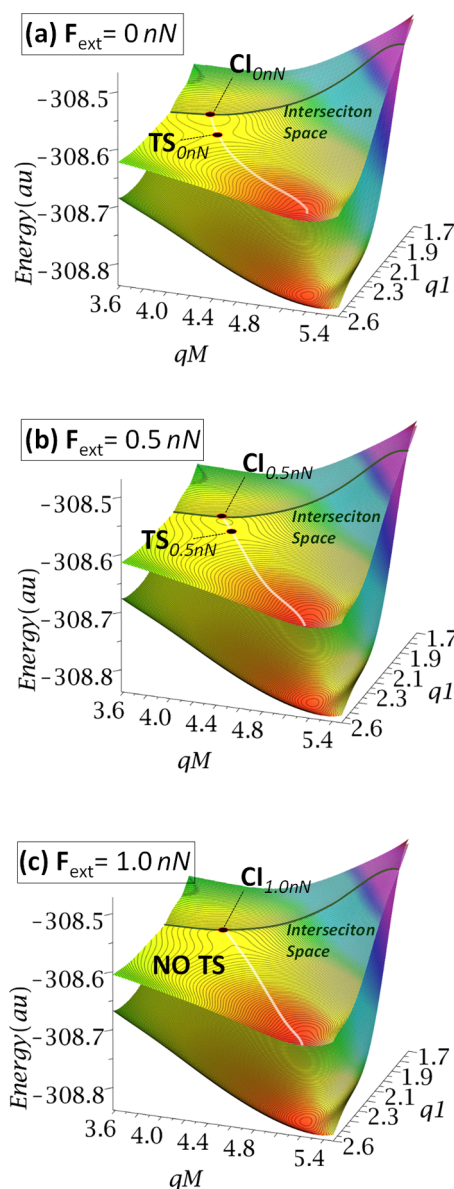


Figure 4. Ground and excited state PESs of 1–3-dimethylbenzene including the mechanical energy term as a function of q_M and q_1 for different external force magnitudes: 0, 0.5, and 1.0 nN. TS on S_1 is present up to ca. 0.7 nN (a and b cases) while it disappears for 1 nN (c case).

the energy barrier from the minimum on S_1 to either the TS or the CI. For instance, at 0.5 nN, the TS barrier is increased by an additional 6.4 kcal/mol, while at 1 nN force, there is no TS, but the CI energy increases up to approximately 13 kcal/mol. Consequently, the nonadiabatic relaxation path under external forces becomes unfavored with respect to the unstressed situation.

CONCLUSIONS

The local CI topology is altered by application of external forces over a given chromophore. Such an effect has different components. On one side, the CI tilt is affected by the work developed over the system by the external forces. Additionally, there is an effect in the CI structure: the exerted force induces a change in the minimum energy CI, eventually changing the three relevant vectors for describing the CI topology, \mathbf{x}_1 , \mathbf{x}_2 , and

s vectors. The effect of that force may produce important changes, as is the case of the benzene-like system, where the application of a 0.7 nN makes the CI change from peaked to sloped providing additional photostability to the system. We show that $(\partial s/\partial q_M)_{CI_{opt}}$ is a fundamental magnitude to understand how the chosen mechanical coordinate is able to effectively modify the CI tilt.

Much work has to be done in order to deeply understand how mechanical forces affect photoreactivity, including the effect on the photoreaction pathways or in the dynamical behavior involving nonadiabatic transitions. The presented results show that the CI topology of the photoreacting systems may be strongly affected, for instance by changing the CI topology from peaked to sloped, with relatively small external forces, suggesting that mechanical forces can be considered as a potential factor controlling the photoreactivity.

■ ASSOCIATED CONTENT

● Supporting Information

Complete reference for Gaussian; Cartesian coordinates of the most relevant structures; and x_1 and x_2 variation with the mechanical coordinate. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jctc.5b00375.

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Notes

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