The Singlet−Triplet Gap in Trimethylenmethane and the Ring-Opening of Methylenecyclopropane: A Multireference Brillouin−Wigner Coupled Cluster Study

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We performed an ab initio study of the singlet−triplet gap in trimethylenmethane (TMM) and of the ring-opening of methylenecyclopropane by the multireference BWCC method. Since the singlet states of TMM and intermediates between TMM and methylenecyclopropane have a strong multiconfigurational character, it is necessary to use a multireference method. The cc-pVDZ and cc-pVTZ basis sets were used. We compared our results with experiments, where available, and with previous calculations performed by MCSCF and spin-flip coupled-cluster-type methods.

1. Introduction

The trimethylenmethane (TMM) is a planar molecule with two nonbonding electrons. It constitutes a typical representative of a non-Kekulé system, the four π electrons being delocalized over the four π molecular orbitals. This unusual electronic system has been known since more than 50 years ago.[1] It was first isolated and its ESR spectrum recorded by Dowd in 1966.[2] Ten years later, the triplet state was confirmed as the ground state by an ESR experiment,[3] and a few years after that, the singlet−triplet gap was obtained from its photoelectron spectra.[4] The TMM derivatives are used, for example, as organic ferromagnets or DNA cleaving agents.[5,6]

As mentioned before, the triplet $^3A'_2$ is the ground state of TMM, which is in agreement with Hund's rule and was confirmed by experimental data. The CCSD[7] or CCSD(T)[8] methods are appropriate for the description of this state.

The equilibrium geometry of the $^3A'_2$ state has D_{3h} symmetry, and the degenerate HOMO orbitals are singly occupied by electrons with parallel spins. The point group symmetry of the $^1B_1$ state is C_{2v} in the equilibrium geometry. The plane of the methylene group is perpendicular to the plane of all other atoms. The two highest occupied orbitals are not degenerate. The state $^1A_1$, similar to the $^1B_1$, has the point group C_{2v}. It is a planar system like the triplet state, but one of the carbon−carbon bonds is longer than the others. The HOMO orbital is doubly occupied, yielding a closed-shell configuration.

The energy of the $^3A'_2 - {}^1A_1$ gap is available from measured ESR spectra, which give 0.699 eV. The experimental data for the $^3A'_2 - {}^1B_1$ gap are not available due to unfavorable Franck−Condon factors.

The methylenecyclopropane (MCP), its derivatives, and the mechanisms of the ring opening had been intensely studied already in 1980.[9,10] MCP is the initial compound for the synthesis of TMM. The ground state of the MCP is $^1A_1$ (C_{2v} symmetry). The trimethylenmethane has the $^3A'_2$ ground state, but when the ring is being opened, the TMM assumes the geometry of the energetic minimum of the $^1A_1$ state, different from the optimum geometry of the ground state. During the conrotation mechanism, the C_2 symmetry is conserved, and the electronic states thus belong to A or B irreducible representations. The transition state of the conrotation has methylene groups rotation angle $\alpha = 50°$, where $\alpha = 0°$ corresponds to the planar TMM and $\alpha = 90°$ to the MCP. During the disrotation, the C_s symmetry is conserved, and the intermediate states are correspondingly classified as A′ and A″. According to the previous theoretical predictions[9] based on MCSCF/STO-3G and SDQ-CI methods, the energy of the conrotatory transition state should be slightly lower than that of the disrotatory transition state.

TMM belongs to the class of chemically interesting compounds which, owing to their quasidegenerate nature, posess a low-lying open-shell singlet state that cannot be successfully treated by standard quantum chemical methods such as CCSD or CCSD(T). It is generally accepted that the necessary accuracy in computation of these structures can be achieved by means of multireference techniques.

Over the years, various approaches on how to treat such problems have been proposed; see ref 11 for an excellent historical overview and extensive bibliography. The multireference coupled cluster (CC) methods had not become so popular in computational chemistry yet due to several problems, mainly their computational complexity, the problem of intruder states, and the lack of size-extensivity. Recently, progress in developing state-specific multireference CC and CEPA methods, which do not suffer the intruder states problem, has been achieved by Mukherjee and collaborators.[12−15] Recently, Krylov et al.[16] developed the spin-flip methods, tailored particularly for multiradical systems, of which TMM is a prominent representative.[17−19] However, our particular interest is focused on the state-specific Brillouin−Wigner CC method,[20−23] which is computationally tractable and does not suffer from intruder states. An efficient implementation of this method has been developed[23] and later extended for an extended number of reference configurations and open-shell ones.[24,25] Hubač and Wilson formulated a simple a posteriori size-extensivity correction for the BWCC method,[26] which turned out to work surprisingly well.[27] Moreover, we have shown that one can construct continuous transitions between MR BWCC and other Hilbert space MRCC approaches, and on this basis set, one can perform an iterative size-extensivity correction, which yields exact extensivity.[28] The performance of the BWCC method has been assessed by calculations on

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several small but "difficult" model systems and diatomic molecules.[24,25,29−34] The efficacy of the implementation[23] and the elimination of the intruder state problem in BWCC have been demonstrated by calculations of chemically interesting systems of moderate size.[35−39] Reviews of the BWCC theory can be found in refs 40 and 41.

The BWCCSD method looks very promising; however, similarly to a standard CCSD, it has its limitations in accuracy concerning the description of dynamic correlation. For highly accurate calculations of systems where both static and dynamic correlation play a role, it seems necessary to include connected triple excitations into the multireference coupled cluster scheme. The importance of connected triple excitations is well-recognized, and they have thus been implemented recently by Musial and Bartlett for the multireference Fock space CC method,[42] as well as for the equation of motion CC method.[43] We have developed an approximation to the iterative MR BWCCSDT, called MR BWCCSDT-α,[44] which improves the accuracy with respect to MR BWCCSD substantially.

In this paper, we computed the splittings between the triplet ground state and two lowest singlet states $^1B_1$ and $^1A_1$ in trimethylenmethane. We also studied the ring opening of methylenecyclopropane by conrotatory and disrotatory paths employing the MR BWCCSD and MR BWCCSDT-α methods.

2. Computational Details

2.1. Method. Since the derivation of the state-specific Brillouin−Wigner coupled cluster theory has already been presented several times,[23,27,44] we describe here only briefly the essence of the method.

Model wave function for the state α is assumed in the form

$$\Psi_\alpha^P = \sum_{\mu=1}^{M} C_\alpha^\mu \, \Phi_\mu \qquad (1)$$

where M is the number of reference configurations, Φ_μ are the reference Slater determinants, and C_α^μ their expansion coefficients. The exact wave function is obtained by applying the state-specific wave operator Ω_α to it

$$\Psi_\alpha = \Omega_\alpha \, \Psi_\alpha^P \qquad (2)$$

while the intermediate normalization condition must be fulfilled

$$\langle \Psi_\alpha | \Psi_\alpha^P \rangle = 1 \qquad (3)$$

The exact energy of selected state $\mathcal{E}_\alpha$ is then obtained as an eigenvalue of the (non-Hermitian) state-specific effective Hamiltonian

$$H^{\mathrm{eff}} \, \Psi_\alpha^P = \mathcal{E}_\alpha \, \Psi_\alpha^P \qquad (4)$$

defined as

$$H^{\mathrm{eff}} = PH\Omega_\alpha P \qquad (5)$$

where

$$P = \sum_{\mu=1}^{M} |\Phi_\mu\rangle\langle\Phi_\mu| \qquad (6)$$

is the projection operator onto the model space spanned by the M reference configurations. For the wave operator Ω_α, we employ the Jeziorski−Monkhorst ansatz[45]

$$\Omega_\alpha = \sum_{\mu=1}^{M} \mathrm{e}^{T(\mu)} |\Phi_\mu\rangle\langle\Phi_\mu| \qquad (7)$$

Each reference configuration has its own cluster operator $T(\mu)$, which can be truncated, for example, to single and double excitations, like in the single-reference CCSD method. Amplitudes corresponding to excitations between reference configurations (so-called internal excitations) are zero, to fulfill the intermediate normalization condition (eq 3). The wave operator must obey the generalized Bloch equation[28]

$$\lambda E_\alpha \Omega_\alpha P + [(1-\lambda)\Omega_\alpha H_0 - H_0 \Omega_\alpha]P = V\Omega_\alpha P - (1-\lambda)\Omega_\alpha P V \Omega_\alpha P \qquad (8)$$

from which one can derive the general equation for BWCC amplitudes with size-extensivity correction

$$\lambda(E_\alpha - \langle\Phi_\mu|H^{\mathrm{eff}}|\Phi_\mu\rangle)\langle\Phi\vartheta|\mathrm{e}^{T(\mu)}|\Phi_\mu\rangle = \langle\Phi\vartheta|H_{\mathrm{N}}(\mu)\mathrm{e}^{T(\mu)}|\Phi_\mu\rangle_{\mathrm{C}} + \lambda\langle\Phi\vartheta|H_{\mathrm{N}}(\mu)\mathrm{e}^{T(\mu)}|\Phi_\mu\rangle_{\mathrm{DC,\,L}} \qquad (9)$$

In this equation, $H_N(\mu)$ is the Hamiltonian normally ordered with respect to Fermi vacuum Φ_μ, and the subscripts C and DC,L denote connected and disconnected but linked diagrams, respectively. The parameter λ serves the continuous transition between Brillouin−Wigner and Rayleigh−Schroedinger perturbation theories[28] and facilitates the size-extensivity correction. A continuous decrease of λ from 1 toward 0 during the CC iterations gives the iterative size-extensivity correction, while the a posteriori size-extensivity correction is performed by iterating of the amplitudes until convergence at $\lambda = 1$, followed by a single iteration setting $\lambda = 0$. The method has been implemented at the singles, doubles, and also approximate iterative triples level in the *ACES II* program,[46] for complete, and recently also for general incomplete, model spaces.[47]

2.2. Trimethylenmethane. TMM has a multiconfigurational character, so computations performed by single reference methods often converged to the wrong state, did not converge at all, or yielded very inaccurate results. The *ACES II* program does not include routines for the MCSCF or CASSCF method. We thus generated initial orbitals for post-HF methods using the CASSCF method within the *GAMESS-UK* package.[48] These orbitals were transformed to the *ACES II* form. In this procedure, special care has to be taken to have consistent orientation of the molecule and the same order of basis functions in both programs and to convert between different normalization conventions of the atomic orbitals (AOs).

Since the analytic gradient code for the MR BWCCSD method is not finished yet, optimizations were performed at the CASSCF level using the *GAMESS-UK* program. These geometries are displayed in Figure 1. As compared with geometries obtained with the CCSD(T)/cc-pVTZ method or SF-DFT/6-31G*,[18] the differences are small, since the potential energy surface is very flat around the equilibrium geometry.

Singlet states need more reference configurations, in particular, the $^1A_1$ state. Both singlet states were described by four references.

Due to the MR character of the $^1A_1$ and $^1B_1$ states (Figure 2), we used the CASSCF MOs for the subsequent BWCC treatment.

2.3. Methylenecyclopropane. The geometry optimization of MCP and all intermediates was performed by the *GAMESS-UK* package employing the CASSCF method, since the inter-

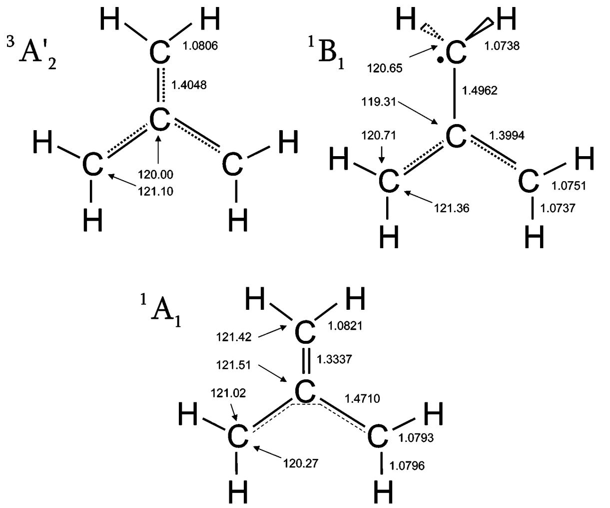

Figure 1. Equilibrium geometries performed by the CASSCF(4,4) method and cc-pVDZ basis set. The $^3A'_2$ state has D_{3h} symmetry; $^1B_1$ and $^1A_1$ states have C_{2v} symmetry.

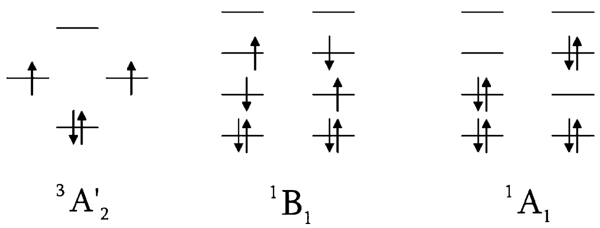

Figure 2. The electronic configuration of TMM states.

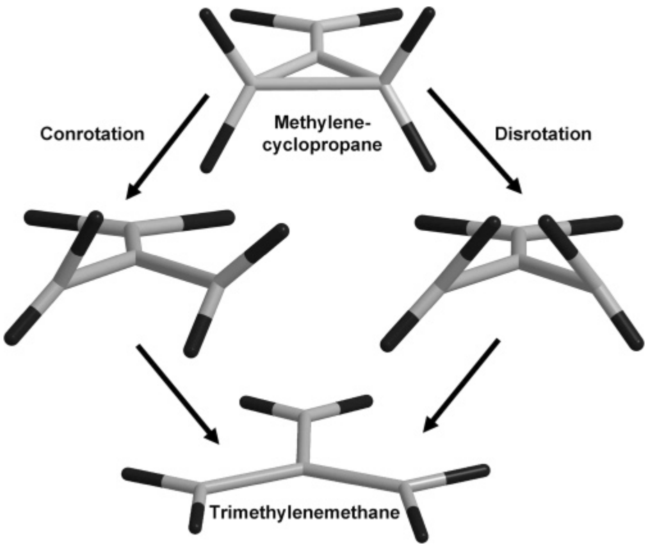

Figure 3. Scheme of the methylenecyclopropane ring opening by two ways—conrotation and disrotation.

mediates have a large multiconfigurational character. We choose the cc-pVDZ basis set for all computations.

As the parameter of the reaction coordinate, we have chosen the dihedral angle α, which is the angle between methylene groups and other atoms in the molecule. For conrotation, the angle is positive for both groups, while for disrotation, it is negative for one of the groups (Figure 3). The planarity of the carbon atoms was enforced by the *Z*-matrix construction, while other geometry parameters were allowed to vary during the optimization, which was performed for the singlet state.

For the optimized geometries, we computed the CASSCF orbitals, which were subsequently used for CCSD and MR BWCCSD methods. The SCF orbitals gave higher CC energies than the CASSCF orbitals, mainly when the geometry was close to the TMM one. The CASSCF active space was formed by the doubly occupied HOMO orbital and three unoccupied LUMO orbitals.

The four reference configurations, employed in the MR BWCCSD method, can be written for the conrotation case, singlet state as

$$(\mathrm{core})(4a)^2(5a)^2(2b)^2(6a)^2(3b)^2(7a)^2(4b)^2(8a)^2(5b)^2(6b)^2(9a)^2$$
$$(\mathrm{core})(4a)^2(5a)^2(2b)^2(6a)^2(3b)^2(7a)^2(4b)^2(8a)^2(5b)^2(6b)^2(7b)^2$$
$$(\mathrm{core})(4a)^2(5a)^2(2b)^2(6a)^2(3b)^2(7a)^2(4b)^2(8a)^2(5b)^2(6b)^2(9a)^{1\alpha}(7b)^{1\beta}$$
$$(\mathrm{core})(4a)^2(5a)^2(2b)^2(6a)^2(3b)^2(7a)^2(4b)^2(8a)^2(5b)^2(6b)^2(9a)^{1\beta}(7b)^{1\alpha}$$

where 9a is the HOMO orbital and 7b the LUMO orbital. In core, we included four orbitals occupied by eight electrons which were excluded from the correlation treatment. Similar configurations were used for the disrotatory case. For comparison of calculated data with experiment, it is necessary to add the difference of zero point energies.

Basis sets cc-pVDZ,[49] aug-cc-pVDZ[50] and cc-pVTZ[51] have been obtained from EMSL.

3. Results and Discussion

3.1. The Singlet−Triplet Gap in the Trimethylenmethane. Results for $^1B_1$ and $^1A_1$ states are given in Table 1. We also present there results from literature[17−19] for comparison.

For the $^1A_1$ state, there is evidently a strong dependence on the level of BWCC approximation. The pronouncedly MR character of this state is confirmed by the difference between single-reference CCSDT (not shown in table) and 4R−BWCCSD methods, 0.109 eV in favor of the latter method. Comparing results in cc-pVDZ and cc-pVTZ basis sets, we see a strong influence of the basis set. MR BWCC/cc-pVTZ give a very good agreement with experiment, but it is possible that the inclusion of higher excitations would lead to an underestimation of the gap. On the other hand, for the $^1B_1$ state, the dependence on the basis set is small, and the MR BWCC methods regardless of the excitation level predict an S−T gap of 0.6 eV, substantially lower than the spin-flip ones.

To investigate the sensitivity of the results on the method used for geometry optimization, BWCC results at CASSCF geometries were compared with those at spin-flip geometries. 4R−BWCCSDT-1α and 4R−BWCCSDT-α predict S−T gaps for both singlets at spin-flip geometries slightly smaller than at CASSCF geometries; however, the differences were at most 0.01 eV.

3.2. The Ring-Opening of Methylenecyclopropane. Figures 4−6 show the energy gap between the ground singlet state of MCP and depending on the torsion angle α. In Figure 4, these curves were obtained by the CASSCF method, while Figures 5 and 6 show the CCSD and 4R−BWCCSD results, respectively.

For conrotation, the attention was paid to the triplet state ^3A and the lowest singlet state ^1A, in the case of disrotation state $^3A'$ and the lowest singlet state $^1A'$. CASSCF energies in Figure 4 correspond to the lowest singlet state.

The transition state according to the BWCCSD method corresponds to the angle ~55°, which is slightly more than that according to CASSCF. On the other hand, it is hard to find the value of α more accurately, since the maximum is flat. When the angle α descends, the energy of the singlet state ^1A increases until the transition state is reached. Worthy of note is the strong growth of the ^1A energy for α higher than approximately 65°.

TABLE 1: The Singlet−Triplet Gap of the TMM: Results and Comparison

basis	method	$E(^3A'_2)$ [a.u.]	$\Delta E(^1B_1 - {}^3A'_2)$ [a.u.]	$\Delta E(^1A_1 - {}^3A'_2)$ [a.u.]
cc-pVDZ	4R−BWCCSD	−155.4529233[e]	0.633	0.800
	4R−BWCCSD it.[a]	−155.4529233	0.631	0.791
	4R−BWCCSDT-1α	−155.4723264	0.626	0.647
	4R−BWCCSDT-α	−155.4727700	0.607	0.678
cc-pVTZ	4R−BWCCSD	−155.5989516[e]	0.634	0.779
	4R−BWCCSD it.[a]	−155.5989516	0.633	0.771
DZP	MCSCF(4,4)[b]	−154.936880	0.643	0.843
	MCSCF(10,10)[b]	−155.010122	0.704	0.834
	SF−CIS(D)[b]	−155.43585	0.987	0.885
cc-pVTZ[c]	SF−CIS[b]	−154.91822	1.017	0.883
	SF−CIS(D)[b]	−155.54809	1.025	0.893
cc-pVTZ	EOM-SF−CCSD[d]	−155.589945	0.554	0.933
	EOM-SF−CC(2,3)[d]	−155.597465	0.697	0.788
	expt − ΔZPE[b]			0.787

[a] 4R−BWCCSD with the iterative correction. [b] From ref 17. [c] cc-pVTZ basis set on carbon; cc-pVDZ basis set on hydrogen. [d] From ref 19. [e] The triplet energies have been obtained for its high spin component by single-reference CCSD method.

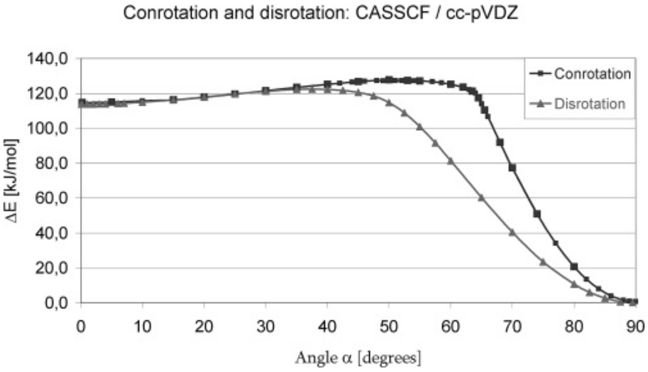

Figure 4. The reaction coordinate computed by the CASSCF/cc-pVDZ method.

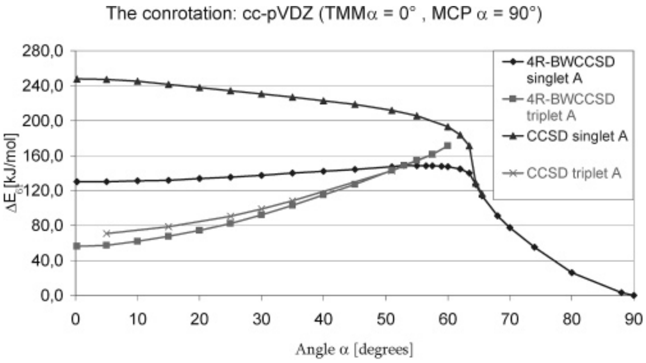

Figure 5. The reaction coordinate characterized by the 4R−BWCCSD and CCSD/cc-pVDZ methods.

States ^{1}A and ^{3}A cross for $\alpha = 53 \pm 1°$. The ^{3}A energy for α up 60° grows strongly, and amplitude equations hardly converge, which can be explained by the fact that for α higher than 60° the MCP is a closed-shell molecule, and the triplet states becomes energetically unfavorable. The limit for $\alpha \rightarrow 0$ is a minimum on the graph for the ^{1}A state, and BWCCSD and CASSCF methods predict it to be very flat. The single-reference CCSD cannot describe this state; on the graph, there is no minimum. The triplet state can be described by CCSD in a good agreement with 4R−BWCCSD, since it has a single-reference character as expected. The activation energy computed by 4R−BWCCSD is 148.6 kJ/mol, while the CASSCF method predicts 126.4 kJ/mol.

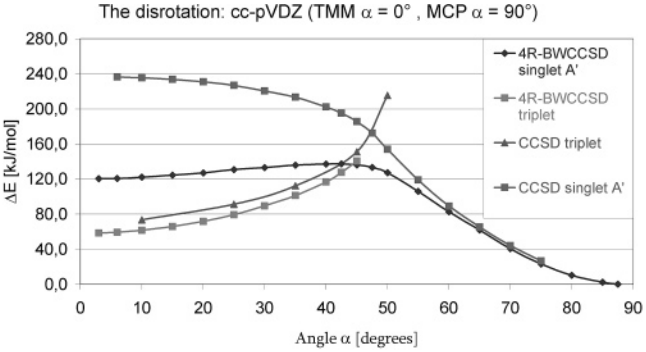

Figure 6. The reaction coordinate characterized by the 4R−BWCCSD and CCSD/cc-pVDZ methods.

TABLE 2: Basis Set Effects on the Reaction Barrier of Conrotation at the CASSCF Level

basis	activation energy [kJ/mol]
cc-pVDZ	126.4
aug-cc-pVDZ	128.1
cc-pVTZ	130.0

From Figure 4, we can find that $\alpha^{\text{CASSCF}} \approx 38°$ and $\alpha^{\text{4R-BWCCSD}} \approx 41°$ correspond to the transition state of the disrotation. When we go from right to left in Figures 5 and 6, then we go from the MCP to the transition state. Just before the ^{1}A′ crosses with the ^{3}A′ state, ^{1}A′ is for $\alpha < 44°$ the lowest state. It is obvious that the CCSD method cannot describe open-shell singlet states, so it gives poorer results when α is lower. On the other hand, the triplet state has a single-reference character again. The activation energy computed by 4R−BWCCSD is 137.0 kJ/mol, again somewhat higher than the 122.5 kJ/mol computed by CASSCF.

For the description of the basis set effect, CASSCF activation energies for aug-cc-pVDZ and cc-pVTZ basis sets were computed. Results for conrotation case are given in Table 2, which shows that the basis set effect is relatively small (4 kJ/mol) and has an increasing trend with larger basis set.

Since we performed the optimizations by the CASSCF method while BWCCSD was used for computations of energies, transition-state geometries and geometries of energetic minimums do not exactly correspond to the true BWCCSD ones. This can be a source of inaccuracy, but the CASSCF method can describe multiconfigurational states qualitatively good, and we do not expect this effect to be significant.

4. Conclusions

Singlet−triplet (S−T) gaps of TMM were studied using the BWCC method. The acquired values for the gap between $^3A'_2$ and $^1A_1$ states computed by 4R−BWCCSD method with the cc-pVTZ basis set are in a good agreement with the experiment.[4] Due to the significant multiconfigurational character of the $^1A_1$ state, the MR method is necessary. In the cc-pVDZ basis set, we have seen a strong dependence of the gap energy on the truncation level of the T operator. Unfortunately, MR BWCCSDT was technically too demanding in the cc-pVTZ basis set. The S−T gap $^3A'_2 - {}^1B_1$ is well-characterized by the 4R−BWCCSD method and does not strongly depend on the truncation of the T operator. The results are somewhat lower than published results of SF methods.[17,19] The single-reference CCSD method describes both singlet states very poorly, and the results are unreasonably high. Single-reference CCSDT performs better, but its results are still unsatisfactory.

We also studied energies of the singlet and triplet states along the reaction coordinate going from MCP to TMM. CASSCF and BWCCSD methods give qualitatively the same behavior. The BWCCSD method predicts higher activation energy for the conrotation than for the disrotation. We found that the disrotation is energetically more favorable than conrotation. The single-reference CCSD cannot describe multireference singlet states for $\alpha < 60°$.

The MR BWCCSD method performs well in describing multiconfigurational states of TMM and singlet intermediates of forming TMM from MCP. For higher precision, it will be necessary to optimize geometries by the MR−BWCCSD method and develop a noniterative approximation to triple excitations, which would be computationally tractable in larger basis sets.

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