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A theoretical determination of the electronic spectrum of Methylenecyclopropene

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Abstract. The vertical electronic spectrum of methylenecyclopropene, the prototype of the nonalternant hydrocarbons known as fulvenes, has been studied using multiconfigurational second-order perturbation theory. The calculations comprise three valence states and the 3*s*, 3*p*, and 3*d* members of the Rydberg series converging to the first π ionization limit. Vertical excitation energies to three valence states are found at 4.13, 6.12, and 6.82 eV. The second of them corresponds to an excitation from the highest occupied σ orbital to a π^* orbital, while the other two are $\pi \rightarrow \pi^*$ excitations. The third transition gives rise to the most intense feature in the electronic spectrum. The results are rationalized within the scheme of two interacting double bonds. Comparisons are made between this and the previous theoretical calculations of the electronic spectra of related systems and also between the available experimental data of methylenecyclopropene in solution.

Key words: Electronic spectrum – Methylene cyclopropene

1 Introduction

Methylenecyclopropene (MCP), the archetype of nonalternant hydrocarbons known as fulvenes, is a molecule of considerable theoretical and experimental interest [1–9]. It was synthesized and characterized for the first time in 1984 by Billups et al. [3] and Staley and Norden [4] independently. The UV spectrum in *n*-pentane at − 78°C was included in the latter study. The electric dipole moment and heavy-atom molecular structure was reported two years later [7]. The experimental value of the dipole moment, $\mu = 1.90 \pm 0.02$ D, is remarkably large for such a small molecule. This has been related to the strong transfer of π-electron density out of the ring by the two double bonds interacting in a T-type arrangement. In addition, the lowest adiabatic (8.15 ± 0.03 eV) and vertical (8.41 ± 0.05 eV) ionization potentials have been determined by photoelectron spectroscopy [8]. Most of the *ab initio* work has been focused on the ground state of the molecule [5–8]. In the early study performed by Johnson and Schmidt [1] on the sudden polarization effect of the system, the low-lying excited states of planar MCP were characterized at the MCSCF level. A limited atomic basis set of double-zeta quality was used.

In the present contribution we report a full theoretical description of the singlet–singlet spectrum of MCP in the energy region below 7 eV. The two low-lying triplet excited states were also considered. Flexible basis sets to describe both valence and Rydberg excited states were employed. The theoretical treatment includes both nondynamic and dynamic electron correlation contributions in order to take into account accurately the differential correlation effects. The theoretical approach uses the Complete Active Space (CAS) SCF method [10] in combination with multiconfigurational second-order perturbation theory by means of the CASPT2 method [11, 12]. The validity of the CASSCF/CASPT2 method in the proper description of the electronic transitions has been demonstrated in a number of earlier applications [13]. Particularly relevant to the present study are the studies of the electronic spectra of *cis*-1,3-butadiene (CB) [14] cyclopentadiene (CP), aromatic five-membered heterocycles [15, 16], and norbornadiene (NB) [17], a formally unconjugated, strained, nonplanar diene. We have previously shown [13, 16, 17] that the electronic spectra of these compounds can be understood on basis the same model, that is, as two double bonds which interact. In this work we shall extend the scheme of two interacting double bonds by considering the theoretical description of the gas-phase electronic spectrum of methylenecyclopropene, the simplest cross-conjugated π-electron system.

2 Computational details

The ground-state geometry determined in gas phase by microwave spectroscopy [7] was employed. Calculations were carried out within C_{2v} symmetry, placing the molecule in the *yz* plane with the *z*-axis bisecting the HCH angle. The generally contracted ANO-type C [4*s*3*p*1*d*]/H[2*s*1*p*] basis set, built from the primitive set C(14*s*9*p*4*d*)/H(8*s*4*p*) [18], was supplemented with a 1*s*1*p*1*d* set of Rydberg functions (each of them contracted from 8 primitive Gaussian functions) placed in the charge centroid of the $^2B_1$ state of the MCP cation. The diffuse functions were specifically designed for the MCP system, following the procedure described elsewhere [13]. This represents a total of 101 basis functions. The SCF energy for the ground state (1^1A_1) of MCP was calculated to be − 153.720618 a.u.

Multiconfigurational wave functions were initially determined at the CASSCF level of approximation [10]. The carbon 1*s* electrons were kept frozen in the form obtained by the ground-state SCF wave function and were not correlated. The active spaces used and the type of states computed are listed in Table 1.

The active space comprising the π-valence MOs (0301) (see footnote a in Table 1) has been used in the computation of the low-lying $^3B_2$ and $^3A_1$ states. The CASSCF (0301) total energy for the ground state was computed to be − 153.766280 au. For the study of the singlet excited states the active space was extended to include the corresponding Rydberg orbitals as appropriate. In order to search for possible valence states arising from excitations out of the $2b_1$ HOMO to the σ^* valence orbitals of a_1 and b_2 symmetries, the CASSCF (5301) ($^1B_1$ states) and CASSCF (0331) ($^1A_2$ states) wave functions include an extra active orbital of symmetry a_1 and symmetry b_2, respectively. It turned out however that the computed extra roots, placed at energies close to 8 eV, had diffuse character. The large strain in the occupied σ orbitals will push them up in energy and make possible excitation from them into the π^* orbitals. One set of calculations have therefore been performed with the highest occupied σ ($4b_2$) orbital active in addition to the four π orbitals. One such excitation will be discussed below. The

Table 1. CASSCF wave functions (number of active electrons) used for valence and Rydberg transitions in methylenecyclopropene

Wave function[a]	States	No. conf.[b]	N^{c}_{states}
CASSCF(0301) (4)	$^3B_2(2b_1 \rightarrow 1a_2^*)$	9	1
CASSCF(0301) (4)	$^3A_1(2b_1 \rightarrow 3b_1^*)$	6	1
CASSCF(0501) (4)	$^1A_1(2b_1 \rightarrow 3p_x, 3d_{xz}, 3b_1^*)$	65	4
CASSCF(5301) (4)	$^1B_1(2b_1 \rightarrow 3s, 3p_z, 3d_{z^2}, 3d_{x^2-y^2})$	175	5
CASSCF(0311) (6)	$^1B_1(4b_2 \rightarrow 1a_2^*)$	9	1
CASSCF(0302) (4)	$^1B_2(2b_1 \rightarrow 1a_2^*, 3d_{xy})$	22	2
CASSCF(0331) (4)	$^1A_2(2b_1 \rightarrow 3p_y, 3d_{yz})$	57	3
CASSCF(1301) (6)	$^1A_2(8a_1 \rightarrow 1a_2^*)$	9	1

[a] Within parentheses the number of active orbitals of symmetry a_1, b_1, b_2, and a_2 of the point group C_{2v}

[b] Number of configurations in the CASSCF wave function

[c] States included in the average CASSCF calculation

first excitation of $^1A_2$ symmetry with clear valence nature, corresponding to the excitation ($8a_1 \rightarrow 1a_2^*$), was found at 7.65 eV at the CASPT2 level. The present study will focus on the main electronic transitions of MCP in the energy region below 7 eV. In order to describe properly the more energetic part of spectrum the $n = 4$ Rydberg transitions should be also considered. The mentioned states located above 7 eV will consequently not be further discussed.

The molecular orbitals for the excited states were obtained from average CASSCF calculations, where the averaging includes all states of interest of a given symmetry. The number of states included in the state average CASSCF calculations together with the number of configurations in the CASSCF wave function are given in Table 1. The transition dipole moments were computed by means of the CASSCF state interaction (CASSI) method [19, 20]. In the formula of the oscillator strength the excitation energy computed at the CASPT2 level was employed.

The CASSCF wave functions were employed as reference functions in the second-order perturbation treatment of each state. The CASPT2 calculations were performed using the full Fock matrix representation of the zeroth-order Hamiltonian [12]. The energy of each excited state is referenced to a ground-state energy computed with the same active space.

The CASSCF/CASPT2 calculations were peformed using the MOLCAS-3 quantum chemistry software [21].

3 Methylenecyclopropene as two interacting double bonds. A qualitative description

For the qualitative description of the electronic transitions expected in the low-energy range of the electronic spectrum of MCP it is helpful to consider the interaction of two independent ethylenic moieties. The interaction of the degenerate bonding, π_b, and antibonding, π_a, MOs of two ethylenic units results in the following four MOs: $\pi_1 = \pi_b + \pi_b$, $\pi_2 = \pi_b - \pi_b$, $\pi_3 = \pi_a + \pi_a$, and $\pi_4 = \pi_a - \pi_a$. With the geometrical arrangement in NB as reference, they lead to the orbital ordering $a_1(\pi_1)$, $b_1(\pi_2)$, $b_2^*(\pi_3)$, and $a_2^*(\pi_4)$ of the C_{2v} point group. Based on this structure the following valence singlet states can be expected and were actually obtained for NB. The one-electron promotions $\pi_2 \rightarrow \pi_3$ and $\pi_1 \rightarrow \pi_4$ yield two states of A_2 symmetry, while $\pi_1 \rightarrow \pi_3$ and $\pi_2 \rightarrow \pi_4$ give two states of B_2 symmetry. The latter two electronic configurations are nearly degenerate and mix to form B_2^- and B_2^+ states. The minus state has the lowest energy and low intensity, while the plus state is pushed up and carries most of the intensity. There is an additional state of A_1 symmetry formed by two electron replacements, mainly the $(\pi_2)^2 \rightarrow (\pi_3)^2$ doubly excited configuration. Similar arguments can be used to rationalize the electronic transitions found in related systems as, for example, the five-atom rings and *cis*- and *trans*-butadiene.

Due to the perpendicular arrangement of the double bonds in MCP, the two antibonding π_a ethylenic MOs cannot interact, because they have different symmetry. Interaction is, however, possible between the π_b MOs. In increasing order of orbital energies, the π-valence orbitals are: $1b_1(\pi_1)$, $2b_1(\pi_2)$, $1a_2^*(\pi_3)$, and $3b_1^*(\pi_4)$. The SCF orbital energies show that configurations involving the first occupied π orbital will not play a significant role in the description of the low-lying excited states. The $1b_1$ MO is around 5.8 eV below the HOMO, $2b_1$, which has a Koopmans' ionization potential of 8.1 eV (C [4*s*3*p*1*d*]/H[2*s*1*p*] results). Electronic states dominated by excitations out of the $1b_1$ MO will consequently not appear in the low-energy part of the spectrum. Two π-derived low-lying singlet and triplet valence excited states can therefore be expected in MCP: $2b_1 \rightarrow 1a_2^*$ gives rise to a state of B_2 symmetry and the excitation $2b_1 \rightarrow 3b_1^*$ results in a state of A_1 symmetry. Due to the localization of the $1a_2^*$ MO on the two carbon atoms of the ring, the transition from the ground state to the first singlet excited state, $^1B_2$ $(2b_1 \rightarrow 1a_2^*)$, is expected with low intensity, contrary to the case of short polyenes in which the corresponding feature is the most prominent. With both the $2b_1$ and $3b_1^*$ MOs spread on the four carbon atoms, the valence transition to the $^1A_1$ $(2b_1 \rightarrow 3b_1^*)$ state is expected to be most intense. In addition, because of the high ring strain inherent to its molecular structure, the σ and σ^* orbitals of MCP are expected to be shifted significantly relative to those of unstrained hydrocarbons, similarly as occurs in cyclopropene [22]. Indeed, the HOMO-1 $(4b_2)$ describes the σ C–C bonds adjacent to the double bond in the cyclic part of the molecule. Valence features involving σ MOs therefore had to be included in the description of the electronic spectrum of MCP, while the σ^* orbitals play a less significant role. Diffuse states arising from excitations out of the HOMO to the 3*s*, 3*p*, 3*d* Rydberg orbitals are predicted to be interleaved among the valence excited states.

4 Results and discussion

The calculated vertical transitions, oscillator strengths, and other properties of the states are collected in Table 2. *Ab initio* transition energies obtained in a previous calculation at the MCSCF level [1] are also included.

The computed dipole moment for the ground state at the individual CASSCF (0301) level, − 1.80 D, is in agreement with the experimental datum, − 1.90 D [7]. The ground-state dipole moment computed in an earlier MCSCF treatment [1] was lower, − 1.33 D. The reason is most probably the different geometry and limited atomic basis set employed.

Three valence singlet states (1^1B_2, 3^1B_1, and 4^1A_1) were located below 7 eV. As expected the lowest singlet excited state is of B_2 symmetry. The vertical excitation

Table 2. Calculated excitation energies (in eV) and other properties of the vertical excited states of methylenecyclopropene.

				Total[b]				Other results
State	CASSCF	CASPT2	μ[a]	$\langle x^2 \rangle$	$\langle y^2 \rangle$	$\langle z^2 \rangle$	Osc. Str.	MCSCF[c]
Ground state (1^1A_1)			− 1.80	− 20.0	− 15.2	− 16.9		
Singlet states								
1^1B_2 ($2b_1 \rightarrow 1a_2^*$)	4.71	4.13	+ 2.07	− 22.6	− 18.8	− 14.4	0.0093	4.71
1^1B_1 ($2b_1 \rightarrow 3s$)	5.04	5.32	+ 2.19	− 41.7	− 36.5	− 32.8	0.0028	
1^1A_2 ($2b_1 \rightarrow 3p_y$)	5.28	5.83	+ 1.23	− 34.7	− 66.2	− 25.6	Forbidden	
2^1B_1 ($2b_1 \rightarrow 3p_z$)	5.52	5.84	+ 1.58	− 36.7	− 32.2	− 64.0	0.0275	
2^1A_1 ($2b_1 \rightarrow 3p_x$)	5.00	5.85	+ 0.78	− 71.7	− 30.7	− 26.7	0.0670	
3^1B_1 ($4b_2 \rightarrow 1a_2^*$)	7.29	6.12	+ 0.01	− 22.2	− 15.8	− 15.8	0.0064	
2^1A_2 ($2b_1 \rightarrow 3d_{yz}$)	5.94	6.54	− 1.86	− 37.6	− 74.4	− 70.1	Forbidden	
4^1B_1 ($2b_1 \rightarrow 3d_{z^2}$)	6.14	6.55	− 5.78	− 42.0	− 54.3	− 86.6	0.0012	
5^1B_1 ($2b_1 \rightarrow 3d_{x^2-y^2}$)	6.19	6.62	− 0.31	− 82.1	− 64.5	− 30.5	0.0005	
3^1A_1 ($2b_1 \rightarrow 3d_{xz}$)	5.77	6.71	− 0.46	− 84.2	− 34.8	− 74.5	0.0062	
2^1B_2 ($2b_1 \rightarrow 3d_{xy}$)	6.53	6.75	− 0.58	− 80.4	− 75.7	− 29.6	0.0035	
4^1A_1 ($2b_1 \rightarrow 3b_1^*$)	8.04	6.82	− 4.81	− 32.2	− 17.7	− 21.6	0.5840	9.36
Triplet states								
1^3B_2($2b_1 \rightarrow 1a_2^*$)	3.50	3.24	+ 0.97	− 20.3	− 17.2	− 15.0		3.32
1^3A_1($2b_1 \rightarrow 3b_1^*$)	4.72	4.52	− 0.85	− 20.8	− 15.6	− 18.2		4.87

[a] Dipole moment (CASSCF) in Debye (experimental value for the ground state is − 1.90 au [7])

[b] Expectation value (CASSCF) of x^2, y^2, and z^2 (in au)

[c] MCSCF results employing a double-zeta basis set from Ref. [1]

energy at the CASPT2 level is computed to be 4.13 eV. The second valence state, $3^1B_1(4b_2 \rightarrow 1a_2^*)$, is placed at 6.12 eV, close to the first vertical $\sigma \rightarrow \pi^*$ transition found in cyclopropene, at 6.36 eV [22]. The third valence excited state, $4^1A_1(2b_1 \rightarrow 3b_1^*)$, appears at 6.82 eV. The computed intensities for the two lowest valence transitions (both involving excitations to the $1a_2^*$ MO) are relatively low, while the third valence transition represents the most intense feature of the system. Compared to the ground state, the expectation values of x^2, y^2, and z^2 reveal the valence nature of the 1^1B_2 and 3^1B_1 states, while the 4^1A_1 state is somewhat more diffuse. The 1^1B_2 and 3^1B_1 states display opposite polarity to that of the ground state, due to the promotion of an electron into the $1a_2^*$ orbital, entirely localized on the three-membered ring. Due to the ionic nature of the 4^1A_1 valence state its computed dipole moment is high, -4.81 D, with the same polarity as the ground state (it is best represented as a carbanion center (CH_2^-) attached to a cyclopropenyl cation). Comparison of the CASSCF and CASPT2 results demonstrates the importance of dynamic correlation effects on the excitation energies. The largest dynamic correlation contribution corresponds to the 4^1A_1 valence state, 1.22 eV. It is therefore not surprising that previous MCSCF calculations using a small atomic basis set [1] placed this state energetically too high, at 9.36 eV.

The calculated vertical transition energy from the ground to the 1^1B_1 ($2b_1 \rightarrow 3s$) Rydberg state is 5.32 eV. It is a weak transition. The $3p$ Rydberg states, 1^1A_2, 2^1B_1, and 2^1A_1, have similar excitation energies. The 2^1A_1 state is placed at 5.85 eV above the ground state. The oscillator strength for the corresponding transition is around 0.07. It is actually the second most intense feature of the spectrum. The five members of the $3d$ series have been computed to lie in the energy range 6.54–6.75 eV. The dipole-allowed $3d$ transitions have lower intensities than the $3p$ transitions. In contrast to the $3s$ and $3p$ Rydberg states (cf. Table 2), the $3d$ states have the same polarity as the ground state. The singlet–triplet gaps are computed to be 0.89 and 2.30 eV for the 1^3B_2 and 1^3A_1 states, respectively. MCP has the smallest singlet–triplet splitting computed for the HOMO → LUMO excited state (0.89 eV), compared to related systems as NB(1.86 eV), CP(2.12 eV), and CB(2.77 eV). It is an additional reflection of the different (localized) nature of the LUMO in MCP.

As far as we are aware, no gas-phase spectroscopic data are available for comparison. The UV spectrum of MCP in *n*-pentane at $-78°C$ is however available [4]. It displays a broad low-intensity band at 4.01 eV, a more narrow low-intensity band at 5.12 eV, and a strong band at 6.02 eV. The position of the first band is strongly solvent dependent, 4.49 eV in methanol at $-78°C$. The solvation effects are smaller for the other absorption bands: 5.00 and 5.90 eV in methanol, respectively. Comparison of the present (gas-phase) results with the available experimental data in solution has to be done with caution. The presence of condensed media perturbs the electronic transitions in different ways. Rydberg states are precluded and bands are usually broad with low resolution. The observed bands of the UV spectrum reported by Staley and Norden [4] should therefore be related to the computed valence transitions. The first band can be identified with the lowest singlet–singlet transition, computed vertically at 4.13 eV in gas phase. The fact that the energy of the excitation increases in a more polar solvent is consistent with the change of sign of the dipole moment (from -1.80 to $+2.07$ D), which makes the interaction with the solvent repulsive in the upper state during the time scale of the excitation. A broad band is also expected due to strong relaxation effects in the solvent. A bathochromic shift is expected for the $1^1A_1 \rightarrow 4^1A_1$ transition, because the dipole moment of the 4^1A_1 valence state is 3 D larger than that of the ground state and with the same sign. Finally, comparison between the observed and calculated intensities of the three valence transitions located below 7 eV supports the identification of the weak band centered at 5.12 eV in *n*-pentane with the second valence transition, which has a computed vertical energy of 6.12 eV in gas phase. The dipole moment is, however, small and one would not expect a solvent red shift of 1 eV. It is, however, possible that other effects than the solvent are important for the differences between the spectrum of MCP in gas phase and solution. One possibility is a nonvertical nature of the transition. Johnson and Schimdt [1] have calculated the low-lying diradical and zwitterionic states of 90° twisted MCP. The exocyclic π-bond twisting leads to a pronounced stabilization with respect to the correlated states of planar MCP. The equilibrium geometries of the excited states are, in general, expected to be twisted. The importance of this phenomenon has been demonstrated in ethylene, and it is by now well established that the maximum of the π–π^* valence band, which occurs at 7.66 eV [23], does not correspond to the vertical transition, which has a best theoretical estimate of about 8 eV [24], but instead to a somewhat twisted molecule. Another possible source of error in the description of the 4^1A_1 state is related to the increased spatial diffuseness of this state compared to the other valence excited states. In cases where there is an erroneous valence-Rydberg mixing at the CASSCF level, the CASPT2 does not lead to an improvement of the excitation energy and larger errors are obtained (about 0.4 eV for the V state of ethylene and 0.3 eV for the lowest singlet–singlet transition of *trans*-butadiene [25]). This possibility was checked in a series of calculations using different active spaces and different basis sets. Additional MRCI calculations were also performed in order to check the behavior of the CASPT2 approach itself. As discussed below, the result of all these studies unambiguously show that the vertical transition energy of the 4^1A_1 state is located in the region 6.5–6.8 eV, where the lower value accounts for a possible error in the CASPT2 energy due to an inappropriate mixing with Rydberg states. The difference between the computed value and the experimental peak position in solution (0.5–0.8 eV) is then explained partly by the bathochromic shift and partly by an assumed non-vertical nature of the transition.

One might argue that if the diffuse functions were removed from the basis set, the fourth state of 1^1A_1 symmetry should be purely valence in nature, because no mixing is then possible with the Rydberg functions. The difference between the excitation energies computed with and without diffuse functions could be related to the error due to the wrong valence-Rydberg mixing. Such a calculation has been performed employing the π-valence CASSCF (0301) wave function, with four active electrons, averaging the lowest two roots (ground and first excited state), using the C[4*s*3*p*1*d*]/H[2*s*1*p*] ANO-type basis set. The computed transition energies at the CASSCF and CASPT2 level are 6.20 and 6.15 eV, respectively, in apparent agreement with the experiment. However, a detailed analysis of the convergence pattern of the excitation energy of the lowest singlet excited valence state of $^1A_1$ symmetry with respect to an increased flexibility of the valence one-electron basis set reveals that this issue is more complex. Table 3 lists the transition dipole moment and excitation energy using different atomic valence basis sets of increasing quality.

Using the double-zeta contraction, the second state is placed at 6.98 eV, with a high value for the transition moment, 2.1 au. As already mentioned the excitation energy drops to 6.15 eV when polarization functions are included (calculation 3). It further decreases to 6.05 eV using an extended basis set including up to *f*-type functions (calculation 4). Interestingly, increasing the number of basis functions the tendency towards diffuseness of the second root increases, while the transition

Table 3. Transition energy (in eV) and properties for the first excited state of $^1A_1$ symmetry of methylenecyclopropene computed using different one-electron basis functions. Average CASSCF (0301) wave functions (four active electrons) obtained averaging two roots were employed as reference for the CASPT2 calculations

			Total[c]					
Basis set[a]	Root	μ[b]	$\langle x^2 \rangle$	$\langle y^2 \rangle$	$\langle z^2 \rangle$	$\lvert M_{ij} \rvert$[d]	CASSCF	CASPT2
1: C [2*s*1*p*]/H [1*s*]	1	− 0.343	− 25.5	− 20.8	− 21.6			
	2	− 2.036	− 24.8	− 20.2	− 23.6	1.851	10.25	9.32
2: C [4*s*2*p*]/H [2*s*]	1	− 0.500	− 20.7	− 15.8	− 17.3			
	2	− 2.168	− 23.7	− 16.5	− 22.5	2.088	8.23	6.98
3: C [4*s*3*p*1*d*]/H [2*s*1*p*]	1	− 1.204	− 19.9	− 14.2	− 16.2			
	2	+ 0.275	− 36.3	− 20.2	− 20.8	1.151	6.20	6.15
4: C [5*s*4*p*3*d*2*f*]/H [3*s*2*p*]	1	− 1.231	− 19.8	− 14.1	− 15.9			
	2	+ 0.258	− 41.5	− 22.2	− 22.2	0.873	5.69	6.05

[a] Number of basis functions. 1:24; 2:48; 3:92; 4:220. SCF energies. 1: 153.28466 au; 2: 153.613828 au; 3: 153.719901 au; 4: 153.734259 au

[b] Dipole moment (CASSCF) in au (experimental value for the ground state is − 0.7475 au [7])

[c] Expectation value (CASSCF) of x^2, y^2, and z^2 (in au)

[d] Transition dipole moment (CASSI) in au

Table 4. Excitation energies (in eV) for the singlet excited states of A_1 symmetry of methylenecyclopropene computed at the MRCI level

Calculation	1^1A_1	$2^1A_1(2b_1 \rightarrow 3p_x)$	$3^1A_1(2b_1 \rightarrow 3d_{xz})$	$4^1A_1(2b_1 \rightarrow 3b_1^*)$
1. MOs: averaged CASSCF				
No. of roots: 4				
No. of ref. states[a]	4	4	4	4
Weight[b]	0.853	0.861	0.861	0.847
MRCI	–	5.58	6.43	7.73
MRCI + Q	–	5.85	6.73	7.58
2. MOs: MRCI-NOs				
No. of roots: 2				
No. of ref. states[a]	2			2
Weight[b]	0.856			0.772
MRCI	–			9.62
MRCI + Q	–			7.12
No. of ref. states[a]	5			5
Weight[b]	0.858			0.836
MRCI	–			7.62
MRCI + Q	–			7.09
3. MRCI + INO results				
No. of roots: 2				
No. of ref. states[a]	3	3		
Weight[b]	0.860	0.863		
MRCI	–	5.84		
MRCI + Q	–	5.95		
CASPT2 results (from Table 2)	–	5.85	6.71	6.82

[a] Number of configurations in the reference space

[b] Total weight of the reference configurations in the MRCI wave function

dipole moment decreases. For comparison, the corresponding values of the transition dipole moment for the transition from the ground state to the $2^1A_1(2b_1 \rightarrow 3p_x)$ and $4^1A_1(2b_1 \rightarrow 3b_1^*)$ are, in absolute value, 0.68 and 1.87 au, respectively (obtained with the original basis set). The results are conclusive: by increasing the flexibility of the atomic valence basis set, convergence of the second root to the $2^1A_1(2b_1 \rightarrow 3p_x)$ state is progressively achieved on both the excitation energy and the transition dipole moment. This is one more example, which illustrates how important it is to choose a one-electron basis, which includes enough flexibility to describe both valence and Rydberg excited states.

The stability of the computed vertical transition to the $4^1A_1(2b_1 \rightarrow 3b_1^*)$ valence state has been checked in several additional ways. At the CASPT2 level, the vertical transition is not significantly sensitive to the enlargement of the active space, in particular including a number σ, σ^* orbitals and all the Rydberg orbitals active. In addition, extended multi-reference CI (MRCI) calculations also support the CASPT2 findings. Table 4 shows the MRCI results, also with addition of the Davidson correction ($+Q$), for the excitation energies to the singlet states of A_1 symmetry, employing different sets of MOs to build the MRCI wave function. For the sake of comparison, the CASPT2 results taken from Table 2 are also included.

We start the analysis by discussing MRCI results obtained with the average CASSCF MOs, obtained averaging four roots of A_1 symmetry. The minimum number of reference configurations (four) were used to describe the four lowest states of A_1 symmetry. At the MRCI level, the diffuseness, nature, and properties of the states are similar as previously indicated (see Table 2). For the Rydberg states the computed excitation energies at the MRCI + Q level are close to the CASPT2 results. The $4^1A_1(2b_1 \rightarrow 3b_1^*)$ state is, however, more different, which can be related to the valence nature of the state. Larger differential correlation contributions can be expected for the valence state and they are apparently not well treated using such a limited set of reference configurations. In order to improve the description of the valence excited state, a set of MRCI natural orbitals (NOs) were subsequently used (calculation 2).

The reference space is now chosen such that only the ground state and the valence excited state are included. As the result only two roots are required in the CI step. The excited state has a clear valence character. With two reference configurations (the closed-shell Hartree–Fock and one singly excited configuration) the excitation energy computed at the MRCI + Q level is slightly larger than the corresponding CASPT2 value, and the Q correction is large. Next, the reference space was enlarged to five configurations. The selection of the reference configurations was made by inspection of the magnitude of the CI coefficients obtained in the smaller calculation. The five reference configurations should take into account the major reorganization effects of the π system. The MRCI + Q (5 ref.) excitation energy is now consistent with the CASPT2 result. In addition, using three reference configurations (full CI 2 electrons within the $2b_1$ and $3b_1^*$ MOs) the Iterative Natural Orbital (INO) procedure for the two lowest roots was carried out. The converged excitation energy after 30 iterations, MRCI + INO results in Table 4, for the second root was 5.95 eV, with a clear diffuse character of the wave function. These results give further support to the previous conclusions: the lowest excited state of A_1 is of Rydberg nature and the vertical excitation energy of the valence state of the same symmetry as the ground state is placed around 7 eV in the gas-phase spectrum.

5 Summary and conclusions

From the present study it can be concluded that the main features of the electronic spectrum of methylenecyclopropene can be rationalized within the scheme of two interacting double bonds. The lowest triplet state is mainly described by the HOMO → LUMO excitation. The energy difference between the π_3 and π_2 orbitals is about the same in MCP, NB, CP, and CB. This is reflected in similar values for the lowest singlet–triplet transition, 3.24, 3.42, 3.15, and 2.81 eV, respectively. The orbital energy model is too crude to allow a more detailed analysis of the small relative energy differences. The corresponding singlet excited state, 1^1B_2, located at 4.13 eV, lies around 1 eV below the corresponding state in the related systems NB(1^1A_2: 5.28 eV), and CP(1^1B_2: 5.27 eV). Orbital energy differences are about the same as in the other diene systems [16]. Thus, the explanation lies in the electron repulsion terms. The excitation moves the electron from an orbital, which is delocalized over all four atoms to an orbital entirely localized on the ring atoms. This greatly reduces the size of the corresponding exchange integral with a corresponding down-shift of the energy for the singlet state and a small singlet–triplet separation.

The strongest vertical transition corresponds to the 4^1A_1 valence state, computed in the high-energy side of the spectrum above the $n = 3$ Rydberg series, with an excitation energy of 6.5–6.8 eV. It is mainly described by the $\pi_2 \rightarrow \pi_4$ configuration, with a small valence-Rydberg mixing. No near degeneracy occurs with excitations involving the lowest π orbital, which can be rationalized considering the large orbital energy spacing with the remaining π orbitals. The T-type interaction between the two double bonds and the intrinsic strain of the molecule makes the system unique with a valence state mainly described by one-electron promotion from the highest σ orbital (HOMO-1) to the LUMO present at a moderate energy, between the 3*p* and 3*d* Rydberg series. The shifts noted between the computed spectrum and the available UV spectrum in *n*-pentane and methanol are most likely due to both the nonvertical nature of the valence bands and solvent effects.

Taking into account that methylenecyclopropene is a highly reactive compound, the experimentally determined gas-phase spectrum might not be easily accessible for some time. The interplay between experiment and theory therefore has importance for gaining further insight into the properties of this fundamental nonalternant hydrocarbon.

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