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Photoelectron Spectroscopy of Organofluorine Compounds

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The analysis of the photoelectron spectra of organofluorine compounds is described. The influence of substitution by fluorine on the electronic structure of the molecules is examined on the basis of experimental data and quantum-chemical calculations. A table of the ionisation energies of organofluorine compounds is presented.
The bibliography includes 170 references.

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I. INTRODUCTION

The wide-scale application of organofluorine compounds in various branches of science and engineering is responsible for the great interest by chemists in the study of their electronic structure and reactivity. The commonest method of securing information about electronic structure is nowadays the photoelectron spectroscopy of molecules (PES),[1-4] which permits a direct comparison with experiment of various quantum-chemical models used for the calculation of the physicochemical characteristics of molecules.

The aim of the present review is the analysis of data obtained for organofluorine compounds by the PES method. Although there are several reviews of a general character (see, for example, Vovna and Vilesov[2] and Rao et al.[5]) as well as reviews for individual classes of compounds,[6,7] data on organofluorine compounds have not been described systematically or discussed. One may mention only two communications[8,9] in which photoelectron spectra (PE spectra) are presented without discussion for a series of fluorine-containing compounds together with tables of experimental and calculated ionisation energies. This review discusses the results of the most detailed investigations, which are naturally available only for not unduly complex molecules. Examples of the application of PES to the study of the correlation between the electronic structure of fluorine-containing molecules and their reactivity are examined. In order to cover fully the studies on the PES of organofluorine molecules, the review presents a table of the first ionisation energies of the molecules of compounds in all the classes considered.

The information which can be extracted from the PES refers strictly speaking not to the neutral molecule but to the corresponding molecular radical-cation, PES yielding the spectrum of the energy states of the molecular ion. However, the PE spectra are frequently interpreted using the Koopmans theorem by comparing the PE spectral bands with a definite molecular orbital (MO) of the ground electronic state of the neutral molecule. In this approximation, PES yields the binding energies of the electrons in different MO (ionisation energies) and the band shape is determined by the character of the localisation of the electron in the corresponding MO (distribution of electron density).

The relation between the ionisation energy (EI) and the orbital energy (ε_ρ) is expressed by the equation

$$IE - (-\epsilon_\rho) = \Delta E_{cor} + \Delta E_{reorg},$$

where ΔE_{cor} is the difference between the correlation energy of the ion and the molecule ($\Delta E_{cor} > 0$) and ΔE_{reorg} is the reorganisation energy ($\Delta E_{reorg} < 0$).[2] For the Koopmans theorem to be valid, the equality $\Delta E_{cor} = -\Delta E_{reorg}$ must hold. A detailed analysis of the Koopmans theorem may be found in two monographs.[2,4] Both non-empirical and semiempirical quantum-chemical calculations, carried out using the Koopmans theorem, sometimes fail to yield a satisfactory agreement with experimental EI. Despite this, the MO concept remains fairly fruitful both in the analysis of the PE spectra and in the study of the reaction mechanisms and of the structure of organic compounds.[10]

The concept of the weighted mean (with respect to the degree of degeneracy of the MO) ionisation energy of the unshared (lone) electron pair of the halogen atoms has been introduced[1] and linear correlations have been established between the ionisation energies and the valence and inner electrons of the halogens, which it has been suggested can be used for the identification of the lone electron pair bands in the PE spectra. The authors of the above study note that, in establishing correlations for fluorine-containing compounds, definite difficulties arise associated with the necessity to re-examine the existing interpretation of a number of spectra in the literature. Apparently, as a result of the marked delocalisation of the unshared (lone) electron pairs (LEP) of the fluorine atom, the proposed correlations must be used with much caution.

II. FLUORINE-CONTAINING ALKANES AND HALOGENOALKANES

Fluorinated halogenomethanes are the most thoroughly investigated compounds of this class.[12-17] The most thorough experimental study of CH_nF_{4-n} is one[17] in which the PE spectra were obtained by excitation with the HeI and HeII lines, the vibrational structure was analysed, a comparison was made with the absorption spectra and photoionisation mass-spectrometric data, and calculations of the

electronic structure were carried out in terms of the Hartree–Fock approximation. The above investigation included also the analysis of the theoretical and experimental data obtained previously.

The substitution of a hydrogen atom by a fluorine atom greatly complicates the PE spectra both as a result of the increase in the number of valence electrons and owing to the decrease in symmetry. Even in the PE spectrum of CH_3F the second band consists of a superposition of two unresolved bands. X-Ray electronic spectra have been obtained[18] in the valence region and the complex bands with Lorentzian profile were resolved using the calculated intensities of the individual bands. The vertical ionisation energies (EI) obtained are used in comparing theory and experiment. Here it is necessary to bear in mind that, owing to the large step (0.16 eV) in the measurement of the PE spectra and the low resolution, the accuracy of the determination of the EI is low and probably does not exceed a level to within 0.2 eV.

Despite the difficulties mentioned, the interpretation of the PE spectra of fluoromethanes can be regarded as fairly reliable. The sequence of the MO for these molecules in order of increasing ionisation energy is presented in Fig.1. Some uncertainty remains in the sequences of the close MO $1b_1$, $3a_1$, and $2b_2$ for CH_2F_2 (in the EI range 18.5–19.8 eV). We present the sequence proposed[19] on the basis of calculations in terms of the $X\alpha$ approximation with overlapping spheres. Another sequence has been obtained for this energy range in other studies.[9,17,18]

The nature of the majority of the MO in CH_nF_{4-n} is complex because of the pronounced mixing of the atomic orbitals of fluorine with the σ orbitals of carbon. On the basis of the results of Du Li et al.,[19] only the MO $3b_2$ and $1a_2$ (EI = 15.2 and 15.6 eV) in CH_2F_2 can be regarded as localised on the fluorine atoms. According to Brundle et al.,[17] the MO $4e$ with EI = 17.2 eV in CF_3H and $1e$ with EI = 18.5 eV in CF_4 are closest to the unshared electron pair of fluorine, while in CH_3F the unshared electron pairs of fluorine do not exist in a pure form. One should note that different methods of calculation yield appreciably different results for the MO populations.[17,19–21] However, the band widths in the PE spectra agree with an appreciable delocalisation of the unshared electron pairs of fluorine.

The character of the highest occupied MO (HOMO) is especially important in the study of reactivity. For all the fluorine-substituted methanes except CF_4, the HOMO is bonding in relation to the C–H bond and antibonding in relation to the C–F bond.[17] In CF_4, the HOMO of the C–F bond must be bonding, since the removal of an electron from this MO is accompanied by the dissociation of the molecular ion.[22]

The PE spectra of C_2H_5F and n-C_3H_7F have been published.[9,23–25] It is seen from these data that the HOMO of the C–C bond in the alkyl fluoride is bonding. The first vertical EI decrease with increase in the length of the alkyl chain but remain approximately 0.4 eV higher than the EI of the corresponding alkanes owing to the high electronegativity of the F atom. The same effect leads to a further increase in EI with increase in the number of F atoms in $C_2H_nF_{6-n}$.[25] However, the spectra become so much more complex that even for $n = 2$ it is possible to distinguish only three bands.

The introduction of a single halogen atom X (X = Cl, Br, or I) into perfluoromethane lowers the molecular symmetry to C_{3v} and leads to the partial removal of the degeneracy of the MO (Fig.2). In the low-energy part of the PE spectrum, the bands of the unshared electron pairs of the X atom, corresponding to the removal of the electron from the HOMO, can be readily differentiated both as regards shape and the characteristic spin–orbital splitting. The first vertical EI decrease appreciably in the sequence Cl, Br, I (13.08, 12.12, and 10.45 eV). The bands of the n_X electrons are followed by the band of the C–X bonding MO with vertical EI of 15.20,

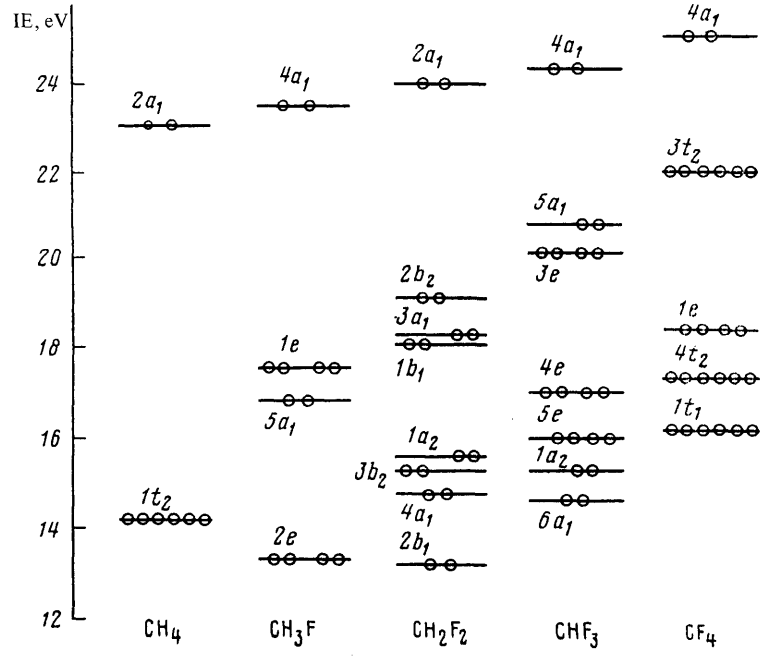


Figure 1. Schematic arrangement of the molecular orbitals of CH_nF_{4-n}.

14.28, and 11.18 eV for Cl, Br, and I respectively. In the region of higher energies, the PE spectra of all three halogenotrifluoromethanes are similar,[14,15,26–29] Despite the large number of bands, one can resolve all the bands whose appearance is possible up to an energy of 24 eV. Analysis of the vibrational structure, the change in band intensity on passing from excitation by the HeI line to excitation by the HeII lines, and comparison with the CF_4 and CF_3H spectra made it possible to interpret all the bands unambiguously.[15,16] The following sequence of MO was obtained: $1a_1$(C2*s*); $1e$(CF_3); mixed orbitals of the unshared electron pairs of the F atom and the C–F bond; $2a_1$, $2e$, and $3e$; $1a_2$(F); $3a_1$(C–X); $4e$(X). Calculations by the extended Hückel (EHM) and CNDO/2 methods for CF_3Cl and CF_3Br yield the reverse sequence of the MO $1a_2$ and $3e$.[20]

An increase in the number of isotypical X atoms in $CF_{4-n}X_n$ leads to a further decrease in EI and to a redistribution of the band intensity in the PE spectra between the high-energy and low-energy parts, since the EI of other halogens are lower than the EI of fluorine. For X = Cl or Br and n = 1–3, it has been possible to differentiate and identify virtually all the stretching vibration bands of the electrons.[13–16,27,28] The following sequence of MO was obtained: $3b_2$, $3b_1$, $2a_2$, $4a_1$, $2b_2$, $2b_1$, $1a_2$, $3a_1$, $1b_1$, $2a_1$, $1b_2$, and $1a_1$ for CF_2X_2 and $1a_1$, $4e$, $3e$, $3a_1$, $2e$, $1e$, $2a_1$, and $1a_1$ for CFX_3. The four highest MO are those of the unshared electron pairs of the atom X. The $(4e)^{-1}$ and $(3e)^{-1}$ bands in PE spectrum of $CFBr_3$ exhibit spin–orbital splitting. The sequence of the MO of the unshared electron pairs of the atoms X in CF_2X_2 and CFX_3 differs from the sequence of the MO of the corresponding X-substituted derivatives of methane not containing fluorine.[12,19,30,31] If the increase in EI on passing from perfluorinated halogenomethanes to the fluorinated derivatives is attributed to the inductive influence of the fluorine atom, then the inductive effect is found to be different for different MO.

The PE spectra of a series of less symmetrical fluorine-containing halogenomethanes have been obtained and interpreted in fair detail: $CHFCl_2$, CHF_2Cl, CH_2FCl, and CF_2BrCl.[12–14,26,28] The HOMO are described satisfactorily by the AO of the unshared electron pair of the Cl atom for the first three molecules and the AO of the Br atom for the last. The most thorough studies of both fluorinated and fluorine-free halogenomethanes have been carried out by a group of Yugoslav spectroscopists,[12–16] who paid special attention to the influence of the changes in the energy of ionising radiation (the HeI and HeII lines) on the spectra. They established that the sensitivity of the bands with an appreciable contribution by the unshared electron pairs of the halogens decreases in the sequence F ≫ Br ≅ I > Cl. This regularity can be usefully borne in mind in differentiating the bands corresponding to the removal of electrons from different halogen atoms.

Successive fluorination of ethane leads to the stabilisation of the HOMO, which is C–C bonding in character.[9,23,25] A fairly complete analysis of the PE spectrum has been carried out only for C_2H_5F.[9] Semiempirical calculations of the electronic structure yielded the following MO sequence: $3a''$(CH), $10a'$(Cl), $9a'$(C–H), $2a''$(F), $8a'$(C–F), $1a''$(F, C–H), $7a'$(F), $6a'$, and $5a'$.[41] However,

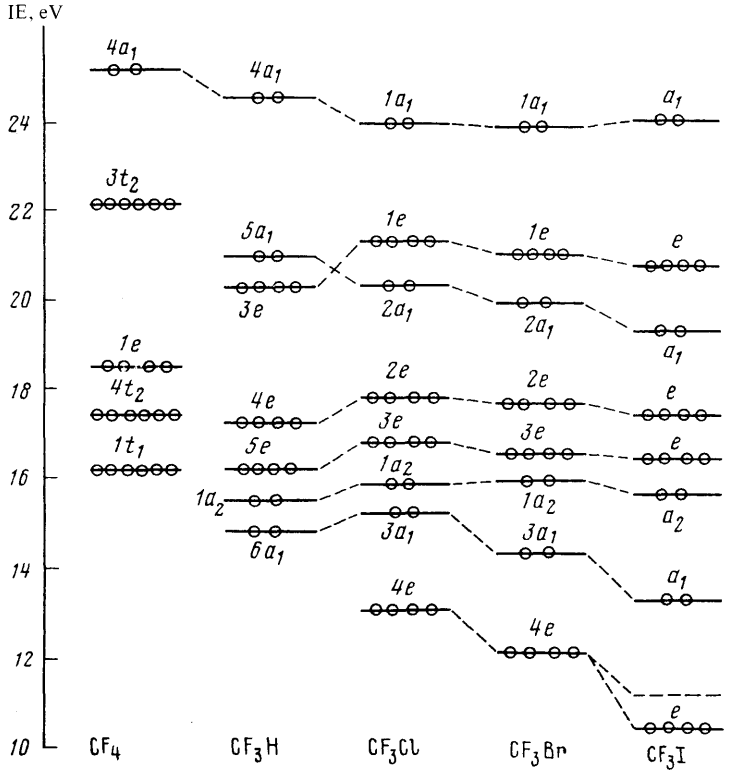


Figure 2. Schematic arrangement of the molecular orbitals of trifluoromethanes CF_3X, where X = H, F, Cl, Br, or I.

the observed regularities in the variation of the first EI in the successive fluorination of methane and ethane agree better if the highest two occupied MO are interchanged.

The introduction of Cl, Br, and I atoms into fully or partly fluorinated ethane entails the same changes in the PE spectrum[26,32-34] as those examined above for methane. The spectra of $(CF_2X)_2$, where X = Cl, Br, or I, have been analysed in greatest detail,[32] but in this case too the number of bands identified is appreciably smaller than expected even when account is taken of only the valence *p* electrons of the atoms.

Analysis of the spectra of halogenoethanes is complicated by the fact that the specimens consist of mixtures of *gauche*- and *trans*-isomers. A structure attributed to the ionisation of individual isomers was discovered only for $(CF_2I)_2$ [32] and CH_2FCH_2Br [33] in the region of the spectra corresponding to the removal of one of the electrons of the unshared electron pairs of I and Br. For $(CF_2I)_2$, EI proved to be higher by 0.1 eV for the *gauche*-isomer, while for CH_2FCH_2Br it proved to be higher by 0.2 eV for the *trans*-isomer. Higher values of the EI for the *anti*-isomers have been obtained also for a series of monofluoro- and monobromo-derivatives of propane and butane and also for *trans*-1-bromo-2-fluorocyclohexane.[33] The bands have been assigned to different conformers[32,33] on the basis of semiempirical calculation. Gounelle et al.[33] took into account only the interaction through space, while Chan and McDowell took into account[32] also the interaction through σ bonds. Possibly the different sequences of the EI of the conformers of derivatives of ethane obtained in these two studies may be associated with this factor.

III. FLUORINE-CONTAINING ALKENES AND HALOGENOALKENES

All the studies on fluorine-containing molecules with an isolated double bond carried out by the PES method concern ethylene derivatives $R^1R^2CCR^3R^4$ (R^1, R^2, R^3, R^4 = H, F, or CF_3). The first EI correspond to the removal of the π electrons of the double bond.

For all the six fluorinated ethylenes,[35-38] the PE spectra were obtained with excitation by the HeI and HeII lines, the variation of the parameter of the angular anisotropy of the scatter of the photoelectrons has been studied for all the spectral bands in the region up to 20 eV, the vibrational band structure has been analysed,[36,38] and empirical and non-empirical calculations, including many-particle calculations, of the electronic structure have been performed.[35,39] This made it possible to interpret fairly reliably the spectra in the region up to 25 eV taking into account all the valence electrons, although some of the ionisation transitions then proved to be somewhat degenerate with respect to energy.

Successive fluorination of ethylene hardly alters the HOMO energies (the vertical EI are in the range 10.38 – 10.69 eV). Such behaviour can be explained by the compensation of the inductive influence of the F atoms and by the interaction through space between the π MO of the C=C bond and the AO of the unshared electron pairs of fluorine ($n-\pi$ conjugation). Indeed, both quantum-chemical calculations[35] and the observed variation of the parameter of angular anisotropy[36] for the series of fluorethylenes indicate an appreciable contribution by the AO of fluorine to the HOMO. The second EI, corresponding to the removal of σ electrons, increase appreciably with increase in the number of F atoms in the substituted ethylene; for example, the second EI of perfluoroethylene is higher by 3 eV than that of the unsubstituted ethylene. The different influences of the substitution of hydrogen by fluorine on the energies of the π and σ MO have been called the perfluoro-effect, the fluorination of ethylene being regarded as the classical example of the manifestation of the perfluoro-effect in planar molecules.[3,4,38] However, more thorough experimental theoretical study[35,39] showed that the shifts of both σ and π MO depend greatly on the nature of the MO and can vary within wide limits (see below). The almost complete agreement between the PE spectra of *cis*- and *trans*-1,2-difluoroethylenes, which agrees well with the many-particle calculations for these molecules, is noteworthy.[35] Semiempirical calculations in terms of the CNDO approximation yield appreciably different MO schemes for the isomers.

Complete fluorination of propene, *cis*- and *trans*-but-2-enes, and 2,3-dimethylbut-2-ene increases the first vertical EI by 1.3 – 4.0 eV.[40-43] However, the variation of the EI with *n* in $C_2H_{4-n}(CF_3)_n$ is irregular and its explanation requires further experimental and especially theoretical studies of the electronic structure. Among other fluoropropene derivatives, only 3-fluoropropene has been studied in fair detail, although a complete interpretation of the spectrum has not been carried out.[44-46] The regularities in the variation of the first ionisation potential in the C_3H_5X series, where X = F, Cl, Br, or I, have been considered as the first semiquantitative demonstration of the existence of "hyperconjugation".[46]

Scott and Russell[47] carried out a joint empirical analysis of the PE spectra and UV absorption spectra of chlorofluoroethylenes. With the aid of the experimental quantities obtained, characterising the successive substitution of hydrogen atoms by fluorine or chlorine atoms, they were able to reproduce the experimental energies of the highest occupied and lowest unoccupied MO of nine chlorofluoroethylenes.[48,49] The introduction of chlorine or bromine atoms into fluorinated ethylenes (the spectra of fluoroiodoethylenes were not obtained) leads to an appreciable (by 0.3 – 1.0 eV) decrease in the first EI corresponding to the removal of π electrons[43,47,49] owing to the effect of $n-\pi$ conjugation. Detailed quantitative studies of this effect for the compounds considered are not described.

A second characteristic feature of fluorohalogenoethylenes is the presence in the PE spectra of the bands due to the LEP of the chlorine and bromine atoms and the bands associated with the C – X bonds. They appear in the energy range (11 – 15 eV) which in the spectra of fluoroethylenes is free from bands and can be readily identified from their characteristic features (see above).

The electronic structure of allene is characterised by the presence of two systems with mutually perpendicular nodal planes. The corresponding MO are degenerate in both allene and perfluoroallene and are HOMO.[50,51] In contrast to fluorinated ethylenes, an appreciable increase (by 1.3 eV) in the first EI is observed, which the authors[51] explained by the predominance of the effect due to negative hyperconjugation and of the inductive effect over $n-\pi$ conjugation.

In 1,1-difluoroallene, the degeneracy of the π MO is removed, since $n-\pi$ conjugation is ruled out for symmetry reasons in the case of the π MO localised on the C(2)=C(3) bond and hyperconjugation is ruled out for the π MO of the C(1)=C(2) bond.[51] As a result, the HOMO is the bonding π MO of the C(1)=C(2) bond. The second π MO of the C(2)=C(3) bond lies 1.5 eV lower. The nonequivalence of the two π bonds in 1,1-difluoroallene [the C(1)=C(2) bond is characterised by an excess electron density, while the C(2)=C(3) bond is characterised by its electron deficiency compared with the bonds in allene and perfluoroallene] is manifested in the chemical reactions of 1,1-difluoroallene.

In tetraflurobutatriene, all the fluorine atoms are located in the nodal plane of the highest occupied π MO of the C(2)=C(3) bond, whose energy (9.3 eV) has not changed compared with butatriene

(the perfluoro-effect).[52] The terminal localised π MO, whose nodal plane is perpendicular to the plane passing through the F atoms, interact effectively with these atoms via the conjugation mechanism. When account is taken of the $\pi-\pi$ conjugation, the delocalised b_{3u} and b_{2u} MO with 12 and 12.5 eV binding energies are obtained. Such interpretation of the spectrum agrees with the quantum-chemical calculations (see Basch et al.[52] and the references quoted therein).

The PE spectra of 1,1,4,4-tetrafluoro- and perfluoro-butadienes were used to identify the sequence of the occupied MO in buta-1,3-diene.[53] The sequence $(\ldots 1a_u\pi 7a_g\sigma 1b_g\pi)$, proposed on the basis of the analysis of the spectra, agrees with semiempirical calculations. Non-empirical calculations as well as later calculations by the modified complete neglect of the differential overlap method yields the $7a_g\sigma$ and $1b_g\pi$ order of MO.[54] Analysis of the PE spectra as well as absorption spectra enabled Brundle and Robin[53] to conclude that the carbon skeleton of tetrafluorobutadiene is planar, while perfluorobutadiene is characterised by the rotation of two π-bonds by an angle of 42° about the C—C bond.

Among cyclic compounds with double bonds, we shall mention the fully fluorinated Dewar benzene—hexafluoro[2.2.0]hexa-2,5-diene. In this case, the PE spectra of the fluorinated compound[55,56] were used to demonstrate the absence of interaction between the isolated π-electron systems.

IV. FLUORINE-CONTAINING ALKYNES AND HALOGENO-ALKYNES

The small number of valence electrons in fluorinated acetylenes leads to fairly simple spectra, which have been interpreted reliably by comparison with quantum-chemical calculations.[57–59] It has been

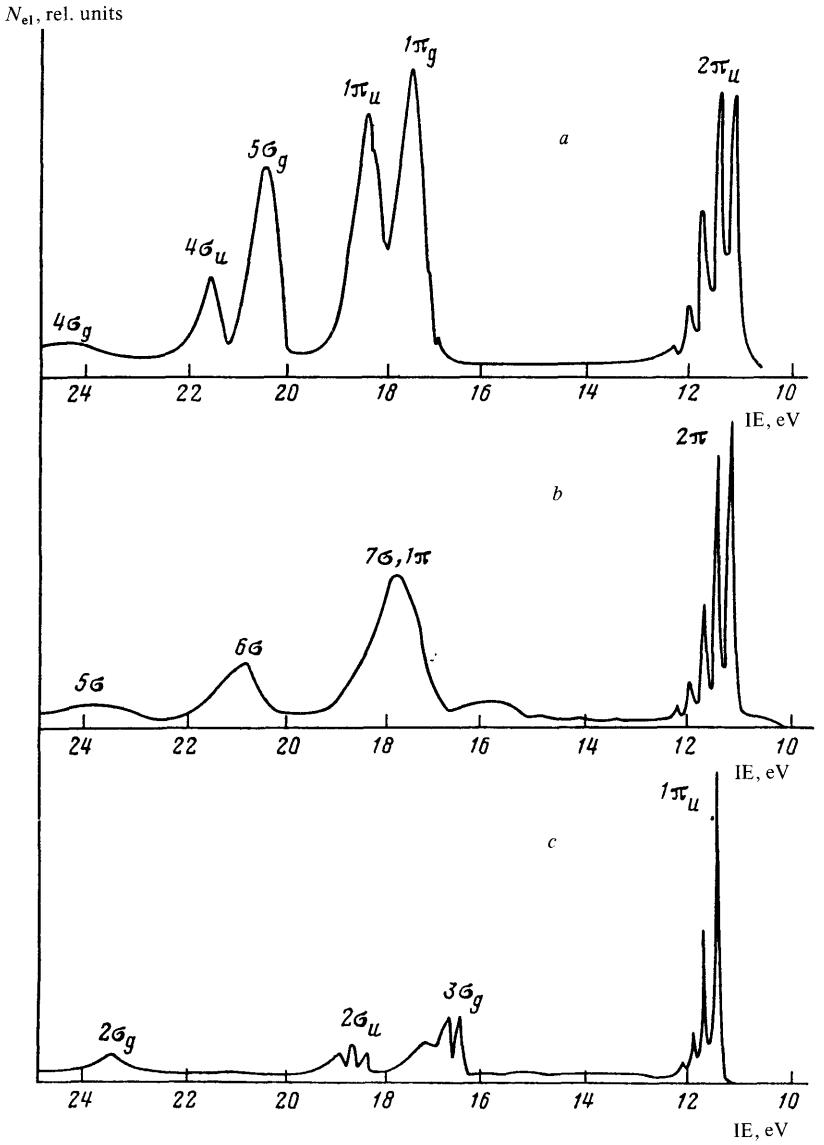


Figure 3. Photoelectron spectra of C_2F_2 (*a*), C_2FH (*b*), and C_2H_2 (*c*).

shown that the HOMO is a C–C bonding MO of the π type with a considerable contribution by the antibonding combination of the $2p\pi$ AO of fluorine (Fig.3). As a result of the cancelling out of the inductive effect and the $n-\pi$ conjugation effect, the first EI of acetylene changes on fluorination by not more than 0.2 eV (the perfluoro-effect). However, approximately the same shift is observed also for the σ(C–H) MO of fluoroacetylene relative to the centre of gravity of two analogous MO of acetylene, which does not agree with a simple treatment of the perfluro-effect. The spectra of other fluorinated alkynes are much more complex and their complete analysis has not been carried out.[9,60–63] In this case, the HOMO are MO of the π type. Fluorination of the methyl groups in propyne and but-2-yne leads to an appreciable (by up to 2.8 eV in perfluorobut-2-yne) increase in the first EI as a result of the inductive influence and negative hyperconjugation.[51]

Similar regularities have been observed also in the spectra of fluorinated dialkynes with conjugated π systems:[9,57,58,60] the fluorination of diacetylene does not change the energy of the HOMO of the π(C≡C) type, but substitution of the hydrogen atoms in the methyl groups of penta-1,3-diyne and hexa-2,4-diyne by fluorine atoms increases appreciably the first EI of their molecules. As an example of the sharp deviation from the usual behaviour of the σ MO on fluorination, we may mention the increase in the EI for the σ(C–C) electron in fluoro- and difluoro-diacetylenes compared with the unsubstituted molecule. This is explained by the interaction of the σ(C–C) MO with the σ(C–H) and σ(C–F) orbitals, the first of which is charactersied by a lower binding energy than the σ(C–C) orbital, while the second is characterised by a higher binding energy.[58]

PES data have been published[61] for the compounds CF_3CCX, where X = Cl, Br, or I. Spin–orbital splitting has been observed in the first bands of bromo- and iodotrifluoropropynes, whose magnitude agrees with the splitting for bromo- and iodoacetylenes[59] and is somewhat smaller than the splitting in the spectra of alkyl halides. This indicates an appreciable $n-\pi$ conjugation in CF_3CCl and CF_3CCBr. Although quantum-chemical calculations have not been made, the HOMO in these two molecules are apparently predominantly np_X AO. For X = Cl, the interaction of the π(C≡C) MO with the p_C AO is weak and the HOMO is in this case an almost pure π(C≡C) MO. The different character of the HOMO for X = Cl and X = Br or I can affect the reactivity of the molecules considered.

V. FLUORINATED AROMATIC COMPOUNDS

Fluorobenzenes have been investigated in greatest detail: the PE spectra have been obtained for different energies of ionising radiation,[9,39,64–66] a thorough analysis of the vibrational structure of the spectra[39] and of the angular distribution of the scattering of photoelectrons removed from different MO [37] has been carried out, and numerous quantum-chemical calculations of the electronic structure have been made.[9,39,54,65,67,68] The PE spectra with excitation by the HeII line have been published[9] for all the fluorobenzenes as well as the results of quantum-chemical calculations taking into account all the valence electrons. In the range of energies less than 25 eV, fluorobenzene has 16 MO according to calculations, but only 11 bands could be resolved in the PE spectra. The situation is still more complex for substituted benzenes with a larger number of fluorine atoms. Despite this, the sequences of the MO quoted[9] are fairly reliable. As an example, we shall quote recommended sequences of MO for fluorobenzene:

$3b_1\pi_{CC}$, $1a_2\pi_{CC}$, $8b_2$, $2b_1\pi_{CC}$, $13a_1$, $7b_2$, $6b_2$, $12a_1$, $5b_2$, $1b_1\pi_F$, $11a_1$, $10a_1$, $4b_2$, $9a_1$, $8a_1$, $3b_2$, $7a_1$, and $6a_1$

and similarly for perfluorobenzene:

$2e_{1g}\pi_{CC}$, $2a_{2u}\pi_{CC}$, $2b_{2u}$, $6e_{2g}$, $1a_{2g}$, $6e_{1u}$, $1b_{2g}\pi_F$, $1e_{2u}\pi_F$, $1e_{1g}\pi_F$, $5e_{2g}$, $1a_{2u}\pi_F$, $5e_{1u}$, $5a_{1g}$, $1b_{2u}$, $4b_{1u}$, $4e_{2g}$, $4e_{1u}$, $4a_{1g}$, $3b_{1u}$, $3e_{2g}$, $3e_{1u}$, and $3a_{1g}$.

In all the fluorobenzenes, the HOMO is the π MO of benzene whose binding energy increases somewhat on fluorination to the maximum value of 9.90 eV in hexafluorobenzene. However, the changes in the first EI on fluorination cannot be accounted for on the basis of the consideration of the conjugation and inductive effects and many-particle calculations are required.[65] Fluoroderivatives of toluene and xylenes have been investigated to a much lesser extent.[65,66,69,70] Detailed analysis of the PE spectra using non-empirical calculations have been carried out and the changes in band intensities in the spectra with excitation by the HeI and HeII lines have been studied only for three $CH_3C_6H_4F$ isomers.[65]

The PE spectra have been obtained and partly identified for a series of fully fluorinated condensed aromatic hydrocarbons[71] as well as 9-fluoroanthracene.[72] For nine substituted anthracenes (apart from fluorine, other halogen atoms as well as CH_3, OCH_3, CHO, etc. were used as substituents), a linear relation has been obtained between the first EI and the Hammett constants.

The comparative analysis of the PE spectra of the *ortho*- and *meta*-substituted benzonorbornadienes carried out by Santiago et al.[73] indicates a different nature of the HOMO in *o*- and *m*-fluorobenzonorbornadienes. The authors attribute the difference between their photochemical activities to this factor.[73]

One of the first studies involving the use of PES to obtain information about the geometrical structure of molecules, is that of Maier and Turner[74] who analysed the spectra of substituted (including seven fluoro-substituted) biphenyls. The difference between the first and fourth EI was used to determine the dihedral angle between the planes of the two benzene groups on the basis of the linear relation $\Delta E = A\cos\theta + B$, where θ is the dihedral angle and A and B are constants. In connection with the hypothesis that the physiological activity of certain biphenyl derivatives (namely chloro-derivatives) is determined by the degree of coplanarity of the molecules, this question has been recently re-examined[75] using new electron diffraction and PES data.

The introduction of chlorine, bromine, and iodine atoms into perfluorobenzene leads to the changes in the PE spectra already examined: the splitting of the first band as a result of the removal of the degeneracy of the HOMO e_{1g} with some decrease (to 0.5 eV for the iodine atom) in the first EI and the appearance of the bands due to the unshared electron pairs of the halogen in the range 11 to 12.5 eV, which is free from bands in the PE spectra of perfluorobenzene.[8,68,76] The sequence of the first five MO in C_6F_5X, namely $a_2\pi$, $b_1\pi$, b_2h_x, $b_1\pi$ (for X = Cl, we have $b_1\pi$, b_2h_{Cl}), π, has been fairly reliably established and confirmed by quantum-chemical calculations.[8,68] The PE spectra of 52 fluorinated compounds containing more than one chlorine or bromine atom, excited by the HeI and HeII lines, as well as the symmetry types of the highest (up to 6) MO, obtained from non-empirical calculations, have been published;[8] they have not so far been analysed. The PE spectra of the *m*-, *p*-, and *o*-isomers of the chloro- and bromo-derivatives of ααα-trifluorotoluene are similar and the first four EI of the different isomers differ by not more than 0.15 eV.[7,66] The first two bands in the spectra correspond to the removal of π electrons and the next two to the removal of the electrons of the unshared pairs of chlorine and bromine.

VI. FLUORINATED ORGANIC COMPOUNDS CONTAINING NITROGEN, OXYGEN, AND SULPHUR HETEROATOMS

Among nitrogen-containing compounds, fluoro-derivatives with the CN group have been investigated in fair detail. The PE spectra of FCN excited by the HeI and HeII lines and the correlation diagram for the first four EI of XCN, where X = I, Br, Cl, or F, have been published.[77] Comparison of the PE spectra of the more complex $CH_2F-C\equiv N$ and $CH_2F-C\equiv CH$ molecules made it possible to assign the bands in the $CH_2F-C\equiv N$ spectrum,[62] although the assignment cannot be regarded as unambiguous because the PE spectrum of $CH_2F-C\equiv N$ is fairly complex owing to the superposition of the bands of the triple bond and the unshared electron pair of the nitrogen atom. For a more accurate interpretation of the spectrum, non-empirical calculations were carried out. The PE spectra, excited by the HeI and HeII lines, of a series of compounds of the type $X-C\equiv C-C\equiv N$, where X = CF_3, F, Cl, Br, or I, have been published.[61] Fig.4 presents the correlation diagram for the EI of cyanoacetylenes on the basis of which the bands in the PE spectra of these substances were assigned. For the bromo-, chloro-, and iodoacetylenes, a strong interaction of the $1\pi_\lambda$ and $2\pi_\lambda$ orbitals is observed. It has been shown that calculations using Green functions predict much better the band sequence and the trend in the variation of EI of cyanoacetylenes than the calculations in terms of the Koopmans approximation.[61]

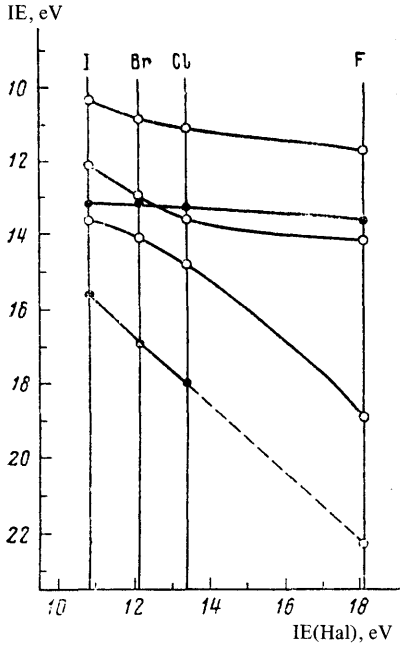


Figure 4. Correlation diagram for the ionisation energies of cyanoacetylenes $X-C\equiv C-C\equiv N$ as a function of the ionisation energy of the halogen atom X = I, Br, Cl, or F.

Comparison of the angular distributions of the photoelectrons, formed on photoionisation of pyridine, pentafluoropyridine, and 2,6-lutidine by the HeI line, made it possible to refine the assignment of the bands in the PE spectrum of pyridine.[78] Thus the first pyridine band was assigned to the a_1n MO, while the fifth band corresponds to the lowest occupied $b_1\pi$ Mo. The asymmetry parameter β of the angular distribution of photoelectrons for pentafluoropyridine hardly changes (in contrast to pyridine and 2,6-lutidine) within the limits of the first band and differs only slightly for different bands: for bands 1–5, β = 0.60, 0.68, 0.65, 0.55, and 0.34 respectively.

The UV absorption spectra and the PE spectra of $(CF_3)_2C=NH$ and other hydrocarbons with the azomethine group have been compared[79] and it has been observed that fluoro-substitution leads to a significant shift, by more than 2 eV, of the n, π, and the first σ ionisation energies for $(CF_3)_2C=NH$ compared with the analogous hydrocarbons. On the other hand, the $\pi^* \leftarrow n$ band shift of the absorption spectra of the corresponding compounds is hardly observed.

Staley et al.[80] used the EI of fluoramines, measured by the PES method, to determine the homolytic dissociation energies of protonated molecules (B), while the difference between the influences of alkyl and fluoroalkyl substitutents on the electronic structure of amines was used to account for the irregularities in the variation of the proton affinities and the values of $D(B^+-H)$ for the test compounds.

The PE spectra of benzonitrile, 1,2- and 1,4-dicyanobenzenes, and their perfluoro-analogues have been studied in detail.[81] The CNDO, INDO, and the linear combination of bond orbital methods were used to assign the bands. It was observed that the difference between the changes in the energies of the σ and π orbitals of benzonitrile on perfluorination is significantly greater than for 1,2- and 1,4-dicyanobenzenes. The fluorescence of perfluorobenzonitrile ions has been observed and investigated;[69] fluorescence has not been observed for benzonitrile itself. The difference is explained by the fact that perfluorination of benzonitrile alters the sequence of the close lying γ^{-1} and π^{-1} ($\tilde{B}$ and $\tilde{C}$) states of the cations.

The study of the influence of the position of fluorine on the PE spectra of fluoroanilines[65] showed that the position of the band corresponding to the removal of an electron from the b_1 MO, in which the contribution by the n_N AO predominates, hardly changes on fluorination in the *ortho*-, *meta*-, and *para*-positions. On the other hand, the HOMO, which is predominantly of the π type, shifts on fluorination towards higher energies, the shift being particularly marked for *meta*-fluoroaniline.

An increase in the number of atoms in a compound usually entails a sharp increase in the complexity of the PE spectrum. However, for molecules with multiple bonds and heteroatoms, the first bands in the PE spectrum are frequently well differentiated. Fig.5 presents the PE spectra of indole and 4,5,6,7-tetrafluoroindole.[82] Fluorination shifts the first four bands by 0.72, 0.60, 0.56, and 0.44 eV respectively and leads to the separation of the fourth band from the remaining group of strongly overlapping bands. The PE spectra of diazanaphthalenes and their fluoro-derivatives have been published.[83] The results of quantum-chemical calculations by the extended Hückel method were used for analysis. Attempts to apply the methods of perturbation theory within the framework of the model involving interactions through the bonds between localised orbitals of the unshared pairs of nitrogen for the description of the splitting of the MO with a considerable contribution by the h_N AO proved unsuccessful for compounds of this class.

Among oxygen- and fluorine-containing hydrocarbons, carbonyl compounds have been studied in greatest detail. The first and second bands in the PE spectra of substituted aldehydes and ketones

usually correspond to the unshared pair of oxygen and the π orbital of the C=O bond. A correlation analysis of the PE spectra of H_2CO, HFCO, and F_2CO has been carried out.[84] The bands in the HFCO spectrum are located in the centre between the corresponding bands of H_2CO and F_2CO. For the carbonyl halides $X_2C=O$, the band of the unshared electron pair of oxygen shifts upwards in the sequence X = H, Br, Cl, F. The first EI of oxalyl halides $(COX)_2$ corresponds to the LEP of the oxygen atom and increases in the sequence X = Br, Cl, F.[85] For $(COBr)_2$ and $(COCl)_2$, groups of four sharp peaks, corresponding to the unshared electron pairs of Br and Cl, are observed at 11.7 and 12.7 eV. A similar sharp structural group is not observed for $(COF)_2$. Comparison of the PES data, the results of the CNDO semiempirical calculation, and the temperature variation of the PE spectra led to the conclusion that these compounds have two isomers. Comparison of the PE spectra of ten chlorofluoroacetones with semiempirical CNDO/2 calculations[86] permitted the assignment of the bands in the PE spectra. The first EI of all the compounds correspond to the removal of one electron of the LEP of oxygen. The second EI for fluoroacetones corresponds to the removal of electrons from the π orbital of the C=O bond, while for chlorofluoroacetones there are several orbitals corresponding to the LEP of chlorine between the above two orbitals.

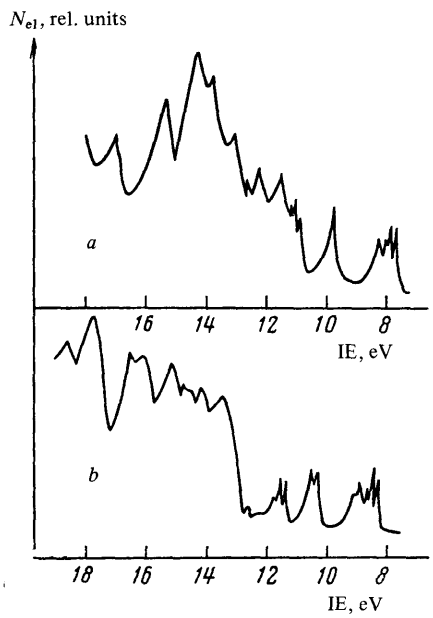


Figure 5. Photoelectron spectra of indole (*a*) and tetrafluoroindole (*b*).

Studies on the PE spectra, excited by the HeI line, of a series of fluoroethers[87] or the type $F[CF(CF_3)CF_2O]_nCHFCF_3$, where $n = -4$ (the E-1, E-2, E-3, and E-4 Freons) showed that they have EI higher by 3.5 eV than the corresponding ordinary ethers. Their vacuum UV absorption spectra begin at energies greater than 10 eV. Both photoelectron and UV spectra are complex, which indicates the existence of several close orbitals of the LEP of oxygen. The EI corresponding to the unshared electron pairs of oxygen and the C–C orbitals must lie close to one another in the region of low EI. The remaining orbitals are difficult to identify from the spectra, since the PE spectra of these compounds are continuous without very distinct bands.

A correlation analysis has been carried out[88,89] and the PES data for *p*-benzophenone and its fluoro-analogues have been compared with the semiempirical calculations by the CNDO/2 and CNDO/S methods. The MO energies have been determined for *p*-benzophenone and have been found to decrease in the sequence $n > n_+ > \pi_+ > \pi_-$, the sequence for *p*-perfluorobenzophenone being $n_+ > n_- > \pi_- > \pi_+$. The perfluoro-effect for these compounds leads to a shift of the *n* orbitals by ~1 eV; the shift of the π orbitals is significantly smaller than that of the *n* orbitals.

The first bands in the PE spectra of fluorine-containing thiocarbonyl compounds correspond, like those for carbonyl compounds, to the LEP of the sulphur atom with a lower EI than for oxygen, while the second band corresponds to the π orbitals of the C=S bond. The bands in the PE spectra of $F_3CS-C(S)-X$, where X = F, Cl, or CF_3, have been assigned on the basis of correlation analysis relative to the PE spectra of halogen-containing carbonyl compounds.[90] Among all the compounds examined, only $F_2C=S$ undergoes $\sigma-\pi$ polarisation. It has been observed that the use of a chlorine atom or the CF_3 group as the substituent results in identical shifts of the PE spectral bands.

The formula relating the first EI of the unshared electron pair of sulphur to the sum of the electronegativities X_α of the substituents has been found from the analysis of the PE spectra of the sulphuranes CF_3SF_3, $(CF_3)_2SF_2$, $(CF_3)_2S$, and others:[91]

$$EI(n_S) = 0.73(\Sigma X_\alpha + 7.10)\ \text{eV}.$$

The outer valence levels in the phenyl and pentafluorophenyl derivatives of bivalent sulphur have been investigated by PES.[92] It has been established earlier for these compounds by X-ray fluorescence spectroscopy that, on passing from phenyl to pentafluorophenyl derivatives of bivalent sulphur, the 3*p* electrons are displaced from conjugation with the aromatic π system, forming a virtually non-bonding level. At first sight, this should promote reactions in which the sulphur atom behaves as a π-electron donor. However, in reality the reactivity of the compounds C_6F_5SX in such reactions is significantly lower than that of their hydrocarbon analogues. The absence of this effect is explained by the increase in EI as a result of the perfluoro-effect.

The influence of the substituents on the EI of the outer occupied molecular orbitals has been investigated for certain groups of compounds containing oxygen and sulphur of the type $X-C_6H_4-Y$, where X is a halogen or another group and Y is a group containing sulphur or oxygen.[93–95] For all the series of compounds, the stabilisation of the HOMO was greatest on substitution of X by fluorine.

With increase in the size of the molecule, the interpretation of the spectrum usually becomes much more complicated owing to the diffuseness of the spectrum and the difficulties in calculations for many-electron systems. However, in many instances the high symmetry of the molecules makes it possible to diminish these difficulties. An example is provided by a comparative study of the PE and vacuum UV absorption spectra of tetrathiofulvalene and related compounds, including tetrakis(trifluoromethyl)tetrathiofulvalene,[96]

where the use of a simple theoretical model and semiempirical calculations made it possible to determine fairly satisfactorily the sequence of orbitals in these compounds.

Ionisation potentials (IP) of fluorine-containing hydrocarbons determined by the EPS method.

Compound	IP, eV	Refs.
C_2F_2	11.18 ± 0.2 a	[58]
"	11.60 v	[9]
C_4F_2	10.05 ± 0.02 a	[58]
"	10.35 v	[9]
CF_4	15.56 ± 0.01 a	[97]
"	16.25 ± 0.04 v	[98]
C_2F_4	10.12 ± 0.01 a	[40]
"	10.56 ± 0.02 v	[36]
$CF_2=C=CF_2$	10.88 a	[5]
"	11.24 v	[50]
$CF_2=C=C=CF_2$	9.30 v	[50]
$CF_3C\equiv CC\equiv CF$	10.58 a	[9]
"	10.85 v	[9, 57]
C_2F_6	14.6 v	[25]
$CF_3CF=CF_2$*	10.60 ± 0.03 a	[40]
"	11.29 v	[43]
Cyclo-C_3F_6*	11.18 ± 0.03 a	[40]
$CF_2=CFCF=CF_2$	9.5 a	[53]
"	10.4 v	[53]
$CF_3C\equiv CCF_3$	12.35 ± 0.01 a	[60]
$CF_3C\equiv C-C\equiv CCF_3$	10.99 ± 0.01 a	[60]
Hexafluorobenzene	9,905 a	[9]
"	10.14 v	[68]
Hexafluorobicyclo[2.2.0]hexa-2,5-diene	10.4 v	[55]
"	10.38 ± 0.01	[56]
C_3F_8	13.38 v	[99]
cis-2-C_4F_8	11.46 v	[42]
trans-2-C_4F_8	11.55 v	[42]
Octafluorotoluene	9.9 ± 0.1 a	[69]
Octafluoronaphthalene	8.85 a	[100]
"	9.05 v	[100]
Octafluoroacenaphthylene	9.1 ± 0.1 v	[71]
Perfluoro-*p*-xylene	9.9 ± 0.1 a	[69]
Decafluoro-1,1-biphenyl	9.40 ± 0.02 a	[74]
"	9.80 v	[74]
Decafluoroanthracene	8.28 ± 0.05 a	[71]
Decafluorophenanthrene	8.75 ± 0.05 a	[71]
"	8.9 v	[71]
Decafluoropyrene	8.36 ± 0.05 a	[71]
$(CF_3)_2C=C(CF_3)_2$	12.61 v	[71]
$CF_2=CF(CF_2)_3CF_3$*	10.48 ± 0.02 a	[101]
$(CF_3)_2C=C=C(CF_3)_2$	12.28 v	[102]
C_2HF	11.26 ± 0.02 a	[58]
"	11.50 v	[9]
CH_3F	12.533 ± 0.006 a	[103]
"	13.038 ± 0.003 v	[103]
C_2H_3F*	10.363 ± 0.015 a	[104]
"	10.56 ± 0.02 v	[36]
C_2H_5F	12.43 v	[105]
$CH_2FC\equiv CH$	10.95 v	[62]
$CH_2=CHCH_2F$	10.11 a	[44]
"	10.38 ± 0.02 v	[45]
$(CH_3)_2CHF$*	11.05 ± 0.02 a	[106]
n-C_3H_7F	11.96 v	[23]
$CF\equiv CC\equiv CH$	10.10 ± 0.02 a	[58]
"	10.25 v	[58]
C_6H_5F*	9.200 ± 0.005 a	[40]
"	9.37 v	[24]
$C_6H_5CH_2F$**	9.12 ± 0.02 a	[107]
"	9.55 v	[108]
o-Fluorotoluene**	8.915 ± 0.01 a	[101, 107]
"	8.93 a	[65]
m-Fluorotoluene**	8.92 ± 0.01 a	[101, 107]
p-Fluorotoluene**	8.78 ± 0.01 a	[101, 107]
"	8.90 a	[65]
2-Fluoroadamantane	9.46 ± 0.05 a	[109]
"	9.85 v	[109]
o-Fluoronorbornadiene	8.66 ± 0.05 v	[73]
m-Fluoronorbornadiene	8.62 ± 0.05 v	[73]
2-Fluoro-1,1-biphenyl	8.20 ± 0.02 a	[74]
4-Fluoro-1,1-biphenyl	8.00 ± 0.02	[74]
11-Fluoro-1,6-methano[10]annulene	8.10 v	[110]
9-Fluoroanthracene	7.46 ± 0.03 v	[72]
2-Fluoroadamantane	9.86 v	[5]
"	9.46 ± 0.05 a	[5, 109]
CH_2F_2	12.72 a	[5, 17]
"	13.29 v	[5]
CD_2F_2	12.79 a	[17]
$CH_2=CF_2$	10.29 ± 0.01 a	[111]
"	10.69 ± 0.02 v	[36]
cis-CHF = CHF	10.23 ± 0.02 a	[37]
"	10.44 ± 0.02 v	[36]
trans-CHF = CHF	10.21 ± 0.02	[37]
"	10.38 ± 0.02 v	[36]
CH_3CHF_2	11.864 ± 0.029 a	[112]
"	12.8 v	[25]

Table (contd.).

Compound	IP, eV	Refs.
$CF_2=C=CH_2$	9.79 ± 0.03 a	[51]
1,2-Difluorobenzene**	9.30 a	[113]
"	9.60 ± 0.03 v	[114]
1,3-Difluorobenzene**	9.35 a	[113]
"	9.60 ± 0.03 v	[114]
1,4-Difluorobenzene**	9.18 a	[113]
"	9.4 v	[9]
$CH_3CF_2CH_3$*	11.42 ± 0.02	[106]
$C_6H_5CHF_2$	9.45 ± 0.02 a	[107]
11,11-Difluoro-1,6-methano[10]annulene	8.19 v	[110]
Difluoromethylenecyclohexane	8.84 a	[115]
2,2'-Difluoro-1,1'-biphenyl	8.35 ± 0.02 a	[74]
"	8.85 v	[5]
3,3'-Difluoro-1,1'-biphenyl	8.35 ± 0.02 a	[74]
"	8.70 v	[5]
4,4'-Difluoro-1,1'-biphenyl	8.00 ± 0.02	[74]
"	8.38 v	[5]
CHF_3*	14.19 ± 0.02 a	[116]
"	14.8 v	[9]
C_2HF_3	10.14 ± 0.02 a	[37]
"	10.54 ± 0.02 v	[36]
CH_3CF_3	13.8 v	[25]
$CF_3C\equiv CH$	11.96 a	[61]
"	12.1 v	[9]
1,2,3-Trifluorobenzene	9.7 v	[9]
1,2,4-Trifluorobenzene**	9.37 ± 0.02 a	[107, 117]
"	9.5 v	[9]
1,3,5-Trifluorobenzene	9.64 a	[37]
"	9.8 v	[9]
Trifluoromethylbenzene***	9.69 ± 0.03 a	[40]
"	9.90 v	[66]
1,3,5-Trifluoro-2,4,6-trimethylbenzene	8.76 ± 0.02 v	[69]
ααα-Trifluoromethylcyclohexane	10.46 ± 0.02	[101]
$CF_2=CHCH=CF_2$	8.98 a	[53]
"	9.38 v	[53]
1,2,3,4-Tetrafluorobenzene	9.56 a	[64]
"	9.78 v	[37]
1,2,3,5-Tetrafluorobenzene	9.56 a	[64]
"	9.6 v	[9]
p-Fluoro-ααα-trifluorotoluene	9.69 ± 0.02 a	[107]
1,2,4,5-Tetrafluorobenzene	9.36 a	[64]
"	9.5 v	[9]
1,2,4,5-Tetrafluoro-2-methylbenzene	9.16 ± 0.02 a	[69]
Pentafluorobenzene**	9.82 a	[118]
"	9.64 a	[64]
"	9.90 v	[68]
Pentafluoromethylbenzene	9.4 ± 0.1 a	[69]
"	9.81 v	[68]
$C_6F_5CH=CH_2$	9.18 ± 0.02	[119]
2,2,3,3,8,8,9,9-Octafluorotricyclo[8.2.2.2]-hexadeca-4,6,10,12,13,15-hexaene	8.90	[120]
CF_3Cl*	12.39 a	[121]
"	12.60 ± 0.02 a	[116]
CF_3Cl*	13.08 ± 0.01 v	[27]
C_2F_3Cl**	9.76 a	[47]
"	9.82 a	[63]
"	10.24 ± 0.01 v	[49]
$CF_3C\equiv CCl$	11.14 ± 0.02 a	[61]
"	11.29 v	[61]
CF_3CF_2Cl	12.96 v	[26]
C_6F_5Cl	9.72 ± 0.02 a	[8]
"	9.94	[68]
CF_2Cl_2*	11.75 a	[122]
"	11.87 ± 0.02 a	[116]
"	12.24 v	[27]
$CF_2=CCl_2$	9.62 a	[63]
"**	9.69 ± 0.01 a	[123]
"	9.84 v	[137]
CF_2Cl-CF_2Cl	12.47 v	[32]
"	12.85 v	[26]
$CF_3CCl=CClCF_3$*	10.36 ± 0.01 a	[101]
"	10.55 ± 0.03 v	[43]
$CFCl_3$	11.46 ± 0.02 a	[116]
"	11.76 ± 0.01 v	[27]
CF_3CCl_3*	11.78 ± 0.03 a	[101]
$CFCl_2CF_2Cl$	12.05 v	[26]
1,3,5-Trichloro-2,4,6-trifluorobenzene	9.48 ± 0.02 a	[8]
"	9.68 ± 0.02 v	[8]
CH_2FCl	11.74	[28]
"	11.9 v	[5]
$CH_2=CFCl$**	9.97 a	[47]
1-Chloro-2-fluorobenzene	9.18 ± 0.02 a	[8]
"	9.37 ± 0.02 v	[8]
1-Chloro-3-fluorobenzene	9.22 ± 0.02 a	[8]
"	9.40 ± 0.02 v	[8]
1-Chloro-4-fluorobenzene	9.24 ± 0.02 v	[8]
"	9.08 ± 0.02 a	[8]
CHF_2Cl*	12.28 ± 0.02 a	[116]
"	12.56 ± 0.05 v	[12]
trans-CHF = CFCl	9.83 ± 0.02 a	[48]
cis-CHF = CFCl	9.86 ± 0.02 a	[48]
$CF_2=CHCl$**	9.76 a	[47]
"	9.84 a	[49]
"	10.04 ± 0.01 v	[49]
$CH_2=CFCl$	9.97	[47]
cis-CHCl = CHF	9.87 ± 0.01	[48, 101]
trans-CHCl = CHF	9.87 ± 0.07	[48, 101]
CH_3CF_2Cl	11.93 ± 0.01 a	[101]
"	12.50 v	[26]

Table (contd.).

Compound	IP, eV	Refs.
1-Chloro-2,4-difluorobenzene	9.17 ± 0.02 a	[8]
"	9.35 ± 0.05 v	[8]
1-Chloro-3,5-difluorobenzene	9.40 ± 0.02 a	[8]
"	9.66 ± 0.02 v	[8]
1-Chloro-2,6-difluorobenzene	9.37 ± 0.02 a	[8]
"	9.53 ± 0.02 v	[8]
1-Chloro-2,5-difluorobenzene	9.19 ± 0.02 a	[8]
"	9.40 ± 0.05 v	[8]
1-Chloro-3,4-difluorobenzene	9.24 ± 0.02 a	[8]
"	9.40 ± 0.05 v	[8]
1-Chloro-2,3,4-trifluorobenzene	9.42 ± 0.02 a	[8]
"	9.59 ± 0.02 v	[8]
1-Chloro-2,4,5-trifluorobenzene	9.27 ± 0.02 a	[8]
"	9.40 ± 0.05 a	[8]
1-Chloro-2,3,6-trifluorobenzene	9.39 ± 0.02 a	[8]
"	9.60 ± 0.02 v	[8]
1-Chloro-2-trifluoromethylbenzene	9.47 a	[7]
1-Chloro-3-trifluoromethylbenzene	9.50 a	[7]
1-Chloro-4-trifluoromethylbenzene	9.56 a	[7]
"	9.80 v	[66]
1-Chloro-2,3,5,6-tetrafluorobenzene	9.58 ± 0.02	[8]
"	10.05 ± 0.05 v	[8]
$CF_3CF_2CF_2CH_2Cl$	10.84 ± 0.02 a	[101]
$CHFCl_2$*	11.75 ± 0.02 a	[116]
"	11.92 ± 0.05 v	[12]
1,2-Dichloro-3-fluorobenzene	9.29 ± 0.02 v	[8]
1,2-Dichloro-4-fluorobenzene	9.16 ± 0.02 a	[8]
"	9.31 ± 0.02 v	[8]
1,3-Dichloro-2-fluorobenzene	9.32 ± 0.02 a	[8]
"	9.32 ± 0.02 v	[8]
1,5-Dichloro-2-fluorobenzene	9.39 ± 0.02 v	[8]
1,4-Dichloro-3-fluorobenzene	9.09 ± 0.02 a	[8]
"	9.28 ± 0.02 v	[8]
2,4-Dichloro-1-fluorobenzene	9.12 ± 0.02 a	[8]
"	9.31 ± 0.02 v	[8]
1,2-Dichloro-3,4-difluorobenzene	9.33 ± 0.02 a	[8]
"	9.50 ± 0.02 v	[8]
1,3-Dichloro-2,4-difluorobenzene	9.27 ± 0.02 a	[8]
"	9.50 ± 0.05 v	[8]
1,3-Dichloro-2,5-difluorobenzene	9.32 ± 0.02 a	[8]
"	9.55 ± 0.05 v	[8]
1,4-Dichloro-2,5-difluorobenzene	9.17 ± 0.02 a	[8]
"	9.37 ± 0.02 v	[8]
2,3-Dichloro-1,4-difluorobenzene	9.32 ± 0.02 a	[8]
"	9.50 ± 0.02 v	[8]
$CF_2ClCHFCl$	12.00 v	[26]
2,4-Dichloro-1,3,5-trifluorobenzene	9.37 ± 0.02 a	[8]
"	9.57 ± 0.02 v	[8]
1,2,3-Trichloro-6-fluorobenzene	9.20 ± 0.02 a	[8]
"	9.37 ± 0.02 v	[8]
1,2,5-Trichloro-4-fluorobenzene	9.16 ± 0.02 a	[8]
"	9.31 ± 0.02 v	[8]
1,3,5-Trichloro-2-fluorobenzene	9.23 ± 0.02 a	[8]
"	9.50 ± 0.02 v	[8]
2,3,5-Trichloro-1-fluorobenzene	9.24 ± 0.02 a	[8]
"	9.40 ± 0.02 v	[8]
1,2,3,4-Tetrachloro-6-fluorobenzene	9.20 ± 0.02 a	[8]
"	9.34 ± 0.02 v	[8]
2,3,5,6-Tetrachloro-1-fluorobenzene	9.19 ± 0.02 a	[8]
"	9.37 ± 0.02 v	[8]
"	9.34 ± 0.02 v	[8]
CF_3Br*	11.76 ± 0.02 a	[116]
"	12.12 ± 0.02 v	[29]
C_2F_3Br	9.67	[63]
"	10.11 ± 0.03 v	[43]
$CF_3C \equiv CBr$	10.81 ± 0.02 a	[61]
C_6F_5Br	9.67 ± 0.02 a	[8]
"	9.8 v	[76]
CF_2Br_2*	10.98 ± 0.02 a	[116]
"	11.17 ± 0.05	[13]
CF_2BrCF_2Br	11.44 ± 0.01 v	[32]
1,2-Dibromo-3,4,5,6-tetrafluorobenzene	9.50 ± 0.02 v	[8]
1,3-Dibromo-2,4,5,6-tetrafluorobenzene	9.45 ± 0.02 v	[8]
1,4-Dibromo-2,3,5,6-tetrafluorobenzene	9.42 ± 0.02 v	[8]
$CFBr_3$	10.67 ± 0.01 a	[101]
"	10.70 ± 0.05	[13]
1,3,5-Tribromo-2,4,6-trifluorobenzene	9.33 ± 0.02 a	[8]
cis-CHF = CHBr	9.75 v	[43]
CH_2FCH_2Br (*gauche*)	10.57 v	[33]
CH_2FCH_2Br (*trans*)	10.77 v	[33]
$CH_2FCH_2CH_2Br$	10.38 v	[33]
CH_3CHFCH_2Br (*gauche*)	10.44 v	[33]
CH_3CHFCH_2Br (*trans*)	10.61 v	[33]
$CH_3CH_2CHFCH_2Br$ (*gauche*)	10.32 v	[33]
$CH_3CH_2CHFCH_2Br$ (*trans*)	10.49 v	[33]
$(CH_3)_2CFCH_2Br$ (*gauche*)	10.28 v	[33]
$(CH_3)_2CFCH_2Br$ (*trans*)	10.42 v	[33]
$CH_3CHFCHBrCH_3$ (*erythro, gauche*)	10.19 v	[33]
$CH_3CHFCHBrCH_3$ (*trans*)	10.34 v	[33]
$CH_3CHFCHBrCH_3$ (*threo, gauche*)	10.21 v	[33]
$CH_3CHFCHBrCH_3$ (*trans*)	10.37 v	[33]
1-Bromo-2-fluoro-*cis*-cyclopentene	10.10 ± 0.02	[124]
1-Bromo-2-fluoro-*trans*-cyclopentene	10.25 ± 0.02	[124]
1-Bromo-2-fluorobenzene	9.11 ± 0.02 a	[8]
"	9.14 v	[7]
1-Bromo-2-fluorobenzene	9.11 ± 0.02 a	[8]
"	9.25 v	[7]
1-Bromo-4-fluorobenzene	9.02 ± 0.02 a	[8]
cis-1-Bromo-2-fluorocyclohexane	10.04 ± 0.02 v	[124]

Table (contd.).

Compound	IP, eV	Refs.
trans-1-Bromo-2-fluorocyclohexane	10.18 ± 0.02 v	[124]
"	10.05 v	[33]
4-Bromo-4′-fluoro-1,1′-biphenyl	8.10 ± 0.02 a	[74]
"	8.40 v	[5]
1-Bromo-2,4-difluorobenzene	9.16 ± 0.02 a	[8]
1-Bromo-2,5-difluorobenzene	9.18 ± 0.02 a	[8]
"	9.38 ± 0.02 v	[8]
1-Bromo-3,4-difluorobenzene	9.19 ± 0.02 a	[8]
"	9.37 ± 0.02 v	[8]
1-Bromo-2,4,5-trifluorobenzene	9.25 ± 0.02 a	[8]
"	9.42 ± 0.02 v	[8]
1-Bromo-2,4,6-trifluorobenzene	9.34 ± 0.02 v	[8]
1-Bromo-2-trifluoromethylbenzene	9.38 a	[7]
1-Bromo-3-trifluoromethylbenzene	9.36 a	[7]
1-Bromo-4-trifluoromethylbenzene	9.48 a	[7]
"	9.55 v	[66]
1-Bromo-2,3,4,6-tetrafluorobenzene	9.50 ± 0.02 a	[8]
"	9.67 ± 0.02 v	[8]
1-Bromo-2,3,4,5-tetrafluorobenzene	9.46 ± 0.02 a	[8]
"	9.55 ± 0.02 v	[8]
1-Bromo-2,3,5,6-tetrafluorobenzene	9.45 ± 0.02 v	[8]
"	9.85 ± 0.05 v	[8]
2,4-Dibromo-1-fluorobenzene	9.05 ± 0.02 a	[8]
"	9.18 ± 0.02 v	[8]
CF_2BrCH_2Br	10.83 ± 0.01 a	[101]
"	10.86 ± 0.01 v	[32]
$CHFBrCH_2Br$	10.75 ± 0.02 a	[101]
1,2-Dibromo-4,5-difluorobenzene	9.13 ± 0.02 a	[8]
"	9.28 ± 0.02 v	[8]
1,4-Dibromo-2,5-difluorobenzene	9.09 ± 0.02 v	[8]
CF_2BrCl*	11.21 ± 0.02 a	[116]
"	11.51 ± 0.05 v	[13]
CF_3I	10.32 ± 0.03 a	[125]
" *	10.38 ± 0.02 a	[116]
"	10.45 ± 0.05 v	[15]
$CF_3C \equiv CI$	10.17 ± 0.02 a	[61]
C_2F_5I	10.65 v	[34]
C_6F_5I	9.54 v	[68]
"	9.84 v	[34]
CF_2ICF_2I (*trans*)	10.11 ± 0.01 v	[32]
CF_3CF_2I (*gauche*)	10.21 ± 0.01 v	[32]
CF_3CH_2I**	9.998 a	[126]
"	9.99 v	[34]
$CF_3(CF_2)_2CH_2I$	9.96 ± 0.02 a	[101]
FCN	13.34 ± 0.02 a	[77]
"	13.65 v	[77]
CF_3CN	13.86 a	[127]
"	14.3 v	[127]
$CF \equiv CCN$	11.51 ± 0.02 a	[15]
3,3-Difluorodiazirine	11.2 ± 0.05	[100]
$CF_3C \equiv CCN$	12.00 ± 0.002 a	[15]
2,4,6-Trifluoro-1,3,5-triazine	11.5 a	[100]
"	12.3 v	[127]
Tetrafluoropyrazine	10.37 v	[128]
Tetrafluoropyridazine	11.15 v	[128]
Tetrafluoropyrimidine	10.82 v	[128]
1,2-Dicyano-3,4,5,6-tetrafluorobenzene	10.60 v	[81]
1,4-Dicyano-2,3,5,6-tetrafluorobenzene	10.65 v	[81]
Pentafluoropyridine	10.08 a	[127]
"	10.3 v	[127]
Pentafluorobenzonitrile	10.1 a	[69]
"	10.45 v	[81]
cis-$CF_3N = NCF_3$	10.5 a	[38]
trans-1,2-Bis(trifluoromethyl)fumaronitrile	11.85 ± 0.05 v	[129]
Hexafluorocinnoline	9.66 v	[130]
2,3,4,5,6,7-Hexafluoro-1,8-naphthyridine	10.01 v	[83]
1,3,4,5,6,8-Hexafluoro-2,7-naphthyridine	9.50 v	[83]
Hexafluorophthalazine	9.90 v	[130]
Hexafluoroquinazoline	9.43 v	[130]
Hexafluoroquinoxaline	9.65 v	[130]
Heptafluoroisoquinoline	9.29 v	[131]
Heptafluoroquinoline	9.51 v	[131]
$(C_2F_5)_3N$*	11.7 a	[56]
CH_2F-CN	12.67 v	[62]
2-Fluoroaniline*	7.95 ± 0.02 a	[107]
"	8.18 v	[132]
3-Fluoroaniline*	7.90 ± 0.02 a	[107]
"	8.32 v	[132]
4-Fluoroaniline*	7.82 ± 0.02 a	[107]
"	8.18 v	[132]
2-Fluorobenzonitrile	9.78 v	[133]
3-Fluorobenzonitrile	9.79 v	[133]
4-Fluorobenzonitrile	9.74 v	[133]
2-Fluoropyrimidine	10.5 a	[128]
4-Fluoroquinazoline	9.22 v	[83]
2-Fluoroquinazoline	9.15 v	[83]
2,3-Difluoropyrazine	10.35 v	[128]
2,6-Difluoropyrazine	10.30 v	[128]
3,6-Difluoropyridazine	10.17 v	[128]
2,4-Difluoropyrimidine	10.65 v	[128]
4,6-Difluoropyrimidine	10.95 v	[128]
2,7-Difluoropyrimidine-1,8-naphthyridine	9.26 v	[83]
2,4-Difluoroquinazoline	9.30 v	[83]
2,3-Difluoroquinoxaline	9.30 v	[130]
2,6-Difluorophenyliminoimidazoline	8.12 v	[134]
4-(Trifluoromethyl)pyridine	10.1 v	[135]
2,4,6-Trifluoropyrimidine	10.93 v	[128]
4,5,6,7-Tetrafluoro-1*H*-indole	8.30 ± 0.015 v	[82]
1,3,6,8-Tetrafluoro-2,7-naphthyridine	9.55 v	[83]

Table (contd.).

Compound	IP, eV	Refs.
5,6,7,8-Tetrafluoroquinoxaline	9.50 v	[130]
2,3,4,5,6-Pentafluoroaniline	8.40 ± 0.02 a	[136]
2-(Pentafluorophenylimino)imidazoline	8.60 v	[134]
$(CF_3)_2C=NH$	11.8 v	[79]
$(CH_3)_2NC(CF_3)=C(CF_3)H$	8.22 a	[63]
$C_6H_5N(CF_3)_2$	10.0 ± 0.03 a	[66]
F_2CO	13.04 a	[137]
"	13.6 v	[138]
$(COF)_2$	12.20 a	[85]
"	12.58 v	[139]
CF_3OF	12.20 a	[5]
"	13.64 v	[5]
2,3,5,6-Tetrafluorocyclohexa-2,5-diene-1,4-dione	10.96 ± 0.05 v	[88]
$(CF_3)_2CO$	11.44 a	[38]
"	12.09 ± 0.02 v	[86]
$(CF_3)_2CCO$	10.67 a	[102]
Tetrafluoro-*p*-benzoquinone	10.7 a	[127]
Difluoromaleic anhydride	11.45 a	[127]
"	11.7 v	[127]
HFCO	12.37 ± 0.02	[84]
"	12.55 v	[5]
CH_3CFO	11.51 ± 0.02 a	[105]
CH_3COCH_2F	10.20 ± 0.02 v	[86]
Fluoromethyloxiran	10.78 v	[140]
$CH_2FCH_2OCH_3$	10.18 v	[105]
2-Fluorophenol	8.66 ± 0.01 a	[101]
"	8.95 v	[141]
"	8.97 ± 0.02 v	[142]
3-Fluorophenol	8.99 v	[141]
"	9.05 ± 0.02	[142]
4-Fluorophenol	8.77 v	[141]
"	8.79 ± 0.02 v	[142]
p-$CH_2FC_6H_4COOCH_3$*	9.09 a	[143]
C_6H_5COF*	9.78 a	[144]
cis-*m*-Fluoroanisole***	8.4134 a	[145]
trans-*m*-Fluoroanisole***	8.4673 a	[145]
2,4-Difluorophenol	8.98 ± 0.02 v	[142]
2,5-Difluorophenol	9.10 ± 0.02 v	[142]
3,5-Difluorophenol	9.04 ± 0.02 v	[142]
CF_3CH_2OH	11.74 v	[5]
CH_3COCF_3	10.67 ± 0.01 a	[146]
"	11.00 ± 0.02 v	[86]
2,3,4-Trifluorophenol	9.19 ± 0.02 v	[142]
2,4,5-Trifluorophenol	9.10 ± 0.02 v	[142]
CF_3COOH	11.46 a	[147]
"	12.00 ± 0.03 v	[148]
"	12.06 v	[149]
CF_3COOCH_3	11.31 a	[147]
"	11.6 v	[147]
$HCOOCH_2CF_3$	11.31 a	[147]
$C_2H_5OCOCF_3$*	11.07 ± 0.03 a	[150]
$CF_3COOC_2H_5$	11.6 v	[147]
$CH_3COOCH_2CF_3$	10.84 a	[147]
$CF_3COCH_2COCH_3$	9.72 a	[5]
"	9.92 ± 0.07 v	[151]
$C_6H_5COCF_3$*	9.72 a	[144]
"	9.92 ± 0.07 v	[151]
$C_6H_5COCF_3$*	9.72 a	[144]
$(CH_3)_3CCOCH_2COCF_3$	9.87 ± 0.07 v	[151]
iso-C_3H_7COOH-CF_3COOH	10.7 v	[5]
p-$CF_3C_6H_4COOCH_3$*	9.55 a	[143]
m-$CF_3C_6H_4COOCH_3$*	9.60 a	[143]
p-$CF_3COC_6H_4COOCH_3$*	9.64 a	[143]
m-$CF_3CH_2C_6H_4COOCH_3$	9.26 a	[143]
$(CHF_2)_2CO$	11.33 ± 0.02 v	[36]
2,3,5,6-Tetrafluorophenol	9.40 ± 0.02 v	[142]
$C_2F_5CH_2OH$	11.67 v	[5]
C_6F_5OH	9.20 ± 0.02 a	[152]
"	9.37 ± 0.02 a	[102]
$C_6F_5OCH_3$	9.10 ± 0.02 a	[152]
$CF_3CH(OH)CF_3$	12.23 v	[153]
Hexafluorocyclobutanone	11.2 a	[154]
$CF_3CF_2CF_2OCHFCF_3$	12.6 a	[87]
p-$C_2F_5C_6H_4COOCH_3$*	9.66 a	[143]
m-$C_2F_5C_6H_4COOCH_3$*	9.67 a	[143]
$(C_2H_5O)_2C=C=C(CF_3)_2$	8.93 a	[102]
CF_3COOCH_3	11.31 a	[147]
"	11.6 v	[147]
$HCOOCH_2CF_3$	11.31 a	[147]
$C_2H_5OCOCF_3$*	11.07 ± 0.03 a	[150]
$CF_3COOC_2H_5$	11.6 v	[147]
$CH_3COOCH_2CF_3$	10.84 a	[147]
$CF_3COCH_2COCH_3$	9.72 a	[6]
"	9.92 ± 0.07 v	[151]
$C_6H_5COCF_3$*	9.72 a	[144]
"	9.92 ± 0.07 v	[151]
$C_6H_5COCF_3$*	9.72 a	[144]
$(CH_3)_3COOCH_2COCF_3$	9.87 ± 0.07 v	[151]
iso-C_3H_7COO-CF_3COOH	10.7 v	[5]
p-$CF_3C_6H_4COOCH_3$*	9.55 a	[143]
m-$CF_3C_6H_4COOCH_3$*	9.60 a	[143]
p-$CF_3COC_6H_4COOCH_3$*	9.64 a	[143]
m-$CF_3CH_2C_6H_4COOCH_3$	9.26 a	[143]
$(CHF_2)_2CO$	11.33 ± 0.02 v	[86]
2,3,5,6-Tetrafluorophenol	9.40 ± 0.02 v	[142]
$C_2F_5CH_2OH$	11.67 v	[5]
C_6F_5OH	9.20 ± 0.02 a	[152]
"	9.37 ± 0.02 a	[102]

Table (contd.).

Compound	IP, eV	Refs.
$C_6F_5OCH_3$	9.10 ± 0.02 a	[152]
$CF_3CH(OH)CF_3$	12.23 v	[153]
Hexfluorocyclobutanone	11.2 a	[154]
$CF_3CF_2CF_2OCHFCF_3$	12.6 a	[87]
p-$C_2F_5C_6H_4COOCH_3$*	9.66 a	[143]
m-$C_2F_5C_6H_4COOCH_3$*	9.67 a	[143]
$(C_2H_5)_2C=C=C(CF_3)_2$*	8.93 a	[102]
p-$CF_3CF_2CF_2C_6H_4COOCH_3$*	9.59 a	[143]
m-$CF_3CF_2CF_2C_6H_4COOCH_3$*	9.63 a	[143]
p-$(CF_3)_2CFC_6H_4COOCH_3$*	9.60 a	[143]
$CF_2H(CF_2)_3CH_2OC(O)CH_3$*	10.61 ± 0.03 a	[150]
p-$(CF_3)_3CC_6H_4COOCH_3$*	9.54 a	[143]
m-$(CF_3)_3CC_6H_4COOCH_3$*	9.51 a	[143]
p-$(CF_3)_3CCH_2C_6H_4COOCH_3$*	9.20 a	[143]
m-$(CF_3)_3CCH_2C_6H_4COOCH_3$*	9.20 a	[143]
$F[CF(CF_3)CF_2O]_2CHFCF_3$	12.78 v	[87]
$F[CF(CF_3)CF_2O]_3CHFCF_3$	12.96 v	[87]
$F[CF(CF_3)CF_2O]_4CHFCF_3$	13.47 v	[87]
$CClF_2COCF_3$	11.71 ± 0.02 v	[86]
$(CF_2Cl)_2CO$	10.71 v	[146]
$CCl_2FCOCClF_2$	11.21 v	[86]
CF_3COCCl_3	10.80 ± 0.01 a	[146]
"	11.24 v	[86]
$CClF_2COCHF_2$	11.33 ± 0.02 v	[86]
$CH_2BrCOCF_3$	10.92 ± 0.02 v	[86]
CF_3NO	10.4 ± 0.01 a	[155]
"	11.6 ± 0.05 v	[156]
$(CF_3)_2NO$	10.7 ± 0.1 v	[157]
trans-C_4F_9NO	8.55 ± 0.01 a	[155]
4-Fluorobenzamide	9.50 v	[158]
o-Fluoronitrobenzene	9.86 v	[159]
m-Fluoronitrobenzene	9.88 a	[159]
"	10.08 v	[159]
p-Fluoronitrobenzene	9.90 a	[159]
"	10.06 v	[159]
7-Fluoro-3,10-dimethylbenzopteridine-2,4-(3*H*, 10*H*)-dione	8.51 v	[160]
CF_3CONH_2	10.8 a	[127]
"	11.3 v	[127]
4-(Trifluoromethyl)pyridine 1-oxide	8.90 v	[135]
2,2,2-Trifluoro-*N*-phenylacetamide	8.93 ± 0.05 v	[161]
2,2,2-Trifluoro-*N*-(2-methylphenyl)acetamide	8.84 ± 0.05 v	[161]
2,2,2-Trifluoro-*N*-(3-methylphenyl)acetamide	8.73 ± 0.05 v	[161]
2,2,2-Trifluoro-*N*-(4-methylphenyl)acetamide	8.61 ± 0.05 v	[161]
2,2,2-Trifluoro-*N*-(2,3-dimethylphenyl)acetamide	8.62 ± 0.05 v	[161]
2,2,2-Trifluoro-*N*-(3,4-dimethylphenyl)acetamide	8.51 ± 0.05 v	[161]
2,2,2-Trifluoro-*N*-(2,4-dimethylphenyl)acetamide	8.56 ± 0.05 v	[161]
2,2,2-Trifluoro-*N*-(3,5-dimethylphenyl)acetamide	8.59 ± 0.05 v	[161]
2,2,2-Trifluoro-*N*-(2,5-dimethylphenyl)acetamide	8.70 ± 0.05 v	[161]
2,2,2-Trifluoro-*N*-(2,6-dimethylphenyl)acetamide	8.99 ± 0.05 v	[161]
5-Trifluoromethyluracil	10.07 v	[162]
$F_2C=S$	10.45 ± 0.01	[163]
"	10.64 v	[164]
CF_3SF_3	12.4 v	[91]
CF_3SCF_3	11.35 v	[91]
$(CF_3)_2C=C=S$	9.96 a	[102]
$(CF_3)_2SF_2$	12.1 v	[91]
$(C_6F_5)_2S$	9.34 v	[92]
$CF_3SC(F)=S$	10.12 v	[90]
$F_3SCF_2SF_3$	12.1 v	[91]
$(CF_3)_2S_3$	10.16 v	[5]
$(CF_3S)_2C=S$	9.25 v	[90]
$(CF_3)_2S_4$	9.75 v	[5]
$C_6S_4(CF_3)_4$	7.95 v	[165]
Tetrakis(trifluoromethyl)tetrathiofulvalene	7.95 a	[96]
C_6F_5SH	9.50 v	[92]
$CH_2=SF_4$	10.65 v	[166]
$C_6F_5SCH_3$	9.16 v	[92]
5-*p*-Fluorophenyl-1,2-dithiole-3-thione	8.14 v	[167]
FClCS	10.20 v	[164]
C_6F_5SCl	9.73 v	[92]
$S=C(Cl)SCF_3$	9.57 v	[165]
$(CH_3)SO_2(F)$	12.53 v	[168]
"	12.61 v	[169]
$FC_6H_4CH=CHSO_2CH_3$	9.05	[169]
11,11-Difluoro-1,6-methano[10]annulene-2-sulphonyl chloride	8.90 v	[110]
10-[3(4-Methyl-1-piperazinyl)propyl]-2-(trifluoromethyl)-10*H*-phenylthiazine	7.31 ± 0.08 v	

Notation. Ionisation potentials: a = adiabatic, v = vertical.

*Photoionisation mass spectrometry.

**Spectroscopic ionisation method.

***Multiphoton ionisation.

The first adiabatic and vertical ionisation energies of all the fluorine-compounds in the classes dealt with in the review which have been investigated up to 1985 are presented in the Table. As a rule, one most reliable value of the ionisation energy is included for each

molecule. The error in the ionisation energy is quoted only when it is given in the original communication. In the remaining cases, it can be estimated as 0.1 eV for values quoted with a single figure after the decimal point and 0.05 eV for those quoted with two figures after the decimal point. The compounds are listed in the Table in order of increasing numbers of the S, O, N, I, Br, Cl, F, H and C atoms (starting with their absence).

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Thus chlorination of organic compounds increases the ionisation energies of almost all the orbitals. This effect is particularly large for perfluorohydrocarbons and can be used for the specific synthesis of compounds with high ionisation potentials.

The observed regularities in the variation of the ionisation energies of the compounds on replacement of all the hydrogen atoms by fluorine (the perfluoro-effect) provide an effective method for the recognition of the character of the MO in certain classes of compounds, despite its limited applicability. Thus the replacement of hydrogen by fluorine in a planar molecule has a much greater stabilising effect on σ MO than on π MO. This effect is most pronounced for non-aromatic hydrocarbons whose fluorination shifts the π MO by 0–0.5 eV and the σ MO by 2–3 eV. For aromatic compounds, the shift of the π orbitals can be somewhat greater. Analysis of a large number of PE spectra demonstrated that detailed analysis of the electronic mechanism which leads ultimately to the perfluoro-effect is fairly complex. This is because, when hydrogen is replaced by fluorine, two competing influences are observed: the greater electronegativity of the fluorine atoms, leading mainly to the polarisation of the σ-skeleton of the molecule, and the repulsive interaction of the unshared electron pairs of fluorine with the π-system to which they are linked. In studying the influence of the perfluoro-effect, it is essential to take into account the molecular symmetry.

The PE spectra of organofluorine compounds differ greatly from the spectra of other halogen-substituted compounds. This is associated with the following properties of the fluorine atom, which distinguish it among the halogens. Firstly, the C–F bonds are appreciably shorter than the C–X bonds, where X = Cl, Br, or I. If the sum of the covalent atomic radii is used to estimate the length of these bonds, then 1.4, 1.7, 1.9, and 2.1 Å are obtained for F, Cl, Br, and I respectively. Secondly, the 2*p* AO of fluorine is smaller (less diffuse) than the AO of the valence *p* electrons of the remaining halogens. Such properties lead to an effective interaction of the AO of fluorine with the MO of the C–C and C–X bonds which have the correct symmetry and hence to an appreciable delocalisation of the unshared electron pairs of fluorine. Therefore the PE spectra of organofluorine compounds do not contain the narrow bands characteristic of the unshared electron pairs of the other halogens. In many instances, there is probably no point at all in considering the unshared electron pairs of fluorine. The differentiation of the corresponding bands in the PE spectrum is a very complex task, especially if account is taken also of the small spin–orbital splitting of these bands. For the other halogens, the spin–orbital splitting is manifested reliably in the spectra and is a satisfactory diagnostic feature for the identification of the bands corresponding to the removal of the electrons of the unshared pairs.

Yet another important difference between the PE spectra of organofluorine compounds and those of other organic substances is the lower frequencies of the corresponding vibrations of the ions when hydrogen atoms are replaced by fluorine. Thus the energies of the vibrational quanta for the stretching vibrations of the C–H and C–F bonds are approximately 3000 and 1300 cm^{-1} respectively. Such a marked change in frequency can alter significantly the shape of the individual bands in the PE spectra, especially when the vibrational structure is resolved.

In comparing the ionisation energies obtained from the PE spectra with theoretical calculations, preference should be given to many-body calculations of ionisation energies. Semiempirical calculations can in certain cases yield appreciably different arrangement of orbitals, especially for different isomers.

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