Photodynamics of Methyl-Vinyl Criegee Intermediate: Different Conical Intersections Govern the Fates of Syn/Anti Configurations†

Ya-zhen Li, Jia-wei Yang, Lily Makroni, Wen-liang Wang, Feng-yi Liu∗

Key Laboratory for Macromolecular Science of Shaanxi Province, School of Chemistry & Chemical Engineering, Shaanxi Normal University, Xi’an 710062, China

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Methyl vinyl ketone oxide, an unsaturated four-carbon Criegee intermediate produced from the ozonolysis of isoprene has been recognized to play a key role in determining the tropospheric OH concentration. It exists in four configurations (anti-anti, anti-syn, syn-anti, and syn-syn) due to two different substituents of saturated methyl and unsaturated vinyl groups. In this study, we have carried out the electronic structure calculation at the multi-configurational CASSCF and multi-state MS-CASPT2 levels, as well as the trajectory surface-hopping nonadiabatic dynamics simulation at the CASSCF level to reveal the different fates of syn/anti configurations in photochemical process. Our results show that the dominant channel for the S1-state decay is a ring closure, isomerization to dioxirane, during which, the syn(C–O) configuration with an intramolecular hydrogen bond shows slower nonadiabatic photoisomerization. More importantly, it has been found for the first time in photochemistry of Criegee intermediate that the cooperation of two heavy groups (methyl and vinyl) leads to an evident pyramidalization of C3 atom in methyl-vinyl Criegee intermediate, which then results in two structurally-independent minimal-energy crossing points (Cls) towards the syn(C–O) and anti(C–O) sides, respectively. The preference of surface hopping for a certain CI is responsible for the different dynamics of each configuration.

Key words: Trajectory surface hopping nonadiabatic dynamics, Criegee intermediate, Dioxirane, Photoisomerization, Minimal-energy crossing point

I. INTRODUCTION

Isoprene (2-methyl-1,3-butadiene) is one of the most abundant volatile organic compound in the atmosphere [1, 2]. Its reaction with ozone has been reported as a major tropospheric removal pathway that plays a significant source of OH in the tropospheric oxidation cycle especially during daytime and winter months [3]. Depending on the position of O3 attacking at the two C=C bonds of isoprene (i.e., C1–C2 or C3–C4), two isomers of C4 Criegee intermediate, namely a methyl-vinyl ketone oxide (MVK-OO, (CH2=CH)(CH3)COO) and a methacrolein oxide (MVCR-OO, CH2=C(CH3)CHOO), with total branching of 23% and 19%, respectively, are formed [4, 5]. The more abundant MVK-OO, also known as methyl-vinyl Criegee intermediate (MVCI), is predicted to have four configurations with respect to the orientations around C3–C4 and C3–O1 bonds (FIG. 1), of which each has considerable abundance [5]. Therefore, the formation, interconversion and atmospheric reactions of MVCI have drawn great attention from chemists [6–8].

Until now, the electronic structure of the simplest Criegee intermediate (SCI) is elusive, therefore, the substitution effect has shown significant difference based on whether it is saturated or unsaturated substituents. It is well understood that the unimolecular reaction of SCI is in favor of ring-closure to a three-membered-ring structure (dioxirane) while against hydrogen atom transfer to terminal oxygen [9–11]. However, the asymmetrical substitution on SCI by a saturated methyl group (-CH3) forming syn- and anti-CH3CHO has shown significantly different reaction pathways in anti/syn configuration [11–15]. More evidently, the addition of unsaturated substituents suggests a totally different channel. A recent theoretical calculation demonstrated that in vinyl-Criegee intermediate (VCI), both the C–O–O ring closure and H transfer are suppressed, while another ring-closure channel to either a four- or five-membered-ring product becomes dominant [11]. In addition to the thermal reactions, the photochemistry of Criegee Intermediates (Cls) also shows strong substituent dependence. The high-level dynamically-weighted complete active space self-consistent field (DW-CASSCF)/MRCI-F12 calculations by Guo and coworkers suggested that the SCI has

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∗Author to whom correspondence should be addressed. E-mail: fengyiliu@snnu.edu.cn

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two spin allowed photo-dissociation branches, i.e., \( \text{H}_2\text{CO}(\text{X}^1\text{A}_1)+\text{O}(\text{I}^3\text{D}) \) and \( \text{H}_2\text{CO}(\text{a}^3\text{A}^\ast)+\text{O}(\text{I}^3\text{P}) \), on the second excited \( \text{S}_2 \) state [16]. Our electronic-structure calculations and nonadiabatic dynamic simulations on SCI, methyl-Criegee intermediate (MCI) and VCI revealed a first excited \( \text{S}_1 \) state involved process that led to dioxirane, in addition to the known \( \text{O}--\text{O} \) bond cleavage. For each conformer/configuration of MCI and VCI, the ring tension, hydrogen bond and conjugation caused by the different orientations of substituents, govern the relative nonadiabatic transition probabilities and product yields [17, 18].

In MCI, there are both methyl and vinyl groups bonded to the carbon site, therefore it provides a unique opportunity to comparatively identify the roles of saturated and unsaturated substituents in a single system. Recently, experimental and theoretical studies combined by Lester et al. has reported that the thermal reactions of MCI are configuration-dependent. The \( \text{syn} \)(CO)-MCI produces OH radical through a hydrogen-atom-transfer mechanism, while the \( \text{anti} \)(CO) configuration is predicted to produce OH via a dioxole pathway, and the former has a much lower barrier height than the latter [15]. All these findings show non-negligible contribution from both saturated and unsaturated substituent effects in MCI. This synergistic effect observed from this study is a quite dissimilar atmospheric fate from other relevant configurations. Therefore, for the unidentified photochemistry of MCI, we have carried out the electronic structure calculations at the state-averaged (SA)-CASSCF and multi-state second-order perturbation theory (MS-CASPT2), along with the CASSCF-level trajectory surface-hopping (TSH) [21, 22] nonadiabatic molecular dynamics, to reveal the potential energy surface (PES) and photodynamics of all configurations of MCI. The contribution of the saturated and unsaturated substituents is expected to be well understood.

II. COMPUTATIONAL METHODS

A. Electronic structure calculations

Electronic structure calculations are carried out at the SA3-CASSCF [19] and MS3-CASPT2 [20] levels of theory, respectively, using \text{def}2-SVP and \text{def}2-TZVP basis set [23]. An active space consists of the \( 2s \) orbital of the middle \( \text{O} \) atom, the lone-pair orbital on terminal \( \text{O} \) atom, \( \sigma/\sigma^\ast \) orbitals of \( \text{O}--\text{O} \) bond, and all the five \( \pi/\pi^\ast \) orbitals, as well as the electrons distributed on them, namely, the \( \text{CAS}(12e; 9o) \), are used (see FIG. S1 in supplementary materials). First, four ground-state \( \text{S}_0 \) configurations of MCI, i.e., the \( \text{anti}--\text{anti} \), \( \text{anti}--\text{syn} \), \( \text{syn}--\text{anti} \), and \( \text{syn}--\text{syn} \) MCI (for convenience, which are respectively abbreviated as AA, AS, SA and SS, in the following discussion), are optimized at the SA-CASSCF/\text{def}2-SVP, MS-CASPT2/\text{def}2-SVP and MS-CASPT2/\text{def}2-TZVP levels, respectively, and their corresponding excitation energies to the low-lying excited states are calculated. To get a systematic understanding of the unimolecular process, one-dimensional (1D) potential energy curves (PECs) and 2D-PESs are constructed with a series of constrained optimizations along the relevant reaction coordinates at the SA3-CASSCF/\text{def}2-SVP level. Moreover, the nonadiabatic processes are further validated by searching for the \( \text{S}_1/\text{S}_0 \)-minimal energy crossing points (CIs) at the CASSCF level. The transition states (TSs) for \( \text{C}--\text{O}--\text{O} \) ring-closure on the ground-state are optimized using the PBE0 density functional with a \text{def}2-SVP basis set. Their relative energies are then refined by MS3-CASPT2 single-point calculation. All CASSCF and MS-CASPT2 calculations are carried out using the MOLCAS program [24], and DFT calculations are obtained in Gaussian 09 [25].

B. Trajectory surface-hopping dynamics

Trajectory surface-hopping (TSH) molecular dynamics simulations, combined with the SA3-CASSCF/\text{def}2-SVP quantum-chemistry calculations, are employed to gain a better understanding of photodynamics of MCI. Here, trajectory dynamics simulation of all the four configurations are carried out to investigate the substitution effects, even though the calculated Boltzmann populations (Table S1 in supplementary materials) show very low percent for SS. For each configuration, 300 initial conditions are respectively generated on the base of the SA3-CASSCF optimized geometry and frequencies, then a Wigner distribution [26] is generated. Both the \( \text{S}_1 \) and \( \text{S}_2 \) states are initially populated based on our previous calculations [17], while the triplet process is excluded due to the negligible spin-orbital coupling effects [27]. Energy windows for each state are set individually considering their different excitation energies (see Table S2 in supplementary materials). Finally, about 100 trajectories are successfully simulated for each of the four configurations from either \( \text{S}_1 \) or \( \text{S}_2 \) state (in detail: 108 for AA, 99 for AS, 73 for SA and 88 for SS from \( \text{S}_1 \) state; and 130 for AA, 131 for AS, 131 for SA and 130 for SS from \( \text{S}_2 \) state). The trajectories are submitted with a time step of 0.5 fs and run up to 400 fs. During the simulation, the “SHARC dynamics” of diagonal potentials and vectorial nonadiabatic couplings [28] are used. The decoherence correction is considered using an energy difference-based correction (EDC) scheme [29], and the standard SHARC surface hopping scheme is used to describe the surface hopping. TSH dynamic simulations are performed by using the SHARC program [30, 31], combined with CASSCF calculations implemented in the MOLPRO package [32].

III. RESULTS AND DISCUSSION

A. Electronic structures and PESs

FIG. 1 presents the four configurations of MCI with key geometrical parameters optimized at the MS3-
The four $S_0$-state configurations of MVCI (where A and S stand for anti and syn, respectively, the first A/S indicate the anti/syn configuration with respect to the orientations of the vinyl group and terminal O atom beside C3–O1 bond; the second one corresponds to that with respect to C3–C4 bond). Geometries optimized at the MS3-CASPT2/def2-TZVP level, along with the important bond lengths (in Å) are shown on the left, and definitions of key (dihedral) angels are shown on the right panel.

CASPT2/def2-TZVP level (structures with more parameters, and those optimized at the DFT-PBE0/def2-SVP, CASSCF/def2-SVP and MS3-CASPT2/def2-SVP levels are shown in FIG. S2). It is seen that all configurations are planar, indicating an extended conjugation moiety caused by the vinyl substituent. Compared with the geometry of SCI calculated at the same level of theory (in which $R$(C–O)$=1.288$ Å and $R$(O–O)$=1.330$ Å), all configurations of MVCI show a systematically elongated O–O bond ($1.347$–$1.370$ Å), suggesting a larger zwitterionic character in the ground state. Also, in both SA and SS configurations that contain the same syn(C3–O1) skeleton, a short O2···H distance is observed. The hydrogen-bond-like interaction shortens the O–O bond (with respect to those in AA and AS, which share the same anti(C3–O1) skeleton), and is expected to stabilize the syn(C–O) configurations. Meanwhile, it is found that in SA and SS configurations, ring tension is also more significant, which is reflected by the large bond angles around the C–O bond (i.e., $\alpha$, $\beta$, and $\gamma$, as defined in FIG. 1). The hydrogen bond and ring tension play opposite roles in stabilizing the configurations, as being found in the VCI [18]. As a result, the MS-CASPT2/def2-TZVP calculations suggest that the relative energies of 0.0, 0.6, 1.3, and 3.7 kcal/mol for AA, AS, SA and SS configurations, respectively, are well consistent with Lester’s computational results at the AN10-R2F//B2PLYP-D3/cc-pVTZ level (in which the relative energies are 0.00, 1.76, 2.57, and 3.05 kcal/mol) [15]. The order of relative stabilities is in a sharp contrast to that of VCI (in which the relative stabilities are SA$\approx$SS$\approx$AA$\approx$AS at the MS-CASPT2/def2-SVP level) [18], caused by the substitution of the more steric methyl group. These differences observed between VCI and MVCI suggest their different fates in photo-induced reactions.

The MS-CASPT2/def2-TZVP calculated excitation energies of the four configurations to the $S_1$ state are in the range of $51.3$–$55.4$ kcal/mol ($516$–$558$ nm), falling into visible region. The $S_2$ excitation, with a $\pi\rightarrow\pi^*$ character in 79.4–84.5 kcal/mol (i.e., $339$–$360$ nm), is comparable with the experimental values ($350$–$381$ nm) [33]. We attempt to optimize all possible minima on the $S_1$ and $S_2$-state PESs, while only SS configuration in $S_1$ state can be found by MS-CASPT2/def2-TZVP and only SA configuration can be found by MS-CASPT2/def2-SVP (both $S_1$-SA and $S_1$-SS can be optimized at the CASSCF level). From the optimized $S_1$-SA and $S_1$-SS structure, we observed significant elongation of the C–O bond ($1.385$ and $1.387$ Å in $S_1$-SA and $S_1$-SS at the MS-CASPT2 level, respectively) compared with that in the ground state, therefore the C–O bond shows a strong tendency to rotate (i.e., O2 atom rotates out of the molecular plane). Such a tendency actually exists in all configurations of MVCI, as being found in SCI and substituted Cls [17, 18].

FIG. 2 shows the $S_1$-PECs constructed by a series of constraint geometry optimizations along the dihedral angle $\phi$ (see FIG. 1 for definition). Ideally, rotations around the C3–C4 and C4–C5 bonds are both possible, while they can be excluded due to either high barrier heights (see FIG. S3 in supplementary materials) or insignificance for distinguishable configurations. As seen in FIG. 2, the C–O rotary PECs show a downhill trend from the Frank-Condon (FC) point of AA and AS configuration to the $S_1$/$S_0$ degenerate region, suggesting a spontaneous decay to possible conical intersections (CIs); while for FC-SA and FC-SS, very mild barriers are observed, therefore the accessing of CIs from these configurations is comparatively less straightforward. At the bottom of each PECs, a pair of CIs is optimized at the CASSCF level. For instance, as seen in FIG. 2(a), two CIs, namely, CI$^-\alpha$ and CI$^+\alpha$ lie on the left and right of 90°, towards the SA and AA side, respectively. In addition to the dihedral angle $\phi$, another major difference between them are the pyramidalization angle $\tau$, which reflects the intensity of C3 popping out of the C4–C6–O1 plane. More specifically, CI$^-\alpha$ and CI$^+\alpha$ show a positive and negative pyramidalization angle ($+6.8^\circ$ and $-6.4^\circ$), respectively.

The findings here are different from that in MCI and VCI (where only one CI is found on the $S_2$-PEC, that is, the photoisomerization from syn and anti conformer/configuration shares the same CI), while being similar to the situation in cis-trans photoisomerization of alkenes [34–36]. Clearly, the three heavy groups (i.e., methyl, vinyl and peroxy groups) bonded on C3 atom increase C3’s pyramidalization intensity, thus the
FIG. 2 The CASSCF/def2-SVP computed $S_1$-state energy profiles along the C3–O2 rotary coordinate (i.e., dihedral angle $\phi$) (a) between SA and AA and (b) between SS and AS, FCs are shown in red triangles, fully optimized $S_1$-SA and $S_1$-SS are shown in red circles; (c) $S_1$-SA, $S_1$-SS and the CIs optimized on the same level, with important geometrical parameters. The CIs are named as follows: subscript S and A stand for the configuration around the unchanged C3–C4 bond, and +/− indicates the dihedral angle $\phi$ larger or smaller than 90°, respectively.

$S_1$/$S_0$ crossing point bifurcates into two geometrically different ones. Due to their inequivalent geometries, the two CIs are expected to play different roles in the syn(C–O)$\rightarrow$anti(C–O) and anti(C–O)$\rightarrow$syn(C–O) photoisomerization processes, which will be verified by TSH dynamics.

The 2D $S_1$-PESs along the dihedral angle $\phi$ and C3–O2 distance (FIG. S4 in supplementary materials), demonstrate the above-mentioned $S_1$-state decay pathways. After $S_1$$\rightarrow$S0 nonadiabatic transition, there exist three possible channels, including the anti(CO)/syn(CO) isomerization, ring closure to dioxirane, and internal conversion (IC) back to the initial configuration in $S_0$ state. Because of the lowest relative energies of dioxirane (more than 21 kcal/mol lower in energy than the respective MVCI configurations, see FIG. S3 in supplementary materials), we can predict the highest ring-closure yields. In the $S_1$/S0-Cl–$S_0$-dioxirane process, obvious shortening of C–O bond (from $\sim$2.1 Å to $\sim$1.3 Å) and continued decrease of bond angle $\alpha$ (from $\sim$95° to $\sim$60°) are seen (FIG. S2 in supplementary materials), and will be further observed in the results of TSH dynamics.

B. $S_1$-state photodynamics of MVCI

The trajectories starting from $S_1$ state for all configurations show an ultrafast transition to $S_0$ state. The averaged $S_1$ lifetimes for the AA, AS, SA and SS configurations, 278.4, 279.7, 486.5, and 337.5 fs (FIG. S5), respectively, are consistent with that observed in VCI [18]. The hydrogen-bonded structures (SA and SS) show slower decay towards the perpendicular CI region, due to the time spent in breaking the hydrogen bond. Similarly, as predicted above in electronic-structure calculations, in SA and SS, the existed $S_1$-state minima at the FC region trap the trajectories and slow down their further decay (see FIG. 2 and discussion in section III A).

The hopping events of $S_1$ trajectories, characterized by the geometric features of the hopping points, as
FIG. 3 Distributions of the hopping points near the $S_0/S_1$-CIs for the trajectories starting from the $S_1$ state of (a) AA, (b) AS, (c) SA and (d) SS configurations, following the dihedral angle $\phi$ and pyramidalization angle $\tau$. The CASSCF/def2-SVP optimized CIs are shown in blue and red ‘+’ symbols, respectively.

shown in FIG. S6 (distributions for various coordinates), can be classified into three types: the majority (63%-71%) corresponds to the $S_1\rightarrow S_0$ hop caused by the C–O bond rotation, which takes place in the vicinity of the CASSCF-optimized CIs. Correspondingly, the hopping points are densely distributed around dihedral angle $\phi=90^\circ$. The second type is the $S_1\rightarrow S_0$ hop occurring, in a few cases (1%-12%), at the FC region, due to the relatively low $S_1$ excitation energy. And the third one takes place along the O–O elongating path, featured by a long O–O distance (>1.7 Å), which then leads to either $S_1\rightarrow S_0$ or $S_1\rightarrow S_2$ hop (1%-5%). Each of the three types of hops forwards the trajectory to different branches and thus generates different products, i.e., ring closure to dioxirane (or syn-anti isomerization to the opposite configuration that shares the same type of hopping points as ring closure), restoring to initial configuration, and forming a methyl-vinyl ketone+singlet O atom, respectively.

FIG. 3 illustrates the distributions of the hopping points for the dominant type (i.e., hops in the vicinity of CI) of MVCI along $\phi$ and $\tau$. It is interesting to find that, for trajectories starting from different configurations, the hopping points favor different CIs. Most of the hopping points of AA and AS (with an initial $\phi$ of 180°) are distributed on the right side of $\phi=90^\circ$, close to CI$_{A+}$ and CI$_{S+}$, respectively; while those of SA and SS configurations (in which $\phi$ is initially 0°), on the contrary, majorly fall on the left or on top of 90°, thus slightly favoring the CI$_{A-}$ and CI$_{S-}$. Directly comparing the distributions in FIG. 3 (a) and (c) (and in FIG. 3 (b) and (d)) makes the fact more notable, that is, the hops of MVCI show a clear preference for the CI at the “reactant” side. Again, it is different from what has been observed in VCI, in which all hops, from either the syn or anti configuration, are evenly distributed around the only CI between each pair of configurations [18]. The dramatic change of the hopping events from VCI to MVCI, emphasizes the heavy-group effect caused by methyl substituent.

The photodynamics after the nonadiabatic decay takes place mainly in the ground state and is thus straightforward. As summarized in FIG. 4 (a detailed analysis of branching ratios based on various geometrical parameters are illustrated in FIG. S7 in supplementary materials), from the CI, two isomerization channels are discovered. In one case, the C–O bond continuously rotates from 0° to 180° (or reversely, from 180° to 0°), a syn-to-anti (or anti-to-syn) isomerization around the C–O bond can be achieved; in the other case, if the C–O–O bending mode is involved, then a ring closure (indicated by the shortened C3–O2 bond and decreased angle $\alpha$) to dioxirane is expected. In principle, a third channel, namely, the internal conversion to initial configuration is possible but not observed in all simulations. For all configurations, the ring closure is the dominant channel in all configurations (the yields are 66%, 67%, 55% and 47 for AA, AS, SA and SS, respectively), which may be attributed to the much lower relative energy of dioxirane. The time spent in the
FIG. 4 The major photoisomerization channels of S₁-state MVCI started from (a) AA (in black) and AS (in purple), (b) SA and SS configurations. Yields for each process relative to the total successful trajectories are shown in light-red and purple background. The relative energies (in kcal/mol) of minima are calculated at the MS3-CASPT2/def2-TZVP level, whereas those of the S₀-TSs and CIs are calculated at the MS-CASPT2/def2-TZVP//PBE0/def2-SVP and MS-CASPT2/def2-TZVP//CASSCF/def2-SVP level, respectively.

ring-closure photoisomerization process is in a range of 120−280 fs. The yields of the syn-anti photoisomerization and O−O bond dissociation products, are relatively small (4%−16% for the former and 1%−5% for the later), which are thus not discussed in detail.

The good consistency between the S₁-PECs and TSH dynamics, confirms the novel finding of photo-induced ring closure of MVCI to dioxirane. More importantly, the newly found preference of hopping for certain CIs, reveals the importance of heavy-group effect on the photoisomerization processes.

C. S₂-state photodynamics of MVCI

FIG. 5 shows the variations of O−O distance in the S₂-trajectories with respect to the simulation time. It is seen, 86%, 86%, 82% and 89% of all successful trajectories in AA, AS, SA and SS configurations that started from S₂ state, respectively, undergo an ultrafast O−O dissociation channel, which is finished in the initial 50 fs of the simulation. Also, during the O−O elongation, the molecules do not always maintain its planar structure, as seen in FIG. S8 in supplementary materials, a mild torsion around C−O bond (ϕ varies in a range of ±30°) are observed. Furthermore, due to the known degeneracy in ground- and low-lying excited states of CIs [16, 17], in MVCI, 12%, 21%, 24% and 12% of AA, AS, SA and SS trajectories, respectively, eventually decay to S₀ state within 300 fs (FIG. S9). Majority of the S₂→S₁ and S₂→S₀ hops, as shown in FIG. S10 in supplementary materials, occur in 50 fs, with an elongated O−O bond length of ∼2.0 Å, while the rest (mainly the S₁→S₀ hop) takes place with an even longer O−O distance. The TSH dynamics well replicate the previous high-level calculations on the dissociation channel [16].

IV. CONCLUSION

In this study, we report the multi-configurational CASSCF and MS-CASPT2 electronic-structure calculations and CASSCF trajectory surface hopping non-diabatic dynamic simulations on the photoinduced uni-
molecular processes of an atmospherically important Criegee intermediate, namely, the methyl-vinyl Criegee intermediate. Important findings and conclusions are drawn as below:

(i) In MVCI, the substitutions by methyl and vinyl groups play a cooperative role in altering the relative stabilities of the four configurations, in which the hydrogen bond between the vinyl H and terminal O atoms decreases whereas the ring tension introduced by the same group increases the relative energies of the syn-anti and syn-syn configurations. Thus, it causes that all four configurations are in considerable abundance, none of which can be neglectable during thermal or photo-induced reactions.

(ii) The dominant channel for the $S_1$-state decay corresponds to a ring closure process to dioxirane, which is much more favored compared to other channels. During the photoisomerization, the hydrogen bond caused by the vinyl group significantly slows down the nonadiabatic photoisomerization, the hydrogen bond between the vinyl H and terminal O atoms much more favored compared to other channels. Duration in Criegee-intermediate chemistry.

The findings here are expected to not only deepen the knowledge on the photochemical processes of the Criegee intermediate, but also inspire the rethinking of the “old” concept of substitution effect, that is, how a usually thought “inert” methyl group would dramatically change the nonadiabatic transition and photodynamics of a conjugated molecule.

Supplementary materials: CASSCF and MS-CASPT2-optimized geometries, PESs, and details of dynamic simulations, as well as the Cartesian coordinates of key structures are provided.

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