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The He(Iα) PE Spectra and Electronic Absorption Spectra of Hexafluorocyclobutanone and of Tetrafluoro-1,2-cyclobutanedione

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The He(Iα) PE and the electronic absorption spectra of hexafluorocyclobutanone (**3**) and tetrafluoro-1,2-cyclobutanedione (**4**) have been recorded. The assignment of the observed bands in both types of spectra is mainly based on the correlation with the corresponding spectra of the parent compounds cyclobutanone (**1**) and 1,2-cyclobutanedione (**2**), and in addition on the results of semiempirical calculations. As a result of the perfluoro effect, the bands in the PE spectra of **3** and **4** are shifted towards higher ionization energies by 1.6 eV and 1.5 eV relative to the corresponding bands in the PE spectra of **1** and **2**. A comparison of the positions of the first band in the electronic spectra of **1** and **3**, as well as of **2** and **4**, shows that this band is shifted bathochromically by about 5000 cm^{-1} as a consequence of the perfluoro substitution. This is explained as being due to a stronger lowering of the LUMO (π*) energy than that of the HOMO (n) energy, induced by the replacement of the H- by F-atoms.

Die He(Iα)-PE-Spektren und Elektronenabsorptionsspektren von Hexafluorcyclobutanon und Tetrafluor-1,2-cyclobutandion

Die He(Iα)-PE-Spektren und die Elektronenabsorptionsspektren von Hexafluorcyclobutanon (**3**) und Tetrafluor-1,2-cyclobutandion (**4**) wurden gemessen. Die Zuordnung der ersten Banden beider Spektrentypen basiert hauptsächlich auf der Korrelation mit den entsprechenden Spektren der unsubstituierten Verbindungen Cyclobutanon (**1**) und 1,2-Cyclobutandion (**2**) sowie auf den Resultaten semiempirischer Rechnungen. Die Banden in den PE-Spektren von **3** und **4** werden im Vergleich zu den PE-Banden von **1** und **2** durch den Perfluor-Effekt um 1.6 bzw. 1.5 eV zu höheren Energien verschoben. Vergleicht man die Energie der ersten Bande in den Elektronenspektren von **1** und **3** bzw. **2** und **4**, so findet man, daß diese Bande bathochrom um etwa 5000 cm^{-1} durch die Perfluor-Substitution verschoben wird. Dies wird dadurch erklärt, daß beim Ersatz der H-Atome durch F-Atome die Energie des LUMOs (π*) stärker abgesenkt wird als die des HOMOs (n).

The He(Iα) photoelectron (PE) spectra and the electronic absorption spectra of the title-compounds hexafluorocyclobutanone (**3**) and tetrafluoro-1,2-cyclobutanedione (**4**) are of some

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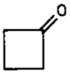
interest, because of the rather peculiar spectroscopic properties of these molecules. Whereas the parent compounds cyclobutanone (**1**) and 1,2-cyclobutanedione (**2**) are colourless, **3** is of a light yellow and **4** of a deep blue colour[1]. Secondly, having reported some time ago He(Iα) PE spectra of a series of α-diketones[2] and of related compounds[3], one expects that those of **3** and **4** will provide additional information concerning the electronic structure of such species. The same is true for the PE spectra of cyclic ketones[4]. Finally, any additional experimental information concerning the photoelectron spectroscopic „perfluoro effect“[5-7] would obviously be welcome.



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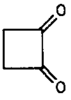

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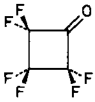

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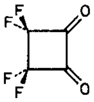

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He(Iα) PE Spectra

The He(Iα) PE spectra of **3** and **4** are shown in Fig. 1 and the positions I_J^m of the first few maxima, which are close to the vertical ionization energies, I_J^v, of **1** to **4**, are collected in Tab. 1 together with the corresponding values for the orbital energies, ε_J, from INDO and HAM/3-calculations[8]. The band assignment assumes the validity of *Koopmans'* theorem i.e. $-\varepsilon_J = I_J^v \approx I_J^m$[9]. Comparing the predicted values with experimental data, it is evident that the INDO-calculation, as well as all other methods we have tried (CNDO/2, EH, MINDO/3), yield rather unreliable results for perfluoro compounds such as **3** and **4**. The reason is rather well understood: Due to the minimal basis set used for fluorine in all these treatments, the electron cloud around each bonded fluorine atom freezes to a non-polarizable spherical charge distribution once the fluorine atom is bonded and can therefore not account for the typical way in which fluorine AOs participate in the different molecular orbitals. Only the inclusion of polarization functions would amend this shortcoming. For this reason the theoretical results are used only as a crude guide-line and the assignments proposed are mainly derived by correlation of experimental data.

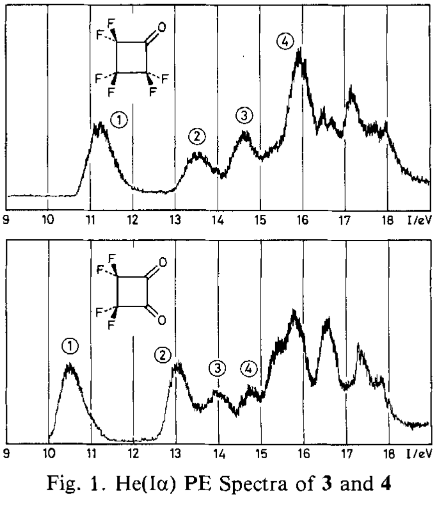


Fig. 1. He(Iα) PE Spectra of **3** and **4**

Bands ② and ③ in the PE spectrum of **2** exhibit vibrational fine structure (spacing ≈ 0.15 eV and ≈ 0.2 eV, respectively), as does band ① in the spectrum of **3** (spacing ≈ 0.17 eV). The PE spectra of **3** show indication of an additional shoulder at approximately 13.8 eV, which, however, can hardly be due to an additional band, as suggested by the integrated intensity of the feature. Finally, the width at half heights (whh) of the first band in the PE spectra is 0.4 eV for **1**, 0.6 eV for **2**, and 0.7 eV for both **3** and **4**.

Table 1. Comparison between Recorded Ionization Energies, I_J^m, of **1** to **4** and Calculated Orbital Energies, ε_J

Compound	Band	Assignment	I_J^m [eV]	$-\varepsilon_J$ [eV] INDO	HAM/3
1	①	$b_2(n)$	9.60	10.39	9.64[a]
	②	$b_1(\pi)$	11.90	13.08	11.83
	③	$b_2(\sigma)$	12.40	13.11	12.02
	④	$a_1(\sigma)$ (?)	12.8 (?)		
2	①	$a_1(n_+)$	9.60	10.80	9.61[b]
	②	$b_2(n_-)$	11.70	12.56	11.62
	③	$a_2(\pi)$	12.85	13.87	12.78
	④	$a_1(\sigma)$	13.7	14.76	13.85
3	①	$b_2(n)$	11.20	13.17	
	②	$b_1(\pi)$	13.45	16.67	
	③	$b_2(\sigma)$	14.60	15.07	
	④	$a_1(\sigma)$	15.90	16.03	
4	①	$a_1(n_+)$	10.45	12.62	
	②	$b_2(n_-)$	13.05	14.58	
	③	$a_2(\pi)$	13.95	16.35	
	④	$a_1(\sigma)$	14.70	15.53	

[a] Experimental geometry. – [b] Geometry as obtained by energy minimization within a MINDO/3 calculation.

Discussion of the PE Spectra

The first band ① of the cyclobutanone spectrum[4] (**1**) is assigned to the 2p "lone-pair" of the carbonyl group. Its vertical ionization energy (9.60 eV) is very close to that for acetone (9.69 eV). Its whh of 0.4 eV, which is large compared to that of other ketones, indicates considerable mixing with one of the Walsh-type orbitals of the cyclobutane ring. The assignment of the overlapping bands ② and ③ is problematic in so far as semiempirical calculations (MINDO/3, CNDO/2, INDO, and HAM/3) yield different results concerning the sequence of the MOs $3b_1(\pi)$, $3b_2(\sigma)$ and $6a_1(\sigma)$. Our assignment of bands ② and ③ to $3b_1(\pi)$ and $3b_2(\sigma)$, respectively (see Tab. 1), is based on HAM/3 calculations performed by *Lindholm*[10] and ab initio calculations using a STO-3G basis[11].

The first bands ②, ③ of the PE spectrum of **2** have already been assigned[3] by comparison either with a MINDO/3 calculation or with the PE spectrum of cyclobutene-1,2-dione and other α-diketones. According to prevailing theory the gap $I_2^m - I_1^m = 2.1$ eV between the $a_1(n_+)^{-1}$ and $b_2(n_-)^{-1}$ bands ①, ② is mainly due to "through-bond" interaction[12]. This is also the reason for the orbital sequence $a_1(n_+)$ above $b_2(n_-)$.

Replacement of all hydrogen atoms in a molecule by fluorine atoms leads to a substantial lowering of all orbital energies, with one notable exception: If all the fluorine atoms happen to lie in the nodal plane of a π-system (e.g. tetrafluoroethene or hexafluorobenzene), the π-orbital energies are little, if at all, lowered[5-7]. For example, the $2b_1(n)^{-1}$ and $1b_2(\pi)^{-1}$ ionization energies of formaldehyde (10.88 and 14.5 eV, respectively) increase to 13.6 eV and only 14.6 eV for the corresponding ionization processes $5b_1(n)^{-1}$ and $2b_2(\pi)^{-1}$ of difluoroformaldehyde[5]. On the other hand the lone-pair and π ionization energies of acetone (9.69, 13.4 eV) increase both by ≈ 2.5 eV when all the hydrogen atoms are replaced by fluorine atoms, i.e. in hexafluoroacetone, which yields 12.08 and 16.0 eV, respectively[5].

In Fig. 2 are shown the shifts of the first bands in the PE spectra of **3** and **4** relative to the corresponding bands of their parent compounds **1** and **2**. For the pair **1**, **3** the shifts of the bands due to the perfluoro effect are ≈ 1.6 eV, i.e. somewhat smaller than for the pair acetone/perfluoroacetone.

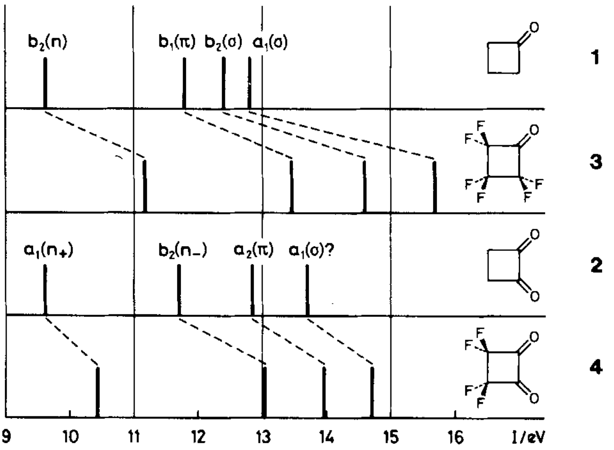


Fig. 2. Correlation between the Low-Energy PE Bands of **1** to **4**

For the other pair **2**, **4** the shifts towards higher energy of corresponding bands in their PE spectrum amounts to about 1 to 1.5 eV, which seems to be reasonable in relation to the shift between **1** and **3**, since there are only four hydrogen atoms replaced by fluorine. The broadening of the first two PE-bands of **3** compared to **1** and of **4** compared with **2**, may be due to the fact, that the n-orbitals get more binding character by increased interaction with the more electronegative Walsh-orbitals of the four-membered ring.

The correlation diagram of Fig. 2 and the assignment given in Tab. 1 assumes that the lone pair orbitals are more influenced by the fluorine substituents than the π-orbitals. Therefore the same orbital sequence is proposed for the perfluoro compounds **3** and **4** as compared to the parent compounds **1** and **2**. These results are in contrast to the INDO results given in Tab. 1, presumably for the reasons discussed above.

Electronic Spectra

As shown in the preceeding paragraph, replacement of all hydrogen atoms in **1** or **2** by fluorine atoms to yield **3** or **4** is accompanied by a large shift towards higher ionization energies of the bands in the PE spectra due to the "perfluoro effect". To explore the influence of this effect on the electronic transitions, we have re-recorded the UV/VIS spectra of **3** and **4** in cyclohexane solution, which are shown, together with those of **1** and **2**, in Fig. 3. (Previous UV/VIS data: **3**[13,14], 379 (ε 14), 195 nm (ε 225); **4**[14], 650, ≈ 580, 207 nm, gas phase). The band positions are compared with those of the parent compounds **1** and **2** in Tab. 2.

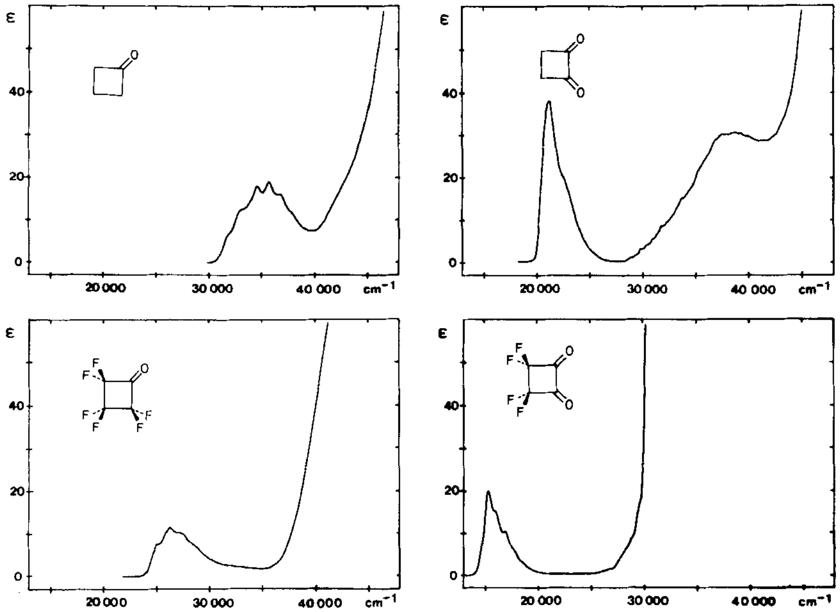


Fig. 3. Electronic Absorption Spectra of **1**–**4**. (The spectra of **1**, **3**, and **4** have been recorded in cyclohexane, that of **2** has been measured in acetonitrile)

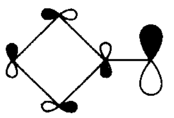
The most noticeable change due to the "perfluoro effect" is a strong bathochromic shift by ≈ 5000 cm^{-1} of the first band in the electronic spectra of **3** and **4** compared to **1** and **2**.

The electronic spectrum of cyclobutanone (**1**) shows a first absorption band at 34500 cm^{-1} [15] of low intensity, typical for the $\pi^* \leftarrow n$ bands of simple ketones[16]. In the case of the diketone **2** this band is split into two bands at 21400 and 37000 cm^{-1} (cf. Fig. 3), both of comparable low intensity. Model calculations of the CNDO/S-CI[17] and INDO-CI[8] type suggest that the first of these two bands in the electronic spectrum of **2** belongs to the π_1^* (LUMO) $\leftarrow n_+$ (HOMO) transition, whereas the second band has to be ascribed to a mixture of $\pi_2^* \leftarrow n_+$ and $\pi_1^* \leftarrow n_-$, the latter formal transitions referring to configurations. This interpretation is supported by investigations of other diketones[18].

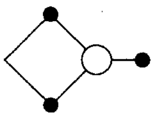
Table 2. Comparison of the Positions of the UV/VIS Absorption Bands of **1** to **4** with Calculated Transition Energies (INDO) of the First Electronic Excited States

Compd.	Band	$\tilde{\nu}_{max}$ [cm^{-1}] (ε_{max} [mol^{-1} dm^3 cm^{-1}])	Symm.	Config. (% Contribut.)	$\tilde{\nu}_{max}$ (calc.) [cm^{-1}]
1	1	30300 (19.1)[15]	A_2	$\pi^* \leftarrow n$ (96%)	21700
2	1	21100 (39.0)	B_1	$\pi_1^* \leftarrow n_+$ (85%)	17600
	2	37000 (30.1)	A_2	$\pi_2^* \leftarrow n_+$ (60%); $\pi_1^* \leftarrow n_-$ (40%)	22750
3	1	26200 (11.7)	A_2	$\pi^* \leftarrow n$ (93%)	16500
4	1	15300 (19.9)	B_1	$\pi_1^* \leftarrow n_+$ (82%)	14500
	2	33200 (8.2)	A_2	$\pi_2'' \leftarrow n_+$ (58%); $\pi_1^* \leftarrow n_-$ (39%)	19100

A simple rationalization of the bathochromic shift of the first band in the electronic spectrum of **3** relative to that of **1** is provided by considering the following, schematic diagrams of the HOMO and LUMO of **1**.



$b_2(n)$



$b_1(\pi^*)$

From these it can be seen that the HOMO $b_2(n)$ is essentially an oxygen lone pair orbital with some admixture of the Walsh-type orbital of appropriate symmetry of the four-membered ring. The shift induced by the fluorine atoms, which lowers the corresponding orbital energy, depends on the distance of the fluorine centres to the atom(s) with the largest orbital coefficients, i.e. in the case of the HOMO $b_2(n)$, the oxygen atom removed by two bond lengths (one CC and one CO) from the nearest fluorine substituted centre. On the other hand the LUMO $b_1(\pi^*)$ has a very large coefficient at the carbon atom removed by only one C–C bond length from the fluorine centres. As a result of this, the lowering of the HOMO $b_1(\pi^*)$ orbital is larger than that of the LUMO $b_2(n)$ orbital, which means that the HOMO – LUMO gap narrows on replacing H by F in **1**, and that the $\pi^* \leftarrow n$ band shifts to lower wave numbers. Similar arguments hold for the explanation of the bathochromic shift of the low energy electronic transitions of **4** relative to **2**.

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1) *D. C. England,* J. Am. Chem. Soc. **83**, 2205 (1961).

2) *D. O. Cowan, R. Gleiter, J. A. Hashmall, E. Heilbronner,* and *V. Hornung,* Angew. Chem. **83**, 405 (1971); Angew. Chem., Int. Ed. Engl. **10**, 401 (1971); *R. Gleiter, R. Bartetzko, P. Hofmann,* and *H.-D. Scharf,* Angew. Chem. **89**, 414 (1977); Angew. Chem., Int. Ed. Engl. **16**, 440 (1977); *R. Gleiter, P. Schang,* and *G. Seitz,* Chem. Phys. Lett. **55**, 144 (1978); *R. Bartetzko, R. Gleiter, J. L. Muthard,* and *L. A. Paquette,* J. Am. Chem. Soc. **100**, 5589 (1978).

3) *P. Schang, R. Gleiter,* and *A. Rieker,* Ber. Bunsenges. Phys. Chem. **82**, 629 (1978); *H.-D. Martin, H.-J. Schiwek, J. Spanget-Larsen,* and *R. Gleiter,* Chem. Ber. **111**, 2557 (1978).

4) *D. Chadwick, D. C. Frost,* and *L. Weiler,* Tetrahedron Lett. **1971**, 4543.

5) *C. R. Brundle, M. B. Robin, N. A. Kuebler,* and *H. Basch,* J. Am. Chem. Soc. **94**, 1451 (1972).

6) *C. R. Brundle, M. B. Robin,* and *N. A. Kuebler,* J. Am. Chem. Soc. **94**, 1466 (1972).

7) *K. Wittel* and *H. Bock,* in "The Chemistry of Functional Groups", Supplement D (*S. Patai* and *Z. Rappoport,* edits.), J. Wiley & Sons Ltd., New York 1983.

8) *M. C. Böhm* and *R. Gleiter,* Theor. Chim. Acta **59**, 127, 153 (1981).

9) *T. Koopmans,* Physica **1**, 104 (1934).

10) *E. Lindholm,* private communication.

11) *D. J. Pasto, D. M. Chipman,* and *J. J. Worman,* J. Phys. Chem. **86**, 3981 (1982).

12) *R. Hoffmann, A. Imamura,* and *W. Hehre,* J. Am. Chem. Soc. **90**, 1499 (1968); *E. Heilbronner* and *A. Schmelzer,* Helv. Chim. Acta **58**, 936 (1975); reviews: *R. Hoffmann,* Acc. Chem. Res. **4**, 1 (1971); *R. Gleiter,* Angew. Chem. **86**, 770 (1974); Angew. Chem., Int. Ed. Engl. **13**, 696 (1974); *M. N. Paddon-Row,* Acc. Chem. Res. **15**, 245 (1982); *H.-D. Martin* and *B. Mayer,* Angew. Chem. **95**, 281 (1983); Angew. Chem., Int. Ed. Engl. **22**, 283 (1983).

13) *B. E. Smart* and *C. G. Krespan,* J. Am. Chem. Soc. **99**, 1218 (1977).

14) *D. C. England,* private communication.

15) *G. Förster, R. Skrabal,* and *J. Wagner,* Z. Elektrochem. **41**, 290 (1937); *S. W. Benson* and *G. B. Kistiakowsky,* J. Am. Chem. Soc. **64**, 82 (1942).

16) *J. N. Murell,* "The Theory of Electronic Spectra of Organic Molecules", Methuen & Co. Ltd., London 1963; *H. H. Jaffé* and *M. Orchin,* "Theory and Application of Ultraviolet Spectroscopy", John Wiley and Sons Inc., New York, London 1962.

17) *H. H. Jaffé,* Acc. Chem. Res. **2**, 136 (1969), and references given therein.

18) *J. F. Arnett, G. Newcome, W. L. Mattice,* and *S. P. Mc Glynn,* J. Am. Chem. Soc. **96**, 4385 (1974); *N. J. Leonhard* and *P. M. Mader,* ibid. **72**, 5388 (1950); *N. J. Leonard* and *E. R. Blout,* ibid. **72**, 484 (1950).

19) *E. Honegger, Z.-z. Yang, E. Heilbronner, W. v. E. Doering,* and *J. C. Schmidhauser,* Helv. Chim. Acta **67**, 640 (1984).

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