Theoret. Chim. Acta (Berl.) 39, 321–328 (1975)
© by Springer-Verlag 1975

Shake up Phenomena in Some Unsaturated Fluorocarbons

David T. Clark and David B. Adams
Department of Chemistry, University of Durham

Received March 10, 1975

Shake up processes accompanying core ionizations for some simple unsaturated fluorocarbon systems have been studied experimentally by ESCA. Comparison has been made of shake up intensities with those calculated theoretically within the sudden approximation using the equivalent cores concept and the INDO SCF MO formalism. The observed transitions are identified as arising from $\pi^* \leftarrow \pi$ excitation accompanying core ionizations and the theoretical calculations give a good overall account of the transition probabilities.

Key words: Fluorocarbons, unsaturated ~ – Shake-up phenomena – ESCA

1. Introduction

There is considerable interest in the investigation and interpretation of shake up and shake off phenomena accompanying core ionizations.[1] The most detailed experimental studies to date relate to the inert gases and simple polyatomic molecules [2, 3]. For these systems the possibility exists of detailed non-empirical theoretical treatments of both transition energies and probabilities. Such studies have shown that the sudden approximation provides a sound basis for the discussion of the data. It may be shown theoretically that the average over the energies of the direct photoionization and associated shake up and shake off peaks is equal to the binding energy appropriate to the unrelaxed system as would be obtained from Koopmans' Theorem [4]. Extensive theoretical studies both in this and other laboratories, have shown that although relaxation energies (given as the energy difference between the computed binding energies including relaxation and Koopmans' Theorem) depend significantly on the local electronic environment, they nonetheless fall within a fairly narrow range (e.g. for C_{1s} levels ~ 1.5 eV) [5]. It may be inferred from this therefore that shake up and shake off processes are perfectly general. Indeed this is already apparent from the literature where shake up phenomena have been studied in transition metal complexes [6], charge transfer complexes [7] and unsaturated organic systems [8].

Although the investigations to date indicate that the observation of shake up phenomena can add a new dimension to information pertaining to structure and bonding as revealed by ESCA, there has been little emphasis placed on systematically exploiting this possibility [9]. An obvious area of application would be for systems in which the information derived from the primary sources of ESCA data viz. absolute and relative binding energies and relative peak intensities, is somewhat limited.

As a first step in investigating the possibility of using shake up data to provide information useful in structural studies, we report here an investigation of some simple unsaturated fluorocarbon systems. The systems studied were perfluorocyclohexene and perfluorocyclohexa-1,3- and 1,4-dienes and for comparison purposes cyclohexene. The rationale for studying these particular systems is threefold. Firstly, the chemical shifts between saturated and unsaturated carbon atoms are sufficiently large such that studies of the satellite structure of the C_{1s} and F_{1s} levels taken together allow an assignment to be made of the shake up transitions involved. Secondly, reliable and computationally inexpensive theoretical models are available for interpreting both shifts and absolute binding energies for such systems, [10], and it is therefore of interest to determine whether calculations at the same level of approximation can be used to interpret shake up phenomena. Finally, these molecules represent prototypes for simple pi-electron systems with one double bond and two double bonds either conjugated or non-conjugated. The materials have the added advantage that their physical properties are such that sample handling is facilitated and measurements of thin films in the solid phase may thus be routinely accomplished. This is an important consideration since the results may then be directly compared with that for more complicated systems such as polymers with a common energy reference (Fermi level).

2. Experimental

Samples were studied as thin films condensed onto a gold substrate using an AEI ES 100 electron spectrometer and $MgK\alpha_{1,2}$ radiation. Under the conditions employed in this work the Au $4f_{7/2}$ levels at 84.0 eV binding energy used for calibration purposes had a FWHM 1.15eV. In the particular case of perfluorocyclohexa-1,3-diene the condensed phase measurements were complemented by gas phase studies carried out on a McPherson ESCA 36 spectrometer. The gas phase spectrum was recorded at a pressure of 0.1 torr and owing to the lengthy nature of data acquisition only the C_{1s} spectrum was recorded. Samples were checked for purity by g.l.c.

3. Computational Details

The theoretical interpretation of the data pertaining to the intensity of the shake up transitions has been within the sudden approximation and INDO formalism [11]. Within this approximation the probability of observing a transition from occupied orbital ψ_i corresponding to an unrelaxed valence electron in the hole state to a virtual orbital ψ_f for the hole state is proportional to $|\langle\psi_i|\psi_f\rangle|^2$. The virtual orbitals for the hole states were simulated in the INDO formalism by taking the appropriate equivalent core species [12]. In the particular case of the F_{1s} levels this involved an extrapolation of the relevant parameters [11] for the equivalent core. This was accomplished by plotting the relevant values for

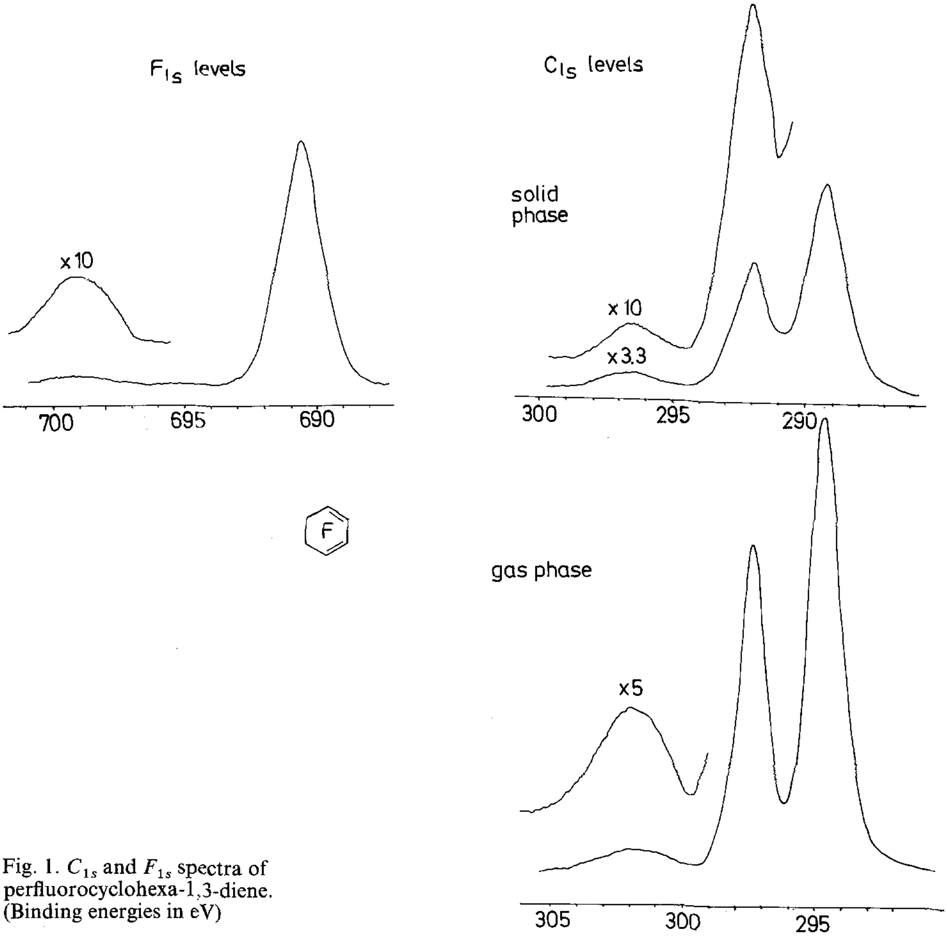


Fig. 1. C_{1s} and F_{1s} spectra of perfluorocyclohexa-1,3-diene. (Binding energies in eV)

the first row elements as a function of atomic number and in all cases the smooth form of the curves allowed a ready determination of the data which was as follows:

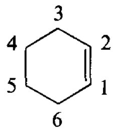
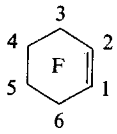
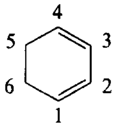
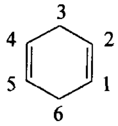
G1 = 0.64, F2 = 0.366, BETA = 50.0, (I + A)/2 (s) = 40.5 and (I + A)/2 (p) = 13.5.

4. Results and Discussion

4.1. Experimental Data

The measured C_{1s} and F_{1s} levels for perfluorocyclohexa-1,3-diene together with the shake up structure as shown in Fig. 1. For comparison purposes the gas phase data pertaining to the C_{1s} levels are also included (the difference in energy scales arises from the different energy reference used for the solid and gas phase viz. Fermi versus vacuum level). Two features are clearly evident. Firstly, there is a substantial shift in binding energy between the CF_2 and $=\overset{|}{C}-F$ environment

Table 1. Molecular core binding energies and shake up data

Molecule	Ring position	Core level	Binding energy in eV	Shake up (%)	ΔE[a] (shake up) in eV
Cyclohexene 	1, 2	C_{1s}	285.0	1.4	7.0
	3, 6 4, 5	C_{1s}	285.0		
Perfluorocyclohexene 	1, 2	C_{1s}	289.6	4.3	6.8
	3, 6 4, 5	C_{1s} C_{1s}	292.3		
	1, 2 3, 6 4, 5	F_{1s}	690.6	1.1	7.2
Perfluorocyclohexa-1,3-diene[b] 	1, 4	C_{1s}	289.2 (294.6)	8.4 (7.7)	7.2 (7.4)
	2, 3 5, 6	C_{1s} C_{1s}	291.9 (297.5)		
	1, 4 2, 3 5, 6	F_{1s}	690.5	3.3	8.2
Perfluorocyclohexa-1,4-diene 	1, 2, 3, 4	C_{1s}	289.4	8.0	7.2
	3, 6	C_{1s}	292.4		
	1, 2, 3, 4 3, 6	F_{1s}	690.5	1.0	8.4

---

[a] Energy separation between centroids of shake up structure and relevant photoionization peak.

[b] Data in parentheses refer to gas phase spectra.

of 2.7 eV and well developed satellete structure to both the C_{1s} and F_{1s} levels. Secondly, the fact that the satellite structure is essentially the same for both the solid phase and gas phase measurements (with respect to both energy separation and relative intensity) strongly suggests that it arises from shake up transitions. A further feature is that the satellite energy separation for the F_{1s} levels corresponds approximately in magnitude with the separation between the satellite structure accompanying the C_{1s} levels and the direct photoionization peak corresponding to the vinylic carbons. Indeed careful measurement shows that the area ratios for the C_{1s} levels $= \overset{|}{\mathrm{C}}\text{–F}/\mathrm{CF}_2$ is somewhat less than expected on simple stoichiometric grounds. This would all seem to point to the fact that the shake up structure is associated with the pi electron system. The differing linewidths for the two peaks in the C_{1s} levels also strongly suggest that the two types of vinylic $=\mathrm{CF}$ groups have slightly differing binding energies (this is most readily apparent in the gas phase spectra FWHM $\mathrm{CF}=1.45$, $\mathrm{CF}_2=1.15$ eV). Deconvolution using standard procedures yields a shift difference of 0.5 ± 0.2 eV with the vinylic carbons attached to CF_2 groups having the higher binding energy. Both the absolute and relative binding energies are in excellent agreement with previously published data on related systems [13].

For all of the compounds studied, well developed satellite structures were evident for the core levels and the relevant data are collected in Table 1.

As a preliminary to the detailed analysis of this data the following observations are of interest.

1. The shake up energies are similar for monoenes and dienes, however the relative intensities are greater for the latter for both C_{1s} and F_{1s} levels.
2. For the isomeric dienes the shake up intensities are comparable.
3. The shake up energies for the F_{1s} satellites are larger than for the C_{1s} satellites, the difference being much smaller for the monoene, however the shake up intensities are greater for the C_{1s} satellites.

4.2. Theoretical

The evidence presented thus far would strongly suggest that the observed satellite structures arise from $\pi^* \leftarrow \pi$ shake up transitions accompanying core ionization. Our prime objective in this work is to systematically explore the possibility of utilizing information derived from shake up data, as an additional tool in developing ESCA for studies of structure and bonding in complex systems such as polymers. Therefore, it is important that any theoretical framework used to discuss the results be in principle applicable to more complicated systems than in the current investigation.

The theoretical discussion is therefore limited to an examination of shake up probabilities calculated using the sudden approximation, the equivalent cores concept and an all valence electron INDO SCF MO model.

Shake up transitions between the highest occupied and lowest unoccupied pi orbitals have been considered and the calculated probabilities for a given core level with respect to the single $\pi^* \leftarrow \pi$ transitions for the monoenes and the four corresponding transitions for the dienes are tabulated in Table 2. Inspection of

Table 2. Calculated shake up intensities and comparison with experiment

Molecule	Ring position	Transition	Shake up probabilities (%)	
			C_{1s}	F_{1s}
Cyclohexene		$a_{2\pi} \leftarrow b_{1\pi}$		
	1, 2		3.7	–
	3, 6		0.02	–
	4, 5		0.3	–
			Total[a] 1.3 Exptl. 1.4	–
Perfluorocyclohexene		$a_{2\pi} \leftarrow b_{1\pi}$		
	1, 2		3.8	1.4
	3, 6		0.02	0.1
	4, 5		0.2	0.01
			Total[a] =CF 3.8 Exptl. 4.3	Total[a] 0.32 Exptl. 1.1
Perfluorocyclohexa-1,3-diene		$b_{1\pi} \leftarrow a_{2\pi}$		
	1, 4		7.7	2.4
	2, 3		1.9	0.3
	5, 6		0.02	0.05
		$a_{2\pi} \leftarrow a_{2\pi}$		
	1, 4		0.6	0.7
	2, 3		0.5	0.0
	5, 6		0.0	0.0
		$b_{1\pi} \leftarrow b_{1\pi}$		
	1, 4		0.7	0.8
	2, 3		0.9	0.2
	5, 6		0.0	0.0
		$a_{2\pi} \leftarrow b_{1\pi}$		
	1, 4		0.1	0.3
	2, 3		0.3	0.0
	5, 6		0.0	0.0
			Total[a] =C–F 6.4 Exptl. 8.4	Total[a] 1.2 Exptl. 3.3
Perfluorocyclohexa-1,4-diene		$b_{1\pi} \leftarrow a_{2\pi}$		
	1, 2, 4, 5		2.8	1.0
	3, 6		0	0
		$a_{2\pi} \leftarrow a_{2\pi}$		
	1, 2, 4, 5		0.1	0.1
	3, 6		0.3	0.0
		$b_{1\pi} \leftarrow b_{1\pi}$		
	1, 2, 4, 5		2.3	0.9
	3, 6		0.1	0.1
		$a_{2\pi} \leftarrow b_{1\pi}$		
	1, 2, 4, 5		0.2	0.1
	3, 6		0	0
			Total[a] =C–F 5.4 Exptl. 8.0	Total[a] 1.1 Exptl. 3.0

[a] The total shake up probabilities, as percentages, are weighted with respect to the number of core levels contributing to the main photoionization peak.

the relevant eigenvectors shows that although strict σ-π separability does not obtain in these systems the description of the transitions as being approximately $\pi^* \leftarrow \pi$ in nature is basically sound. For convenience the transitions have formally been labelled in terms of the local symmetry of the π system ($C2v$) although of course for some of the hole states the symmetry is lowered.

Considering firstly the monoenes, in the case of perfluorocyclohexene (for which the chemical shift difference is sufficiently large to allow a direct determination of the shake up intensity with respect to the vinylic carbons), the calculated and experimental shake up intensities for the C_{1s} levels are in excellent agreement. That the approximate designation as $\pi^* \leftarrow \pi$ for the transitions is entirely adequate is shown by the low calculated transition probabilities for the CF_2 carbons indicating the small extent of through space and through bond interactions in these systems. This is reinforced by the good agreement between theory and experiment for the parent cyclohexene the calculated probabilities being almost identical to those for the perfluoro compound.

For perfluorocyclohexa-1,3-diene the calculations would indicate that the shake up structure accompanying photoionization of the C_{1s} levels arises predominantly from $b_{1\pi} \leftarrow a_{2\pi}$ transitions for C_1 and C_4. This is not entirely unexpected since this corresponds to the HOMO-LUMO transition in the neutral molecule and should formally be monopole forbidden. The large electronic reorganization accompanying core ionization however, lowers the symmetry such that the transition acquires considerable intensity. The calculated intensity is in reasonable agreement with experiment and moreover the calculations correctly reproduce the large increase in intensity on going from monoenes to dienes. For the unconjugated diene the calculated shake up intensities are again in very good overall agreement with experiment and reproduce the close similarity in intensities with respect to the conjugated diene.

Turning now to the F_{1s} satellites it is clear that although the model successfully reproduces the substantial increase in shake up intensity on going from monoene to dienes on an absolute scale the intensities are consistently underestimated by a factor of ~ 3. This can almost certainly be attributed to the parametrization employed for the equivalent core species and could no doubt be improved by judicious optimization of parameters. It is clear, however, that the model employed in this work is successful in interpreting the major features of the relative intensities of the shake up satellites and therefore forms the basis for discussing more complicated systems. No attempt has therefore been made to adjust the parameters to improve the quantitative agreement since our main objective is to have a reliable model for interpreting trends and differences.

Acknowledgements. Thanks are due to S.R.C. for provision of equipment.

References

1. Cf. Proceedings of international conference on electron spectroscopy, Namur 1974. Caudano,R. Verbist,J., (Eds.) J. Electron Spectry. **5**, (1974) and Refs. therein
2. (a) Siegbahn,K., et al.: ESCA applied to free molecules. Amsterdam: North Holland 1969
   (b) Carlson,T.A., Nester,C.W.: Phys. Rev. A **8**, 2887 (1973)
3. (a) Gelius,U., Allan,C.J., Allison,D.A., Siegbahn,H., Siegbahn,K.: Chem. Phys. Letters **11**, 224 (1971)
   (b) Aarons,L.J., Barber,M., Guest,M.F., Hillier,I.H. McCartney,J.H.: Mol. Phys. **26**, 1247 (1973)
4. (a) Lundquist,B.I.: Phys. Kondens. Materie **9**, 236 (1969)
   (b) Langreth,D.C.: Phys. Rev. **B1**, 471 (1970)
   (c) Manne,R., Aberg,T.: Chem. Phys. Letters **7**, 282 (1970)

5. Clark,D.T., Scanlan,I.W., Muller,J.: Theor. Chim. Acta (Berl.) **35**, 341 (1974)
6. Barber,M., Connor,J.A., Hillier,I.H.: Chem. Phys. Letters **9**, 570 (1971)
7. (a) Aarons,L.J., Barber,M., Conner,J.A., Guest,M.F., Hillier,I.H., Ikemoto,I., Thomas,J.M. Kuroda,H.: J. Chem. Soc. Faraday II, **69**, 270 (1973)
   (b) Grobman,W.D., Pollak,R.A., Eastman,D.E., Maas,E.J., Scott,B.A.: Phys. Rev. Letters **32**, 534 (1974)
8. (a) Pignataro,S., Distefano,D.: J. Electron Spectry **2**, 171 (1973)
   (b) Clark,D.T., Adams,D.B., Scanlan,I.W., Woolsey,I.S.: Chem. Phys. Letters **25**, 263 (1974)
   (c) Aarons,L.J., Connor,J.A., Hillier,I.H., Schwarz,M., Lloyd,D.R.: J. Chem. Soc. Faraday II **70**, 1 (1974)
   (d) Barber,M., Broadbent,S.J., Connor,J.A., Guest,M.F., Hillier,I.H., Puxley,H.J.: J. Chem. Soc. Perkin 11 1517 (1972)
9. Chambers,R.D., Clark,D.T., Kilcast,D., Partington,S.: J. Pol. Sci., Polymer Chem. Edn. **12**, 1647 (1974)
10. Clark,D.T., Kilcast,D., Adams,D.B.: Faraday Disc. **54**, 182 (1972)
11. Pople,J.A., Beveridge,D.: Approximate molecular orbital theory. New York: McGraw-Hill 1970
12. Aarons,L.J., Guest,M.F., Hillier,I.H.: J. Chem. Soc. Faraday II, **11**, 1866 (1972)
13. Cf. Reference 10 and Clark,D.T., Feast,W.J., Kilcast,D. Adams,D.B., Preston,W.E.: J. Fluorine Chem. **2**, 199 (1972)

Dr. D.T. Clark
Department of Chemistry
University of Durham
Science Laboratories, South Road
Durham, DH1 3LE, U.K.