Conical Intersections Studied by the Configuration-Interaction-Corrected Tamm–Dancoff Method

Lei Xu,* Victor M. Freixas, Flavia Aleotti, Donald G. Truhlar, Sergei Tretiak, Marco Garavelli, Shaul Mukamel, and Niranjan Govind*

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ABSTRACT: Conical intersections directly mediate the internal energy conversion in photoinduced processes in a wide range of chemical and biological systems. Because of the Brillouin theorem, many conventional electronic structure methods, including configuration interaction with single excitations from a Hartree–Fock reference and time-dependent density functional theory in either the linear response approximation (TDDFT) or Tamm–Dancoff approximation (DFT-TDA), have the wrong dimensionality for conical intersections between the ground state (S_0) and the first excited state (S_1) of the same multiplicity. This leads to unphysical state crossings. Here, we implement and assess the configuration-interaction-corrected Tamm–Dancoff approximation (CIC-TDA) that restores the correct dimensionality of conical intersections by including the coupling between the reference state and the intersecting excited state. We apply the CIC-TDA method to the S_1/S_0 conical intersections in ammonia (NH₃), ethylene (C_2H_4), bithiophene ($C_8H_6S_2$), azobenzene ($C_{12}H_{10}N_2$), and 11-cis retinal protonated Schiff base (PSB11) in vacuo. We show that this black-box approach can produce potential energy surfaces (PESs) of comparable accuracy to multireference wave function methods. The method validated here can allow cost-efficient explorations of photoinduced electronically nonadiabatic dynamics, especially for large molecules and complex systems.

Conical intersections (CoIns)^{1–10} play a central role in many crucial photochemical and photobiological processes, such as photosynthesis and light-harvesting,¹¹ photocatalysis,¹² photo-isomerization in the primary event of vision,^{13,14} and ultraviolet light-induced DNA damage.^{15–17} CoIns are a common feature of molecular potential energy surfaces (PESs) when two or more electronic states become degenerate. At and near the CoIn seams, the Born-Oppenheimer approximation breaks down, resulting in strongly coupled electronic and nuclear degrees of freedom. The dynamics of polyatomic molecules in excited states are often driven by internal energy conversion at CoIns and frequently leads to photodissociation or photoisomerization processes. The strong coupling at the intersections may bifurcate the nuclear wave packet such that each portion evolves along a different PES, and the ultrafast nonradiative decay in the vicinity of a CoIn often controls the proportions of the various photoproducts. Therefore, the development of efficient computational techniques for the proper description of CoIns is crucial for studying photochemical processes in molecular systems.

Multireference (MR) electronic structure methods are important for treating the correlation of degenerate and nearly degenerate states, and they are often used to compute consistent PESs of the ground and excited states.^{18,19} Such methods include multistate complete active space perturbation theory (MS-CASPT2),²⁰ based on complete active space selfconsistent field (CASSCF) reference functions, and multireference configuration interaction (MRCI).^{21–23} However, MR methods require a careful selection of orbitals in the active space, and their intrinsic complexity often requires systemspecific specialized knowledge for their effective application. In addition, MR computations are often very expensive, making them less than ideal for running nonadiabatic dynamics on moderate-sized and large molecules especially when the dynamics calculations require extensive ensemble averaging and/or long time scales.

Considering the favorable combination of computational cost and semiquantitative accuracy of Kohn–Sham density functional theory (KS-DFT),^{24,25} time-dependent density functional theory (TDDFT)^{26,27} is a popular method for treating electronically excited states of molecules, where calculations may be performed in the linear-response approximation (KS-LR) or the Tamm–Dancoff approximation (KS-TDA). In the rest of this article, we will follow the usual convention of labeling KS-LR simply as TDDFT. Unlike MR methods, TDDFT and KS-TDA are based on singly excited

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Slater determinants. The working equation of TDA closely resembles that of conventional configuration interaction with single excitations from a Hartree–Fock reference (HF-CIS).²⁸ In this framework, doubly excited configurations are missing in the response state, so the coupling between the ground state and singly excited states is always zero according to the Brillouin theorem.²⁹⁻³¹ We note that if doubly excited states are included in the configuration interaction, the ground and singly excited states could mix indirectly through the doubly excited states. The identically zero coupling of the approximate ground singlet state (S_0) and the first singly excited singlet state (S_1) , gives the wrong dimensionality to the CoIn seam between them.¹⁸ In particular, if a molecule has F internal nuclear degrees of freedom, the CoIn seam should have a dimension of F - 2, but HF-CIS, TDDFT, and KS-TDA all predict a seam of dimension F - 1. Likewise, conventional algebraic-diagrammatic construction (ADC) methods, which usually rely on the HF ground state as the starting point, are unable to reproduce the correct dimensionality and conical shape of an S_1/S_0 surface crossing.^{32,33} For coupled-cluster theory, such as the equation-of-motion coupled-cluster (EOM-CC) and multireference coupled-cluster (MR-CC), problems in the vicinity of accidental same-symmetry intersections can be anticipated due to the inherent non-Hermitian character of the ansatz.^{34–36}

Various modifications of TDDFT have been proposed to improve the description of excited states in the context of CoIns. Grimme and Waletzke³⁷ presented a semiempirical approach in which the configuration interaction matrix elements are constructed empirically by using the exact operator and corrections from DFT. Gräfenstein and Cremer³⁸ proposed the CAS-DFT method which allows an economical, simultaneous treatment of static and dynamic correlation effects for systems with MR character. Spin-flip TDDFT^{39,40} methods that describe target multiconfigurational states as spin-flipping excitations from a single-configurational high-spin triplet reference have shown good performance for CoIns in ethylene-like and uracil molecules.^{41–43} More recently, mixedreference spin-flip TDDFT extensions have been introduced by Park et al.⁴⁴ to tackle this problem.

Another approach is multiconfiguration pair-density functional theory (MC-PDFT)^{45,46} in which a multiconfiguration reference wave function is combined with DFT to provide a better treatment of strongly correlated systems. However, MC-PDFT is a single-state method in which the final MC-PDFT energies do not come from the diagonalization of a modelspace Hamiltonian matrix, thus this can lead to the wrong topology at CoIns.^{47,48} Multistate extensions of MC-PDFT have been developed, such as compressed multistate PDFT^{47,48} (CMS-PDFT) and linearized PDFT⁴⁹ (L-PDFT), in order to recover the correct topology of CoIn. But for the structures of nearly linear molecules, the CMS-PDFT energies are nonunique and can be discontinuous.⁴⁹ L-PDFT does not fail for the degenerate states of nearly linear molecules and its computational cost scales as a constant with the number of states included in the state averaging.⁴⁹ It was recently demonstrated that L-PDFT can be used for the study of azomethane nonadiabatic molecular dynamics.⁵⁰

Maitra and co-workers^{51,52} have explored the dressed TDDFT (D-TDDFT) model which explicitly included two hole–two particle states (i.e., double excitations) by adding frequency-dependent terms from many–body theory to the adiabatic exchange-correlation kernel. Huix-Rottlant intro-

duced an approach called Brillouin-corrected dressed TDDFT (b-D-TDDFT) as an extension to D-TDDFT.⁵³ A parametrized treatment combining HF-CIS or a parametrized semiempirical TDDFT with one doubly excited configuration has also been proposed to recover the correct dimensionality of CoIns.^{54,55}

Most of the above enhancements involve an increase in computational effort and complexity that may limit their applicability to nonadiabatic dynamics simulations. An additional drawback of semiempirical TDDFT approaches is the quality and transferability of the parameters upon which these theories are based. This issue is even more critical for nonadiabatic dynamics simulations, which explore regions far away from those employed for parametrization.

Simple alternatives to the above approaches are configuration-interaction-corrected TDA (CIC-TDA)⁵⁶ and dualfunctional TDA (DF-TDA)⁵⁷ in which another set of orbitals is used instead of KS self-consistent orbitals when building the KS-TDA Hamiltonian. The CIC-TDA method offers a welldefined and cost-effective way to remedy the incorrect dimensionality of CoIns within KS-TDA. Here we investigate the CIC-TDA method to treat PESs corresponding to bond making and bond breaking processes of large molecules mediated by CoIns and compare our results to those obtained by wave function calculations.

In order to explain the significance of the calculations presented here, we recall some features of conical intersections. Let F be the number of internal degrees of freedom of a molecular species; F is equal to $3N_{\text{atoms}} - 6$, where N_{atoms} is the number of atoms. In the absence of spin-orbit coupling (which is neglected in the present article) conical intersections are (F - 2)-dimensional hypersurfaces.^{1,58} In the vicinity of conical intersections, the potential energies show locally avoided crossings. Locally avoided crossings are a signature of conical intersections since a local minimum in the energy gap between two adjacent potential energy curves (along some path through the F-dimensional internal coordinate space) almost always indicates that one is on the shoulder of a conical intersection (which is an unavoided crossing).⁵⁹ Thus, truly avoided crossings would be a rare exception; crossings are avoided locally along paths when one is on the shoulder of a true intersection. Because of the reduced dimensionality of true crossings, an arbitrary path is unlikely to pass precisely through a conical intersection. Methods that do not treat the topology of conical intersection correctly often introduce errors where potential surfaces exhibit crossings or double crossings along arbitrary paths rather than the smoothly avoided crossings one should see on the shoulder of a conical intersection. In the present work we employ the CIC-TDA method that introduces the coupling (missing in KS-LR and KS-TDA) that produces intersections in F - 2 dimensions, and we demonstrate that the behavior of adjacent (in energy) potential energy surfaces along paths close to conical intersections show smooth local avoidance (without double crossings).

THEORY

Within TDDFT, the excitation energies are obtained by solving the following non-Hermitian eigenvalue equation:^{26,27,60,61}

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \omega \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix}$$
(1)

Here, **A** and **B** denote matrices that can be represented in a basis of occupied and unoccupied eigenstates of the ground-state Kohn–Sham equations, ω is the excitation energy, and the eigenvectors **X** and **Y** represent the transition amplitudes associated with the excitations. When using a global-hybrid exchange-correlation (xc) functional with a fraction $c_{\rm HF}$ of Hartree–Fock exchange (where 0 < $c_{\rm HF}$ < 1), the matrix elements A and B are given as^{62,63}

$$A_{ia,jb} = \delta_{ij}\delta_{ab}(\epsilon_a - \epsilon_i) + (ialbj) - c_{\rm HF}(ijlab) + (1 - c_{\rm HF})(ialf_{\rm xc}|bj)$$
(2)

$$B_{ia,jb} = (ialjb) - c_{\rm HF}(iblaj) + (1 - c_{\rm HF})(ialf_{\rm xc}|jb)$$
(3)

where (ij|ab) is a two-electron integral, *i* and *j* indices denote occupied orbitals, *a* and *b* denote unoccupied orbitals, ϵ_a is an orbital energy, and f_{xc} is the exchange-correlation kernel given as the second derivative of the ground-state functional. Neglecting the contributions from the **B** block and diagonalizing only **A**, yields the Tamm–Dancoff approximation (TDA):⁶³

$$\mathbf{A}\mathbf{X} = \boldsymbol{\omega}\mathbf{X} \tag{4}$$

The TDA includes only single excitations from occupied to virtual orbital, whereas the full linear response of eq 1 also allows virtual to occupied de-excitations. The TDA is a well established and widely used simplification to the full time-dependent DFT response problem. For studying photochemical dynamics, KS-TDA is often preferred to TDDFT because it is more resilient and more stable near state interactions.^{64–66}

In wave function theory, the TDA corresponds to configuration interaction (CI) in which only single excitations from a Hartree–Fock determinant are included (HF-CIS). The matrix corresponding to **A** in HF-CIS theory (built from HF orbitals) is

$$\begin{aligned} H_{ia,jb} &= \langle \Phi_i^a | H | \Phi_j^b \rangle \\ &= \delta_{ij} \delta_{ab} (\epsilon_a - \epsilon_i) + (ailjb) - (ablji) \end{aligned}$$

where Φ_i^a denotes the singly excited determinant with an electron excited from occupied orbital *i* to virtual orbital *a*. The matrices **A** of eq 4 and *H* of eq 5 involves all single determinants except the ground-state determinant Φ_0^{HF} , which is not needed because the coupling between the ground-state determinant and any single excited determinant vanishes by virtue of Brillouin's theorem:

$$H_{0,ia} = \langle \Phi_0^{\rm HF} | H | \Phi_i^a \rangle = (a | f^{\rm HF} | i) \equiv 0$$
⁽⁶⁾

where $f^{\rm HF}$ is the Fock operator as defined as

$$f^{\rm HF} = h + \sum_{i}^{N^{\rm eff}} 2J_i - \sum_{i}^{N^{\rm eff}} K_i$$
(7)

where *h* is the core operator (kinetic energy plus external potential), J_i is the Coulomb operator, K_i is the exchange operator, and the sum is over all doubly occupied HF orbitals. The argument has just been given for HF-CIS, but the same situation holds for KS-TDA because the KS reference ground state Φ_0^{HF} does not couple to singly excited determinants.

The lack of coupling of $\Phi_0^{\rm HF}$ to singly excited determinants in HF-CIS does not mean that there are no singly excited

determinants in the exact ground state. The $|\Phi_i^a\rangle$ and $|\Phi_0$ can couple indirectly through the doubly excited determinants by including the matrix elements $\langle \Phi_0^{\rm HF}|H|\Phi_i^a\rangle$ and $\langle \Phi_0^{\rm HF}|H|\Phi_{ij}^{ab}\rangle$ in the configuration interaction Hamiltonian.^{29,31} The artificial decoupling between ground state and singly excited state is the cause of the incorrect (F - 1) dimensionality of CoIns between the ground state and the excited state in HF-CIS and KS-TDA.

In order to correct the dimensionality of CoIns obtained from KS-TDA for the calculation of excited states, we adopt the configuration interaction-corrected TDA (CIC-TDA) method proposed earlier.⁵⁶ The CIC-TDA method introduces a nonzero coupling between the DFT ground state and singleexcitation TDDFT response states by expanding A to a new matrix A' defined by

$$\mathbf{A}' = \begin{pmatrix} E^{\mathrm{KS}} & \mathbf{c}^T \\ \mathbf{c} & \mathbf{A} \end{pmatrix}$$
(8)

where E^{KS} is the energy of reference ground-state, **c** is a $(N^{\text{occ}} \cdot N^{\text{virt}})$ -dimensional column vector and **c**^T corresponds to the transpose of **c**:

$$\mathbf{c}^{T} = \begin{pmatrix} 0 & \cdots & 0 & A_{0,ia}^{\text{CIC}} & 0 & \cdots & 0 \end{pmatrix}$$
(9)

The c vector has only one nonzero element, $A_{0,ia}^{\text{CIC}}$, which is in the row of the dominant determinant of the intersecting excited state of the CoIn. The element $A_{0,ia}^{\text{CIC}}$ adds the coupling between the closed-shell determinant of the ground state and the intersecting dominant singly excited determinant. It can be explicitly calculated according to wave function theory by assuming that the KS and the TDA determinants both approximate wave functions of the real system:

$$A_{0,ia}^{\text{CIC}} = \langle \Phi_0^{\text{KS}} | H | \Phi_i^a \rangle = (a | h + \sum_{n=1}^{N^{\text{occ}}} 2J_n - \sum_{n=1}^{N^{\text{occ}}} K_n | i)$$

= $(a | h + \sum_{n=1}^{N^{\text{occ}}} 2J_n + v_{\text{xc}} | i) - (a | \sum_{n=1}^{N^{\text{occ}}} K_n | i) - (a | v_{\text{xc}} | i)$
= $(a | f^{\text{KS}} | i) - (a | \sum_{n=1}^{N^{\text{occ}}} K_n | i) - (a | v_{\text{xc}} | i)$
= $-(a | \sum_{n=1}^{N^{\text{occ}}} K_n | i) - (a | v_{\text{xc}} | i)$ (10)

where f^{KS} is the KS operator and v_{xc} is the exchangecorrelation potential defined as the functional derivative of the xc functional E_{xc} with respect to electron density. Since the KS orbitals are not eigenvectors of the Fock operator, $A_{0,ia}^{\text{CIC}}$ in eq 10 does not vanish, and its magnitude is usually small as discussed in ref 56 and is equal to the difference between the matrix elements of the HF exchange potential and the KS xc potential.⁵⁶ This introduces a state coupling that is not present in the linear response approximation of time-dependent DFT but that is very important in regions of strong state coupling. Introducing the coupling term $A_{0,ia}^{\text{CIC}}$ between the KS ground state and its first single excitations is essential to recover the correct dimensionality and thus the double cone topology of the PESs near the S_1/S_0 CoIn.^{56,57} Note that we construct the coupling term $A_{0,ia}^{\text{CIC}}$ using the HF exchange functional in this work; in fact, other choices would also be possible.⁵⁷



Figure 1. (a) Geometry of planar NH₃ with the distance of N–H dissociation. (b) Geometry of NH₃ with N–H bond stretching r_1 at $\beta = 89^{\circ}$. Nitrogen and hydrogen atoms are represented by gray and pink colors, respectively. (c,d) PESs of NH₃ near S₁/S₀ conical intersection along the N–H dissociation distance and N–H bond stretching r_1 as calculated by MRCI, CIC-TDA, and KS-SCF/KS-TDA methods.

The eigenvalues of CIC-TDA Hamiltonian eq 8 are found by using the Davidson iterative algorithm,⁶⁷ which is significantly less expensive than a direct diagonalization.

COMPUTATIONAL DETAILS

We compare and discuss results obtained with KS-SCF/KS-TDA, CIC-TDA, MRCI, and CASPT2. Calculations were performed on test cases with increasing molecular sizes. All calculations were performed with $6-31+G(d)^{68-70}$ basis set. In the discussion of the results, we note that (1) in KS-SCF/KS-TDA, the S_0 , S_1 , and S_2 states correspond to the KS ground singlet state (KS-SCF) and the first and second excited singlet state (KS-TDA), respectively; (2) in CIC-TDA, the S_0 , S_1 , and S_2 states correspond to the three lowest eigenvalues of singlet states obtained by diagonalizing CIC-TDA Hamiltonian.

We implemented the CIC-TDA method in a development version of the NWChem^{71,72} computational chemistry program. We used the PBE0 exchange-correlation functional,⁷³ which has $c_{\rm HF}$ equal to 0.25. We also used a variation of PBE0 where $c_{\rm HF}$ is equal to 0.33,^{74,75} which will be referred to as PBE33. In the test cases considered here, the first excited electronic state S_1 is dominated by a transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). Thus, the corresponding single coupling matrix element and its transpose are calculated and added to the KS-TDA A matrix.

The MRCI calculations were carried out with the molpro quantum chemistry package.⁷⁶ The CASPT2 calculations on the PSB11 system were carried out with the OpenMolcas⁷⁷ package with the same active space, i.e., 12 π -electrons in 12 π -orbitals, as reported in ref 78 with state averaging over the two lowest-energy singlet states (S_0 and S_1) and using an imaginary shift of 0.2 $E_{\rm h}$ and the IPEA shift set to zero.

RESULTS AND DISCUSSION

Ammonia. The PESs and CoIns of ammonia (NH₃) have been very well discussed in previous studies. 54-57,79-81 For NH₃, we investigate the PESs around two geometries. One is the minimum-energy CoIn (MECI) planar geometry with C_1 symmetry optimized by CASPT2 in ref 57. The corresponding PESs in Figure 1c were calculated along N–H bond distance stretch, as indicated in Figure 1a. The other is the geometry used previously^{56,81} as indicated in Figure 1b: r_1 , r_2 , and r_3 are the N-H bond lengths, θ (θ_1 , θ_2 , and θ_3) are the H-N-H bond angles, β is the angle between the vector trisecting the three N-H bonds and any of the N-H bonds. The PESs in Figure 1d was calculated along the N–H bond stretching r_1 with $r_2 = r_3 = 1.04$ Å, $\theta = 120^\circ$, and $\beta = 89^\circ$. For the MRCI calculations of NH₃, we used an active space of eight electrons in seven orbitals in the CASSCF calculations and the stateaveraged self-consistent field (SCF) optimization was carried out for an average of three singlet states associated with this

manifold; on top of the CASSCF reference, the MRCI expansion additionally includes single and double excitations.

In Figure 1c the KS-SCF/KS-TDA PES shows two spurious crossings between S_0/S_1 around N-H distance 2.1 and 2.3 Å. In contrast, CIC-TDA provides the correct crossing of CoIn around 2.1 Å and compares well with the CoIn around 1.95 Å predicted from MRCI results. Similarly, in Figure 1d, the KS-SCF/KS-TDA PES gives an unphysical S_0/S_1 crossing at N-H bond stretching $r_1 = 2.21$ Å. This unphysical crossing is corrected by the CIC-TDA, opening a small energy gap around 0.06 eV between S_0 and S_1 , which is consistent with the gap of 0.13 eV between S_0 and S_1 around $r_1 = 2.00$ Å obtained from MRCI results.

It should be noted that as shown in Figure 1c,d, the PESs of S₀ obtained from MRCI results increase initially then decrease as the N-H bond is stretched, eventually reaching a plateau at large internuclear distances [$r(N-H) \sim 2.5$ Å in Figure 1c and $r(N-H) \sim 2.3$ Å in Figure 1d]. However, for example, in Figure 1c the PESs of S₀ calculated from KS-TDA increase continuously then reaching a plateau at N-H dissociation, and the corresponding dissociation energy [the energy difference of S_0 between r(N-H) = 1.0 and 3.0 Å] is 7.15 eV for KS-TDA; the CIC-TDA brings slight decrease of such dissociation energy by 0.008 eV. The example indicates that CIC-TDA corrects the S_0/S_1 crossing of KS-TDA without changing the dissociation energy. The incorrect dissociation energy results because the determinant of a double excitation relevant for describing bond dissociation is not included in the CIC-TDA Hamiltonian.

Ethylene. The PESs and CoIns of ethylene have also been extensively studied. $^{54-57,82-85}$ For C₂H₄, we use the geometry optimized with CASPT2 as in ref 57. The PESs computed by KS-SCF/KS-TDA, CIC-TDA, and MRCI methods along the pyramidalization angle as indicated in Figure 2a, are shown in Figure 2b. The reference for the MRCI calculations used an active space of two electrons in two orbitals (HOMO and LUMO) and averaging of three singlet states; all electrons were correlated. We notice that the KS ground-state solutions are relatively unstable near state crossings and in regions where the KS closed-shell reference is not the ground state, thus it is difficult to converge to smooth potential energy curves for KS-SCF/KS-TDA and CIC-TDA, as also pointed out in an earlier study.56 The PESs calculated from KS-SCF/KS-TDA and CIC-TDA using the PBE0 functional show jumps (see Figure S1 in Supporting Information). The smooth PESs shown in Figure 2b were obtained using the PBE33 functional ($c_{\rm HF}$ = 0.33). The artificial crossing between S_0 and S_1 obtained from KS-SCF/KS-TDA around pyramidalization angle 2° is corrected by the CIC-TDA method. The CIC-TDA method gives a tiny energy gap around 0.13 eV between S_0 and S_1 at 2° , which agrees well with 0.08 eV at around 0° as predicted by MRCI calculations.

Bithiophene. The photophysical properties of thiophenebased materials are used in a variety of different applications,⁸⁷ such as light emitting devices⁸⁸ and polymer-based organic solar cells.⁸⁹ The radiationless-decay of the thiophene molecule after excitation is mainly associated with internal conversion via its singlet electronic states through a CoIn.⁸⁶ For bithiophene, the photodeactivation path is dominated by an intersystem crossing (ISC) according to the study in ref 86. The optimized ground state geometry with the B3LYP functional with 6-311G^{**} basis set, as shown in Figure 3a, was reported in ref 86. Along the reaction path, two S₁





Figure 2. (a) Geometry of pyramidalization with carbon and hydrogen atoms represented by brown and pink colors, respectively. (b) PESs of C_2H_4 near S_1/S_0 conical intersection along the pyramidalization angle as calculated by MRCI, CIC-TDA, and KS-SCF/KS-TDA methods. For the CIC-TDA and KS-SCF/KS-TDA calculations, the PBE33 functional ($c_{HF} = 0.33$) was used.

minimum-energy structures were optimized with CASSCF calculations with the 6-31G* basis sets: the S_1 -min-*a* and S_1 -min-*b*, corresponding to closed-ring and open-ring structures as shown in Figure 3b,c, respectively.

The PESs for the S_0 , S_1 , and S_2 states along the linear interpolation coordinate starting from the S₀ equilibrium structure to the S_1 -min-*a* structure and continuing to the open ring S1-min-b structure, are calculated by KS-SCF/KS-TDA and CIC-TDA methods. The corresponding results are shown in Figure 3d,e. Both KS-SCF/KS-TDA and CIC-TDA yield an S_1/S_0 crossing at interpolation coordinate $\xi = 1.9$. However, for the crossing with KS-SCF/KS-TDA, the energy of S_1 state drops below that of S_0 state, corresponding to negative excitation energy, which is spurious and unphysical. With CIC-TDA method, the unphysical crossing is corrected at the same interpolation coordinate ξ without changing the overall profile of PESs. The CoIn obtained from CIC-TDA shown in Figure 3e is in good agreement with the published results using the equation of motion-coupled cluster singles and doubles method (EOM-CCSD)⁸⁶ and the TDDFT-1D⁵⁵ method. Azobenzene. The most interesting feature of the

Azobenzene. The most interesting feature of the azobenzene and its derivatives is their ability to undergo fast, efficient, and fully reversible photoisomerization. Absorption of photons leads to internal rotation of the phenyl rings about the azo bond, converting the molecule from the *trans* to the *cis* conformation. The photoconversion between the *trans* and *cis* isomers is related to the torsion around the N=N bond and in-plane inversion of one of the two CNN angles. Previous



Figure 3. (a-c) Optimized geometries of bithiophene molecule in ref 86 including: (a) the optimized ground state geometry at the B3LYP/6-311** level S_0 -min, two S_1 minimum structures at the CASSCF/6-31* level: (b) S_1 -min-*a*, and (c) S_1 -min-*b*. Carbon, sulfur, and hydrogen atoms are represented by brown, yellow, and pink colors, respectively. (d,e) Potential energy surfaces for the S_0 , S_1 , and S_2 states of the bithiophene molecule along the linear interpolation coordinate ξ calculated using PBE0/KS-SCF/KS-TDA (left) and PBE0/CIC-TDA (right). The interpolation coordinate $\xi = 0$ corresponds to the geometry of S_0 -min, $\xi = 1$ corresponds to the geometry of S_1 -min-*a* and $\xi = 2$ corresponds to the geometry of S_1 -min-*b*. For KS-SCF/KS-TDA, there is a conical intersection with unphysical crossing at $\xi = 1.9$. For CIC-TDA, this conical intersection is corrected to an avoided crossing.



Figure 4. (a,b) The optimized geometries of gas phase azobenzene in ref 90: (a) *cis*-azobenzene, and (b) *trans*-azobenzene. The CNNC torsion and NNC/CNN symmetric angles are indicated. Carbon, nitrogen, and hydrogen atoms are represented by brown, gray, and pink colors, respectively.

work⁹⁰ has analyzed the PESs of S_0 and S_1 of azobenzene in the three-dimensional space spanned by CNNC torsion and the two CNN bending angles at single-state and multistate RASPT2 levels of theory. The optimized ground-state geometries of *trans-* and *cis-*azobenzene isolated isomers in gas phase reported in ref 90 (as indicated in Figure 4), obtained with Møller Plesset perturbation theory (MP2), were chosen as the starting coordinates for the rigid scan of selected torsional and bending angles.

We chose the CNNC torsion angle at 180° , 100° , and 0° , and for these selected values of CNNC dihedral, we scanned the two CNN/NNC bending angles from 100° to 160° with steps of 2°. We additionally chose the CNN bending angle at 156° with CNNC angle changing from 0° to 180° with steps of 10°. The corresponding PESs obtained from KS-SCF/KS-TDA, CIC-TDA, and RASPT2 calculations are shown in Figure 5a-h. The RASPT2 points of S_0 and S_1 connected by dashed lines were digitized from ref 90. The curves for a CNNC angle of 0° in Figure 5e,f have discontinuous derivatives due to the merging of the trans and cis rigid scans.⁹⁰ The KS-SCF/KS-TDA results give unphysical S_1/S_0 crossings as demonstrated in Figure 5a,c,e,g. The CIC-TDA results, however, correct this and provide topologically correct CoIns without changing the overall profile of the PESs, as shown in Figure 5b,d,f,h.

Furthermore, we compared the positions of CoIns to the RASPT2 results. For the PESs with the CNNC angle equal to 180° in Figure 5a,b, the CIC-TDA method gives the avoided crossing at CNN angle of 152°, in good agreement with the crossing at a CNN angle of 150° in the RASPT2 results. At a CNNC angle of 100°, the avoided crossing of CIC-TDA is around a CNN angle of 134°, in line with 144° in the RASPT2 results. We notice that there is a discontinuity starting from a CNN angle of 154° in the KS-SCF S₀ PES. The CIC-TDA results, in contrast, have smooth PESs with a very narrow S_1/S_0 gap around 0.2 eV after the CNN CoIn angle >134°. Similarly, the RASPT2 results show an S_1/S_0 gap of the same magnitude around 0.1 eV after a CNN CoIn angle >144°. Both CIC-TDA and RASPT2 results give PESs with steep gradient at a CNNC angle of 0° as shown in Figure 5f. The S_1/S_0 CoIn of the CIC-TDA results is around a CNN angle of 159°, which is similar to 156° in RASPT2 results. The PESs of S_1 and S_0 at a CNN angle of 156° are rather flat in Figure 5h. The RASPT2 results indicate a wide crossing seam covering CNNC angles from 0° to 30° and a possible CoIn around a CNNC angle of 100° . CIC-TDA results show a narrow S_1/S_0 gap around 0.2 eV at CNNC angles from 0° to 30° and a CoIn at a CNNC angle of 100°.

11-cis Retinal Protonated Schiff Base (PSB11). PSB11 is the chromophore of rhodopsin proteins. Rhodopsin is a light-sensitive protein that converts light into electrical signals



Figure 5. (a–h) Azobenzene PESs in the space of CNNC torsion and symmetric CNN bending angles as calculated by KS-SCF/KS-TDA, CIC-TDA, and RASPT2 methods. The dashed lines corresponding to the RASPT2 results were digitalized from ref 90. The regions calculated from the *trans*- and *cis*-derived coordinates are separated by vertical black lines in (e,f).

that the brain interprets as vision. The biological activity of rhodopsins is triggered by the ultrafast light-induced *cis-trans* isomerization of the corresponding retinal chromophores. In this process, the retinal chromophores transform the

absorption of light into a physiological signal through conformational changes that initiate a complicated signaling cascade, resulting in electrical impulses sent to the brain and ultimately leading to visual perception.⁹¹ The photoisomeriza-



Figure 6. (a) Geometry of PSB11 with carbon, hydrogen, and nitrogen atoms represented by brown, pink, and gray colors, respectively. The red arrows indicate the stretching and torsion of C_6-C_7 and $C_{11}-C_{12}$ bonds along the CASSCF/6-31G* optimized reaction coordinate as reported in ref 78, i.e., the twisting of the β -ionone ring on C_6-C_7 single bond and rotation about the $C_{11}-C_{12}$ double bond. (b) CASPT2-calculated PESs of PSB11 near S_1/S_0 conical intersection along the reaction coordinate ξ estimated based on that reported in ref 78. We used the coordinates of β -ionone ring frozen (PSB11_{frozen}) structure provided in ref 78 and adjusted the bond lengths and torsion angles as indicated in (a) according to the values in the Figure 2 of ref 78. (c,d) The PESs calculated with KS-SCF/KS-TDA and CIC-TDA methods along the estimated and extrapolated reaction coordinate ξ using PBE0 and CAM-B3LYP functionals, respectively. The geometries of the reaction coordinates $\xi \leq 21$ are the same as these in (b). The geometries of reaction coordinates $\xi > 21$ were extrapolated.

tion of the retinal chromophore has been intensively studied.^{14,78,91,92} The reaction mechanism can be characterized by two modes (first stretching then torsion), and the corresponding photoisomerization path on the spectroscopic state S_1 essentially drives the system into a central double bond twisted S_1/S_0 CoIn.

Using a complete active space of 12 π -electrons in 12 π -orbitals with the 6-31G* basis set, unconstrained CASPT2/ CASSCF minimum energy path (MEP) computations were performed in a previous study,⁷⁸ where the structure of the S_1 / S_0 CoIn was found with a twisting angle of -39° for the β ionone ring and a rotation of -80° about the $C_{11}-C_{12}$ double bond, as indicated in Figure 6a.

To assess how well the CIC-TDA method describes the CoIn of PSB11, we computed the PESs of S_0 and S_1 along the estimated and extrapolated mass-weighted reaction coordinate ξ [bohr(amu)^{1/2}] based on that reported in ref 78. In particular, we used the coordinates of the β -ionone ring frozen (PSB11_{frozen}) structure provided in ref 78 and adjusted the bond lengths and torsion angles as indicated in Figure 6a according to the values in the Figure 2 of ref 78 for reaction coordinate $\xi \leq 21$. We further extrapolated the bond lengths and torsion angles up to ξ around 25. The results of the CASPT2, CIC-TDA/KS-SCF/KS-TDA methods are shown in Figure 6b,c. In Figure 6b, the CASPT2 results predict a S_1/S_0

CoIn at $\xi \approx 20.5$, which is in line with the PESs obtained from CASPT2/CASSCF optimized reaction coordinate in ref 78.

In Figure 6c, the overall profiles of PESs derived from KS-SCF/KS-TDA and CIC-TDA results are consistent with that in Figure 6b. The KS-SCF/KS-TDA results give a minimumenergy gap (MEG) around 0.44 eV at $\xi \approx 21.4$, whereas the CIC-TDA results increase this MEG to 1.07 eV without significantly changing the energy profiles far from this point.

In addition to comparing the KS-SCF/KS-TDA and CIC-TDA results discussed in Figure 6c, we computed the PESs using the PBE33 functional (see Figure S2 in Supporting Information). The MEG of S_0 and S_1 PESs derived from KS-SCF/KS-TDA becomes as small as 0.16 eV. However, the CIC-TDA method has the tendency to increase the MEG by decreasing and increasing the S_0 and S_1 PESs, respectively. Better descriptions of the PESs including MEG between S_0 and S_1 can be obtained with appropriate or improved xc functionals, for which the CIC-TDA method should correct the spurious crossing of KS-SCF/KS-TDA method at the S_1/S_0 CoIn point.

We note that the photoisomerization path on the spectroscopic state S_1 is essentially barrierless and drives the system into a central double bond twisted S_1/S_0 CoIn funnel according to the CASPT2/CASSCF results in ref 78. However, for the KS-SCF/KS-TDA and CIC-TDA results as shown in Figure 6c, there is a barrier of around 0.7 eV characterized by

the energy difference between ξ at 0 and 14. There is a chargetransfer process on S_1 upon photoexcitation,⁷⁸ where the positive charge migrates from the nitrogen-containing moiety toward the other half of the chromophore. Global hybrid functionals with a fixed fraction of HF exchange mixed with a local or semilocal xc functional are not optimal for describing both short-range and long-range interactions simultaneously. Range-separated functionals explicitly handle the distance dependence of interactions, $^{93-95}$ which makes them better suited for describing charge transfer processes. In order to demonstrate this, we calculated the PESs with the CAM-B3LYP^{96,97} functional as shown in Figure 6d. For the PES of the S_1 state, an extended energy plateau emerges from ξ at 0 up to 5 and the barrier of the energy difference between ξ at 0 and 14 is around 0.1 eV. Similar PES profiles and barriers of the S_1 state were also obtained with long-range corrected PBE (LC-PBE) and long-range PBE0 (LC-PBE0) functionals, respectively.^{98–100} (see additional details in Figures S3 and S4 in SI). Further improvements may be possible with tuned rangeseparated functionals.¹⁰⁰⁻¹⁰⁵

CONCLUSIONS

We have shown that the CIC-TDA method, which includes the coupling between the ground state and the intersecting response excited state, can correct the artificial S_1/S_0 state crossings of the KS-SCF/KS-TDA method. We tested the CIC-TDA method from molecules ranging from small to relatively large, in particular, ammonia, ethylene, bithiophene, azobenzene, and the rhodopsin chromophore. The calculated PESs of S_1 and S_0 , including the molecules for which PESs involving bond making and breaking processes, are comparable to those of multireference wave function methods. We performed TDDFT calculations with the PBE0 functional and calculated the CIC coupling element $A_{0,ia}^{\text{CIC}}$ with HF exchange. Additionally, we assessed the efficacy of rangeseparated functionals in the rhodopsin chromophore system. In principle, the CIC-TDA method can be applied with any xc functional, thus further improving the accuracy as possible by using an appropriately selected functional or extensions. The CIC-TDA method is applicable to quite large molecules and can be considered as a promising alternative to semiempirical and multireference wave function methods, making feasible the simulation of the photochemical dynamics of complex molecular systems. Future planned developments include nonadiabatic coupling vectors, which would allow the simulation of wave packet dynamics, and energy gradients, which would in turn allow the simulation of nonadiabatic molecular dynamics for larger molecular systems using curvature-driven trajectory surface hopping methods.^{50,106}

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jctc.4c01768.

Associated coordinates and geometric parameters of ammonia, ethylene, bithiophene, azobenzene, and PSB11; and PESs of ethylene and PSB11 using the PBE0 functional with the variation of the HF exchange fraction (PDF)

AUTHOR INFORMATION

Corresponding Authors

- Lei Xu Physical and Computational Sciences Directorate, Pacific Northwest National Laboratory, Richland, Washington 99352, United States; Email: lei.xu@pnnl.gov
- Niranjan Govind Physical and Computational Sciences Directorate, Pacific Northwest National Laboratory, Richland, Washington 99352, United States; Department of Chemistry, University of Washington, Seattle, Washington 98195, United States; orcid.org/0000-0003-3625-366X; Email: niri.govind@pnnl.gov

Authors

- Victor M. Freixas Department of Chemistry and Department of Physics and Astronomy, University of California, Irvine, California 92697-2025, United States
- Flavia Aleotti Dipartimento di Chimica Industriale "Toso Montanari", University of Bologna, Bologna 40129, Italy; orcid.org/0000-0002-7176-5305
- Donald G. Truhlar Department of Chemistry, Chemical Theory Center, and Minnesota Supercomputing Institute, University of Minnesota, Minneapolis, Minnesota 55455-0431, United States; © orcid.org/0000-0002-7742-7294
- Sergei Tretiak Physics and Chemistry of Materials, Theoretical Division and Center for Integrated Nanotechnologies, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, United States; orcid.org/ 0000-0001-5547-3647
- Marco Garavelli Dipartimento di Chimica Industriale "Toso Montanari", University of Bologna, Bologna 40129, Italy; orcid.org/0000-0002-0796-289X
- Shaul Mukamel Department of Chemistry and Department of Physics and Astronomy, University of California, Irvine, California 92697-2025, United States; Occid.org/0000-0002-6015-3135

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.jctc.4c01768

Notes

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Supporting Information: Conical Intersections Studied by the Configuration-Interaction-Corrected Tamm-Dancoff Method

Lei Xu,¹ Victor M. Freixas,² Flavia Aleotti,³ Donald G. Truhlar,⁴ Sergei

Tretiak,^{5,6} Marco Garavelli,³ Shaul Mukamel,² and Niranjan Govind^{1,7}

¹Physical and Computational Sciences Directorate,

Pacific Northwest National Laboratory, Richland, WA 99352, USA*

²Department of Chemistry and Department of Physics and Astronomy,

University of California, Irvine, California 92697-2025, USA

³Dipartimento di Chimica Industriale "Toso Montanari",

University of Bologna, Via Piero Gobetti 85, Bologna 40129, Italy

⁴Department of Chemistry, Chemical Theory Center, and Minnesota Supercomputing Institute,

University of Minnesota, Minneapolis, MN 55455-0431, USA

⁵Physics and Chemistry of Materials, Theoretical Division,

Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA

⁶Center for Integrated Nanotechnologies, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA

⁷Department of Chemistry, University of Washington, Seattle, WA 98195, USA[†]

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Cartesian coordinates of molecules

We used the coordinates of planar NH_3 and C_2H_4 indicated in Fig.1(a) and Fig.2(a), respectively, as reported in Ref.[1], corresponding to the optimized minimumenergy conical intersection (MECI) geometry by multistate CASPT2/6-311+G(2d,p). The relevant xyz coordinates at MECI are given in Table S1 and Table S3. The coordinates of NH₃ with N-H bond stretching indicated in Fig.1(b) are given in Table S2. The optimized geometries of bithiophene molecule, *i.e.*, S_0 -min and two S_1 minimum structures, were reported in the Supporting Information of Ref. [2]. The corresponding coordinates are given in Table S4, Table S5, and Table S6. The optimized geometries of gas phase *cis*- and *trans*-azobenzene were reported in Ref.[3]. The corresponding coordinates are provided in Table S7 and Table S8. For the geometries of PSB11 discussed in main text, we used the coordinates of β -ionone ring frozen (PSB11_{frozen}) structure reported in Ref.[4] and the xyz coordinates are given in Table S9. The bond lengths and torsion angles indicated in Fig.6(a) were digitalized and extrapolated according to the values in the Fig.2 of Ref.[3]. The corresponding numbers are listed in Table S10.

TABLE S1. The xyz coordinates of planar NH_3 optimized at MECI as reported in Ref.[1] with units in Å.

atoms	Х	Y	Z
Ν	0.00	0.00	0.00
Н	-0.38152359	0.94882791	0.00
Η	-0.76127515	-0.68787230	-0.00019546
Н	1.94065126	0.00	0.00

TABLE S2. The xyz coordinates of NH₃ with N–H bond stretching at $r_1 = 2.0$ Å. Units in Å.

	-		
atoms	Х	Y	Z
Ν	0.00	0.00	0.00
Н	1.99970000	0.00	-0.03490000
Н	-0.51942087	-0.89966335	-0.01813305
Η	-0.51942087	0.89966335	-0.01813305

TABLE S3. The xyz coordinates of C_2H_4 optimized at MECI as reported in Ref.[1] with units in Å.

atoms	Х	Y	Z
С	0.00	0.00	0.00
\mathbf{C}	1.39256669	0.00	0.00
Η	-0.16311333	-0.86899057	-0.72061431
Н	-0.15689386	-0.86646844	0.72855820
Н	1.96657058	0.92903077	0.00000000
Н	2.01361377	-0.90061491	-0.00046903



FIG. S1. (a) The geometry of pyramidalization with carbon and hydrogen atoms represented by brown and pink colors, respectively. (b) PESs of C_2H_4 near S_1/S_0 conical intersection along the pyramidalization angle as calculated by MRCI, CIC-TDA, and KS-SCF/KS-TDA methods. For the CIC-TDA and KS-SCF/KS-TDA calculations, PESs with PBE0 functional (the factor of Hartree-Fock exchange functional as 0.25) are not smooth.



FIG. S2. The PESs of PSB11 along the reaction coordinate ξ as discussed in main text. In these CIC-TDA and KS-SCF/KS-TDA calculations, the PBE33 functional (the factor of Hartree-Fock exchange functional as 0.33) was used.



FIG. S3. The PESs of PSB11 along the reaction coordinate ξ as discussed in main text. In these CIC-TDA and KS-SCF/KS-TDA calculations, the long-range corrected PBE (LC-PBE) functional was used.



FIG. S4. The PESs of PSB11 along the reaction coordinate ξ as discussed in main text. In these CIC-TDA and KS-SCF/KS-TDA calculations, the long-range corrected PBE0 (LC-PBE0) functional was used.

TABLE S5. The xyz coordinates of optimized S_1 -min-a bithiophene structure as reported in Ref.[1] with units in Å.

atoms	Х	Y	Z
С	0.11152670	0.67910799	0.00
\mathbf{C}	-0.11152670	-0.67910799	0.00
\mathbf{C}	1.35854305	1.39188333	0.00
\mathbf{C}	-1.35854305	-1.39188333	0.00
\mathbf{C}	1.20054730	2.77778907	0.00
\mathbf{C}	-1.20054730	-2.77778907	0.00
\mathbf{C}	-0.14525417	3.16629087	0.00
\mathbf{C}	0.14525417	-3.16629087	0.00
\mathbf{S}	-1.22808900	1.82619831	0.00
\mathbf{S}	1.22808900	-1.82619831	0.00
Н	2.30497134	0.88846443	0.00
Н	-2.30497134	-0.88846443	0.00
Н	2.01071451	3.47941856	0.00
Н	-2.01071451	-3.47941856	0.00
Н	-0.53070359	4.16426731	0.00
Η	0.53070359	-4.16426731	0.00

TABLE S4. The xyz coordinates of optimized S_0 -min bithiophene structure as reported in Ref.[1] with units in Å.

atoms	Х	Y	Z
С	0.12027495	0.71571272	0.05493598
\mathbf{C}	-0.12027495	-0.71571272	0.05493598
\mathbf{C}	1.28405149	1.39848545	0.31831287
\mathbf{C}	-1.28405149	-1.39848545	0.31831287
\mathbf{C}	1.14725255	2.81093789	0.22642491
\mathbf{C}	-1.14725255	-2.81093789	0.22642491
\mathbf{C}	-0.11806895	3.20124774	-0.10405096
\mathbf{C}	0.11806895	-3.20124774	-0.10405096
\mathbf{S}	-1.16742554	1.84040127	-0.32994087
\mathbf{S}	1.16742554	-1.84040127	-0.32994087
Н	2.20396213	0.90011764	0.59494876
Н	-2.20396213	-0.90011764	0.59494876
Н	1.95488123	3.50702862	0.41043484
Н	-1.95488123	-3.50702862	0.41043484
Н	-0.50356180	4.20093034	-0.23160591
H	0.50356180	-4.20093034	-0.23160591

 TABLE S6.
 The xyz coordinates of optimized S_1 -min-b

 bithiophene structure as reported in Ref.[1] with units in Å.

Х	Y	Z
0.15920037	0.31045414	0.11753307
0.01117539	-1.11654281	0.11760603
1.17195966	1.18365704	0.11728153
-1.17204183	-1.80712782	0.11724081
1.08380471	2.64822426	0.11728655
-0.99523942	-3.23130300	0.11736937
-0.00745488	3.47248692	0.11767141
0.31574076	-3.59409371	0.11785437
-1.66135095	2.99914200	0.11825485
1.37586054	-2.22042866	0.11813181
2.17868542	0.79137481	0.11696539
-2.12632155	-1.31722121	0.11690313
2.03849073	3.14655214	0.11700621
-1.80636944	-3.93357219	0.11710284
0.18395691	4.53058491	0.11763454
0.72141233	-4.58491083	0.11801480
	$\begin{array}{c} X \\ 0.15920037 \\ 0.01117539 \\ 1.17195966 \\ -1.17204183 \\ 1.08380471 \\ -0.99523942 \\ -0.00745488 \\ 0.31574076 \\ -1.66135095 \\ 1.37586054 \\ 2.17868542 \\ -2.12632155 \\ 2.03849073 \\ -1.80636944 \\ 0.18395691 \\ 0.72141233 \end{array}$	XY 0.15920037 0.31045414 0.01117539 -1.11654281 1.17195966 1.18365704 -1.17204183 -1.80712782 1.08380471 2.64822426 -0.99523942 -3.23130300 -0.00745488 3.47248692 0.31574076 -3.59409371 -1.66135095 2.99914200 1.37586054 -2.22042866 2.17868542 0.79137481 -2.12632155 -1.31722121 2.03849073 3.14655214 -1.80636944 -3.93357219 0.18395691 4.53058491 0.72141233 -4.58491083

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TABI	LE S7.	The xy	$z \cos \theta$	ordinates	s of	optimized	l ci	s-azober	nzene
struct	ure in	dicated	in F	$\operatorname{Fig.4(a)}$	as	reported	in	Ref.[3]	with
units	in Å.								
-									

 TABLE S8.
 The xyz coordinates of optimized transazobenzene structure indicated in Fig.4(b) as reported in Ref.[3] with units in Å.

atoms	Х	Υ	Z
С	0.00	0.00	0.00
\mathbf{C}	1.40778	0.00	0.00
\mathbf{C}	2.12914	-1.20526	0.00
\mathbf{C}	1.43609	-2.42458	0.09846
\mathbf{C}	0.02765	-2.43644	0.13519
\mathbf{C}	-0.68616	-1.22315	0.06504
Ν	2.16663	1.22177	-0.09950
Ν	1.96300	2.15411	0.75105
\mathbf{C}	1.07163	1.91440	1.85850
\mathbf{C}	0.05209	2.85556	2.07705
\mathbf{C}	-0.84582	2.66582	3.14218
\mathbf{C}	-0.68438	1.57323	4.01705
\mathbf{C}	0.38451	0.67440	3.82705
\mathbf{C}	1.26519	0.83900	2.74611
Н	-0.04341	3.70716	1.39623
Н	-1.66030	3.37971	3.30057
Н	-1.37559	1.43417	4.85356
Н	0.53109	-0.15866	4.52173
Н	2.08654	0.13770	2.58452
Н	3.22208	-1.17346	-0.04837
Н	1.99357	-3.36609	0.12840
Н	-0.51096	-3.38660	0.19814
Н	-1.78068	-1.22969	0.06333
Н	-0.54677	0.94446	-0.03962

atoms	Х	Y	Z
С	0.00	0.00	0.00
\mathbf{C}	1.41312	0.00	0.00
\mathbf{C}	2.12973	-1.21332	0.00
\mathbf{C}	1.43696	-2.43679	0.00
\mathbf{C}	0.02907	-2.44482	0.00
\mathbf{C}	-0.68280	-1.22494	0.00
Ν	2.22340	1.17081	0.00
Ν	1.54400	2.25707	0.00
\mathbf{C}	2.35434	3.42797	0.00
\mathbf{C}	1.63796	4.64138	0.00
\mathbf{C}	2.33082	5.86476	0.00
\mathbf{C}	3.73874	5.87267	0.00
\mathbf{C}	4.45044	4.65269	0.00
\mathbf{C}	3.76743	3.42788	0.00
Η	0.54470	4.60292	0.00
Η	1.77566	6.80791	0.00
Η	4.28198	6.82257	0.00
Н	5.54520	4.66192	0.00
Η	4.30349	2.47707	0.00
Н	3.22297	-1.17497	0.00
Н	1.99203	-3.38001	0.00
Н	-0.51402	-3.39483	0.00
Н	-1.77756	-1.23459	0.00
Н	-0.53629	0.95067	0.00

atoms	Х	Y	Z
Ν	-0.029429	0.017858	0.074216
С	-0.007019	0.006393	1.415582
С	1.152627	0.039737	2.160031
\mathbf{C}	1.267612	0.030386	3.620895
\mathbf{C}	2.539165	0.069767	4.128204
\mathbf{C}	3.050269	0.074779	5.517506
\mathbf{C}	2.366786	0.040364	6.696459
\mathbf{C}	2.955688	0.048606	8.026973
\mathbf{C}	2.063313	0.007793	9.114704
\mathbf{C}	2.429039	0.008279	10.448629
\mathbf{C}	1.473708	-0.035053	11.573839
\mathbf{C}	0.662629	1.017122	11.845135
\mathbf{C}	-0.319136	1.004167	12.997569
\mathbf{C}	-0.592171	-0.388087	13.553164
\mathbf{C}	0.720525	-1.142561	13.720375
\mathbf{C}	1.474984	-1.345128	12.393182
\mathbf{C}	0.810497	-2.461087	11.563294
\mathbf{C}	2.912919	-1.780869	12.732129
\mathbf{C}	0.691213	2.332857	11.100932
\mathbf{C}	4.444200	0.090461	8.252431
С	0.024985	-0.020705	4.482883
С	-1.227264	-0.016577	-0.740317
Η	-1.285132	0.869481	-1.361060
Η	-1.223652	-0.893139	-1.377016
Η	-2.095529	-0.052669	-0.099332
Η	0.843974	0.052242	-0.408107
Η	-0.974738	-0.031302	1.873385
Η	2.079562	0.076857	1.613587
Η	0.022747	-0.906234	5.108585
Η	-0.883916	-0.047273	3.900350
Η	-0.038613	0.851258	5.124257
Η	3.335130	0.103844	3.405621
Η	4.122023	0.113104	5.554308
Η	1.297166	0.002930	6.687250
Η	5.007140	0.105221	7.333477
Η	4.765959	-0.777628	8.818672
Η	4.718229	0.973586	8.819785
Η	1.011150	-0.000602	8.891182
Η	3.473509	-0.053700	10.694917
Н	-1.244989	1.471028	12.670558
Н	0.073405	1.646974	13.784324
Н	-1.259217	-0.928401	12.888414
	Continued	d on next page	

TABLE S9: The xyz coordinates of $PSB11_{frozen}$ structure reported in Ref.[4] with units in Å.

atoms	Х	Υ	Z
Н	-1.103055	-0.310756	14.507259
Н	0.549361	-2.113099	14.176377
Н	1.355574	-0.585071	14.405424
Н	-0.217669	-2.223569	11.314930
Н	1.343371	-2.631063	10.632593
Н	3.471324	-2.089507	11.853689
Н	0.814428	-3.395272	12.116111
Н	2.887708	-2.630910	13.405623
Н	3.463966	-0.985802	13.225725
Н	1.509905	2.421781	10.400380
Н	-0.238522	2.481465	10.557507
Н	0.773155	3.152078	11.809492

TABLE S9 – continued from previous page

ξ	$\Theta(C_6-C_7)$	$\Theta(C_{11}-\mathbf{C}_{12})$	$d(C_{11} - C_{12})$	$d(C_6-C_7)$	
0.0	-68.75	-0.26	1.36371	1.49418	
1.0	-65.98	-0.54	1.46112	1.47605	
2.0	-63.24	-1.47	1.47406	1.47106	
3.0	-59.56	-2.39	1.47711	1.46812	
4.0	-50.97	-5.84	1.47512	1.45710	
5.0	-48.78	-6.68	1.47518	1.45506	
6.0	-46.41	-7.79	1.47419	1.45108	
6.6	-44.10	-13.81	1.47619	1.44894	
7.2	-42.89	-17.12	1.47714	1.44999	
7.7	-42.60	-23.42	1.48298	1.44810	
8.3	-41.53	-25.98	1.48209	1.44905	
8.8	-40.87	-31.77	1.48304	1.44910	
9.9	-39.13	-33.58	1.48505	1.45006	
10.5	-38.90	-36.14	1.48705	1.45111	
11.1	-38.57	-37.73	1.48610	1.45102	
11.7	-37.02	-40.52	1.48706	1.44897	
12.2	-36.65	-43.23	1.48711	1.44908	
12.8	-36.18	-43.18	1.48711	1.44803	
13.4	-34.16	-47.98	1.48921	1.44714	
13.9	-34.86	-48.77	1.48712	1.44714	
14.5	-33.55	-50.96	1.48818	1.44720	
15.1	-34.62	-55.07	1.48818	1.44810	
15.6	-32.19	-55.67	1.48724	1.44811	
16.2	-33.91	-59.17	1.48634	1.45011	
16.8	-32.56	-62.34	1.48714	1.45011	
17.3	-32.74	-63.36	1.48595	1.45021	
17.9	-32.22	-67.00	1.48630	1.45152	
18.5	-32.36	-70.50	1.48466	1.45327	
19.0	-31.61	-72.41	1.48417	1.45337	
19.7	-31.65	-77.44	1.48267	1.45542	
20.3	-31.65	-80.34	1.47933	1.45842	
21.0	-30.99	-85.37	1.47585	1.46022	
21.2	-30.70	-87.95	1.47508	1.46195	
21.4	-30.55	-89.76	1.47400	1.46304	
21.6	-30.40	-91.64	1.47286	1.46420	
21.8	-30.25	-93.60	1.47165	1.46543	
22.0	-30.08	-95.65	1.47039	1.46672	
22.2	-29.91	-97.79	1.46907	1.46809	
22.4	-29.73	-100.01	1.46768	1.46953	
22.6	-29.55	-102.34	1.46622	1.47104	
22.8	-29.35	-104.76	1.46470	1.47263	
Continued on next page					

TABLE S10: The digitalized and extrapolated torsion angles $[\Theta(C_6-C_7) \text{ and } \Theta(C_{11}-C_{12}) \text{ unit in degree}]$ and bond lengths $[d(C_{11}-C_{12}) \text{ and } d(C_6-C_7) \text{ unit in } Å]$ indicated in Fig.6(a) along the reaction coordinate ξ according to the Fig.2 in Ref.[4].

TABLE 510 – continued from previous page						
ξ	$\Theta(\mathrm{C}_6\mathrm{-C}_7)$	$\Theta(C_{11}{-}C_{12})$	$d(C_{11} - C_{12})$	$d(C_6-C_7)$		
23.0	-29.15	-107.28	1.46311	1.47430		
23.2	-28.94	-109.91	1.46144	1.47605		
23.4	-28.72	-112.65	1.45970	1.47789		
23.6	-28.49	-115.51	1.45789	1.47982		
23.8	-28.25	-118.48	1.45600	1.48183		
24.0	-28.00	-121.58	1.45403	1.48394		
24.2	-27.74	-124.80	1.45197	1.48614		
24.4	-27.47	-128.16	1.44984	1.48844		
24.6	-27.19	-131.66	1.44761	1.49084		
24.8	-26.89	-135.29	1.44530	1.49334		
25.0	-26.59	-139.07	1.44290	1.49595		

TABLE S10 – continued from previous page

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- * lei.xu@pnnl.gov
- [†] niri.govind@pnnl.gov
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