Electron-Energy-Loss Spectroscopy and Theoretical Study of Triplet and Singlet Excited States of Fulvene

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Triplet and singlet excited states of fulvene and 6,6′-dimethylfulvene were studied in the gas phase by electron-energy-loss spectroscopy. Two valence triplet states were observed for each compound, with vertical transition energies of 2.35 and 3.10 eV for fulvene and 2.35 and 3.00 eV for 6,6′-dimethylfulvene. The states are assigned as $^3B_2$ and $^3A_1$. The $^1B_2$ and $^1A_1$ valence singlet states and two Rydberg bands, known from photoabsorption spectroscopy, were also observed. To support the assignments multiconfigurational second-order perturbation calculations (CASSCF/CASPT2) were performed. The calculated energies of the first two valence triplet and singlet transitions are within 0.19 eV of the experiment.

Introduction

Fulvene was first synthesized at the beginning of the century.[1] The fact that fulvene is a nonalternant cross-conjugated cyclic hydrocarbon and at the same time valence isomer of benzene motivated particular interest in its electronic structure. The specific conjugation pattern of fulvene results in unusual and interesting properties of its excited states and is manifested in various types of spectra.

Singlet excited states of fulvene were studied by photoabsorption spectroscopy,[2−4] which revealed four electronic transitions in the region from 550 to 168 nm. The lowest, with an absorption maximum at 360 nm (3.44 eV), lies in the visible. It is responsible for the yellow color of fulvene and is assigned as a valence $^1B_2$ transition. It is weak ($f < 0.01$) and is generally reported to be structureless. Weak sharp vibrational structure with an origin at 19685 cm^{-1} (2.44 eV) was observed, however, in the gas phase absorption with a very long path length and in the crystal absorption spectra of Domaille *et al.*[3] The vibrational structure has several unusual properties: (i) it shows blue-shaded sequences, indicating an excited state potential “stiffer” than the ground state, with respect to a vibration proposed to be a b_1 ring out-of-plane bend, and (ii) it is shifted toward the blue in the crystal spectra. The second band lies in the ultraviolet with a maximum at 235 nm (5.28 eV), has vibrational structure, and is assigned as a valence $^1A_1$ transition. Two transitions with sharp vibrational structure are further observed at $\lambda_{0-0} = 202$ nm (6.14 eV) and $\lambda_{0-0} = 178$ nm (6.97 eV). They were shown to be Rydberg by matrix isolation and high-pressure perturbation spectra,[4] but ambiguity exists about their assignment.

Less information is available on the triplet states. The lowest excited triplet state of 6,6′-dimethylfulvene (a more stable derivate of fulvene, hereafter referred to as dimethylfulvene) was recently observed in the electron-energy-loss (EEL) spectrum in the condensed phase, with the sample deposited at low temperature on a thin film of argon.[5] Preliminary gas phase EEL spectra of dimethylfulvene were recorded in our laboratory but remained unpublished.[6]

The electronic structure of fulvene has been the subject of various semiempirical and *ab initio* studies which have been reviewed elsewhere.[5,7] Vibronic structure of the valence singlet bands was calculated by Negri and Zgierski,[8] who concluded that the vibrational structure of the S_1 and S_2 bands can be rationalized without invoking out-of-plane vibrations. Bearpark *et al.*[9] calculated the S_1 potential surface and concluded that the methylene group is 90° twisted in this state. There are only a few studies of triplet and Rydberg states. Dreyer and Klessinger[7] recently presented semiempirical and *ab initio* calculations of excitation energies and excited state geometries including triplet states. They predicted two low lying triplet states, $^3B_2$ at 2.45 eV and $^3A_1$ at 3.04 eV. The higher of these states is calculated to be strongly stabilized by torsion around the exocyclic double bond. Energies of singlet excited valence and Rydberg states were calculated by Galasso.[10]

In the present contribution we present a combined experimental and theoretical study of the triplet and the singlet excited states of both the parent compound fulvene and of dimethylfulvene in the gas phase.

The experimental study employs a magnetically focused electron impact spectrometer to record EEL spectra in the gas phase. In its standard continuous mode of operation this instrument measures the sum of electrons scattered into 0° and 180° and is capable of detecting dipole-allowed transitions at higher residual energies as well as dipole- or spin-forbidden transitions at low residual energies. To further enhance the visibility of triplet states in cases of overlapping transitions, we recorded selected spectra at a scattering angle of 180° alone, using a newly developed “electron mirror” device.[11]

In the theoretical part we calculated the excitation energies of both fulvene and dimethylfulvene using the complete-active-space self-consistent-field and multireference second-order perturbation method (CASSCF/CASPT2).[12−15]

Experimental Section

The trochoidal electron spectrometer used in this work has been described in detail previously.[16] It collimates the electron beam by an axial magnetic field and uses trochoidal monochromators[17] both to prepare a quasimonoenergetic incident electron beam and to analyze the energies of the scattered electrons. This spectrometer can be operated in a continuous and a pulsed mode. In both modes of operation electrons

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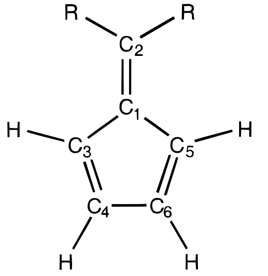

Figure 1. Atom numbering in fulvene (R = H) and dimethylfulvene (R = CH_3).

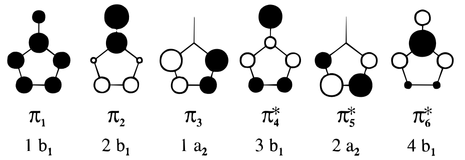

Figure 2. Numbering and symmetry specification of the valence π-orbitals of fulvene. The π-orbitals of dimethylfulvene centered on the fulvene moiety are qualitatively similar, and therefore the same numbering is used. The pseudo π-orbitals of dimethylfulvene (C−H bonding and antibonding orbitals) are labeled π_{CH} and π_{CH}*.

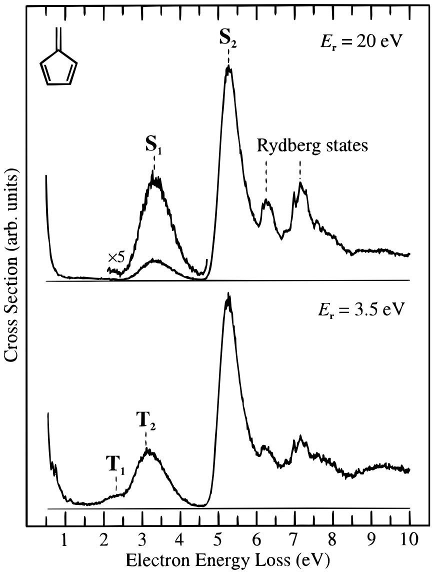

Figure 3. Global energy-loss spectra of fulvene, recorded with a constant residual energy of 20 and 3.5 eV. Singlet−triplet excitations are enhanced at low residual energies.

scattered into 180° are reflected by a potential barrier, re-enter the target chamber, and ultimately also reach the analyzer. In the standard continuous mode of operation a superposition of electrons scattered into 0° and 180° is measured. We have recently developed a pulsed mode of operation, where electrons scattered into 0° and 180° are separated using the difference in their arrival time at the detector. The details of this new technique are described elsewhere.[11,18] The pulsed mode of operation is used here in some cases to enhance the visibility of the triplet states by recording spectra where only electrons scattered into 180° were detected. The energy resolution employed in this work was about 50 meV, and the energy scale is accurate to within 30 meV.

Fulvene was prepared by the technique of Jones and Kent[19] involving the gas phase thermal rearrangement of hexa-1,5-diyne and purified by preparative gas chromatography. The 96% pure fulvene was stored at 200 K. Hexa-1,5-diyne was obtained from Aldrich Chemical. Dimethylfulvene was purchased from Aldrich Chemical at a stated purity of 98%. The purity of the samples was checked by gas chromatography coupled with mass spectrometry (GC−MS). The samples were degassed by repeated freeze−thaw cycles under vacuum and measured at room temperature, where they showed no signs of decomposition.

Computational Methods

The structure and atom numbering of fulvene and dimethylfulvene are given in Figure 1. The ground state geometries of fulvene and dimethylfulvene were optimized using the density functional theory (DFT) B3LYP[20,21] method in combination with a triple-ζ plus double polarization (TZ2P)[22] basis set. During optimization, the molecules were forced to preserve C_{2v} symmetry, this assumption being justified by earlier experimental[23,24] and theoretical[5,7,25] studies.

To calculate the electronic spectra we used atomic natural orbital (ANO) type basis sets[26] of triple-ζ quality for the first-row atoms (C/4s3p2d, H/3s1p). The CASSCF/CASPT2 method[12−15] was used for all excited state calculations. This method is a two-step procedure to calculate state energies corrected by second-order perturbation theory with a CASSCF wave function constituting the reference function. In general, the active space is chosen to include all strongly correlating orbitals, i.e., orbitals with occupation numbers appreciably different from 2 or 0. Thereby all static correlation and near-degeneracy effects are included in the CASSCF reference function, and consequently there will be no large terms in the perturbation expansion. The dipole transition moments are computed using the CAS state interaction (CASSI) method.[27] Energy differences corrected by CASPT2 are used in the oscillator strength formula.

The strongly correlating orbitals in fulvene are the six valence π-orbitals (Figure 2), of which the three lowest in energy (π_1−π_3) are doubly occupied in the ground state SCF wave function. Therefore the minimal active space for fulvene comprised six π-orbitals (four of b_1 and two of a_2 symmetry) with six active electrons. Due to the appearance of intruder states,[28] the active space was enlarged by four orbitals (two of b_1 and two of a_2 symmetry). The basic CASSCF wave functions were thus constructed by distributing the six π-electrons in all permissible ways among 10 π-orbitals.

In comparison to fulvene dimethylfulvene possesses additional pseudo π-orbitals (C−H bonding and antibonding orbitals). At first all 10 π-electrons and the corresponding 10 π-orbitals were kept active. We soon realized that the two lowest (pseudo) π-orbitals remained almost doubly occupied, and they were therefore moved to the inactive space. To avoid problems caused by intruder states, two orbitals (one of b_1 and one of a_2 symmetry) were added to the active space. This resulted in six active electrons distributed among 10 active orbitals (six of b_1 and four of a_2 symmetry).

The calculations have been performed with the MOLCAS-3 program package[29] on IBM RS/6000 workstations except for the DFT geometry optimizations, which used the GAUSSIAN 94 program package.[30]

EEL Spectra of Fulvene

Valence States. Representative EEL spectra of fulvene are shown in Figure 3. The top spectrum, recorded at a high residual energy of 20 eV when optically allowed transitions predominate, is in accord with the photoabsorption measurements. The transition energies are summarized in Table 1. The two bands at 3.34 and 5.27 eV are due to the valence singlet−singlet transitions S_1 and S_2. The bands above 6.0 eV with partly resolved vibrational structure are due to Rydberg states.

TABLE 1: Experimental Vertical (Unless Otherwise Noted) Excitation Energies (ΔE_{exp}) of Fulvene (Oscillator Strengths f Are Given in Parentheses

	ΔE_{exp} (eV)			
	photoabsorption			EEL
band	solution[a]	vapor[b]	matrix[c]	vapor[d]
T_1				2.35
T_2				3.10
S_1	3.42 (0.008)	3.44 (0.0042)	3.44	3.34
S_2	5.12 (0.34)	5.28	5.30	5.27
Rydberg		6.14[e]		6.16[e]
Rydberg				6.75
Rydberg		6.97[e]		7.15[f]

[a] References 31 and 32. [b] References 2 and 3. [c] Reference 4. [d] Present work. [e] 0−0 excitation energy. [f] 0−0 excitation energy is 6.99 eV.

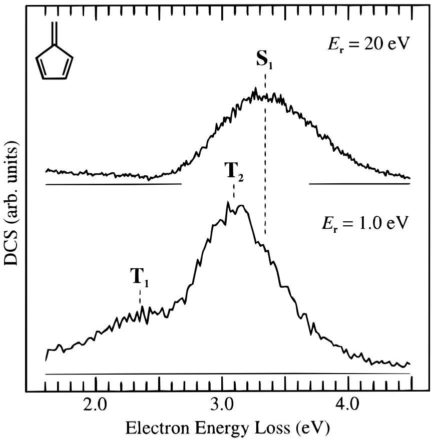

Figure 4. Energy-loss spectra of fulvene recorded in the range of the lowest singlet and triplet transitions at a constant residual energy of 1.0 and 20 eV. The E_r = 1.0 eV spectrum was recorded at a scattering angle of 180°, using the pulsed mode of operation.

The spectrum recorded at the lower residual energy of 3.5 eV shows the excitation of both the triplet and the singlet states, and the bands that are new with respect to the E_r = 20 eV spectrum may thus be assigned to triplet states. (The signal below 1.5 eV is due to excitation of high vibrational levels of the electronic ground state and will not be further discussed.) The shoulder at 2.35 eV is due to the lowest triplet state T_1. The maximum of the next band moved to lower energy by 0.18 eV in comparison with the E_r = 20 eV spectrum, indicating the presence of the second triplet state T_2, partially overlapping with the S_1 state.

Angular distributions of scattered electrons are characteristic of the nature of the electronic states excited. Optically allowed transitions are characterized by a forward peaked behavior, while spin-forbidden transitions show a more isotropic or even backward peaked angular behavior, resulting in a relative enhancement of triplet signal at high scattering angles. We therefore used the capability of our spectrometer to record exclusively the backward signal in the pulsed mode of operation to enhance the triplet transition in the region of overlap. The result is shown in the bottom part of Figure 4. The shoulder with an onset at 1.8 eV and a vertical transition energy of 2.35 ± 0.10 eV is attributed to the lowest triplet excited state T_1. The subsequent band peaks at 3.10 eV, significantly below the peak of the S_1 band at 3.34 eV in the E_r = 20 eV spectrum, confirming the presence of the T_2 state. The determination of the vertical transition energy of the T_2 state is complicated by the overlap with the S_1 band; it could lie up to 0.2 eV below the maximum of the band. We put it at 3.10 ± 0.2 eV.

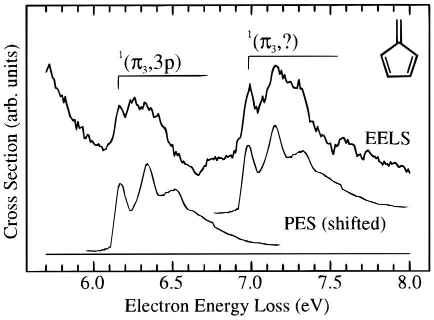

Figure 5. Electron-energy-loss spectra of fulvene recorded with a constant residual energy of 20 eV compared with the profile of the first ionization band in the photoelectron (PE) spectrum. The adiabatic ionization energy is 8.36 eV.[33] The PE band is shown shifted by −2.20 and −1.38 eV.

Rydberg States. The similarity of the band envelope of the bands at 6.26 and 7.15 eV with the band envelope of the lowest UV-photoelectron band,[33] illustrated in Figure 5, suggests that these bands are due to Rydberg states associated with the lowest ionization energy. The two bands are well-known from the photoabsorption spectra, but there is no generally accepted assignment. Originally these two bands were attributed by Harman *et al.*[4] to 3s-Rydberg states of $^1B_1$ symmetry, denoted as $^1(\pi_2,3s)$ and $^1(\pi_2,4s)$. Robin[34] proposed the assignment $(\pi_3,3p)$ and $(\pi_3,4p)$. This assignment of the first Rydberg band is now relatively undisputed and results in a quantum defect of $\delta = 0.51$, conforming with a 3p assignment. It also agrees with the calculated energies of Galasso[10] (6.43 eV for $3p_x$, 6.59 eV for $3p_y$, both having about the same oscillator strength). It may be of interest to note that the highest occupied molecular orbital (HOMO) of fulvene π_3 is predominantly localized on the *cis*-butadiene-like substructure and is reminiscent of the HOMO of cyclopentadiene ($IE_1 = 8.58$ eV).[35] In fact, the EEL spectra of cyclopentadiene[11,36] show a feature at 6.3 eV, reminescent of the present band in fulvene, which has also been assigned to two 3p-Rydberg type transitions.[36,37] Galasso[10] pointed out that the assignment of the second Rydberg band to $(\pi_3,4p)$ results in a quantum defect of $\delta = 0.86$, too large for a p-type orbital. An alternative assignment is $^1(\pi_3,3d)$. It is in agreement with the calculated transition energy[10] (7.22 eV for $3d_{xy}$, which carries the largest oscillator strength of all the 3d-orbitals), but in disagreement with the calculated oscillator strengths[10] (3d is calculated weaker than 4p). The assignment of the 7.15 eV band thus remains uncertain. Note that no band of similar intensity is observed in the appropriate energy region of the EEL spectra of cyclopentadiene. Finally, a shoulder is observed in our spectra at 6.75 eV, the right energy for an assignment as $^1(\pi_2,3s)$, calculated to be at 6.95 eV and to have a substantial oscillator strength.[10]

EEL Spectra of Dimethylfulvene

Valence States. Representative EEL spectra are shown in Figure 6, and the transition energies are summarized in Table 2. The general features of the spectra are very similar to those of fulvene. The first two bands in the spectrum with E_r = 20 eV, with maxima at 3.35 and 4.74 eV, are attributed to the two lowest valence singlet−singlet transitions S_1 and S_2, known already from optical measurements in solution (3.45 and 4.68 eV)[38] and from EEL spectra of condensed dimethylfulvene (3.35 and 4.9 eV).[5] In comparison to the fulvene spectrum, the S_2 band has gained considerably in intensity especially with respect to the two Rydberg bands at 5.88 and 6.95 eV.

The shoulder at 2.35 eV in the spectrum with E_r = 3.5 eV is assigned to the T_1 state. A shift of the maximum of the

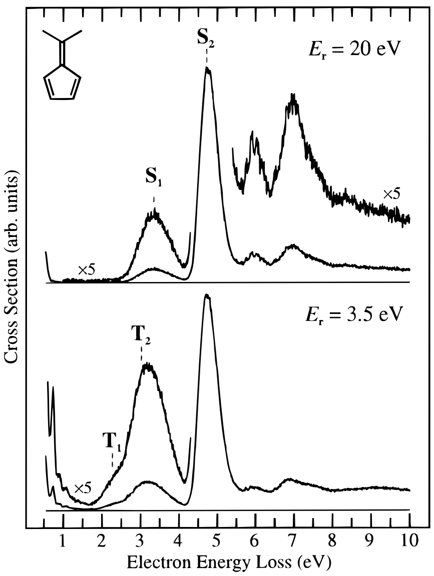

Figure 6. Survey electron-energy-loss spectra of dimethylfulvene.

TABLE 2: Experimental Vertical Excitation Energies (ΔE_{exp}) for the Excited States of Dimethylfulvene

	ΔE_{exp} (eV)		
	photoabsorption	EEL	
band	solution[a]	thin film[b]	vapor[c]
T_1		2.3	2.35
T_2			3.00
S_1	3.45	3.35	3.35
S_2	4.74	4.9	4.74
Rydberg			5.89[d]
Rydberg			6.51
Rydberg			6.95

[a] Reference 38. [b] Reference 5. [c] Present work. [d] Further peaks at 5.76 (0−0) and 6.02 eV.

subsequent band by 0.15 eV to lower energies in the $E_r = 3.5$ eV spectrum indicates the presence of the T_2 state. An attempt to resolve the overlapping T_2 and S_1 bands has been made using spectra (Figure 7) where electrons scattered into the forward and the backward directions are separated. The spectra show the presence of the T_2 and S_1 bands very clearly, and the best enhancement of the T_2 band over the S_1 band is attained at 180° and a residual energy of 1 eV, placing T_2 at 3.0 eV.

Rydberg States. The similarity of the band profile of the 5.88 eV energy-loss band with the profile of the first photoelectron band (Figure 8) identifies it as Rydberg converging to the first IE (8.08 eV, vertical).[39] The quantum defect of $\delta = 0.48$ indicates a $^1(\pi_3,3p)$ assignment. The vibrational structure is surprisingly clear in view of the fact that two overlapping allowed transitions (p_x and p_y) are expected. The Rydberg assignment of this band is confirmed by its absence in the condensed phase EEL spectra of Swiderek *et al.*[5] (Figure 9).

The vibrational structure of the more intense band peaking at 6.95 eV is much less pronounced, a fact that can be explained by several overlapping Rydberg transitions, although a contribution from a valence transition cannot be excluded. Problems encountered while attempting to assign this band are similar to those already discussed for fulvene. The possible assignments include $^1(\pi_3,4p)$ and $^1(\pi_3,3d)$, an unambiguous assignment not being possible at this stage. Finally the peak at 6.51 eV could be assigned as $^1(\pi_2,3p)$ or $^1(\pi_3,3d)$.

Calculations

Geometries. The calculated bond distances and angles of fulvene and dimethylfulvene are given in Table 3 and compared

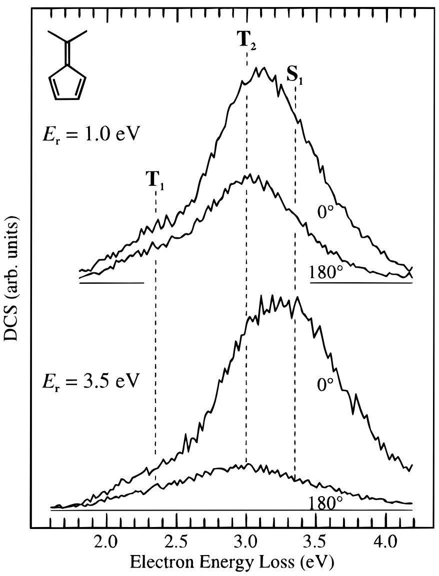

Figure 7. Electron-energy-loss spectra of dimethylfulvene in the range of the lowest singlet and triplet transitions, recorded at constant residual energies of 1.0 and 3.5 eV. The spectra were recorded at 0° and 180°, using the pulsed mode of operation. The most complete suppression of the S_1 state, and thus the best visibility of the T_2 state, is achieved at 180° and $E_r = 1.0$ eV.

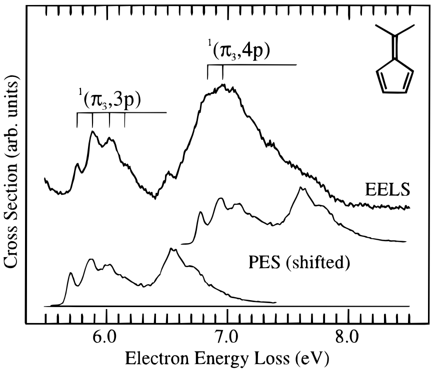

Figure 8. Electron-energy-loss spectra of dimethylfulvene recorded with a constant residual energy of 20 eV compared with the profile of the first two ionization bands in the photoelectron (PE) spectrum. (The adiabatic ionization energies are 7.89 and 8.72.)[6] PE bands are shown shifted by −2.19 and −1.12 eV.

to a selection of earlier theoretical[5,25] and experimental[23,24] structure determinations. A detailed discussion of the previous theoretical studies on the geometry of fulvene can be found in the paper of Dreyer *et al.*[7] For fulvene the B3LYP results agree well with the experimental values. The comparison in Table 3 shows that the B3LYP results are of quality similar to the MP2 geometry, but they were attained at a fraction of the computational cost. For dimethylfulvene the differences between calculation and experiment are larger but still reasonable. Both AM1 and B3LYP predict the C_1-C_2 and C_3-C_4 bonds to be longer than in fulvene, while the experiment determines them to be shorter. Noticeable deviations between theory and experiment are also found for the C−C−H angles.

Transition Energies. This study concentrates on the low lying valence excited singlet and triplet states and does not attempt to treat the Rydberg states correctly. The calculated transition energies of fulvene and dimethylfulvene are given in Table 4 and Table 5. The present results are compared to previous *ab initio* calculations in Table 6.

The weight ω of the CASSCF reference function in the first-order perturbed wave function is an indication of a balanced treatment of electron correlation, and the values of ω were

TABLE 3: Optimized and Experimental Ground State Geometries (in Å and deg) and Total Energies *E* (in au) for Fulvene and Dimethylfulvene (C_{2v} Symmetry Assumed) (See Figure 1 for Atom Numbering)

	fulvene				dimethylfulvene		
	AM1[a]	MP2[b] (6-31G*)	B3LYP[c] (TZ2P)	expt[d]	AM1[a]	B3LYP[c] (TZ2P)	expt[e]
C_1C_2	1.332	1.348	1.350	1.349	1.346	1.366	1.347
C_1C_3	1.483	1.466	1.479	1.470	1.482	1.478	1.476
C_3C_4	1.363	1.358	1.361	1.355	1.365	1.365	1.340
C_4C_6	1.476	1.468	1.480	1.476	1.472	1.469	1.462
C_2C_7					1.484	1.511	1.510
$C_3C_1C_5$	105.2	106.6	106.3	106.6	104.8	105.6	106
$C_1C_3C_4$	108.6	107.7	107.8	107.7	108.8	108.3	108
$C_3C_4C_6$	108.8	109.2	109.0	109.0	108.8	108.9	109.0
C_1C_2R		122.0	122.0	122.0		122.9	122.0
$C_1C_3H(3)$		123.4	124.5	124.7		125.6	123
$C_3C_4H(4)$		127.3	126.5	126.4		126.2	120
E		−231.3983	−232.1682			−310.7804	

[a] Reference 5. [b] Reference 25. [c] Present work. [d] Reference 24. [e] Reference 23.

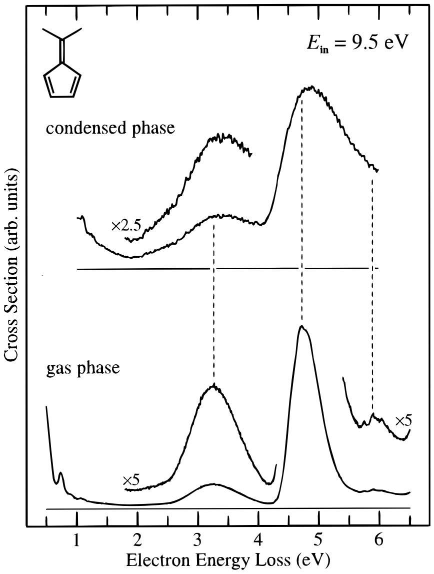

Figure 9. Comparison of the present gas phase EEL spectra of dimethylfulvene with the EEL spectra obtained for less than a monolayer of dimethylfulvene deposited on frozen argon by Swiderek *et al.*[5] Both spectra were recorded with a constant incident energy of 9.5 eV.

TABLE 4: Calculated Excitation Energies Δ*E* (in eV) and Wave Functions of the $\pi \rightarrow \pi^*$ Excited States of Fulvene (Ground State Energies (in au) Are −230.808 485 (CASSCF) and −231.576 083 (CASPT2))

	Δ*E*				
state	CASSCF	CASPT2	*f*[a]	*ω*[b]	wave function[c]
		Singlet States[d]			
1^1A_1	0.00	0.00		0.79	86% $\pi_1^2\pi_2^2\pi_3^2$
1^1B_2	4.07	3.29	0.005	0.77	72% $\pi_3 \rightarrow \pi_4^*$ 13% $\pi_2\pi_3 \rightarrow \pi_4^{*2}$
2^1A_1	5.94	5.30	0.060	0.75	20% $\pi_2 \rightarrow \pi_4^*$ 17% $\pi_3^2 \rightarrow \pi_4^{*2}$ 13% $\pi_1 \rightarrow \pi_4^*$ 12% $\pi_3 \rightarrow \pi_5^*$
3^1A_1	6.78	5.75	0.248	0.76	52% $\pi_2 \rightarrow \pi_4^*$ 14% $\pi_1 \rightarrow \pi_4^*$ 10% $\pi_3^2 \rightarrow \pi_4^{*2}$
2^1B_2	7.77	6.46	0.020	0.73	52% $\pi_2\pi_3 \rightarrow \pi_4^{*2}$ 18% $\pi_3 \rightarrow \pi_4^*$
3^1B_2	7.16	6.88	0.150	0.76	87% $\pi_3 \rightarrow \pi_6^*$
		Triplet States[d]			
1^3B_2	2.51	2.27		0.78	86% $\pi_3 \rightarrow \pi_4^*$
1^3A_1	3.09	2.97		0.78	84% $\pi_2 \rightarrow \pi_4^*$
2^3A_1	5.27	5.06		0.77	44% $\pi_3 \rightarrow \pi_5^*$ 28% $\pi_1 \rightarrow \pi_4^*$
2^3B_2	6.15	5.65		0.74	40% $\pi_3 \rightarrow \pi_6^*$ 36% $\pi_2\pi_3 \rightarrow \pi_4^{*2}$

[a] Oscillator strength in au. [b] The weight of the CASSCF reference function in the first-order wave function. [c] Excitations that contribute more than 10% to the CASSCF wave function are listed. [d] For each symmetry/spin group the lowest *n* states were included in the state-average CASSCF calculation: $n = 3$ ($^1A_1$), 3 ($^1B_2$), 2 ($^3A_1$), and 2 ($^3B_2$).

therefore included in Tables 4 and 5. They should ideally be the same for the ground and all excited electronic states under consideration. The present values of *ω* for valence excited states are satisfactory, although they are generally somewhat smaller than for the ground state, reflecting the larger importance of dynamic electron correlation effects.

Tables 4 and 5 also indicate the wave functions in terms of molecular orbitals (MOs). Although the MOs are not identical for states of different spin or symmetry in a CASSCF calculation, a qualitative comparison of the contributing configurations is still useful and legitimate, since the nodal properties of the MOs are preserved.

Singlet States. In fulvene the lowest valence excited singlet state (1^1B_2) is calculated at 3.29 eV, in excellent agreement with the experimental value of 3.34 eV. It corresponds to the $\pi_3 \rightarrow \pi_4^*$ (HOMO → LUMO) excitation and is predicted to be the weakest ($f = 0.005$) of the four dipole-allowed transitions, in agreement with its low intensity in the spectrum. Two singlet excited states (2^1A_1 and 3^1A_1) are calculated in the 5−6 eV range, where the most intense singlet band is observed. They are a mixture of singly and doubly excited configurations. The assignment of the intense singlet band at 5.27 eV (labeled S_2 in the spectrum of Figure 3) thus remains somewhat ambiguous at this stage. The assignment to 2^1A_1 results in a good agreement in terms of transition energy, but a discrepancy in terms of intensity (Table 6). The observed large intensity and large calculated oscillator strength make an assignment to 3^1A_1 more preferable, but the discrepancy of calculated and observed transition energies (Table 6) is larger than is customary for the CASPT2 model. Finally the relatively strong transition to the 3^1B_2 state ($f = 0.150$) is calculated at 6.88 eV, which is likely to be hidden underneath the Rydberg transitions in the crowded spectral region around 7 eV.

The situation in dimethylfulvene is very similar to that in fulvene. Note that now both the 2^1A_1 and the 3^1A_1 states are calculated somewhat higher in energy than the observed intense singlet band, indicating that the present calculation neglecting the Rydberg states provides only an approximate description of the higher lying singlet states.

Note that the calculation correctly reproduces the fact that the 1^1B_2 state is at essentially the same energy in dimethylfulvene and in fulvene. In contrast, the energies of both $^1A_1$ states

TABLE 5: Calculated Excitation Energies Δ*E* (in eV) and Wave Functions of the $\pi \rightarrow \pi^*$ Excited States of Dimethylfulvene (Ground State Energies (in au) Are −308.908 494 (CASSCF) and −309.994 187 (CASPT2))

	Δ*E*				
state	CASSCF	CASPT2	f^a	ω^b	wave function[c]
		Singlet States[d]			
1^1A_1	0.00	0.00		0.73	86% $\pi_1^2 \pi_2^2 \pi_3^2$
1^1B_2	4.22	3.29	0.006	0.71	78% $\pi_3 \rightarrow \pi_4^*$ 10% $\pi_2 \pi_3 \rightarrow \pi_4^{*2}$
2^1A_1	5.80	4.93	0.134	0.69	36% $\pi_2 \rightarrow \pi_4^*$ 13% $\pi_3 \rightarrow \pi_5^*$ 11% $\pi_3^2 \rightarrow \pi_4^{*2}$
3^1A_1	6.61	5.40	0.243	0.69	37% $\pi_2 \rightarrow \pi_4^*$ 21% $\pi_1 \rightarrow \pi_4^*$ 13% $\pi_2^2 \rightarrow \pi_4^{*2}$ 10% $\pi_3^2 \rightarrow \pi_4^{*2}$
2^1B_2	6.60	6.52	0.046	0.72	87% $\pi_3 \rightarrow \pi_{CH}^*$
3^1B_2	7.33	7.22	0.081	0.71	85% $\pi_3 \rightarrow \pi_{CH}'^*$
		Triplet States[d]			
1^3B_2	2.41	2.34		0.72	87% $\pi_3 \rightarrow \pi_4^*$
1^3A_1	2.94	2.93		0.72	88% $\pi_2 \rightarrow \pi_4^*$

[a] Oscillator strength in au. [b] The weight of the CASSCF reference function in the first-order wave function. [c] Excitations that contribute more than 10% to the CASSCF wave function are listed. [d] For each symmetry/spin group the lowest *n* states were included in the state-average CASSCF calculation. $n = 3$ ($^1A_1$), 3 ($^1B_2$), 1 ($^3A_1$), and 1 ($^3B_2$).

TABLE 6: Excitation Energies (in eV) and Oscillator Strengths (in au, in Parentheses) for the Low Lying Excited States of Fulvene and Dimethylfulvene

state (band)	CIPSI[a]	CIPSI[a]	CAS[c]	CAS[d]	CASPT2[e]	expt[e]
			Fulvene			
1^3B_2 (T_1)	2.76		2.62	2.45	2.27	2.35
1^3A_1 (T_2)	3.44		3.26	3.04	2.97	3.10
1^1B_2 (S_1)	3.82 (0.006)	4.15 (0.023)	4.24	3.72	3.29 (0.005)	3.34
2^1A_1 (S_2)[f]	5.82 (0.09)	5.82 (0.721)	6.15	5.89	5.30 (0.060)	5.27
3^1A_1 (?)[f]			7.48	6.93	5.75 (0.248)	
			Dimethylfulvene			
1^3B_2 (T_1)					2.34	2.35
1^3A_1 (T_2)					2.93	3.00
1^1B_2 (S_1)					3.29 (0.006)	3.35
2^1A_1 (S_2)[f]					4.93 (0.134)	4.74
3^1A_1 (?)[f]					5.40 (0.243)	

[a] Reference 40. [b] Reference 10. [c] Reference 5. [d] Reference 7. [e] Present work. [f] Assignment uncertain (see text).

are calculated to red-shift upon methyl-substitution by 0.37 and 0.35 eV, respectively. This red shift compares favorably with the 0.53 eV shift of the observed S_2 band. Note also that the calculated oscillator strength of the $1^1A_1 \rightarrow 2^1A_1$ transition has increased upon methyl-substitution, possibly a consequence of the larger contribution by the $\pi_2 \rightarrow \pi_4^*$ configuration to the 2^1A_1 wave function.

Triplet States. The agreement of the experimental and calculated transition energies for the lowest two triplet states is excellent both in fulvene and in dimethylfulvene. The calculation also reproduces correctly the somewhat unexpected fact that both triplet transitions do not shift noticeably upon methyl-substitution. The calculation indicates that the doubly excited configurations contribute less to the triplet state wave functions than to the singlet state wave functions.

Discussion and Conclusions

The calculated excitation energies for the three lowest excited states of both fulvene and dimethylfulvene agree with experiment to within 0.13 eV, which is about equal to the uncertainty of localizing the maximum of the broad experimental bands, thus confirming that CASPT2 is a very precise method for calculating excitation energies. The agreement is less satisfactory for the second, intense singlet band. For both compounds, the calculation predicts two excited states, 2^1A_1 and 3^1A_1, both with substantial oscillator strength (Table 6), whereas only one band (labeled S_2 in Figures 3 and 6) is observed in the spectra. The present calculation thus does not entirely account for the observations; it either strongly exaggerates the oscillator strength of the 3^1A_1 transition or predicts both the 2^1A_1 and 3^1A_1 states too high in energy (by different amounts) and the S_2 band is in reality an overlap of both transitions. The same problem has already been encountered by Swiderek *et al.*[5] in their CAS calculations, but does not appear in the RPA calculations of Galasso.[10] At the present time we have not identified the cause of the discrepancy between experiment and the results of our calculations. We confine ourselves to noting that it may be necessary to include the Rydberg orbitals more extensively in the calculation to obtain the energies of the higher lying singlet states with better precision and that it may further be necessary to optimize the MOs separately for each excited state in order to obtain accurate oscillator strengths.[41]

Comparison of the spectra of fulvene and dimethylfulvene reveals that three of the valence bands, T_1, T_2, and S_1, experience no shift upon methylation (within the ±0.1 eV uncertainty of localizing the maxima of the broad bands), whereas S_2 shifts substantially, by 0.53 eV toward lower energy. The behavior of the singlet bands has already been discussed and qualitatively explained by Straub *et al.*[32] The lack of shift of the two triplet states, although correctly reproduced by the CASPT2 calculations, is interesting and somewhat surprising when orbital energy differences alone are regarded. Tables 4 and 5 show that the electron is promoted from the π_3-and π_2-orbitals in the T_1 and T_2 states, respectively, and that both transitions have the same final orbital π_4^*. The ionization energies from the π_2- and π_3-orbitals experience substantially different shifts upon methyl substitution (0.79 and 0.47 eV)[39] so that, on the basis of orbital energy differences alone, T_1 and T_2 would be expected to shift by different amounts.

Very interesting is the comparison of the present gas phase spectrum with the frozen thin film spectrum of Swiderek *et al.*[5] shown for dimethylfulvene in Figure 9. The spectra are very similar in their general aspect, but differ in a number of interesting details. Perhaps the most interesting is the consistently larger width of the individual electronic bands in the thin film spectrum. This observation has already been made with the matrix spectra of benzene[42] and the thin film spectra of butadiene[43] and can be expected to occur generally. The increased width of the $^1E_{1u}$ state of benzene has been ascribed to a drastic reduction of its lifetime due to autoionization.[42] We note that the increased width of, in particular, the low lying triplet bands could also be due to an increase of the Franck−Condon width caused by the excitation of molecule−matrix stretch vibrations in the thin film spectrum, induced by the increased size and thus larger fulvene−matrix equilibrium distance in the electronically excited state.

The Rydberg band at 5.7−6.0 eV is expectedly absent in the thin film spectrum. The fact that the T_1 band is relatively weaker in the present spectrum at an incident energy of 9.5 eV could be caused by the different scattering angles employed in the two experiments and is thus not further significant until more detailed measurements of angular distributions are made. The present results indicate that a comparison of gas phase and frozen thin film spectra for a wider range of compounds could yield interesting information on host−substrate interactions and help to identify Rydberg character of electronic transitions in the future.

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References and Notes

(1) Thiele, J. *Ber. Dtsch. Chem. Ges.* **1900**, *33*, 666.

(2) Brown, R. D.; Domaille, P. J.; Kent, J. E. *Aust. J. Chem.* **1970**, *23*, 1707.

(3) Domaille, P. J.; Kent, J. E.; O'Dwyer, M. F. *Chem. Phys.* **1974**, *6*, 66.

(4) Harman, P. J.; Kent, J. E.; O'Dwyer, M. F.; Smith, M. H. *Aust. J. Chem.* **1979**, *32*, 2579.

(5) Swiderek, P.; Michaud, M.; Sanche L. *J. Chem. Phys.* **1995**, *103*, 8424.

(6) Schafer, O. Ph.D. Thesis, University of Fribourg, Switzerland, 1992.

(7) Dreyer, J.; Klessinger, M. *J. Chem. Phys.* **1994**, *101*, 10655.

(8) Negri, F.; Zgierski, M. Z. *J. Chem. Phys.* **1995**, *102*, 5165.

(9) Bearpark M. J.; Bernardi, F.; Olivucci, M.; Robb, M. A.; Smith, B. R. J. Am. Chem. Soc. **1996**, *118*, 5354.

(10) Galasso, V. *Chem. Phys.* **1993**, *171*, 171.

(11) Asmis, K. R. Ph.D. Thesis, University of Fribourg, 1996.

(12) Roos, B. O.; Andersson, K. *Chem. Phys. Lett.* **1995**, *245*, 215.

(13) Roos, B. O. In *Advances in Chemical Physics; Ab Initio Methods in Quantum Chemistry-II*, Lawley, K. P., Ed.; John Wiley & Sons Ltd.: Chichester, England, 1987; Chapter 69, p 399.

(14) Andersson, K.; Malmqvist, P.-A.; Roos, B. O.; Sadlej, A. J.; Wolinski, K. *J. Phys. Chem.* **1990**, *94*, 5483.

(15) Andersson, K.; Malmqvist, P.-A.; Roos, B. O. *J. Chem. Phys.* **1992**, *96*, 1218.

(16) Allan, M. *J. Electron Spectrosc. Relat. Phenom.* **1989**, *48*, 219.

(17) Stamatovic, A.; Schulz, G. *J. Rev. Sci. Instrum.* **1970**, *41*, 423.

(18) Asmis, K. R.; Allan, M. *J. Phys. B*, in press.

(19) Kent, J. E.; Jones, A. J. *Aust. J. Chem.* **1970**, *23*, 1059.

(20) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(21) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(22) (a) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293. (b) Dunning, T. H. *J. Chem. Phys.* **1971**, *55*, 716. (c) We used the standard Huzinaga and Dunning triple-ζ basis set of contracted Gaussian functions augmented with three sets of Cartesian d-like polarization functions in a 2,1 contraction on the carbons ($\alpha_d(C) = 1.375, 0.407; 0.340$) and three sets of p-type polarization functions in a 2,1 contraction on the hydrogens ($\alpha_p(H) = 1.220, 0.284; 0.260$).

(23) Chiang, J. F.; Bauer H. S. *J. Am. Chem. Soc.* **1970**, *92*, 261.

(24) Baron, P. A.; Brown, R. D.; Burden, F. R.; Domaille, P. J.; Kent, J. E. *J. Mol. Spectrosc.* **1972**, *43*, 401.

(25) Replogle, E. S.; Trucks, G. W.; Staley, S. W. *J. Phys. Chem.* **1991**, *95*, 6908.

(26) Widmark, P.-O.; Malmqvist, P.-Å.; Roos, B. O. *Theor. Chim. Acta* **1990**, *77*, 291.

(27) Malmqvist, P.-Å.; Roos, B. O. *Chem. Phys. Lett.* **1989**, *155*, 189.

(28) Roos, B. O.; Fülscher, M.; Malmqvist, P.-Å.; Merchán, M.; Serrano-Andrés, L. *Quantum Mechanical Electronic Structure Calculations with Chemical Accuracy*; Langhoff, S. R., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1995; p 357.

(29) Andersson, K.; Fülscher, M. P.; Karlström, G.; Lindh, R.; Malmqvist, P.-Å.; Olsen, J.; Roos, B. O.; Sadlej, A. J.; Blomberg, M. R. A.; Siegbahn, P. E. M.; Kellö, V.; Noga, J.; Urban, M.; Widmark, P.-O. *MOLCAS Version 3*; Dept. of Theor. Chem., Chem. Center, Univ. of Lund: P.O.B. 124, S-22100 Lund, Sweden, 1994.

(30) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94* (Revision B.3); Gaussian, Inc.: Pittsburgh, PA, 1995.

(31) Thiec, J.; Wiemann, J. *Bull. Soc. Chim. Fr.* **1956**, *23*, 177.

(32) Straub, P. A.; Meuche, D.; Heilbronner, E. *Helv. Chim. Acta* **1965**, *49*, 517.

(33) Heilbronner, E.; Gleiter, R.; Hopf, H.; Hornung, V.; de Meijere, A. *Helv. Chim. Acta* **1971**, *54*, 783.

(34) Robin, M. B. *Higher Excited States of Polyatomic Molecules*; Academic Press: New York, 1985; Vol. 3.

(35) Derrick, P. J.; Åsbrink, L.; Edqvist, O.; Jonsson, B. Ö.; Lindholm, E. *Int. J. Mass Spectrom. Ion Physics* **1971**, *6*, 203.

(36) Frueholz, R. P.; Flicker, W. M.; Mosher, O. A.; Kuppermann, A. *J. Chem. Phys.* **1979**, *70*, 2003.

(37) Serrano-Andrés, L.; Merchán, M.; Nebot-Gil, I.; Roos, B. O.; Fülscher, M. *J. Am. Chem. Soc.* **1993**, *115*, 6184.

(38) Meuche, D. *Helv. Chem. Acta* **1966**, *49*, 145.

(39) Brogli, F.; Clark, P. A.; Heilbronner, E.; Neuenschwander M. *Angew. Chem.* **1973**, *85*, 414.

(40) Rancurel, P.; Huron, B.; Praud, L.; Malrieu, J. P.; Bertier, G. *J. Mol. Spectrosc.* **1976**, *60*, 259.

(41) Roos, B. O. In *Lecture Notes in Quantum Chemistry*; Roos, B. O., Ed.; Springer Verlag: Berlin, Heidelberg, 1992; p 237.

(42) Sanche, L.; Michaud M. *Chem. Phys. Lett.* **1981**, *80*, 184.

(43) Swiderek, P.; Michaud, M.; Sanche L. *J. Chem. Phys.* **1993**, *98*, 8397.