

Efficient Strategies for Accurate Calculations of Electronic Excitation and Ionization Energies: Theory and Application to the Dehydro-*m*-xylylene Anion

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In the dehydro-*m*-xylylene (DMX) anion [Munsch; et al. *J. Org. Chem.* **2004**, *69*, 5735], three nearly degenerate orbitals host four electrons, which results in a large number of nearly-degenerate electronic states. By using this challenging example, we assess the performance of the multireference “brute force” approach and the two-step schemes based on single-reference methods for calculating accurate energy differences. Different schemes for calculating adiabatic ionization potential (IP) of DMX[−] are also investigated. IP calculated by single-reference based schemes is in excellent agreement with experiment.

1. Introduction

An accurate ab initio calculation of energy differences, such as electronic excitation and ionization energies, as well as heats of formation is a challenging task, which can be addressed by different strategies depending on the electronic structure of species involved.

In the most straightforward “brute force” approach one calculates total energies of relevant states as accurately as possible and then computes energy differences. This is often performed using multireference (MR) state-specific techniques such as multiconfigurational self-consistent field (MCSCF)^{1–3} or, more appropriately, MR methods that include dynamical correlation, e.g., configuration interaction (MRCI),⁴ perturbation theory (MRPT),^{5–7} or MR coupled-cluster (MRCC).^{8,9} Along with obvious advantages of this approach, such as flexibility and potentially high accuracy, there are obvious disadvantages, e.g., the ambiguity of choosing the active space, the factorial scaling, and the reliance on having almost exact total energies.¹⁰ In some situations, an accurate single-reference (SR) approach such as coupled-cluster single and double with perturbative triples [CCSD(T)]¹¹ can be used.

Alternatively, a multistate method, such as a single-reference equation-of-motion CC (EOM-CC) or closely related to it CC linear response theory,^{12–15} can be employed to directly compute energy differences. EOM can describe many multiconfigurational wave functions within a single-reference formalism.^{16,17} The built-in error cancellation ensures accuracy of EOM energy differences. Moreover, its accuracy can be systematically improved (up to the exact full CI results) by including higher excitations explicitly or perturbatively, at the price of increased computational scaling (e.g., EOM-CCSD scales as N^6 where N is the number of basis functions, and explicit inclusion of triples brings it up to N^8).

Yet another approach employs energy additivity schemes in which different effects, e.g., those of expanding the one-electron basis or of higher excitations, are extrapolated separately from series of smaller calculations. Of this type are G3 energy additivity scheme,^{18,19} W3 scheme for accurate thermochemistry,²⁰ and basis set extrapolations.^{21–23}

Furthermore, accurate thermochemistry can be calculated by employing isodesmic or isogyric reactions, and high-low spin

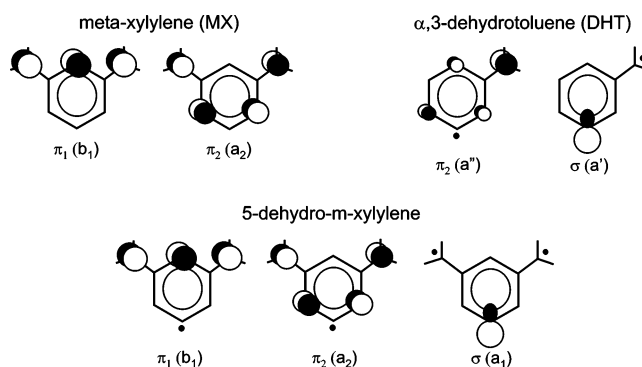


Figure 1. Molecular orbitals of the MX and DHT diradicals and of the DMX triradical.

pathways.^{24,25} In general, this is not a “black-box” approach, as it requires thorough understanding of electronic structure of species involved, and it can be rather ambiguous. However, its potential accuracy is very high.

In this work, we investigate the performance of “brute force” approaches and that of schemes based on a combination of ground-state single-reference and EOM methods on the example of the electronic excitation and ionization energies of the dehydro-*m*-xylylene (DMX) anion.

The structure of the paper is as follows: the electronic structure of DMX and DMX[−] is discussed in section 2; methodology of calculating electronic states of DMX[−] is given in section 3, and computational schemes for calculating accurate ionization potential are presented in section 4. The results are in section 5 and our final remarks are given in section 6.

2. Electronic Structure of DMX and DMX[−]

2.1. DMX[−] Genealogy. Recently, we reported joint experimental/theoretical study of two intriguing molecules, the DMX triradical and its negative anion, DMX[−].^{25,26} The molecular orbitals (MOs) of DMX are shown in Figure 1. The lowest in energy is a σ -type a_1 (in-plane) orbital formed by the sp^2 hybridized carbon orbital. Two π -orbitals are formed by atomic p-orbitals on the methylene carbons and include contributions from the benzene π -system. Two nondisjoint π -orbitals of DMX give rise to the triplet coupling of the two π -electrons, as in the ground state of the π - π diradical analogue of DMX, *m*-xylylene

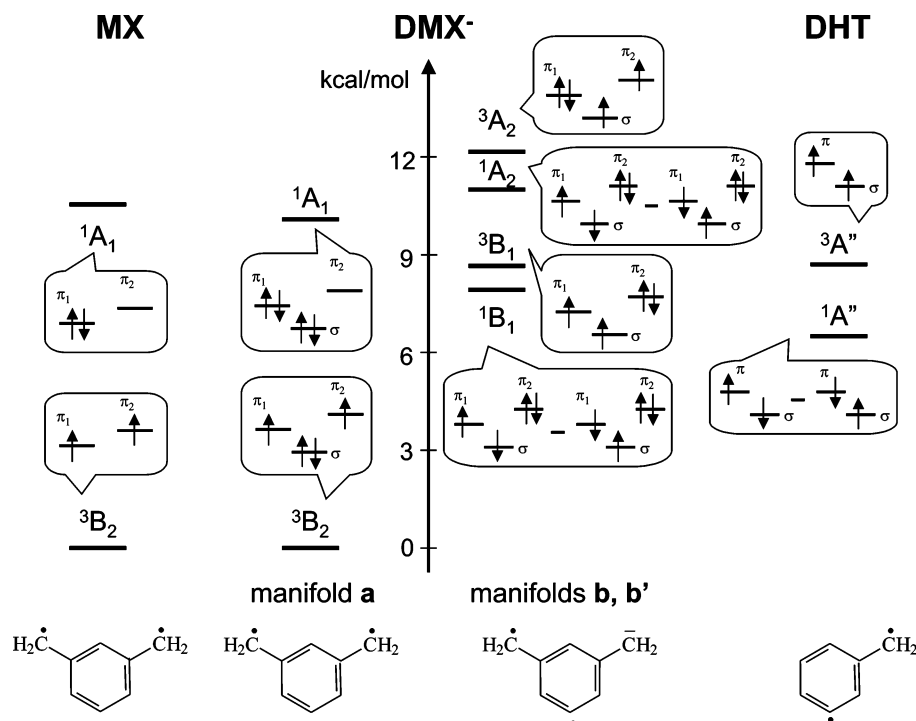


Figure 2. Low-lying electronic states of MX (left panel), DHT (right panel), and DMX⁻ (middle) at C_{2v} geometries. The energy separation in the DMX⁻ states originating from the phenyl anion and the MX diradical moieties (structure **a**) are similar to that of MX's states, and the states correlating with a combination of the benzyl anion and the m-DHT diradical (manifolds **b** and **b'**) resemble the electronic states of the DHT diradical.

(MX). The σ -type a_1 orbital, however, does not overlap with any of the π orbitals, which leads to the anti-ferromagnetic coupling between the σ - and π -electrons. The corresponding σ - π diradical, *m*-didehydrotoluene (DHT), has a singlet ground state. The molecular orbitals of MX and DHT are also shown in Figure 1. Thus, both triplet coupling between π -electrons and singlet coupling between π - and σ -centers are in favor of the open-shell doublet ground state for DMX, in which each of the triradical orbitals is singly occupied and the unpaired electrons are coupled anti-ferromagnetically.

Qualitatively, DMX can be described as consisting of either (i) phenyl and MX or (ii) benzyl and DHT moieties. This suggests that, depending on which orbital an extra electron is placed, the electronic states of the DMX⁻ will belong to one of the following types, that is, (i) states originating from the phenyl anion and the MX diradical moieties (structure **a**) or (ii) states derived from the benzyl anion and the DHT diradical (structures **b** and **b'**). In the latter case, we can distinguish two different structures, **b** and **b'**, depending on which of the two π orbitals is doubly occupied. One may expect that the properties and energy separations between states of type (i), or manifold **a**, would be similar to those of the MX diradical, whereas the states of type (ii), or manifolds **b** and **b'**, would be similar to the electronic states of the DHT diradical.

Figure 2 shows the electronic states of MX, DHT, and DMX⁻ (left, right, and center parts, respectively).²⁷ The ground electronic state of MX is triplet, which is confirmed by both the experimental and theoretical studies.^{28–31} The lowest singlet is of a closed-shell type, the adiabatic singlet–triplet gap being about 10–11 kcal/mol.^{30,31} The open-shell singlet is considerably higher in energy. Such state ordering—triplet, closed-shell singlet, open-shell singlet—is typical for diradicals with non-disjoint frontier MOs (e.g., see methylene example in ref 32).

The state ordering in DHT, a σ - π diradical, is different due to the nodal structure of σ and π orbitals. This results in an

open-shell singlet ground state. The triplet state is about 1–3 kcal/mol higher in energy.^{33,34} The closed-shell singlet state is much higher in energy (about 62 kcal/mol vertically)³⁴ due to its ionic character that results from the electron transfer between the spatially separated σ and π orbitals.

The electronic states of DMX⁻ at planar C_{2v} geometries are shown in the middle of Figure 2. States corresponding to the **a** and **b/b'** manifolds, i.e., MX and DHT like states, are shown on the left and right sides, respectively. Overall, the electronic states from manifold **a** are rather similar to those of MX. Indeed, the lowest electronic state of **a** is triplet, whereas the closed-shell singlet lies 10.1 kcal/mol higher in energy. This energy difference is very similar to the singlet–triplet gap in MX. As mentioned above, **b** and **b'** manifolds are derived by placing an extra electron on either π_1 (b_1) or π_2 (a_2) molecular orbitals, respectively. Though the Aufbau principle would favor placing an extra electron on the slightly lower π_1 orbital, a more diffuse character of π_2 favors a negative charge residing on π_2 . In **b** and **b'**, singlets are 0.2–0.8 and 1.2 kcal/mol lower than triplets, which is close to singlet–triplet energy separation in DHT. To summarize, there is a remarkable similarity between the electronic states of DMX⁻ and those of MX and DHT.

2.2. Equilibrium Geometries of the Lowest Electronic States of DMX⁻. As discussed in ref 26, several low-lying electronic states of DMX⁻ do not preserve the C_{2v} symmetry. The driving force for the symmetry lowering in DMX⁻ is more efficient charge delocalization at twisted geometries due to the lifting of symmetry imposed constraints. In DMX⁻, the energy gain due to the more extensive delocalization appears to be more significant than energy penalty for breaking the conjugation in the π -system at nonplanar geometries. In a more rigorous way, the symmetry breaking can be explained in terms of vibronic interactions between the state of interest and those near it. If the state of interest lies *below* a state of different symmetry, and the vibronic interaction is appreciable, which usually

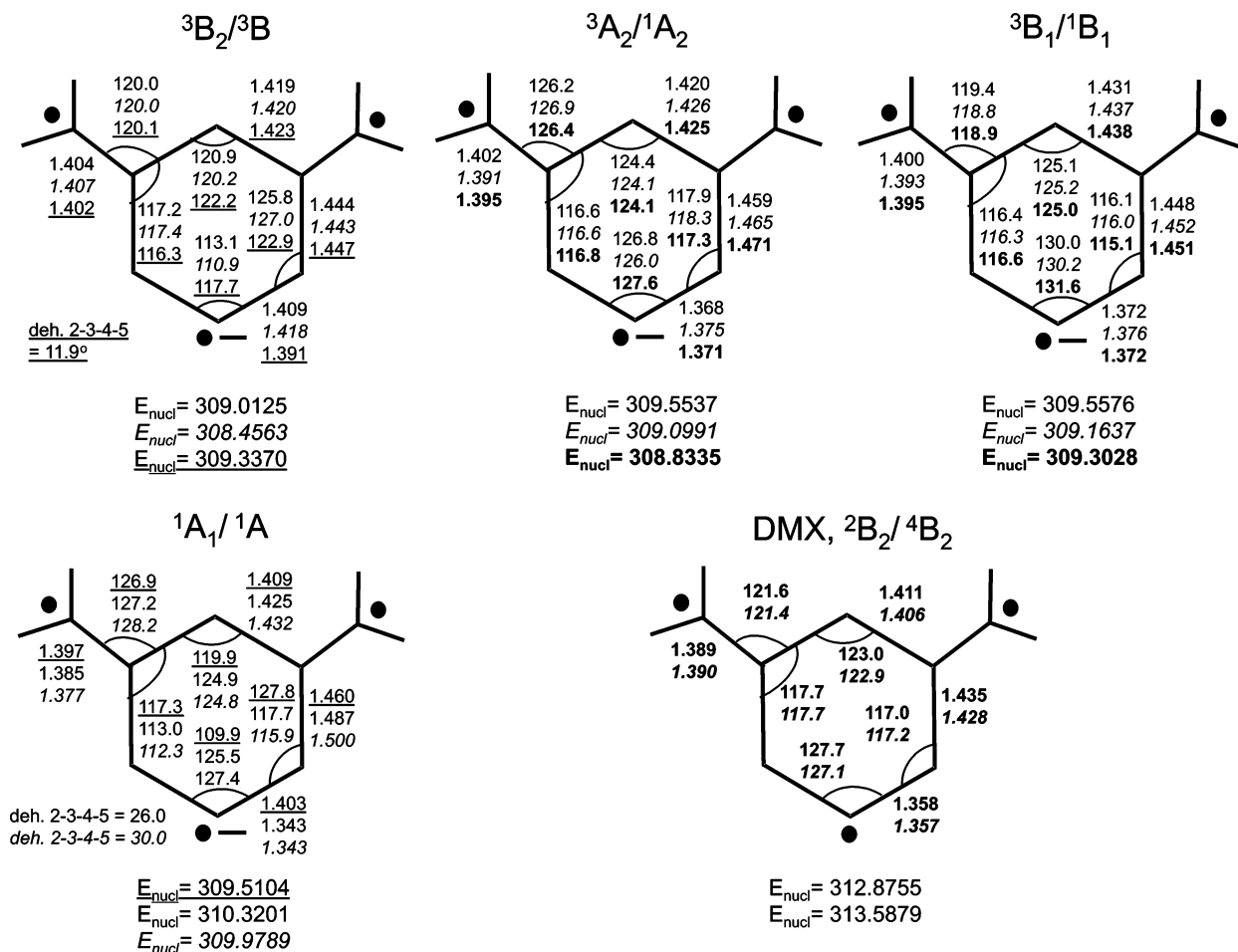


Figure 3. Equilibrium geometries of the lowest electronic states of DMX^- . B3LYP/6-311+G* and CCSD/6-31G* (*italic*) were used to calculate the geometries of all the triplets and the ${}^1A_1/{}^1A_1$ singlet, EOM-CCSD/6-31+G* (**bold**) was used for the 1A_2 and 1B_1 open-shell singlets. Both the C_{2v} constrained (at the B3LYP/6-311+G* level, underlined) and C_2 equilibrium geometries of 1A are shown. A structure corresponding to the artificial symmetry breaking in 3B_2 (observed at the B3LYP/6-311+G+ level, underlined) is also given. Only the C_{2v} constrained structures of 3B_2 and 1B_1 are reported.⁵⁶

happens when the energy separations between the states are small enough, the force constants of the appropriate symmetry (that is, the direct product of the irreducible representations of the two states in question) can become very small or negative, the latter case causing a reduction in symmetry. Alternatively, if the state of interest lies *above* the interacting state, the force constants are increased. Therefore, the *vertical* ordering of states determines type of vibronic interactions and, consequently, resulting equilibrium structures. Below we demonstrate that discrepancies between equilibrium structures calculated by different methods can be explained by different electronic states' ordering computed by those methods.

In the 3B_2 and 3B_1 triplet states, charge delocalization can be enhanced by lowering the symmetry from C_{2v} to C_2 , where these triplets can interact, as in a lower C_2 symmetry group they become 3B . At the C_{2v} geometry of 3B_2 , the 3B_1 state lies about 27 kcal/mol higher, and the vibronic interaction between these states is weak. As a result, 3B_2 remains planar at the CCSD and CCSD(T) levels of theory. However, at the DFT level, it distorts to C_2 . We believe that this lowering the symmetry of 3B_2 at the DFT level is artificial. As follows from equilibrium geometries of the low-lying electronic states of DMX^- (see Figure 3), the overall (artificial) geometry distortion of 3B_2 at the B3LYP level is very small (e.g., the out-of-plane angles do not exceed 12°) and has negligible effect on the computed excitation energies.²⁶

At its C_{2v} geometry, 3B_1 lies lower than other two triplets, and the corresponding vertical energy separation between 3B_1 and 3B_2 is less than 1 kcal/mol. As a result, 3B_1 distorts to C_2 . In this case, there is an agreement between CC and DFT methods.

At the B3LYP level, the 3A_2 triplet lowers the symmetry to planar C_s (where it interacts with 3B_1), and the corresponding C_{2v} structure has a huge imaginary frequency of 1824i cm^{-1} . However, at the CCSD and CCSD(T) levels, 3A_2 remains C_{2v} ! This behavior can be explained by the different relative order of the 3A_2 and 3B_1 states (at C_{2v} geometry of 3A_2) computed by different methods. At the B3LYP level, 3A_2 lies slightly lower than 3B_1 , which leads to symmetry breaking, but the order of these states is reverse at the CCSD and CCSD(T) levels, resulting in stabilization of the C_{2v} structure of 3A_2 . This striking example demonstrates the importance of accurate high-level treatment of the electronically excited states in such a nontrivial system as DMX^- . Indeed, small errors of 1–2 kcal/mol in calculation of the relative excitation energies can result in tremendous differences in structures and properties of the excited state.

The closed-shell singlet state with the doubly occupied σ and π_1 orbitals (the closed-shell singlet from manifold **a**, see Figure 2) has the C_2 equilibrium geometry, at which C_5 no longer hosts the phenyl-type sp^2 hybridized orbital, but rather two sp -hybridized and two π orbitals making double bonds with C4

and C6 carbons. Thus, the lower part of the molecule (C4–C5–C6) resembles the 1,2-propadiene and is only marginally charged. The majority of the charge is localized on the upper part of the molecule, which resembles the pentadienyl anion. Both moieties are connected by the two single carbon–carbon bonds between C3–C4 and C6–C1 (see Figure 3). A similar structure is observed, for example, in deprotonated cyclooctatetraene, which also forms an allene and a delocalized anion.³⁵ The equilibrium bond lengths and the NBO analysis of 1A are consistent with this bonding scheme.

For the completeness, low-lying open-shell singlets of DMX^- should be discussed. Though the 1B_2 state (from manifold **a**) is rather high in energy relative to 3B_2 , other two open-shell singlets, 1A_2 and 1B_1 , lie lower than the corresponding triplets, 3A_2 and 3B_1 . We will limit the discussion to the latter states. As will be discussed in detail in section 3.2, an accurate treatment of the open-shell singlets is much more difficult than that of triplets and closed-shell singlets because the open-shells are of multiconfigurational character.

It is often assumed that structures and properties of the states with same spatial occupancies are similar, as in the case of the triplet and open-shell singlet states of DHT,³⁴ the quartet and the open-shell doublet of DMX,²⁵ and the A_2 states of DMX^- (the latter two states do not exhibit any distortion from C_{2v}). Moreover, the C_{2v} constrained structures of the B_1 singlet–triplet pair of DMX^- 's states obey the same rule. However, charge delocalization and vibronic interactions patterns in the 1B_1 open-shell are different from those in the 3B_1 triplet. Although the 3B_1 triplet experiences the C_2 distortion, the 1B_1 open-shell distorts to planar C_s ! The triplet distorts to C_2 because at its C_{2v} geometry it strongly interacts with the closely lying 3B_2 state, whereas the energy separation between the 1B_1 and 1B_2 singlets is too large to result in any significant interaction which could be sufficient for the reducing the symmetry of 1B_2 to C_2 . Instead, 1B_1 strongly interacts with the almost degenerate (only 1.6 kcal/mol higher) 1A_2 state and distorts to C_s (both 1B_1 and 1A_2 become the A'' states at the planar C_s symmetry).

In contrast to 1B_1 , 1A_2 preserves its C_{2v} geometry, likely because its interaction with 1B_1 , which is vertically about 9 kcal/mol higher, is not sufficiently strong for symmetry breaking.

3. Accurate Excitation Energies of the Electronic States

3.1. General Methodology. Adding an extra electron into the three-electrons-on-three-orbitals system of the DMX triradical leads to the four-electrons-on-three-orbitals pattern in DMX^- . This results in the extensive electronic degeneracies and heavily multiconfigurational wave functions. However, if the interaction between a doubly occupied orbital and two others is weak due to symmetry/nodal considerations or a spatial separation, the complexity of the DMX^- electronic structure reduces to the familiar 2-electrons-in-2-orbitals diradical case. For example, all three nonbonding orbitals are of different symmetry at C_{2v} geometries which, along with a weak overlap between the σ - and π -systems, strongly impede the electron transfer between the σ - and π -orbitals.

Extensive electronic near-degeneracies make the choice of an electronic structure method extremely important: an appropriate model should provide a qualitatively correct description of an electronic wave function (nondynamical correlation), and also include dynamical correlation, which is crucial for quantitative accuracy, especially in anions. Moreover, a balanced description of several states of interest is required; therefore, our preference is to use multistate rather than state-to-state methods.

For molecules such as DMX or DMX^- , traditional strategy is to employ MR techniques. Indeed, with a reasonably chosen active space, MCSCF provides appropriate zero-order wave functions for both DMX and DMX^- . To achieve quantitative accuracy, these zero-order wave function should be augmented by dynamical correlation, e.g., by using configuration interaction (MRCI) or perturbation theory (MRPT). This approach is formulated to provide an equal quality description of all the relevant electronic states. Both one-state-at-a-time and state-averaging procedures can be used.³⁶

In EOM approach,^{12,14–17,37,38} several target states are calculated simultaneously, by diagonalizing the so-called similarity transformed Hamiltonian $\bar{H} = e^{-T}He^T$:

$$\bar{H}R(k) = E_k R(k) \quad (1)$$

where T and $R(k)$ are general excitation operators with respect to the reference determinant $|\Phi_0\rangle$. By combining different types of excitation operators and references $|\Phi_0\rangle$, different groups of target states can be accessed. For example, electronically excited states can be described when the reference $|\Phi_0\rangle$ corresponds to the ground-state wave function, and operators R conserve the number of electrons and a total spin.^{12–14} In the ionized/electron attached EOM models, operators R are not electron conserving—these models can accurately treat ground and excited states of doublet radicals and some other open-shell systems.^{39–41} Moreover, singly ionized EOM method, EOM-IP-CCSD, is useful for determining ionization energies. Finally, the EOM-SF method^{15,42} in which the excitation operators include spin-flip allows one to access diradicals, triradicals, and bond-breaking.

To summarize, EOM approach enables one to describe many *multiconfigurational* wave functions within a *single-reference* formalism.^{16,17} The EOM models are rigorously size-extensive, and their accuracy can be systematically improved (up to exact FCI results) by including higher excitations explicitly or perturbatively. Moreover, the EOM methods are multistate schemes—several target states are obtained in the single diagonalization step. The built-in error cancellation significantly improves the accuracy of EOM.

3.2. Adiabatic Excitation Energies of DMX^- . Accurate calculation of the adiabatic excitation energies in DMX^- is nontrivial due to significantly different equilibrium geometries and character of its electronic states. Indeed, whereas the wave functions of the three triplets and the 1A singlet are dominated by a single electronic configuration, the open-shell singlets are two-configurational. Therefore, it is impossible to describe all six lowest electronic states of DMX^- with an equal quality by using a single-reference technique. To address this problem, we employ two different approaches. In the “brute force” approach, the total energies of all the states are calculated by MCSCF and MRPT, and excitations energies are calculated as differences between the total energies of states. In the second approach, we combine a high-level single-reference method, e.g., CCSD(T), and a single-reference excited state method, EOM-EE-CCSD, to accurately describe energy differences between the states.

As the single-reference approach, we use CCSD(T) to calculate the total energies of all the triplets, 3B_2 , 3B_1 , and 3A_2 , and the closed-shell singlets, 1A and 2^1A_1 . The latter singlet, 2^1A_1 , with electronic configuration $a_1^0b_1^2a_2^2$ (see Figure 1 for orbital notations), can be used as a reference in EOM-EE-CCSD calculations of the open-shell states. Indeed, both open-shell singlets, 1B_1 and 1A_2 , along with the corresponding triplets, 3B_1 and 3A_2 , are singly excited states with respect to this state. Note

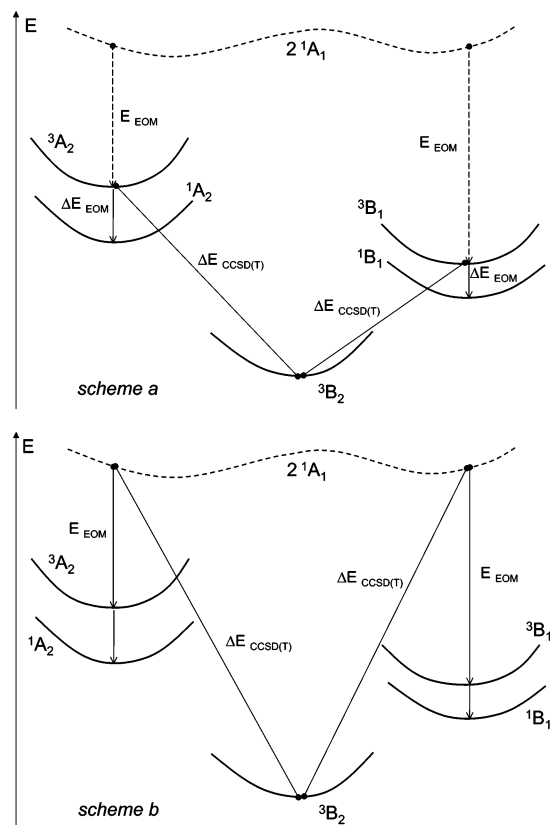


Figure 4. Calculation of the adiabatic excitation energies in DMX^- .

that in the CCSD(T) calculations, the single-configurational high-spin $M_s = 1$ components of the 3B_1 and 3A_2 triplets are used. Alternatively, in EOM-EE/SF calculations, the low-spin $M_s = 0$ components of these triplets are found.

Thus, to calculate the adiabatic excitation energies of DMX^- , we suggest two schemes shown in Figure 4. In both schemes, the energy differences between the states are calculated in two steps. In scheme a, we calculate the adiabatic energy difference between the triplet states and the 1A_2 – 3B_2 energy difference by CCSD(T). The excitation energies of 1A_2 and 1B_1 are calculated by subtracting the energy separations $\Delta E^{^1B_1-^3B_1}$ and $\Delta E^{^1A_2-^3A_2}$ from the CCSD(T) energies of the corresponding triplets. The latter singlet–triplet gaps are calculated at the geometries of the corresponding triplets, by EOM-EE-CCSD from the $^2^1A_1$ reference. Because the singlet–triplet pairs of the B_1 and A_2 states have the same spatial configurations, each pair is described by EOM-EE-CCSD with an equal quality. The main source of uncertainty and possible errors in scheme a is accuracy of CCSD(T) for treatment of different triplet states. All triplets are moderately spin-contaminated, which can result in a loss of accuracy by CCSD(T). However, we believe that scheme a gives an accurate estimate of the excitation energies of DMX^- .

In scheme b, we use CCSD(T) to calculate the energy difference between the lowest triplet 3B_2 and the two closed-shell singlets, 1A_1 and $^2^1A_1$. Then we employ the latter state as the reference in the EOM-EE-CCSD calculations and obtain the excitation energies of the B_1 and A_2 triplets and singlets relative to the $^2^1A_1$ state. Thus, in scheme b, we eliminated the main drawback of scheme a — using CCSD(T) for spin-contaminated triplets. However, scheme b also contains a source of potential error. Whereas, as discussed above, the energy separation between each pair of the B_1 and A_2 states is accurately described by EOM-EE-CCSD, it may not be so for the energy separation between different pairs of these states. For example,

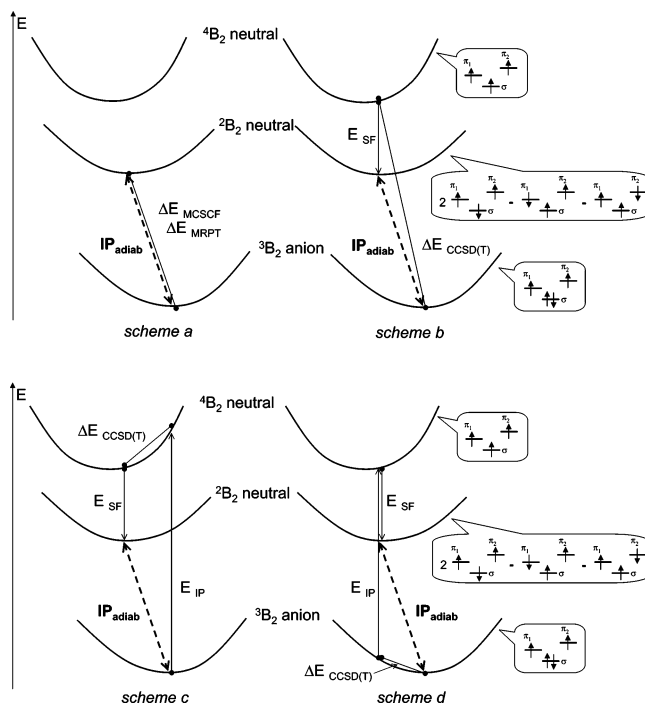


Figure 5. Evaluation of the adiabatic ionization potential of DMX^- .

if one pair of states has a little larger doubly excited character than the other, it will appear higher in energy relative to the other pair of states.

Numerical results of schemes a and b, as well as MR data are presented and discussed in section 5.

4. Ionization Potential of DMX^-

Accurate evaluation of the ionization energy is a challenging task as it requires a balanced description of two different species, a neutral molecule and its negative ion. Using a single-reference method such as DFT or CCSD(T) is possible only if both the anion and the neutral are well behaved systems, e.g., when the neutral is a closed-shell molecule, and the anion does not exhibit symmetry breaking. And this is certainly not the case for DMX and DMX anion!

To calculate the adiabatic ionization energy of DMX^- , we employed several schemes shown in Figure 5. In the simplest and the most straightforward scheme a, the energy difference between the 2B_2 state of DMX and the 3B_2 state of DMX^- is calculated by MCSCF and MRPT, i.e., methods that can describe the electronic structure of both the neutral and the anion qualitatively correct. Scheme b is a two-step procedure. First, we calculate the energy difference between the high-spin states, the 3B_2 state of the anion and the 4B_2 state of the neutral, by CCSD(T). Then, the energy difference between the 4B_2 and the 2B_2 states of DMX is calculated by EOM-SF-CCSD. In schemes c and d, we first use EOM-IP-CCSD for accurate evaluation of the vertical ionization energy between the 3B_2 state of the anion and the 4B_2 state of the neutral.⁴³ Next, to make a transition from the vertical to adiabatic energy differences, the CCSD(T) energies of anion (scheme c) or neutral (scheme d) are calculated at the equilibrium geometries of 3B_2 and 2B_2 . Finally, the vertical energy differences between the 2B_2 and 4B_2 states of neutral DMX are calculated by the EOM-SF-CCSD method. Schemes c and d are of similar quality, they differ by the geometry (3B_2 or 2B_2) at which the EOM-IP-CCSD energy is calculated and by the potential surface (3B_2 or 4B_2) at which the adiabatic shift

TABLE 1: Total (hartree) and Adiabatic (kcal/mol) Excitation Energies of the Lowest electronic states of DMX^{-a}

state	CCSD(T)	EOM-CCSD		EOM-CC(2,3) using scheme b	MCSCF	MRQDPT
		using scheme a	using scheme b			
³ B ₂	-308.250087				-307.011621	-308.016713
¹ A ₁ ^b	11.90				14.56	6.30
¹ A	1.48				4.91	-2.00
¹ B ₁ ^c		8.53	15.45	7.16	11.56	4.37
³ B ₁	8.71	8.71	15.63	7.61	12.28	4.89
¹ A ₂ ^d		11.18	11.39	7.37	12.96	6.43
³ A ₂	12.15	12.15	12.36	9.17	16.35	7.84
2 ¹ A ₁	77.53	-308.061178	-308.061178	-308.064657		
@ ³ B ₁ geom ^e						
2 ¹ A ₁	75.93	-308.062815	-308.062815	-308.066671		
@ ³ A ₂ geom ^e						

^a 6-311+G* basis set was employed for all calculations. B3LYP/6-311+G* geometries used (see Figure 3); see text for details. ^b The ¹A state at the C_{2v} constrained geometry. ^c Calculated at the geometry of ³B₁. ^d Calculated at the geometry of ³A₂. ^e This state has the electronic configuration a₁⁰ b₁² a₂² and used as a reference for EOM-EE-CC calculations of the B₁ and the A₂ states.

is calculated. Numerical results are presented and discussed in the next section.

5. Results and Discussion

Equilibrium geometries of the triplet and closed-shell singlet states of DMX⁻ were optimized at the CCSD/6-31G*^{44,45} and B3LYP/6-311+G*⁴⁶⁻⁴⁸ levels, geometries of the open-shell singlets were obtained by EOM-EE-CCSD/6-31+G*.^{45,48} Geometries of lowest electronic states of DMX⁻ calculated by appropriate methods are shown in Figure 3. Interestingly, the C_{2v} constrained B3LYP geometries of the triplets are very similar to the CCSD ones. Also, there is not much difference between the B3LYP and CCSD C₂ geometries of the ¹A state. Moreover, the C_{2v} geometries of both open-shell singlets, ¹A₂ and ¹B₁, are similar to those of the corresponding triplets, ³A₂ and ³B₁. Therefore, adiabatic excitation energies were calculated using the B3LYP/6-311+G* C₂ geometry for the ¹A state and the B3LYP/6-311+G* C_{2v} constrained geometries for all the other states; i.e., the energies of the ¹A₂ and ¹B₁ singlets were calculated at the geometries of the corresponding triplets.⁴⁹

Adiabatic excitation energies and ionization potential of DMX⁻ were calculated by the CCSD(T), EOM-EE-CCSD, EOM-SF-CCSD, EOM-IP-CCSD, as well as MCSCF and MRPT in the 6-311+G* basis set (see sections 3.2 and 4 for details). The active space for the MR calculations consisted of nine orbitals, i.e., three triradical orbitals shown in Figure 1, and three doubly occupied and three virtual benzene π orbitals, and included ten or nine electrons for DMX⁻ and DMX, respectively. No root averaging was used, i.e., only one solution was sought in each calculation.

In addition, we employed the active space EOM-EE-CC(2,3),^{50,51} i.e., the EOM-CC model in which the cluster amplitudes *T* are truncated at the second order and the excitation operator *R* includes zero, single, double, and triple excitations. In the active space variant of this method, EOM-EE-CC(2,3), only a small subset of triple excitations, determined by the choice of the active space, is included. As an active space for the EOM-EE-CC(2,3) calculations of DMX⁻, we chose three triradical orbitals shown in Figure 1. This small active space includes the leading excitations of the B₁ and A₂ states. Moreover, it takes care of the instability of the reference, the 2¹A₁ state, which is not the lowest closed-shell singlet. As it was shown in the benchmark study,⁵¹ in the case of strong nondynamical correlation, the accuracy of EOM-EE-CC(2,3) significantly exceeds that of EOM-EE-CCSD.

Most of the calculations were performed by using the Q-CHEM⁵² and ACES II⁵³ electronic structure packages. Multireference results were obtained by using GAMESS.⁵⁴

Scheme a was applied to calculate the excitation energies shown in Figure 2. To compare the DMX⁻ states of manifold a with the MX ones, we calculated the vertical rather than adiabatic energy separation between the ³B₂ and ¹A (¹A₁ in C_{2v}) states of DMX⁻. Because at C_{2v} the ¹A singlet has larger multiconfigurational character than at C₂, the EOM-SF-CCSD method, employing ³B₂ state as the reference, was used for calculating the ³B₂-¹A₁ energy separation.

The adiabatic excitation energies of DMX⁻ calculated by different schemes are given in Table 1.⁵⁵ MCSCF and MRPT results are shown in the last two columns of the table. For all excited states, the difference between the MCSCF and MRPT values is 6–9 kcal/mol (0.26–0.40 eV). It is interesting that for the single-reference states, the CCSD(T) values lie between the MCSCF and MRPT ones. MRPT places the ¹A state as the ground state, in contradiction both to other computational methods and to the experiment.²⁶ Thus, the applied multireference methods fail to give an unambiguous answer about the order of electronic states of DMX⁻. This unsatisfactory behavior of the multireference methods in description of the electronic states of DMX⁻ can be explained by no or insufficient level of correlation in MCSCF and MRPT, or by different shapes of potential energy surfaces produced by these methods, i.e., favoring looser structures, which also can result in erroneous adiabatic excitation energies.

It appears that in schemes a and b (see Figure 4), the order of the B₁ and A₂ states is different: whereas scheme a places the B₁ states lower than the A₂ ones, scheme b yields the reverse order. To clarify this, we improved the accuracy of scheme b by replacing the EOM-EE-CCSD method by EOM-EE-CC(2,3). With the inclusion of triples, the general state order in scheme b coincides with that in scheme a; i.e., the B₁ pair of states lies lower in energy than the A₂ pair. However, the absolute order of the states is still different in scheme a and improved scheme b, i.e., the state ³B₁ lies lower than ¹A₂ in scheme a, but higher than that in scheme b. We believe this is because improved scheme b still underestimates the separation between the B₁ and A₂ pairs of states. Indeed, the energy splitting between the triplets ³B₁ and ³A₂ is +3.4 kcal/mol in scheme a (i.e., at the CCSD(T) level), this splitting is -3.3 kcal/mol (reverse order!) in scheme b (i.e., at the EOM-CCSD level), and it becomes +1.6 kcal/mol in improved scheme b (i.e., at the EOM-CC(2,

TABLE 2: Energy Differences (kcal/mol) Used for Calculating Adiabatic Ionization energy of DMX⁻

method	state	geometry	ΔE
CCSD(T)	³ B ₂	³ B ₂ - ² B ₂	14.13
	⁴ B ₂	³ B ₂ - ² B ₂	6.70
IP	³ B ₂ - ⁴ B ₂	³ B ₂ - ² B ₂	24.29
	³ B ₂ - ⁴ B ₂	³ B ₂	35.07
SF	³ B ₂ - ⁴ B ₂	² B ₂	13.83
	⁴ B ₂ - ² B ₂	² B ₂	3.78
MCSCF	³ B ₂ - ² B ₂	³ B ₂ - ² B ₂	-8.85
MRPT	³ B ₂ - ² B ₂	³ B ₂ - ² B ₂	17.73

TABLE 3: Adiabatic Ionization Potential (kcal/mol) of DMX⁻ Calculated by Different Schemes

scheme	method	IP _{adiab}
scheme a	MCSCF	-8.85
	MRPT	17.73
scheme b	CCSD(T), EOM-SF-CCSD	20.51
scheme c	CCSD(T), EOM-SF-CCSD, EOM-IP-CCSD	24.58
scheme d	CCSD(T), EOM-SF-CCSD, EOM-IP-CCSD	24.18
exp ^a		24.9 ± 2.0

^a Reference 26.

$\bar{3}$) level). It is an obvious tendency of increasing the energy separation between the ³B₁ and ³A₂ states with increase of correlation, and inclusion of triples in EOM significantly improves results of scheme b and approaches them to the results of CCSD(T)-based scheme a. It is also possible that the relative energetics in scheme b is not fully converged at the EOM-EE-CC(2, $\bar{3}$) level. However, even at this level of theory, the differences in excitation energies from the improved scheme b and scheme a are less than 3 kcal/mol.

To summarize, we believe scheme a, i.e., the scheme based on the CCSD(T) total energies for the triplet states, is the most reliable, and the state ordering in DMX⁻ is as follows: ³B₂, ¹A₁, ¹B₁, ³B₁, ¹A₂, ³A₂.

Tables 2 and 3 present the results of calculations of the DMX⁻ adiabatic ionization potential. The MCSCF results (scheme a) are erroneous. MRPT gives the IP value that is 7 kcal/mol (0.3 eV) lower than the experimental one. The results of two-step scheme b are also lower than the experimental value. As expected, the ionization energies calculated by schemes c and d are very similar, 24.6 and 24.2 kcal/mol, respectively. These results are in excellent agreement with the experimental value of 24.9 ± 2.0 kcal/mol.²⁶ Thus, the most balanced three-step procedure for calculating the adiabatic ionization potential of DMX⁻ yields accurate results.

6. Conclusions

Accurate description of electronic states of DMX⁻, a four-electrons-in-three-orbital system, is a challenging task for any ab initio method. This is even more so for the determining the DMX⁻'s ionization potential, when, additionally, the ground state of neutral DMX, a three-configurational open-shell doublet wave function, should be described accurately. We demonstrate that the "brute force" approach, i.e., calculation of the total energies of the excited states by MCSCF and MRPT, fails to give the correct order of the electronic states and accurate IP. Contrarily, the EOM based two-step schemes produce correct state ordering and reliable excitation energies. The results of the three-step schemes for calculation of adiabatic IP, which include EOM-IP-CCSD, EOM-SF-CCSD, and CCSD(T), are in excellent agreement with experiment.

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Whereas this uncertainty in excitation energies may not be important when vertical excitation energies are calculated, it can become an issue when the adiabatic excitation energies are of interest. For example, at some points of PES, it may be possible to calculate one root in a time, whereas at other points, degeneracy between the states may require root-averaging.

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