

## 2. The Photoelectron Spectrum of Tetrafluorobutatriene<sup>1)</sup>

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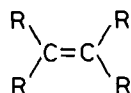
Dedicated to the memory of *Heinrich Labhart*

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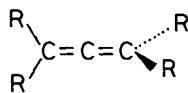
### Summary

The He(I $\alpha$ ) and He(II $\alpha$ ) spectra of tetrafluorobutatriene **3(F)** have been recorded for comparison with those of butatriene **3(H)**. *Ab initio* double-zeta basis self-consistent field (SCF) and configuration interaction calculations on butatriene show that, contrary to previous assignment, no shake-up band is expected to appear in the 9–10 eV energy range of the photoelectron spectrum. Further, such SCF calculations on tetrafluorobutatriene support the use of the perfluoro effect in assigning the purely  $\pi$  orbital ionizations. It is argued that **3(F)** is a key compound for the study of the perfluoro effect. This is supported by a qualitative comparison of its photoelectron-spectroscopic results with those of other perfluoro systems.

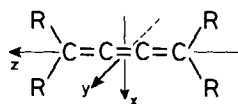
**Introduction.** – Some time ago we reported the valence shell photoelectron spectrum of butatriene (C<sub>4</sub>H<sub>4</sub>) and related derivatives **3(R)** [1].



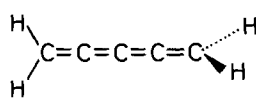
**1(R)**, R=H, F



**2(R)**, R=H, F



**3(R)**, R=H, D, Me, tBu



**4**

1) Part 1 of: 'Some Comments on the Perfluoro Effect'.

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Using both SPINDO [2] and *ab initio* single configuration molecular orbital calculations of the STO-3G and 4-31G types [3], it was possible within the framework of *Koopmans'* theorem to assign the photoelectron spectrum of butatriene based on the usual one-to-one correspondence between molecular orbitals and spectral bands only if an 'extra' band  $\textcircled{\oplus}$  was disregarded. This band was identified with the very second spectral feature at 9.63 eV; the first (vertical) ionization energy being at 9.30 eV (band  $\textcircled{\ominus}$ ).

The extra, low energy 'mystery band'  $\textcircled{\oplus}$  was then assigned as follows. As in the simpler case of ethylene [4], twisting one methylene group about the carbon frame z-axis in  $\text{C}_4\text{H}_4$  by  $90^\circ$  (coordinate system oriented as in formula **3(R)**) causes the highest occupied ( $1b_{3g}$ ) and lowest unoccupied ( $2b_{2u}$ )  $\pi$ -type molecular orbitals (MO's) of planar butatriene **3(H)** to become degenerate (forming the  $3e$  MO) in the twisted  $D_{2d}$  geometry. In consequence, the first ionization process, (corresponding to band  $\textcircled{\ominus}$  at 9.30 eV) which leads to the ground state of the radical cation **3(H)**<sup>+</sup>, can be considered as arising from a transition to the lower branch component of the doubly degenerate  ${}^2E$  state of **3(H)**<sup>+</sup> but in essentially the planar  $D_{2h}$  configuration ( ${}^2B_{3g}$  state). The mystery band was then assumed to be due to an ionization process terminating in the corresponding, presumably very low-lying, upper branch surface ( ${}^2B_{2u}$  state). This being a simultaneous ionization-excitation process, it had to be postulated that it was presumably made allowed by configuration interaction in the neutral ground and/or  ${}^2B_{2u}$  manifold of cation electronic states. Such two electron processes are known as satellites or shake-up bands. The previous one electron assignment of the photoelectron spectrum of **3(H)** is summarized in *Table 1*.

Subsequently, the investigation of the series ethylene **1(H)** [5], allene **2(H)** [6] and butatriene **3(H)** [1] was continued by recording of the photoelectron spectrum of pentatetraene **4** [7]. Correlating the observed positions of both  $\pi$ - and  $\sigma$ -bands of all four molecules with STO-3G orbital energies clearly indicated that the

Table 1. Photoelectron spectrum and calculated ionization energies of butatriene **3(H)** (in eV)

Assignment	Experimental		$-e_j(\text{STO-3G})$	$-e_j(\text{DZ})$	$I^+(\text{SCF})^b$
	$(I_j^v)$				
$1b_{3g}(\pi_2)$	9.30	$\textcircled{\ominus}$	7.40	9.16	8.56
$2b_{3u}$	9.98	$\textcircled{\textcircled{2}}$	8.41	10.12	8.73
$1b_{2u}(\pi_1)$	11.78	$\textcircled{\textcircled{3}}$	11.49	13.26	12.25
$1b_{2g}$	14.2	$\textcircled{\textcircled{4}}$	15.13	16.44	13.86
$1b_{3u}$	(15.0)?	$\textcircled{\textcircled{5}}$	15.81	17.14	
$5a_g$	15.5	$\textcircled{\textcircled{6}}$	15.85	17.86	17.08
$4b_{1u}$	16.8 <sup>c</sup>	$\textcircled{\textcircled{7}}$	17.23		
$4a_g$	20.6 <sup>c</sup>	$\textcircled{\textcircled{8}}$	22.49		
$3b_{1u}$	23.0 <sup>c</sup>	$\textcircled{\textcircled{9}}$	25.99		
$3a_g$			27.99		
$1b_{3g}^{-2}(\pi_2)2b_{2u}^{+1}(\pi_3)$	9.63	$\textcircled{\oplus}^a$			13.86

a) Previous assignment from [1].

b) Direct energy differences from single configuration SCF calculations on both initial and final states in the DZ basis.

c) From He(II $\alpha$ ) spectrum.

'mystery band' ① at 9.63 eV in the spectrum of **3(H)** was indeed the odd-man-out [7]. However, no ancillary information concerning its origin could be adduced.

In a relevant study, *von Niessen et al.* [8] calculated the vertical valence ionization potentials of butatriene (as well as those of ethylene and allene) directly by a many-body *Green's* function method which involves electron correlation. The calculated results showed only two ionization processes (both one electron) in the region of the photoelectron spectrum of **3(H)** where the three bands ① ① ② are observed. The authors, therefore, tentatively assigned the 'extra' band to a vibrational phenomenon where the second and third spectral features (① and ② in *Table 1*) are one composite band due to formation of the first  ${}^2B_{2u}$  cation state. The satellite line assignment for ① proposed by us [1] was rejected on the grounds that such shake-up processes were calculated not to occur in the energy region below 15 eV; hence no band corresponding to a shake-up process would be visible below this value.

Recently *Cederbaum et al.* [9] have shown definitely that the 'mystery band' ① in the photoelectron spectrum of **3(H)** arises from the vibronic coupling between the  ${}^2B_{3g}$  and  ${}^2B_{3u}$  states of **3(H)**<sup>+</sup>, *i.e.* the two radical cation states giving rise to the

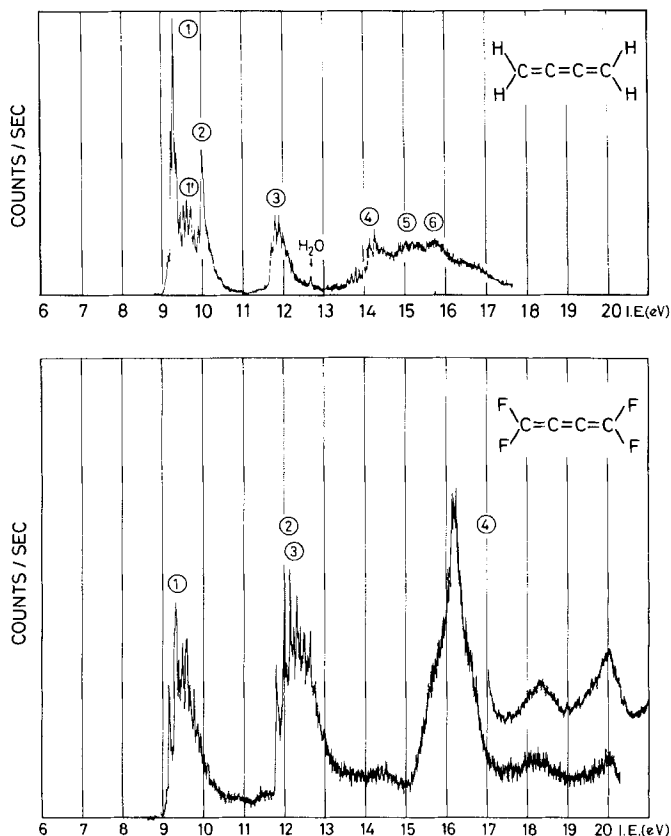


Fig. 1. *He(1s)* photoelectron spectra of butatriene (**3(H)**) and tetrafluorobutatriene (**3(F)**)

two bands ① and ② at 9.30 and 9.98 eV respectively. Thus, the tentative assignment proposed previously [1] has to be discarded.

The work reported in this paper was primarily undertaken in an attempt to shed additional light on the assignment of the 'extra' band in butatriene by a variety of techniques. Although this problem has now been solved by *Cederbaum et al.* [9], we believe that our results are of interest, in particular with regard to the so-called 'perfluoro effect' in photoelectron spectroscopy (*cf.* [10] for a summary). Therefore, the photoelectron spectrum of tetrafluorobutatriene **3(F)** [11] is reported here for the first time and the 'perfluoro effect' is used to identify the one electron  $\pi$  ionization potentials in the parent compound **3(H)**, the He(II $\alpha$ ) photoelectron spectrum of which has also been recorded for further comparison with theoretical results. *Ab initio* self-consistent field and configuration interaction (CI) calculations have been performed for **3(H)** in an attempt to predict the energy of the lowest-lying shake-up state. In addition, double-zeta basis SCF calculations on **3(F)** have been carried out with regard to correlating the 'perfluoro effect' shift of the ionization potentials and the corresponding location of the lowest energy shake-up state.

**Experimental results.** - We compare in *Figure 1* the photoelectron spectrum of butatriene **3(H)** to that of tetrafluorobutatriene **3(F)** [11]. Furthermore, expanded recordings of the bands ① and ② ③ of **3(F)**, using He(I $\alpha$ ) radiation are shown in *Figure 2*.

The photoelectron spectrum of **3(H)** has been discussed in detail previously [1] as well as those of the substitution products **3(R)** with R = D, Me, *t*Bu. The spectrum of **3(F)** consists of three well separated band-systems in the interval from 9 to 18 eV. The first band ①, at 9.3 eV exhibits well resolved vibrational fine structure (see *Fig. 2*) with spacings of  $\tilde{\nu}_1 = 1380 \text{ cm}^{-1}$  and  $\tilde{\nu}_2 = 710 \text{ cm}^{-1}$  (both values  $\pm 40 \text{ cm}^{-1}$ ). The second double band ②, ③ around 12 eV presents a fine-structured

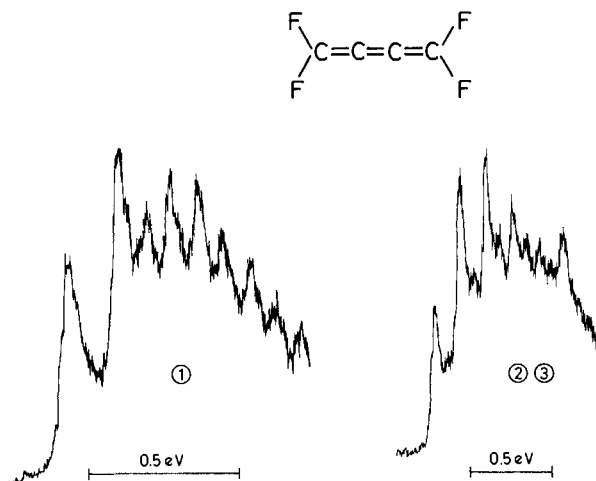


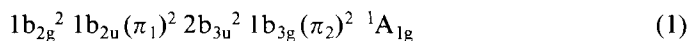
Fig. 2. Expanded recordings of the bands ① and ②, ③ of the photoelectron spectrum of tetrafluorobutatriene **3(F)**

low energy flank with spacings of  $\bar{\nu}_1 = 1360 \text{ cm}^{-1}$  and  $\bar{\nu}_2 = 730 \text{ cm}^{-1}$ , again  $\pm 40 \text{ cm}^{-1}$ . The high energy part of the band system ②, ③ is much less well resolved and is overlapped in part by a small band due to traces of water in the sample. As will be shown these three bands ①, ② and ③ can be safely assumed to be those which correspond to the removal of an electron from one or another of the three highest occupied  $\pi$ -orbitals localized mainly on the carbon atoms. The band system labeled ④, positioned at 16 eV in the spectrum of **3**(F), is mainly due to the ejection of an electron from the fluorine 2p-orbitals, presumably the 2p<sub>y</sub>-linear combinations (the molecule lying in the x, z plane). This is strongly supported by comparing the characteristic shape of this band to that of the band found at 16.3 eV in the photoelectron spectrum of **2**(F) [6c]. In both cases this band consists of a strong component near 16.0 to 16.3 eV preceded by a weaker and broader band. In the case of tetrafluoroethylene **1**(F) [5], we observe a similar band in the interval 16 to 17 eV which is mainly due to ionization from the fluorine 2p dominated  $\pi$ -orbitals. However, this band overlaps with other bands which have to be correlated with  $\sigma$ -orbitals of **1**(F).

**Theoretical procedure and results.** - *Ab initio* self-consistent field calculations were carried out on the planar equilibrium geometry ground electronic states of butatriene **3**(H) and tetrafluorobutatriene **3**(F). The expansion bases consist of the double-zeta (DZ) quality set of Huzinaga's 9<sup>s</sup>5<sup>p</sup> gaussian orbitals for carbon and fluorine [12] using the contraction coefficients of Dunning [13], and the previously reported double-zeta 4<sup>s</sup> basis for hydrogen [14]. For butatriene the STO-3G optimized geometry determined previously [1] was used which gave bond distances very close to the experimental values reported by Bastiansen & Traetteberg [15]. The STO-3G calculations for **3**(F) were performed with the use of the Gaussian 70 program [3] using the standard geometry proposed by Gordon & Pople [16], i.e. r(CF)=133 pm, r(CC,middle)=128 pm and r(CC, terminal)=131 pm with an FCF angle of 120°. For the other calculations of **3**(F) and **3**(F)<sup>+</sup> slightly reduced bond-lengths of r(CF)=130 pm, r(CC,middle)=126 pm and r(CC,terminal)=130 pm were used.

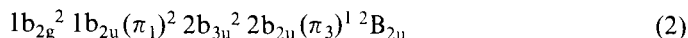
The DZ basis ground state orbital energies for **3**(H) are tabulated in Table 1, together with the previously reported He(Ia) ionization energies and the new He(IIa) higher ionization energies. Table 2 contains the STO-3G and double-zeta basis orbital energies for **3**(F) as well as the experimental ionization energies.

The ground electronic structure of the parent system **3**(H), considering just the four highest occupied molecular orbitals, can be written as the state configuration



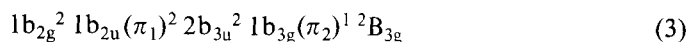
The  $\pi$  electron system consists of two doubly occupied molecular orbitals [ $1b_{2u}(\pi_1)$  and  $1b_{3g}(\pi_2)$ ] the nodal plane of which contains all the nuclei of the eight atoms (z, x-plane) and of the occupied 'in plane'  $\pi$ -orbital  $2b_{3u}$  mainly localized in the central CC double bond. In addition there are two unoccupied MO's, one of which [ $2b_{2u}(\pi_3)$ ] is relatively low-lying in energy and therefore readily accessible for forming low energy excited electronic states. Accordingly, as discussed

in the introduction, the 'mystery band' ① in the photoelectron spectrum of 3(H) had been interpreted [1] as arising from an electron ionization to form the

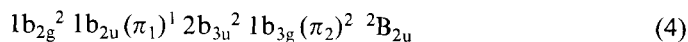


state configuration from the neutral ground state. Note that this assignment, in fact, means that formally this state involves changes (both ionization and excitation) within only the 'out-of-plane'  $\pi$  molecular orbital manifold, relative to the neutral ground state. Now that this assignment has been shown to be untenable [8] [9], it is of interest to obtain an estimate for the ionization energy range in which a photoelectron band corresponding to state configuration (2) could possibly occur.

In the single electronic configuration approximation the first ionization process, giving rise to band ① at 9.30 eV leads to the

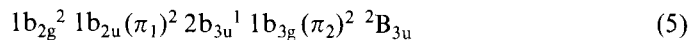


primary ion state configuration, whereas the third  $\pi$  electron ionization corresponding to band ③ at 11.78 eV, leads to the



primary ion state configuration.

For the ground ( ${}^1A_{1g}$ ) and cation butatriene states of interest ( ${}^2B_{3g}$ ,  ${}^2B_{3u}$ , and  ${}^2B_{2u}$ ) multi-configuration SCF calculations were carried out for the single configuration hole states (1)-(4), as well as the



electronic configuration allowing variable occupancy only of spin-paired sets of electrons among the six orbitals of the set  $\{1b_{2u}, 2b_{3u}, 1b_{3g}, 2b_{2u}, 2b_{2g}, \text{ and } 2b_{3g}\}$ , with the occupancy of the singly occupied orbitals (in the ion states) fixed as such [17]. Thus, in the neutral molecule ground state there are 3 spin-paired sets of electrons to be distributed among 6 orbitals leading to 10 configurations if only spin-paired double excitations from electronic configuration (1) are considered. For the cation states 2 pairs of electrons are distributed among 5 orbitals (the sixth orbital containing the odd electron) giving rise to 7 configurations.

Using the calculated MCSCF wave functions configuration interaction calculations were then carried out allowing all single and double excitation states from the respective parent configurations within the same 6 molecular orbital variable occupancy set. For the states of  ${}^2B_{2u}$  symmetry corresponding calculations were carried out starting from both (2) and (4) as the primary ion state configurations where in the CI step both configurations were used as parents simultaneously. The energies are tabulated in *Table 3* and assignments in *Table 4*.

For tetrafluorobutatriene 3(F) only single configuration SCF calculations were carried out in the double-zeta basis for the lowest few cation states as well as for the shake-up state arising from configuration (2). The resulting direct SCF ionization energies are presented in the last column of *Table 2*.

Table 2. Photoelectron spectrum and calculated ionization energies of tetrafluorobutatriene 3(F) (in eV)

Assignment	Experimental			$-e_j(\text{STO-3G})$	$-e_j(\text{DZ})$	$I^+(\text{SCF})^a)$
	$(I_j^+)$					
$2b_{3g}(\pi_2)$	9.30	①		6.32	9.95	9.41
$5b_{3u}$	11.95	②		9.59	12.79	10.98
$2b_{2u}(\pi_1)$	12.5	③		11.05	14.42	13.52
$8a_g$				13.33	18.78	18.33
$7b_{1u}$	15.7	④		13.79	19.22	
$4b_{2g}$	16.2			13.86	19.14	18.47
$4b_{3u}$				13.86	19.16	
$1b_{1g}$				14.31	19.71	
$1a_u$				14.32	19.71	
$1b_{3g}$				17.12	21.86	
$1b_{2u}$				17.37	21.97	
$3b_{2g}$				17.62	22.70	
$3b_{3u}$				17.88	22.83	
$7a_g$				18.71	24.18	
$6b_{1u}$				19.40	23.44	
$6a_g$				22.09	26.27	
$5b_{1u}$				25.98	29.67	
$5a_g$				28.15	31.68	
$2b_{3g}(\pi_2)^{-2}3b_{2u}(\pi_3)^{+1}$						14.78

<sup>a)</sup> See footnote <sup>b)</sup> in Table 1.

Table 3. Results of MCSCF and CI calculations on the ground and cation states of butatriene<sup>2</sup> (3(H) and 3(H)<sup>+</sup>)

State	Single configuration SCF energy <sup>b)</sup>	MCSCF energy	CI energy	Number of configurations
$^1A_{1g}$	-153.64553 <sup>c)</sup>	-153.69188	-153.72343 <sup>h)</sup>	15
$^2B_{3g}$	-153.33844 <sup>d)</sup>	-153.37002	-153.40878	31
$^2B_{3u}$	-153.32013 <sup>e)</sup>	-153.35170	-153.38530	32
$^2B_{2u}$	-153.19678 <sup>f)</sup>	-153.24295	-153.30736 <sup>i)</sup>	52
			-153.19114 <sup>k)</sup>	
$^2B_{2u}$	-153.13685 <sup>g)</sup>	-153.19273	-153.29151 <sup>j)</sup>	52
			-153.21091 <sup>k)</sup>	

<sup>a)</sup> All energies are in atomic units (= Hartrees); <sup>b)</sup> Actually the respective diagonal single configuration energies in the converged MCSCF calculations; <sup>c)</sup> State configuration (1); <sup>d)</sup> State configuration (3); <sup>e)</sup> State configuration (5); <sup>f)</sup> State configuration (4); <sup>g)</sup> State configuration (2); <sup>h)</sup> With wave function of the form,  $0.94951|(1)\rangle - 0.20367|(6)\rangle + \dots$ , where the kets represent state configurations; <sup>i)</sup> With wave function of the form,  $0.84638|(2)\rangle + 0.42040|(4)\rangle + \dots$ ; <sup>j)</sup> With wave function of the form,  $0.69239|(2)\rangle + 0.53929|(4)\rangle + \dots$ ; <sup>k)</sup> Second lowest energy solution.

**Discussion.** - We will first discuss the shake-up calculations for butatriene 3(H) and then proceed to the experimental and theoretical aspects of the comparison with tetrafluorobutatriene 3(F). Table 3 shows that vertical energy separation between the two cation state configurations  $^2B_{3g}(3)$  and  $^2B_{2u}(2)$  is calculated to be about 5.5 eV both on the single configuration SCF and CI levels. Actually, the CI results for the  $^2B_{2u}$  states show heavy mixing between the single electronic configurations (2) and (4), as evidenced by the large energy lowering as a result of

Table 4. CI calculations on the photoelectron spectrum of butatriene 3(H)

Band <sup>a)</sup>	I <sub>j</sub> <sup>y a)</sup> b)	Assignment	CI results <sup>b)</sup> c)
①	9.30	1b <sub>3g</sub> (π <sub>2</sub> )	8.56
②	9.63		
②	9.98	2b <sub>3u</sub>	9.20
③	11.78	1b <sub>2u</sub> (π <sub>1</sub> )	11.32, 11.59
④	14.2	1b <sub>2g</sub> and shake up	14.48, 13.59 <sup>d)</sup>

<sup>a)</sup> See [1]; <sup>b)</sup> In eV; <sup>c)</sup> From Table 2; <sup>d)</sup> Just the shake-up part; <sup>e)</sup> Double entries for bands ③ and ④ are for the two different results obtained using different state configurations as parents in the MCSCF calculations.

CI. However, for either choice of (2) or (4) as the primary state configuration in the SCF and MCSCF steps the predominant configuration (see footnotes to Table 3) for the lowest energy <sup>2</sup>B<sub>2u</sub> state is state configuration (2). Configuration interaction between (1) and the doubly excited configuration

$$1b_{2g}^2 1b_{2u}(\pi_1)^2 2b_{3u}^2 2b_{2u}(\pi_3)^2 {}^1A_{1g} \quad (6)$$

is found to be relatively moderate, indicating that 'initial state' configuration interaction is not the primary intensity giving mechanism for the additional <sup>2</sup>B<sub>2u</sub> state.

To reduce the vertical <sup>2</sup>B<sub>3g</sub>-<sup>2</sup>B<sub>2u</sub> energy separation in butatriene from the calculated 5-6 eV to the approximately 0.32 eV that would have been required by our previous assignment (*cf.* Table 1) is difficult to envisage. It should be pointed out that the comparable energy separation in 1(H) has been calculated [18] using a minimal exponential-type function (ETF) basis (very similar to the STO-3G basis) giving 7.77 eV at the single configuration SCF level. The calculations of *Buenker et al.* [19], as nearly as can be deduced from their double-zeta basis SCF and CI potential curves, do not appear to reduce this figure dramatically.

On the other hand, the very strong configuration mixing between single electronic state configurations (2) and (4) in 3(H) to give two new <sup>2</sup>B<sub>2u</sub> electronic states separated by a calculated 2-3 eV, each of substantial primary ion character (state configuration (2)), predicts the prominent appearance of an extra band in the photoelectron spectrum due essentially to the existence of the ionization-excitation state configuration (4). The precise location of this second <sup>2</sup>B<sub>2u</sub> state is therefore expected to be found at an energy no higher than 2-3 eV from the first <sup>2</sup>B<sub>2u</sub> electronic state. This argument leads to the assignments suggested in Table 4, which identifies the shake-up state together with the 1b<sub>2g</sub><sup>-1</sup> one-electron process in the region of the observed 14.2 eV spectral feature, ④, in the photoelectron spectrum.

In Figure 3 we show a correlation diagram for the states corresponding to bands ①, ② and ③ in 3(R), R = tBu, Me, H, and F. This correlation essentially uses *Koopmans'* approximation in reverse by setting  $-I_j^y = \epsilon_j$  and identifying each radical cation state with the removal of an electron from a doubly occupied MO. For convenience, the orbitals of substituted species are not renumbered but are labeled with the symbol used for the parent compound 3(H). Band ② corresponding



to an ionization from an in-plane (mainly carbon atom)  $\pi$ -type orbital ( $2b_{3u}$ ) in **3(H)** will also simply be referred to as mainly a carbon atom  $\pi$  orbital, although, strictly speaking, only the  $1b_{3g}$  and  $1b_{2u}$  are  $\pi$ -type orbitals.

The observed shifts of the three  $\pi$ -type orbitals are:

Orbital	Shifts in eV		
	<b>3(Me)</b>	<b>3(<i>t</i>Bu)</b>	Ratio
$1b_{3g}(\pi)$	1.6 <sub>0</sub>	2.0 <sub>5</sub>	1.3
$2b_{3u}(\pi)$	1.0 <sub>5</sub>	1.6 <sub>0</sub>	1.5
$1b_{2u}(\pi)$	1.2 <sub>0</sub>	1.7 <sub>0</sub>	1.4

(7)

Both the sizes of the shifts and the ratio of those observed for **3(*t*Bu)** relative to those of **3(Me)** are completely consistent with previous experience [20]. In particular the influence of methyl substitution on the ionization energies of allene **2(H)** has been previously discussed in detail [5 b]. There the situation was somewhat complicated by the fact that the allene radical cation **2(H)<sup>+</sup>** is *Jahn-Teller* unstable and that substituted allenes, although no longer of  $D_{2d}$  symmetry are subject to a pseudo *Jahn-Teller* effect. This obviously makes the analysis less straightforward, but within the limits of error imposed by this complication, the results derived

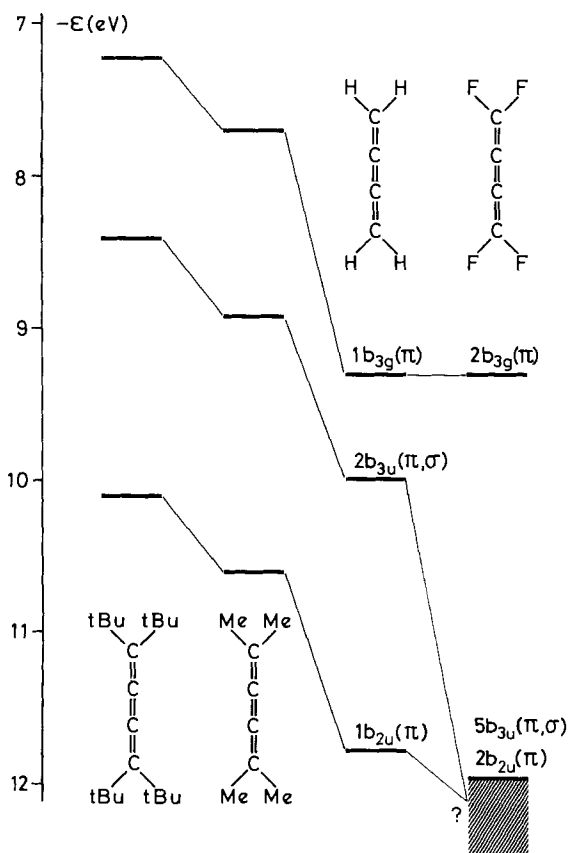


Fig. 3. Orbital correlation diagram for tetra-substituted butatrienes. The orbital energies have been obtained by applying Koopmans' approximation in reverse to the observed ionization energies  $I_j^m$

for this lower homologue of **3**(H) agree perfectly with the shifts listed in (7). Thus, the left side of the correlation diagram of *Figure 3* clearly indicates that the bands ① ② and ③ in the spectrum of **3**(H) are indeed  $\pi$ -bands.

This assignment is made conclusive by the comparison of the spectra of **3**(H), **3**(Me) and **3**(*t*Bu) with that of tetrafluorobutatriene **3**(F), *i.e.* using what is now known as the 'perfluoro effect' [10] [21] [22].

Following some fundamental observations by *Bralsford, Harris & Price* in pre-photoelectron-spectroscopic times [22], the 'perfluoro effect' has been mainly investigated by *Robin et al.* [21] [23] [24]. Put in simplest terms, this 'perfluoro effect' consists in the observation that in-plane substitution of an aromatic or unsaturated hydrocarbon by one or more fluorine atoms (*e.g.* ethylene, vinylfluoride, ..., tetrafluoroethylene [25]) will leave the  $\pi$ -ionization energies more or less unaffected, but will shift the  $\sigma$ -ionization energies towards higher values by up to 4 eV [23]. Typical examples are the fluoroderivatives of ethylene [25], butadiene [24] or benzene [23] [26]. 'In plane' substitution means that all the fluorine atoms lie in the nodal plane of the  $\pi$ -system or, by an obvious extension, on the molecular axis of a linear molecule, *e.g.* fluoroacetylenes [27]. Whereas the above rule relates only to planar or linear systems, 'out-of-plane' substitution of hydrogen atoms by fluorine atoms (*e.g.* toluene/trifluoromethylbenzene) will lead to substantial and almost equal shifts towards higher values of both the  $\sigma$ - and  $\pi$ -ionization energies. Typical examples which exemplify these rules are shown in *Figure 4*, which is self-explanatory.

The detailed electronic mechanism which is at the root of the 'perfluoro effect' is presumably not simple, as evidenced by recent experimental data derived from the photoelectron spectra of a variety of fluorinated systems [28]. This lack of

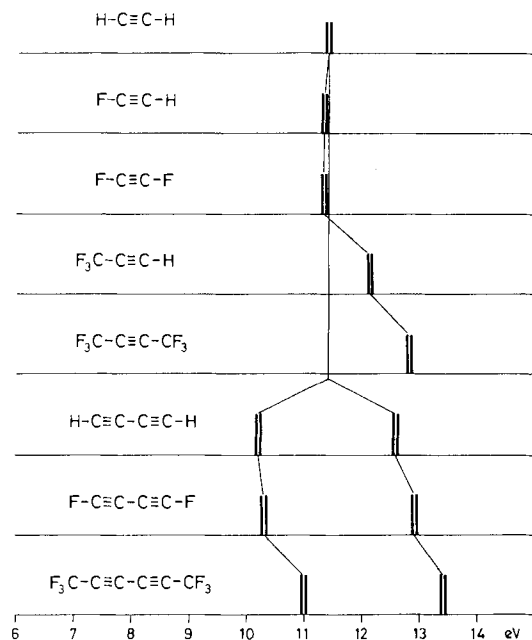


Fig. 4. Shifts of photoelectron  $\pi$ -band positions under the influence of fluorosubstitution

simplicity is due to the competitive interplay between the high electronegativity of the fluorine atoms, which tends to polarize mainly the  $\sigma$ -frame of the molecule, and the strong repulsive interactions of the fluorine lone pairs with the  $\pi$ -system to which they are attached [26] [29]. With regard to this situation, tetrafluorobutatriene **3(F)** is clearly a key compound, presenting within the same molecule the rather unique situation of four fluorine atoms which lie in the nodal plane of two  $\pi$ -orbitals ( $2b_{3g}(\pi)$  and  $2b_{2u}(\pi)$ ; cf. Table 2) and at the same time in a plane which is strictly perpendicular to the nodal plane of another  $\pi$ -orbital ( $5b_{3u}$ ).

With reference to Figures 1, 3 and 5 we note first of all that the position of band ① corresponding to the ground-state of the radical cation **3(F)**<sup>+</sup> is at exactly the same place (9.3 eV) as that of the parent radical cation **3(H)**<sup>+</sup>. Furthermore, the third band ③ in the photoelectron spectrum of **3(F)** is shifted only marginally by 0.1 to 0.3 eV relative to the corresponding band in the spectrum of **3(H)**. As shown in Figure 5 this is what has been observed with respect to the  $\pi$ -bands in the photoelectron spectrum of butadiene and of 1,1,4,4-tetrafluorobutadiene [24] which are found at  $I_1^y=9.1$ ,  $I_2^y=11.6$  eV and  $I_1^y=9.5$ ,  $I_2^y=12.0$  eV respectively [24]. Note that the situation in this pair of molecules, as far as the  $\pi$ -orbitals are concerned, is exactly the same as for the  $\pi$ -orbitals  $nb_{3g}(\pi)$  and  $nb_{2u}(\pi)$  of **3(H)** ( $n=1$ ) and **3(F)** ( $n=2$ ). This is strong evidence that the assignment of this pair of orbitals is correct, especially in conjunction with the alkyl-group induced shifts.

The expected influence of fluorosubstitution on the  $2b_{3u}(\pi)$  orbital of **3(H)** (i.e. the one associated with band ② at 10 eV) can be assessed in a straightforward manner from the data obtained for the pair **2(H)**, **2(F)** by Thomas & Thompson [6c]. As shown in the following diagram, the vicinal fluorine atoms in position 1 lie in the nodal plane of the two-centre  $\pi$ -orbital  $\pi_a$  but in a plane perpendicular to the nodal plane of  $\pi_b$ .

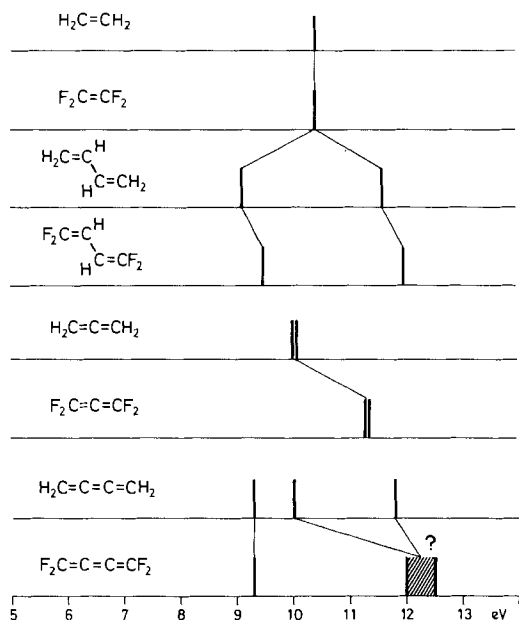
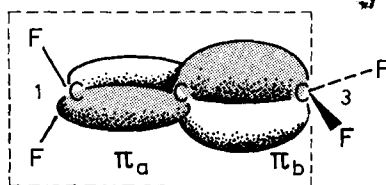


Fig. 5. Shifts of photoelectron  $\pi$ -band positions under the influence of fluoro-substitution



We expect thus, in accordance with previous experience, that their stabilizing influence on the basis orbital energy of  $\pi_a$  will be negligible but rather severe for  $\pi_b$ . For symmetry reasons the same argument holds for the pair of fluorine atoms in position 3. The net result is, that the  $e(\pi)$  orbital of **2(H)** should be shifted towards lower energies in **2(F)**. This is indeed the case; the observed increase in the first vertical ionization energy, going from **2(H)** to **2(F)** being 1.3 eV [6c]. From this result we conclude that the stabilizing influence of the four fluorine atoms in **3(F)** on the  $2b_{3u}(\pi)$  orbital should be about twice the value observed in **2(F)**, *i.e.*  $-2.6$  eV, this being an upper limit because of the absence of the (slight) stabilization of the type 'fluorine-atom-in-position-1-vs.- $\pi_a$ ' present in **2(F)** and also because the 'inductive' stabilization is known not to be strictly additive. However, the above argument would place the  $2b_{3u}(\pi)$  orbital of **3(F)** slightly above  $-10$  eV  $-2.6$  eV =  $-12.6$  eV. This is what one observes, as shown in *Figures 3* and *5*.

To summarize: both the alkyl- and the fluoro-substitution induced shifts of the three bands ①, ② and ③ leave hardly any doubt that they are associated with the removal of an electron from the orbitals  $1b_{3g}(\pi)$ ,  $2b_{3u}(\pi)$  and  $1b_{2u}(\pi)$  respectively. It is gratifying that this assignment, based essentially on experimental observations and using simple correlation techniques, is fully supported by the results of the theoretical calculations reported by *von Niessen et al.* [8] and ourselves (*cf.* [1] and *Tables 1* to *4*). All calculations are in agreement that the first 3 bands in **3(H)** and **3(F)** correspond to ionization from the  $b_{3g}(\pi_2)$ ,  $b_{3u}$  and  $b_{2u}(\pi_1)$  orbitals. Comparing the results in *Table 1* for **3(H)** and *2* for **3(F)** with *Figure 3* shows that, although the calculated ionization energies somewhat overestimate the shift of the purely  $\pi$  levels upon perfluorination, the relative shift of the  $b_{3u}$  orbital is well reproduced.

One problem, however, remains unsolved, namely the relative sequence of the states  ${}^2B_{3u}$  and  ${}^2B_{2u}$  of **3(F)**<sup>+</sup> which are obtained by removal of an electron from the orbital  $b_{3u}$  or  $b_{2u}(\pi_1)$  of **3(F)**. Whereas the theoretical calculations place  ${}^2B_{2u}$  above  ${}^2B_{3u}$ , the semi-quantitative argument, based on the shifts observed for the pair **2(H)** and **2(F)** seems to favour the inverse sequence. Unfortunately, the two corresponding bands in the photoelectron spectrum of **3(F)** overlap completely so that a conservative assessment of the situation would be that both states are almost accidentally degenerate, *i.e.* lie within a few tenths of an eV of each other. As shown above, the vibrational spacings of the fine-structure of band ① and of the low energy part of the composite band system ②, ③ of the photoelectron spectrum of **3(F)** are the same, whereas in the high energy part of the latter band system, no vibrational spacing is discernible. In comparison the bands ① and ③ in the photoelectron spectrum of **3(H)** have closely related spacings of the vibrational fine structure ( $\tilde{\nu}=540$  cm<sup>-1</sup> and 790 cm<sup>-1</sup>, respectively) and band ② is rather poorly resolved. These facts would seem to indicate that the sequence of the states

corresponding to the double band  $\textcircled{2}$ ,  $\textcircled{3}$  in the spectrum of  $\mathbf{3(F)}$  is  ${}^2\text{B}_{2u}$  below  ${}^2\text{B}_{3u}$ , rather than the one predicted by the theoretical treatments. Obviously, this problem can only be solved if ancillary information becomes available.

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