Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

High-Energy Spectroscopic Studies of the Electronic Structures of Organic Systems Formed from Carbon and Fluorine by UPS, Vacuum-UV Optical Spectroscopy, and NEXAFS: Poly(hexafluoro-1,3-butadiene) $[C(CF_3) = C(CF_3)]_n$, Fluorinated Graphites (CF, C_2F, and C_6F), Perfluoroalkanes n-C_nF_{2n+2}, Poly(tetrafluoroethylene) $(CF_2)_n$, and Fluorinated Fullerenes ($C_{60}F_x$ and $C_{70}F_x$)

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Version of record first published: 24 Sep 2006

To cite this article: Kazuhiko Seki, Ryuichi Mitsumoto, Eisuke Itoc, Tohru Araki, Yoko Sakurai, Daisuke Yoshimura, Hisao Ishii, Yukio Ouchi, Takayuki Miyamae, Tadashi Narita, Shin Nishimura, Yasutaka Takata, Toshihiko Yokoyama, Toshiaki Ohta, Shigeaki Suganuma, Fujio Okino & Hidekazu Touhara (2001): High-Energy Spectroscopic Studies of the Electronic Structures of Organic Systems Formed from Carbon and Fluorine by UPS, Vacuum-UV Optical Spectroscopy, and NEXAFS: Poly(hexafluoro-1,3-butadiene) $[C(CF_3) = C(CF_3)]_n$, Fluorinated Graphites (CF, C_2F, and C_6F), Perfluoroalkanes n-C_nF_{2n+2}, Poly(tetrafluoroethylene) $(CF_2)_n$, and Fluorinated Fullerenes ($C_{60}F_x$ and $C_{70}F_x$), Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 355:1, 247-274

Mol. Cryst. Liq. Cryst., Vol. 355, pp. 247-274
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(Received February 28, 2000; In final form April 03, 2000)

Various systems formed by carbon and fluorine were studied by UV photoelectron spectroscopy (UPS), vacuum-ultraviolet (VUV) optical spectroscopy, and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy. New data were measured for poly(hexafluoro-1,3-butadiene) (PHFBD), which is actually poly(hexafluoro-2-butyne), and fluorinated graphites CF, C_2F, and C_6F. These data were analyzed together with reported data for *n*-$C_{24}F_{50}$, poly(tetrafluoroethylene) (PTFE), and fluoninated fullerenes $C_{60}F_x$ and $C_{70}F_x$. The electronic structures deduced from UPS, VUV optical spectra, and MO calculations could be understood in terms of degree of σ delocalization, inductive effects of F and CF_3 groups, and the molecular conformation with possible steric hindrance. The ionization threshold energy of PHFBD (10.3eV) is the largest one for unsaturated systems. The well polarized NEXAFS spectra of CF and C_2F were analyzed by the comparison with related compounds. The NEXAFS results of C_6F showed that the F atoms are neither in molecular form nor covalently bonded to carbon atoms.

Keywords: fluorine; UPS; NEXAFS; vacuum-UV spectra; electronic structure; poly(hexafluoro-1 3-butadiene) PTFE; $C_{60}F_x$ $C_{70}F_x$ CF; C_2F; C_6F

1. INTRODUCTION

Fluorine is an element at the right-top corner of the periodic table, with the largest electronegativity. This gives fluorine compounds unique properties as exemplified by those of poly(tetrafluoroethylene) (PTFE) $(CF_2)_n$, known by the trade name Teflon, such as the high chemical durability, good electrical insulation, low dielectric constant, and low surface tension. Many of such properties should be related to the nature of fluorine atom, such as the large electron-withdrawing ability as a substituent. From the combination of the two elements C and F, also several other classes of compounds can be formed. They belong to various forms of (a) 1-dimensional polymers, (b) 2-dimensional layer compounds, and (c) spherical molecules with 2-dimensionally extended carbon networks. In (a), we can list perfluoroalkanes *n*-$CF_3(CF_2)_{m-2}CF_3$ (**Fig. 1(a)**), their long-chain limit PTFE (**Fig. 1(b)**), and poly(hexafluoro-1,3-butadiene) (PHFBD), which is actually known to have the structure of poly(hexafluoro-2-butyne) $[C(CF_3)=C(CF_3)]_n$ (PHFBY) [1–3] (**Fig. 1(c)**). They have low-dielectric constants, and this makes these materials also attractive for the future applications to insulating materials in electronic devices.

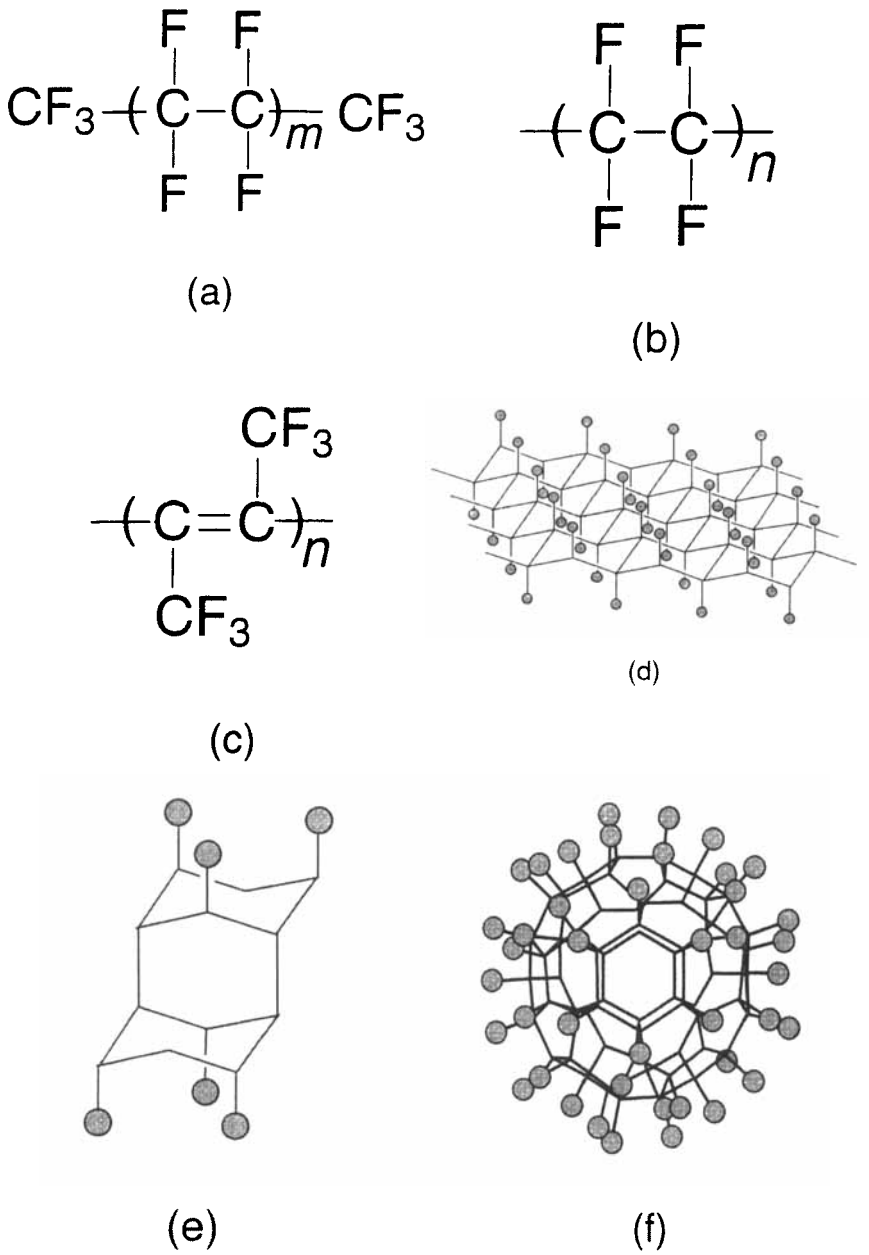

FIGURE 1 The chemical structures of the systems studied in this work. (a) perfluorotetracosane (n-$C_{24}F_{50}$), (b) poly(tetrafluoroethylene) $(CF_2)_n$, (c) poly(perfluorodimethylethyne) $[C(CF_3)=C(CF_3)]_n$, (d) a sheet of CF, (e) basic unit of a C_2F sheet, and (g) $C_{60}F_{48}$

In (b), the layered compounds formed by the fluorination of graphite are included. By increasing the degree of fluorination, layered compounds from ionic (*e.g.* C_6F) [4] to covalent (e.g. C_2F and CF) [5] bonding are formed. The carbon atoms in CF retain the hexagonal network of graphite, but the form of hybridization is changed from sp^2 to sp^3, with an additional F atom attached to each carbon atom. As a result, the carbon framework of each hexagon in the network becomes similar to that of cyclohexane in the chair form (**Fig. 1(d)**). In C_2F, the carbon network in each layer is the same as that in CF, but they form bilayers (**Fig. 1(e)**). The CF bonds at the inner side of the two layers in CF are replaced by single bonds connecting the C atoms in the two layers, and the CF bonds at the outer side of the bilayer remain the same as those in CF. Thus the dimensionality of CF slightly exceeds two. These materials have been extensively studied, with possible practical applications to battery electrodes. [5] In C_6F, the materials of stage 2 is formed, where the fluorine layer is inserted between two pairs of graphite layers. [4] It shows larger electric conductivity than that of graphite due to the electron-transfer from graphite to fluorine.[4] Electrical measurements also showed that it is an ion conductor, [6] and the characterization of the chemical state of F atoms in this material is interesting.

In group (c), fluorinated fullerenes $C_{60}F_x$ (**Fig. 1(f)**) and $C_{70}F_x$ are included. The number x of F atoms can be controlled by the fluorination conditions, and the maximum x without breaking the C_{60} cage is known to be around 48.[7–9] Studies of these materials are also going on for applications *e.g.* to battery electrodes. [10]

As for perfluoroalkane n-$C_{24}F_{50}$ and PTFE [11–15], and also fluorinated fullerenes, [16] we already reported studies examining their electronic structures by methods such as UV photoemission spectroscopy (UPS), vacuum-ultraviolet (vacuum-UV) absorption spectroscopy, near-edge X-ray absorption fine structure (NEXAFS) spectroscopy, and some theoretical calculations. A NEXAFS spectrum corresponds to the excitation from core levels to various vacant orbitals, and we can obtain information about the structures of the vacant electronic states and the local chemical environment around the excited atoms.[17]

In this paper, we report new results by these methods for PHFBD and polarized NEXAFS spectra for fluorinated graphites, and compare them with those of other C-F compounds for obtaining unified insight into the electronic structures of these materials. Although complete set of data are not yet available (*e.g.* the lack of UPS data for CF and C_2F due to the experimental difficulty of charging), we could develop a rather unified insight into the electronic structures of these compounds. Also the systematic comparison of NEXAFS spectra, including the polarization dependence of the spectral features for well-oriented specimen,

helped the interpretation of the spectra, and several useful information (*e.g.* the character of the LUMO) about these classes of compounds could be deduced.

2. EXPERIMENTAL AND THEORETICAL

The sample of PHFBD was synthesized through the polymerization from perfluoro-1,3-butadiene as already reported. [1,2] The samples of CF, C_2F, and C_6F were prepared by fluorination of highly oriented pyrollitic graphite (HOPG) with fluorine of 1 atmospheric pressure at 600 °C for 6 hours and 370 °C for 290 hrs, respectively. The sample of C_6F was prepared by placing HOPG under fluorine atmosphere of 1 atm at 50 °C in a sealed Ni tube for about one month.

The UPS measurements of PHFBD were performed using a film of 10 nm thickness *in situ* evaporated in a vacuum chamber under vacuum of 10^{-8} Torr range. The UPS spectra were measured using the combination of a rare gas discharge lamp with a retarding-field type electron energy analyzer. Energy analysis of photoelectrons was performed with ac modulation technique, [18] with a modulation amplitude of 0.2 V peak-to-peak. The resonance lines of HeI (21.2 eV) and Ar I (11.7 eV) were used. The energy resolution of the system was estimated to be 0.2 eV from the measurements of the Fermi edge of gold.

The NEXAFS spectra of PHFBD and fluorinated graphites were measured at the Photon Factory of Institute for Materials Structure Research in Tsukuba, using a Grasshopper monochromator at beamline 11B and also at UVSOR facility of Institute for Molecular Science, also using a Grasshopper monochromator at beamline 2A. The spectra were measured in the total electron yield mode for film (thickness 100 nm) samples evaporated in a separated chamber for PHFBD. For obtaining well-oriented specimen for examining the polarization dependence of PHFBD, we also used a technique used for $(SN)_x$ [19] and polydiacetylene. [20] In this method, small amount of PHFBD is at first evaporated onto the metal substrate, and its surface was rubbed with a cloth. Then PHDBD was again evaporated onto this precoated and rubbed material.

For fluorinated graphites, a flake of each compound was attached to the substrate using a conductive double-sided adhesive tape, and the surface layer of the specimen was pealed off using a sticking tape for obtaining a clean surface just before the evacuation of the chamber. The photoelectrons were detected either with a channeltron or as the drain current through a picoammeter. The light intensity was measured as the photoemission intensity from a Au mesh in the light path as the drain current through a picoammeter. The polarization dependence of the absorption spectra were examined by changing the incidence angle of

the horizontally polarized synchrotron radiation by rotating the vertically held sample surface around a vertical axis of the sample manipulator.

The vacuum-UV reflection spectra of PHFBD were measured at the beamline 1B of UVSOR using a Seya-Namioka type monochromator for a compressed pellet at near-normal incidence angle of 8.75 degrees. The absolute value of reflectivity was calibrated by measuring the reflectivity of a gold evaporated film as a reference. The obtained spectra were converted via Kramers-Kronig relation using the method by Ahrenkiel [21] to the absorption spectrum and the complex dielectric constants.

For the help of the interpretation of the observed UPS spectra of PHFBD, the electronic structures of a series of oligomers were deduced using semiempirical PM-3 molecular orbital (MO) calculations. Since the structure of PHFBD is actually close to that of PHFBY $[C(CF_3)=C(CF_3)]_n$ as mentioned above, the calculations were performed for molecules $CF_3[C(CF_3)=C(CF_3)]_mCF_3(m = 2 - 6)$, which are oligomers of polyacetylene substituted by a CF_3 at every carbon atom. Their molecular geometries were also estimated by PM-3. The density of states (DOS) for the occupied states was estimated by convoluting the delta functions at the orbital energies of the obtained MOs with a Gaussian function of 0.8 eV FWHM.

3. RESULTS AND DISCUSSION

3.1. Occupied States Probed by UPS

In **Fig. 2(a)**, the UPS spectra of PHFBD obtained by HeI and Ar I discharges ($h\nu$ = 21.2 eV and 11.7 eV) are shown. The abscissa is solid state ionization energy I_s relative to the vacuum level. The right-hand cutoff gives the ionization threshold energy of 10.3 eV defined by a clear peak A at 10.9 eV. Additional features B and C are seen in the higher binding energy region.

In **Fig. 2(b)**, we show the simulated DOS for $CF_3[C(CF_3)=C(CF_3)]_2CF_3$ by PM-3 calculation. The orbital energies of the obtained MOs are indicated by vertical bars on the energy axis. For a better fit with the spectrum in **Fig. 2(a)**, these results are rigidly shifted by 0.65 eV to the lower binding energy side. The geometry optimization of the oligomers $CF_3[C(CF_3)=C(CF_3)]_mCF_3$ ($m = 2 - 6$) gave twisted helical geometries, presumably due to the steric hindrance among the bulky CF_3 groups. This twisted structure suggests that there is little π-conjugation along the polyacetylene backbone. Actually the derived DOS was little different for m = 2 to 6, although a strong variation is expected if the conjugation is

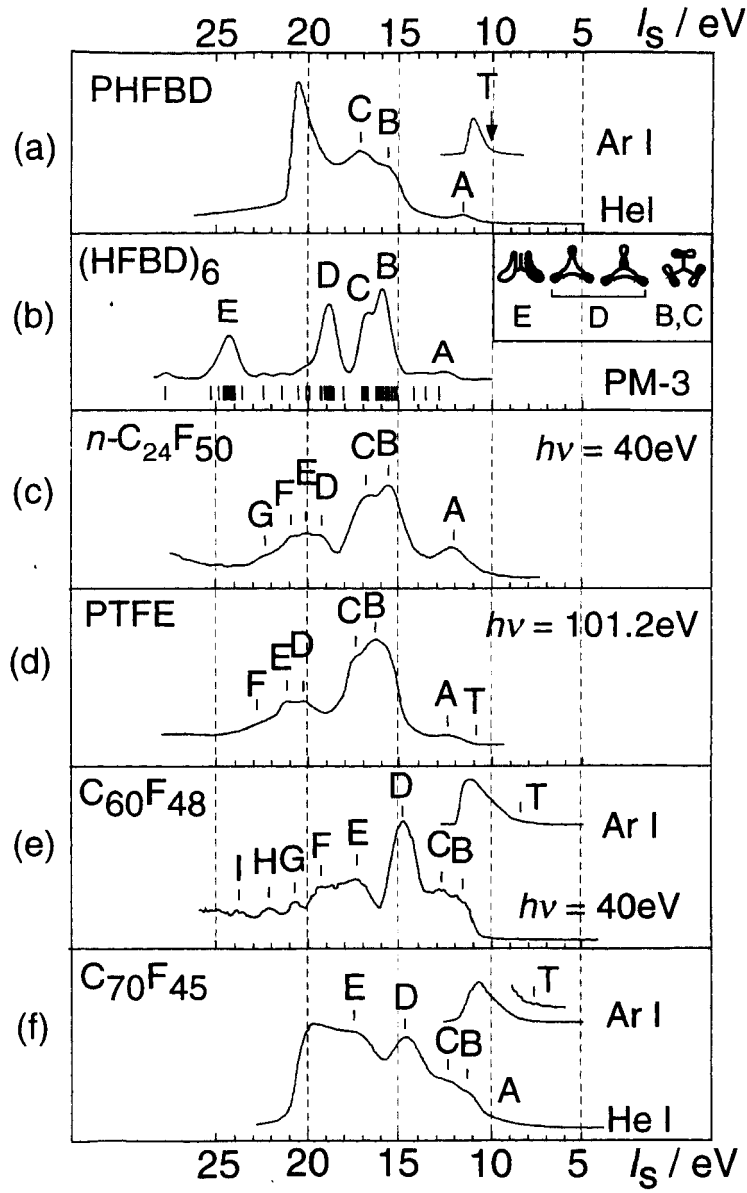

FIGURE 2 The UPS spectra of C-F systems. The abscissa is the solid ionization energy I_s relative to the vacuum level. (a) PHFBD $[C(CF_3)=C(CF_3)]_n$ measured by He I ($h\nu = 21.2$ eV) and Ar I ($h\nu = 11.7$ eV) resonance lines. (b) orbital energies of $CF_3[C(CF_3)=C(CF_3)]_2CF_3$ by PM-3 calculation and the DOS derived from them, (c) n-$C_{24}F_{50}$ at $h\nu = 40$ eV, [15] (d) PTFE at $h\nu = 101.2$ eV, [11] (e) $C_{60}F_{48}$ at $h\nu = 40$ eV and $h\nu = 11.7$ eV (Ar I), [16] and (f) $C_{70}F_{45}$ by He I ($h\nu = 21.2$ eV) and Ar I ($h\nu = 11.7$ eV) resonance lines.[16]

operative. By the comparison between the UPS spectrum in **Fig. 2(a)** and the DOS in **Fig. 2(b)**, we can assign the spectral features in Fig. 2(a). We note that the uppermost part of the occupied states are formed by the C2p and F2p orbitals, although there is some contribution from the C2s orbitals. In a repeating unit, there are four C atoms containing 8 2p electrons (or 16 electrons as the C2p + C2s electrons) and 6 F atoms with 30 F2p electrons. Thus we can expect that the spectrum is dominated by the contribution from the electrons in the F atoms. The MO results indicate that the peak A is derived from the rather isolated π orbitals, and the peaks B and C can be ascribed to the F 2p lone pair orbitals in the CF_3 groups as depicted in the inset of **Fig. 2(b)**. The region between A and B corresponds to the antibonding σ orbitals formed by the C2p and F2p orbitals. These states will be discussed in more detail below.

TABLE I Ionization Energies (in eV) of the UPS Spectral Features

Compound	*PHFBD*[a]		*n-*$C_{24}F_{50}$		*PTFE*[b]		$C_{60}F_{48}$		$C_{70}F_{45}$	
Structure	$[C(CF_3)=C(CF_3)]_n$				$(CF_2)_n$					
Figure	2(a)		2(c)		2(d)		2(e)		2(f)	
hν/eV	11.7, 21.2		40.0		101.2		11,7, 40.0		11.7, 21.2	
Character	*features and their energies / eV*									
Threshold	T	10.3	T	10.3	T	10.6	T	8.4	T	7.8
π	A	11.8					A ca.10		A	ca.9.5
σ*(C2p-F2p)			A	12.0[c]	A	12.0	B	12.0	B	11.6
							C	13.0	C	13.5
F2p lone pair	C	15.9	B	15.6	B	16.4	D	15.0	D	14.8
	C	17.5	C	16.6	C	17.5				
σ (C2p-F2p)			D	19.3[c]	D	19.9	E	17.5	E	17.4
			E	20.1[c]	E	20.8	F	19.6		
			F	21.0[c]						
C2s			G	22.4[c]	F	22.8	G	20.8		
					G	27.0	H	22.1		
							I	23.8		
Reference	This work			15		11		16		16

a. poly(hexaluoro-1,3-butadiene). Actually this polymer has a structure corresponding to poly(hexafluoro-2-butyne) $[C(CF_3)=C(CF_3)]_n$.

b. poly(tetrafluoroethylene).

c. These values were obtained from normal emission spectrum at $h\nu = 40$eV for a well oriented sample. The energies of these peaks significantly depend on the photon energy due to the intramolecular energy band dispersion. [15]

Now we compare the results of PHFBD with those of other CF systems and other substituted polyacetylenes. In **Figs. 2(c) – (f)**, we show the UPS spectra for PTFE, [11] n-$C_{24}F_{50}$, [15] $C_{60}F_{48}$, [16] and $C_{70}F_{45}$. [16] The threshold ionization energies (I_{th}) and the ionization energies of the spectral features are listed in **Table I**. The assignment of these features were carried out also by the comparison with theoretical calculations by *ab-initio* (for PTFE [11] and *n*-$C_{24}F_{50}$ [15]) and ZINDO for fluorinated fullerenes methods [16].

In all of these compounds, strong spectral features derived from the F2p lone pair orbitals appear, as the peaks B and C at 15–18 eV for perfluoroalkanes (**Figs. 2(c)(d)**) and the peak D at 15 eV for the fluorinated fullerenes (**Figs. 2(e)(f)**), respectively. This is consistent with our assignments of peaks B and C of PHFBD at 15.9 and 17.5 eV to the F2p lone pair states, since the energy of the non-bonding F2p orbitals will not strongly depend on the compound.

In the spectra of perfluoroalkanes and fluorinated fullerenes in **Figs. 2(c) – (e)** using high energy synchrotron radiation, we can also see spectral features at larger ionization energy. From the comparison with theoretical calculations, the features D-F in **Fig. 2(c)**and D and E in **Fig. 2(d)** for fluoroalkanes are ascribed to levels formed from the bonding combinations of the F2p and C2p atomic orbitals, while G in **(c)** and F in **(d)** to the states derived from the C2s orbitals. Recent calculations by Bulusheva and collaborators[22] indicated that the features E and F in the spectrum of $C_{60}F_{48}$ in **Fig. 2(e)** are derived from the radial orbitals in the C-F bonds (E) and the mixed contributions from the tangential orbitals from the C-F and C-C bonds (F), respectively. We can expect to see analogous features for PHFBD by the use of higher photon energy. Actually, the DOS in **Fig. 2(b)** derived by PM-3 calculation shows additional features. Namely, the peak D and E are mainly derived from the C-F bonds in the CF_3 groups., which have decreasing number of nodal planes in the CF3 groups, as shown in the inset of **Fig. 2(b)**. The bonding F2p + C2p σ orbitals and the C2s-derived levels delocalized along the chain are distributed across the feature E up to just below D.

On the other hand, in the lower ionization energy region than the F2p lone pairs, we can expect (1) the π states for unsaturated compounds, and (2) the antibonding σ states formed from the F2p orbitals and C2p orbitals, as shown in **Fig. 3**.

As for the π-states, the studies of $C_{60}F_x$ indicated that the topmost part of the occupied state at around 9 eV comes from the π states formed by the residual double bonds left after the fluorination. [16] As shown in **Figs. 3(f)(g)(i)**, the threshold energy is increased from 7.6 eV to 8.4 eV at increasing degree of fluorination from $C_{60}F_{30}$ to $C_{60}F_{48}$, corresponding to the decreased π-conjugation among the double bonds. In $C_{60}F_{48}$ we can still expect 6 double bonds, and their distribution on the spherical cage is not yet clear at present. Thus the splitting

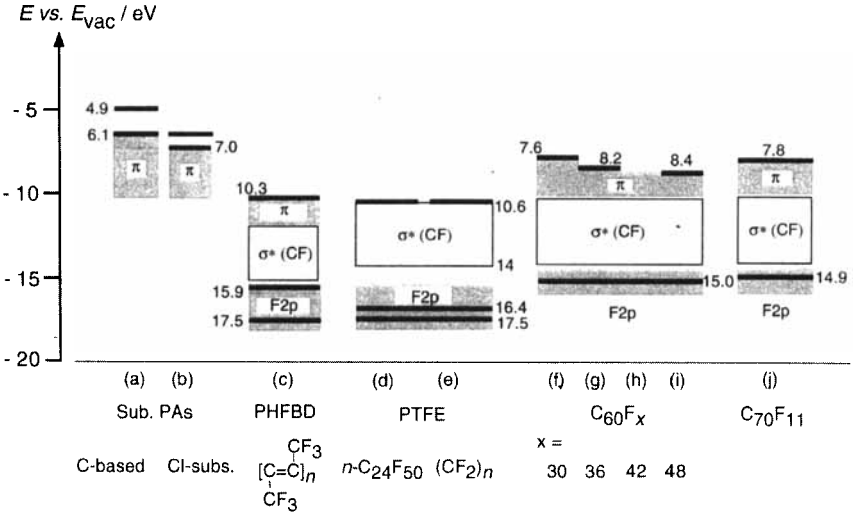

FIGURE 3 The occupied electronic states revealed by UPS and the excitation energies obtained by electronic spectra in C-F systems. (a) polyacetylene substituted by C-based pendants, (b) polyacetylenes substituted by Cl-containing pendants, (c) PHFBD $[C(CF_3)=C(CF_3)]_n$, (d) perfluoroalkane n-$C_{24}F_{50}$,[14] (e) PTFE $(CF_2)_n$,[16] (f)-(i) $C_{60}F_x$, with x = 30, 36, 42, and 48,[16] and (j) $C_{70}F_{45}$.[16] The horizontal bold bars at the top denote the ionization threshold energies, and those at 15-17.5 ev indicate the F2p lone-pair-derived states

among the π levels of these double bonds may affect the ionization threshold energy of $C_{60}F_x$. For $C_{70}F_{45}$, we also obtained a comparable value of 7.8 eV (**Fig. 3(j)**).[16]

We can also examine the values of I_{th} for other substituted polyacetylenes. The study of 26 polymers by UPS and visible-UV absorption[23] revealed that the degree of π-conjugation is more or less decreased from unsubstituted to substituted polyacetylene, probably by the steric hindrance among the substituents. The values of I_{th} for carbon-based substituents range from 4.9 to 6.1 eV (**Fig. 3(a)**).[23] Introduction of electron-withdrawing Cl atoms further increases the ionization energy to 6.1 – 7.0 eV (**Fig. 3(b)**).[23]

As for the systems without unsaturated bonds, the results for PTFE[11] and n-$C_{24}F_{50}$[15] indicate that the σ*(CF) states extend from 14 eV to 10 eV (**Figs. 3(d)(e)**). Theoretical calculations show that their highest occupied states are formed by the combination of C2p orbitals along the main chain. The values of I_{th} for PTFE (10.6 eV) and n-$C_{24}F_{50}$ (10.3 eV) are very similar, although the accuracy of this value is slightly less in the latter due to the use of electrostatic energy analyzer. This similarity indicates that the energy splitting due to the

1-dimensional delocalization along the chain is already almost saturated for the occupied states at 24 carbons. We can expect similar degree of splitting of the σ states in PHFBD. For the fluorinated fullerenes, we may expect a little more effective splitting of the σ states due to the 2-dimensionally extended carbon networks. The comparison with the ZINDO calculations for several structurally plausible isomers of $C_{60}F_{36}$ [16] indicated that the top of the σ states is at around 10 eV, slightly depending on the detailed structure of the isomers (**Figs. 3(f) – (i)**).

The presently observed value of of I_{th} =10.3 eV for PHFBD is much larger than these values for all these substituted polyacetylenes (4.9 – 7.0 eV) and even those of fluorinated fullerenes (7.6 – 8.4 eV). It is almost the same as that of perfluoroalkanes (10.6 eV) (**Figs. 3(d)(e)**) without π electrons. Actually this is the largest ionization threshold energy known to date for an organic compound with a C=C double bond.

We will examine the origin of this high ionization energy with the gas-phase ionization threshold energies of various fluorinated systems in **Fig. 4**. [24,25] For discussing these data, we note that the ionization energy of a molecule in the solid state is lowered from that of the gas phase, due to the electronic polarization of the molecules surrounding the ionized molecule. [26,27] For ordinary organic solids, this lowering is around 1.7 eV, [28] and the estimated value for perfluorinated long-chain alkane is 1.1 eV. [11] Thus we can expect a value of 1.4 eV ± 0.3 eV also for PHFBD, and the gas phase ionization threshold energy of PHFBD is estimated to be 11.7 ± 0.3 eV.

By fluorination of planar π-conjugated hydrocarbons, the π ionization energies are not much affected, [29] in contrast to the large increase of the σ ionization energies. [30] This so-called perfluoro-effect is clearly seen in **Fig. 4(a)** for the fluorinated ethylenes. The π ionization energy is mostly unchanged from 10.5 eV for ethylene to 10.3 eV for tetrafluoroethylene. [24] This invariance is ascribed to the cancellation of the inductive effect by the electron-withdrawing F atom and the antibonding effect between the C and F 2p orbitals. [30] The F 2p orbital along the CF bond does not participate the bonding, since it is on the nodal plane of the C 2p orbital. On the other hand, the substitution by CF_3 group significantly increases both π and σ ionization energies. The CF_3 group is more electron-withdrawing than the F atom. As seen in **Fig. 4(a)**, ethylenes with two or four CF_3 groups have ca. 1.3 and 2.3 eV larger π ionization energies than those of the corresponding F-substituted compounds.

Similar trend is seen when the π system becomes nominally conjugated, as seen in **Fig. 4(b)**. As expected from the perfluoro-effect, perfluorobutadiene has similar ionization threshold with that of butadiene, which is smaller than that of ethylene due to the interaction between the two double bonds. Although the data

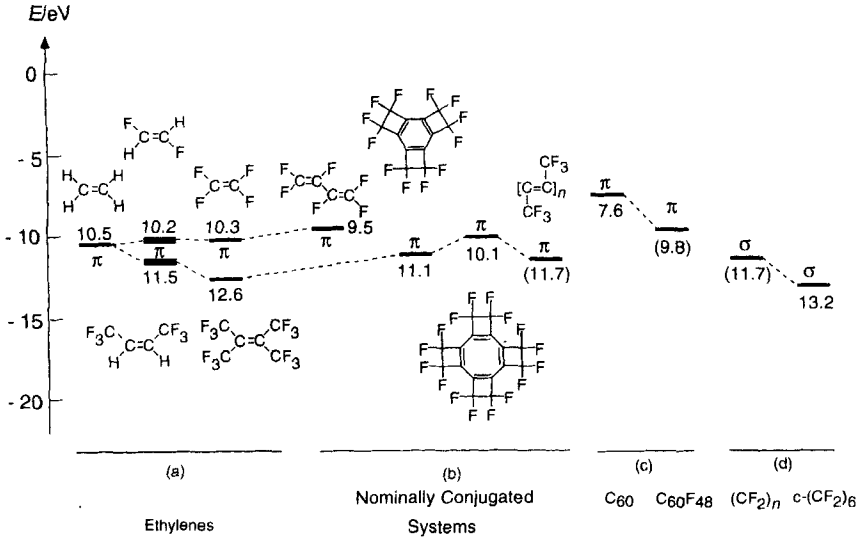

FIGURE 4 The gas-phase ionization threshold energies of compounds related to this work. (a) ethylenes and F- and CF_3-substituted ethylenes, (b) π-conjugated systems and their substituted compounds, (c) $C_{60}F_x$ and $C_{70}F_{45}$, and (d) perfluoroalkanes. The values estimated from the values for the solid state are shown in brackets, and the splitting by π- and σ-conjugation are shown by gray boxes. The data were taken from the following: C_2H_4, *trans*-$C_2H_2F_2$, C_2F_4, and *cis*-$CF_3CH{=}CHCF_3$, [24] $(CF_3)_2C{=}C(CF_3)_2$, [43] $CF_2{=}CF\text{-}CF{=}CF_2$, [25] $C_{12}F_{12}$, $C_{16}F_{16}$, [31] $[C(CF_3){=}C(CF_3)]_n$ from present work, C_{60}, [33] $C_{60}F_{48}$, [16] $(CF_2)_n$, [11] and $(CF_2)_6$. [32]

of corresponding CF_3-substituted compound is not available, we can see the trend of high π ionization energy in cyclic polyenes with a $-CF_2-CF_2-$ substituent at each double bond, with ionization threshold energies of 11.1 and 10.1 eV for six- and eight-membered rings. [31] We note that the larger ring has smaller ionozation energy, indicating the effect of π-delocalization. The ionization energy of PHFBD is much larger than these values, and we can understand the large ionization threshold based on the strong electron-withdrawing power of the CF_3 groups and the large steric hindrance among the CF_3 groups leading to the nonplanarity of the carbon main chain.

A somewhat similar situation is realized in fluorinated fullerenes. In this case, the F-substitution has two effects : [16] (1) breaking of the π-conjugated system by the conversion from sp^2 bonding to sp^3, and (2) the inductive effect by the electron-withdrawing F atoms. Unlike in the planar π-systems, the F atoms are not in the molecular plane of the π system, and can strongly affect the π ionization energies. These effects lead to a significant increase of ionization energy, *e.g.* from 7.6 eV of C_{60} to 9.8 eV for $C_{60}F_4$. [16] Still the ionization energy of PHFBD

is larger than this value by about 1.3 eV. This difference may be due to (1) the larger inductive effect of CF_3 than F, and (2) possible conjugation among the double bonds in fluorinated fullerenes. The latter will be further discussed in analyzing the results of vacuum-UV spectra in the next section.

As for the saturated systems, the ionization threshold energy of PTFE estimated as the value of the long-chain perfluoroalkanes (11.7 eV) is the same as that of PHFBD. This value is significantly smaller than that of cyclic $(CF_2)_6$, (13.2 eV), [32] indicating an effective σ-delocalization along the chain in perfluoroalkanes. This explains why perfluoroalkanes have a similar ionization energy to that of PHFBD although they have no π electrons.

3.2 HOMO-LUMO Transitions Probed by Vacuum-UV Absorption Spectra

In **Fig. 5(a)**, we show the vacuum-UV reflection spectrum of a pressed pellet of PHFBD in a wide photon energy range of 2 – 26 eV. The real and imaginary parts of the dielectric constants and the absorption spectrum derived from this reflection spectrum are shown in **Figs. 5(b)** and **5(c)**, respectively. The absorption spectrum shows several spectral features, with the lowest energy peak at 6.7 eV. In **Fig. 6**, we compare the low energy part of the absorption spectrum of PHFBD with those of PTFE **(b)**, [14] *n*-$C_{24}F_{50}$ **(c)**, [14] and $C_{60}F_{42}$ in perfluoromethylcyclohexane solution **(d)**. [16] For *n*-$C_{24}F_{50}$ and PTFE, uniaxially oriented samples could be prepared by vacuum evaporation and mechanical rubbing, respectively, [14] with the molecular axes vertical and parallel to the substrate surface, respectively. Using these samples, the polarization dependence of the absorption spectra could be also examined as shown in **Figs. 6(b)** and **(c)**. In **Fig. 6(b)**, the drawn-out and broken lines correspond to the cases where the electric vector of the light ***E*** parallel and inclined to the molecular axes, respectively, while in (c) to ***E*** mostly parallel and vertical to the molecular axes, respectively.

We will concentrate on the lowest energy excitations appearing as clear peaks, since the assignments of the transitions at higher energies are difficult. They will correspond to the HOMO to LUMO excitations, and their energies E_{ex} are listed in **Table II**. These data can be discussed with the information about the gas-phase ionization threshold energies and electronic excitation energies summarized in **Fig. 7**.

The peaks of PHFBD and the fluorinated fullerenes should correspond to the π-π^* transitions. Using the values of E_{ex}, we can obtain some feeling about the degree of π-conjugation. As shown in **Fig. 7(a)**, the value of E_{ex} for ethylene C_2H_4 is 7.65 eV, [24] while the value for *trans*-polyacetylene $(CH{=}CH)_n$ is 1.9

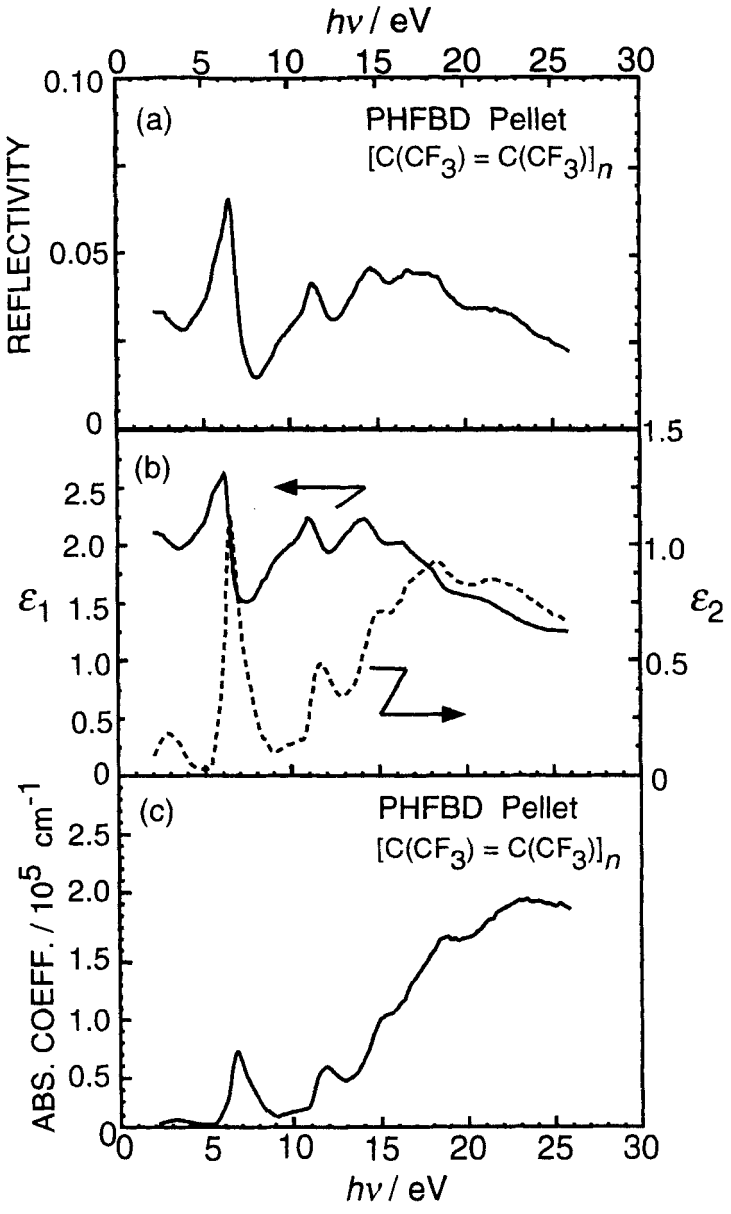

FIGURE 5 The vacuum-ultraviolet optical spectra of PHFBD $[C(CF_3)=C(CF_3)]_n$ pressed pellet using synchrotron radiation. (a) near-normal reflection spectrum at an incidence angle of 8.75 degrees, (b) real (ε_1) and imaginary (ε_2) parts of the dielectric constant, and (c) absorption coefficient. The results of (b) and (c) are derived from (a) by the Kramers-Kronig transformation following the method by Ahrenkiel.[21]

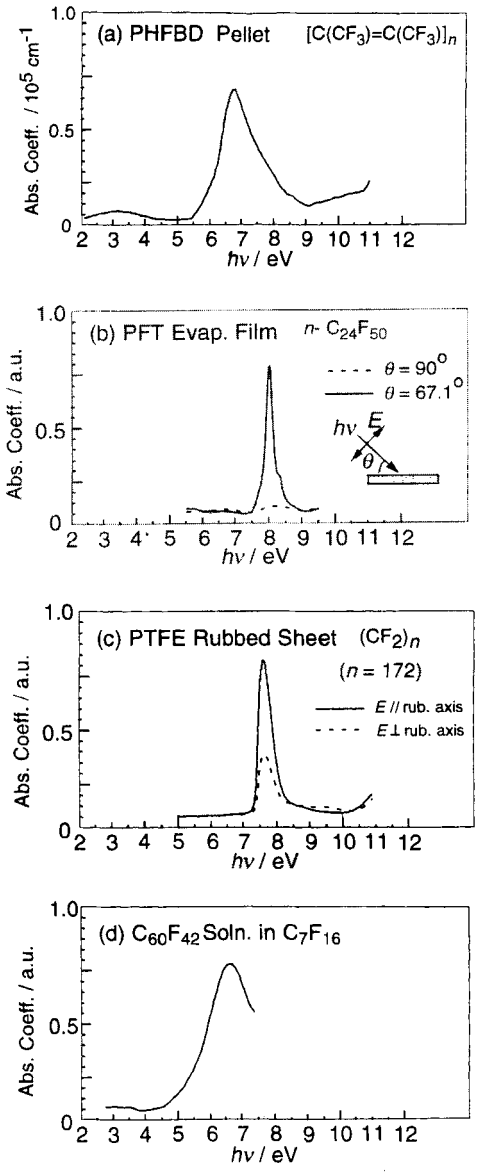

FIGURE 6 The vacuum-ultraviolet absorption spectra of C-F systems. (a) $[C(CF_3)=C(CF_3)]_n$ pressed pellet, (b) n-$C_{24}F_{50}$ evaporated film, [14] (c) rubbed PTFE $(CF_2)_n$ sheet,[14] and (d) $C_{60}F_{42}$ solution in perfluoromethylcyclohexane. [16] In (b), the molecular chains are vertical to the substrate, and the broken and real lines correspond to the electric vector of the light $\boldsymbol{E}$ vertical and inclined to the chain direction. In (c), the molecular axes are mostly aligned parallel to the substrate surface and the rubbing direction, and the spectra with $\boldsymbol{E}$ parallel (drawn-out line) and vertical (broken line) at normal incidence are shown

eV,[33] which gives the value in the fully conjugated system. In between, we see that E_{ex} = 5.93 eV for butadiene C_4H_6. [24] To be compared with this, E_{ex} of perfluorinated compound is lowered by 2.6 eV from tetrafluoroethylene C_2F_4 (8.88 eV)[24] to *cis*-perfluorobutadiene C_4F_8 (6.29 eV).[24] Thus the conjugation of two double bonds leads to a lowering of excitation energy by at least 1.7 eV.

TABLE II Energies of the Lowest Energy Absorption Peaks

Compound	*PHFBD*[a]	*n-$C_{24}F_{50}$*	*PTFE*[b]	*$C_{60}F_{42}$*	*$C_{60}F_{36}$*	*C_{60}*	*PA*
Figure	6(a)	6(b)	6(c)	6(d)	--	--	--
Structure	$[C(CF_3)=C(CF_3)]_n$		$(CF_2)_n$				$(CH=CH)_n$
hν/eV	6.7	8.05	7.68	6.7	6.5	2.0	1.9
Character	$\pi \rightarrow \pi^*$	$\sigma \rightarrow \sigma^*$	$\sigma \rightarrow \sigma^*$	$\pi \rightarrow \pi^*$	$\pi \rightarrow \pi^*$	$\pi \rightarrow \pi^*$	$\pi \rightarrow \pi^*$
Reference	This work	14	14	16	16	33	35

a. poly(hexafluoro- 1,3-butadiene). Actually this polymer has a structure corresponding to poly(hexafluoro-2-butyne) $[C(CF_3)=C(CF_3)]_n$.
b. poly(tetrafluoroethylene).

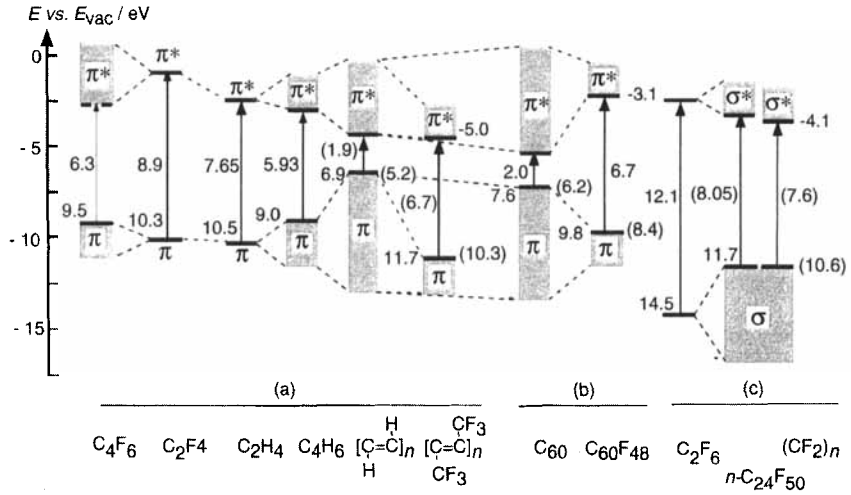

FIGURE 7 The gas-phase ionization threshold energies and electronic excitation energies of compounds related to this work. (a) π-conjugated systems and their F- and CF_3-substituted compounds (perfluoro-1,3-butadinene, tetrafluoroethylene, ethylene, *trans*-1,3-butadiene, polyacetylene, and PHFBD$[C(CF_3)=C(CF_3)]_n$]. (b) C_{60} and $C_{60}F_{48}$, and (c) perfluoroalkanes *n*-$C_{24}F_{50}$ and PTFE. The values for the solid state are shown in brackets, and the splitting by π- and σ-conjugation are shown by gray boxes. The ionization energies were taken from the same sources as in Fig. 3 except for butadiene, [44] polyacetylene[45] (a polarization energy of 1.7 eV [28]was assumed), and hexafluoroethane. [46]

The value of E_{ex} = 6.7 eV for PHFBD is much larger than those for other substituted polyacetylenes in the range of 2.3 – 5.3 eV.[23] This indicates an effective break of the conjugation, in consistency with the discussion of the UPS results. The value of E_{ex} is still slightly smaller than the corresponding values in ethylene and F- or CF_3-substituted ethylenes (ca. 7.6 eV). [24] However, the lowering of E_{ex} by 0.9 eV is smaller than the above-mentioned value of 1.7 eV, suggesting that the degree of conjugation is smaller than 2.

In another extensively π-conjugated system of C_{60}, we have the gas phase ionization threshold energy of 7.6 eV[34] and the lowest energy electronic excitation energy of 2.0 eV (in solution), [35] although the latter is forbidden by molecular symmetry. These are shown in **Fig. 7(b)**. In the absorption spectrum of $C_{60}F_{42}$ shown in **Fig. 6(d)**, where the conjugation is mostly lost, we see a peak at around 6.7 eV, [16] with a long tail at lower energy side. If we take the peak as the HOMO-LUMO gap, the similarity of the transition energies with that of PHFBD (6.7 eV) suggests that the degree of conjugation among the double bonds is also similar. The consideration about the excitonic effect discussed below, however, suggests that the HOMO-LUMO gap may actually correspond to the low-energy tail in the absorption spectrum. In this case, the conjugation is slightly larger than that in PHFBD. Such similar or larger degree of conjugation is consistent with the conclusion in the discussion of the UPS results.

On the other hand, PTFE and *n*-$C_{24}F_{50}$ have no π levels, and the peaks in their spectra are ascribed to the σ-σ* transitions. As expected, their values of $E_{ex}$are higher than the π-π* transitions in PHFBD and fluorinated fullerenes, as shown in **Fig. 7(c)**. The value of E_{ex} for PTFE (7.6 eV) [11,14] is slightly lower than that of *n*-$C_{24}F_{50}$ (8.05 eV), [14] indicating that the effect of conjugation is not yet saturated at the carbon number of 24. Since the values of the ionization energies are similar, as mentioned above, we can expect that the *n*-dependence mostly comes from the variation of the LUMO. Actually the MO and band calculations indicate that the LUMO is delocalized along the chain, [23 14] and electron transmission spectra of short perfluoroalkanes show a rapid lowering of the LUMO energy with carbon-number. [36] The lowest energy excitation was found to be polarized to the chain axis, as shown in **Figs. 6(b)** and **(c)**, and this is consistent with the expectation from *ab-inito* energy-band calculations. [14]

From simple assumption that the value of E_{ex} corresponds to the HOMO-LUMO gap, we can estimate the energy of the LUMO in the gas phase from the values of I_{th} and E_{ex} to be –5.0, –3.1, and –4.1 eV for PHFBD, $C_{60}F_{48}$ (the absorption data of $C_{60}F_{42}$ in **Fig. 6(d)** is used), and PTFE, respectively. The LUMO of PHFBD is the lowest, presumably due to the large electron-withdrawing ability of CF_3 group. In PTFE, the σ conjugation significantly lowers the LUMO, making it even lower than that of $C_{60}F_{48}$.

Finally, we will also briefly discuss the excitonic effect in these systems, which corresponds to the binding energy between the excited electron in the LUMO and the hole in the HOMO in the same molecule. Its magnitude can be estimated from the data in systems where the absolute energy of the LUMO can be independently estimated from other experiments. In fluorinated fullerenes, the LUMO energy in the gas phase was estimated to be 4.06 eV from the Fourier transform ion cyclotron resonance mass spectrometry. [37] With the estimated gas-phase ionization threshold energy, the HOMO-LUMO gap can be deduced to be 5.7 eV, which is similar to the energy at the low-energy tail in the absorption spectrum. Thus the electron-hole binding energy may be small, but it is difficult to deduce the exciton binding energy further, since we cannot see a clear feature in this part of the spectrum,

On the other hand, the results for PTFE and perfluoroalkane give large exciton binding energy. The examination of the carbon number dependence of the ionization threshold energy and electron affinity of perfluoroalkane oligomers[11] gave values of 11.7 eV and −0.2 eV, respectively, leading to a HOMO-LUMO gap of 11.9 eV. This value and the peak energy of absorption at 7.7 eV gives a binding energy of 4.2 eV. [23] Although similar data are not available for PHFBD, the similarity with perfluoroalkanes in the 1-dimensional nature suggests a significantly large value also for this polymer.

3.3 NEXAFS Spectra

3.3.1 Carbon K-edge NEXAFS

In **Figs. 8(a) – (d)**, the carbon K edge NEXAFS spectra of PHFBD, C_6F. CF, and C_2F are shown. The polarization dependence is also shown, with the grazing incidence (GI) and normal incidence (NI) of light shown by the drawn-out and broken lines, respectively. We can see many fine structures with significant polarization dependence. For PHFBD, we cannot tell the details of the preferred orientation due to the expected nonplanar twisted structure. Still the large polarization dependence clearly demonstrates that the "rubbing+evaporation" technique gave rather well oriented sample.

For the help of assignments, these spectra can be compared with the reported spectra of *n*-$C_{24}F_{50}$, [12], $C_{60}F_{40}$, [16] graphite, [38]and diamond, [38] as shown in **Fig. 9**, with insets showing the type(s) of carbon atoms in these compounds. The energies and deduced characters of the spectral features for the C-F systems are listed in **Table III(a)**. Since the spectra of PTFE[12] and $C_{70}F_{11}$ [16] are similar to those of *n*-$C_{24}F_{50}$ and $C_{60}F_{40}$, respectively, they are not shown.

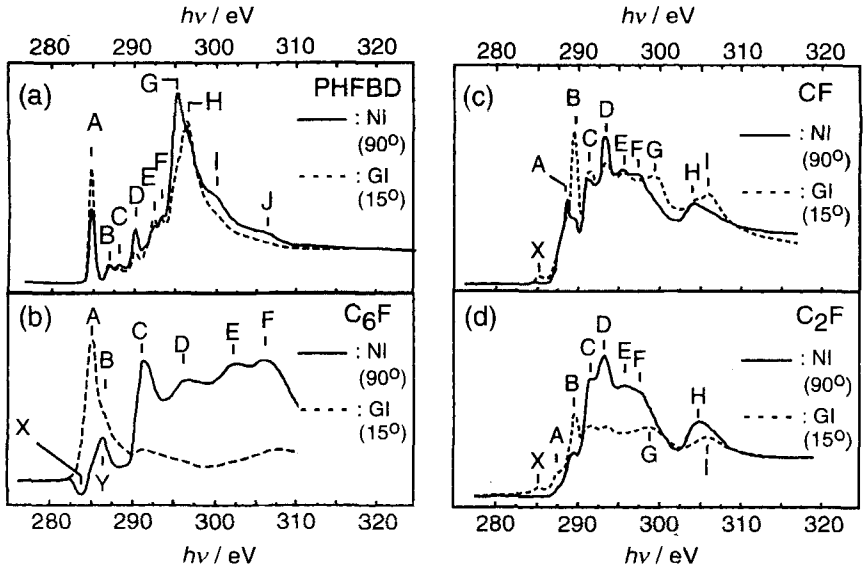

FIGURE 8 Detailed carbon K-edge NEXAFS spectra of newly measured compounds. (a) poly(hexafluoro-1.3-butadiene) (PHFBD) $[C(CF_3)=C(CF_3)]_n$oriented evaporated film, (b) fluorinated graphite C_6F, (c) fluorinated graphite CF, and (d) fluorinated graphite C_2F. The oriented PHFBD sample was prepared by vacuum evaporation onto pre-evaporated PHFBD film which was rubbed away by a cloth. The spectra with normal incidence (NI; $\theta = 90°$) and grazing incidence (GI; $\theta = 15°$ for fluorinated graphites and 30° for PHFBD) are shown by drawn-out and broken lines, respectively

In the spectra of PHFBD, $C_{60}F_{40}$, C_6F, and graphite, we see a sharp peak A at low energy of ca. 285 eV, which can be ascribed to the Cls to π^* LUMO excitations. The appearance of this peak for $C_{60}F_{40}$ (and also for $C_{70}F_{11}$) clearly demonstrates that there are still double bonds in these fluorinated fullerenes. We also see a similar low-energy feature even in the spectra of CF and C_2F (denoted by X), although we do not expect π^* orbitals for the ideal structure shown in **Figs. 1(d)** and **(f)**. Probably the actual specimens contain some double bonds due to the incomplete fluorination.

At higher energy regions of the spectra we expect various σ^*excitations. For assigning the spectra of newly measured PHFBD, C_6F. CF, and C_2F, previous studies of other compounds shown in **Fig. 9** are helpful. From the polarized spectra of evaporated *n*-$C_{24}F_{50}$, in which the molecules are vertically standing on the surface, we see that the peaks A and C are polarized vertical to the molecular axis, while the peak B is polarized parallel to the axis, leading to the assignments of A and C to ls -> σ^*(CF) excitations and peak B to a σ^*(CC) excitation. [12] The orbital character of the LUMO obtained by *ab-initio* calculation is consistent with the vertical polarization to the chain. [23]

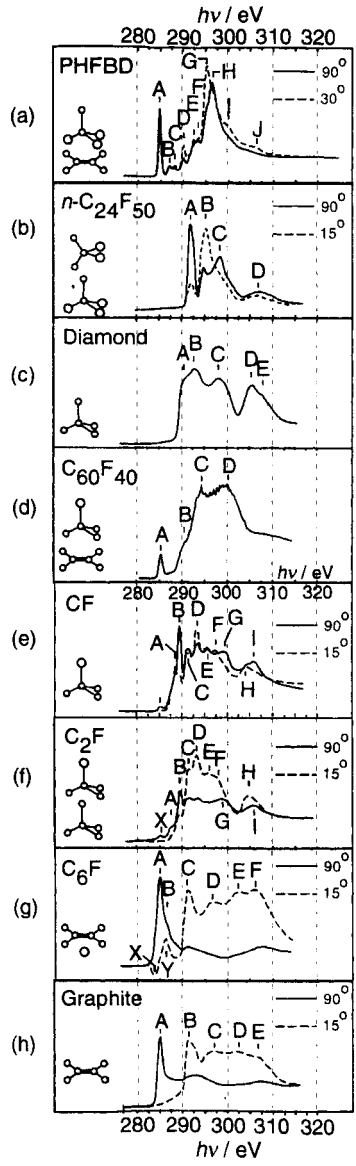

FIGURE 9 Comparison of the carbon K-edge NEXAFS spectra of various C-F systems and related compounds, (a) poly(hexafluoro-1.3-butadiene) (PHFBD) $[C(CF_3)=C(CF_3)]_n$, (b) *n*-$C_{24}F_{50}$, [12](c) diamond, [38] (d) $C_{60}F_{40}$, [16] (e) CF, (f) C_2F, (f) C_6F, and (g) graphite.[38] The spectra at normal incidence (NI; $\theta = 90°$) and grazing incidence (GI; $\theta = 15°$ except for PHFBD, where $\theta = 30°$) are indicated by drawn-out and broken lines, respectively. The insets show the type(s) of coordination around the excited carbon atom, with the small and large circles denote the carbon and fluorine atoms, respectively. The spectral features X and Y for C_6F are not intrinsic features of these systems

TABLE III Excitation Energies and the Assignments of the NEXAFS Spectral Features of C-F Systems

(a) Carbon K-Edge

Compound Structure	*PHFBD*[a] *$[C(CF_3)=C(CF_3)]_n$*		*n-$C_{24}F_{50}$*		*$C_{60}F_{40}$*	
Feature	*hν / eV*	*Character*	*hν / eV*	*Character*	*hν / eV*	*Character*
A	284.8	π^*(C=C)	291.9	σ^*(C-F)	284.1	π^*(C=C)
B	287.0	?	295.3	σ^*(C-C)	288.7	σ^*(C-F)?
C	288.3	σ*(C-C)?	298.4	σ*(C-F)	291.7	C skeleton?
D	290.3	σ*(C-F)?	307.0	EXAFS?	297.2	C skeleton?
E	292.5	?				
F	293.4	?				
G	295.5	σ^*(C-C)				
H	296.6	σ^*(C-F)				
I	300	?				
J	307	EXAFS?				
Reference	This work		12		16	

Compound	*CF*		*C_2F*		*C_6F*	
Feature	*hν / eV*	*Character*	*hν / eV*	*Character*	*hν / eV*	*Character*
X	285.1	extrinsic	285.3	extrinsic	283.8	extrinsic
A	288.6	C skeleton?	287.5	C skeleton?	285.0	π^*(C=C)
Y					286.4	extrinsic
B	289.6	σ*(C-F)	296.3	σ*(C-F)	286.6	π*(C=C)?
C	2931.1	C skeleton?	291.5	C skeleton?	291.2	C skeleton
D	293.4	σ^*(C-C)	293.4	σ^*(C-C)	296.2	C skeleton
E	295.6	C skeleton?	295.8	C skeleton?	302.2	C skeleton
F	297.4	C skeleton?	297.7	C skeleton?	306,0	C skeleton
G	299.3	σ^*(C-F)	299.0	σ^*(C-F)		
H	304.1	EXAFS?	304.9	EXAFS?		
I	305.1	EXAFS?	305.8	EXAFS?		
Reference	This work		This work		This work	

a. poly(hexafluoro-1,3-butadiene). Actually this polymer has a structure corresponding to poly(hexafluoro-2-butyne) $[C(CF_3)=C(CF_3)]_n$.

(b) Fluorine K-Edge

Compound Structure	*PHFBD*[a] $[C(CF_3)=C(CF_3)]_n$		*n*-$C_{24}F_{50}$		*CF*	
Feature	*hν* / eV	*Character*	*hν* / eV	*Character*	*hν* / eV	*Character*
A	692.8	σ*(C-F)	687.3	σ*(C-F)	684.7	σ*(C-F)
B	721.1		690.4	σ*(C-F)	689.1	σ*(C-F)?
C			691.3	σ*(C-C)?	690.6	C skeleton?
D			698.6		694.3	C skeleton?
E			702.5		696.5	
F			716.5	EXAFS?	700.3	
G			720.5	EXAFS?	702.9	
H			742	EXAFS?	711.8	EXAFS?
I			743	EXAFS?	722.9	EXAFS?
J					743	
Reference	This work		12, 39		16	

Compound	*C_2F*		*$C_{60}F_{40}$*		*C_6F*	
Feature	*hν* / eV	*Character*	*hν* / eV	*Character*	*hν* / eV	*Character*
A	685.8	σ*(C-F)	691.4	σ*(C-F)?	694.3	?
B	689.7	σ*(C-F)	708.0		707	
C	693.5	C skeleton?	730	EXAFS?	723	
D	698.1	σ*(C-F)				
E	700.2	C skeleton?				
F	726.3	EXAFS?				
Reference	This work		This work		This work	

In CF, the carbon skeleton and the CF bonds are parallel and vertical to the sample surface, respectively. Thus the peak B, which strongly appears at grazing-incidence, can be ascribed to the σ*(CF) excitation. This peak should correspond to the peak A in the spectrum of *n*-$C_{24}F_{50}$ in view of the expected smaller Cls ionization energy in CF (C with one F atom) than that of *n*-$C_{24}F_{50}$ (C with two F atoms) (see insets in **Fig. 9**). In the spectrum of C_2F, we can see a similar feature B, which is also intense at grazing incidence. The shoulder B in the spectrum of $C_{60}F_{40}$ may also correspond to a σ*(CF) excitation, although polarization dependence is not available for this compound.

On the other hand, the peak D in the spectrum of CF and C_2F are at similar energy and strong at normal incidence, indicating that this is a σ*(CC) excitation.

Again this should correspond to the peak B in n-$C_{24}F_{50}$ with slightly larger excitation energy.

As for the other features A, C, and E-I in CF and C_2F, we tentatively ascribe them to the excitations in the carbon networks, since the spectrum of diamond shows excitations in the same energy region. The feature G is strong at grazing incidence, suggesting the possibility that it corresponds to another σ^*(CF) excitation C in the spectrum of n-$C_{24}F_{50}$. We note that the lowest energy peak A in C_2F is polarized vertical to the CF bond and parallel to the carbon layers. This polarization is different from those of n-$C_{24}F_{50}$ and CF, which are polarized along the CF bonds. Unlike the 1- and 2-dimensional carbon frameworks of n-$C_{24}F_{50}$ and CF, the carbon skeleton has some 3 dimensional character, and this might lead to larger delocalization of the bonds leading to a LUMO of σ^*(CC) character.

In the spectra of PHFBD, we see two strong features G and H with opposite polarization dependence to each other. Also the feature G shows opposite polarization dependence to that of the peak A, which corresponds to the π^* excitation. The π^* excitation is strong for $\boldsymbol{E}$ vertical to the plane of the double bond, while all the C-C bonds around this group are in this plane. Thus we can expect that the σ^*(CC) excitation shows opposite polarization dependence, suggesting that the peak G corresponds to this, with a similar excitation energy with the corresponding peak A for n-$C_{24}F_{50}$. The peak H may corresponds to a σ^*(CF) excitation C of n-$C_{24}F_{50}$. Since the molecular structure and the orientation are not yet well elucidated, detailed assignments of other features are not feasible at present.

The spectrum of C_6F largely preserve the characteristics of the spectrum of graphite, indicating that the carbon network of graphite is not much affected by the reaction with this small amount of fluorine.

3.3.2. Fluorine K-edge NEXAFS

In Figs. **10(a)-(g)**, we show the F K-edge NEXAFS spectra of PHFBD, n-$C_{24}F_{50}$.[39], CF, C_2F, $C_{60}F_{40}$,[16] F_2,[40] and C_6F. The energies of the spectral features for the C-F systems are listed in **Table III(b)**. The spectrum of $C_{70}F_{11}$[16] is similar to that of $C_{60}F_{40}$, and not shown here. The spectra of n-$C_{24}F_{50}$ (**Fig. 10(b)**) agree well with those reported by Ziegler and collaborators[41] for drawn PTFE. We see that the lowest energy part (features A and B) is strong at normal incidence, corresponding to σ^*(CF) excitations. This is consistent to the conclusion from C K-edge spectra that the LUMO is of σ^*(CF) character, as also pointed out by Ishii *et al.* from the data of short perfluoro-n-alkanes in the gas phase.[36]

In the spectra of CF and C_2F (**Figs. 10(c)** and **(d)**), we now see that the intensities for the lowest-energy features A and B are larger for grazing incidence, again corresponding to the σ^*(CF) excitations. In the higher energy region, there are

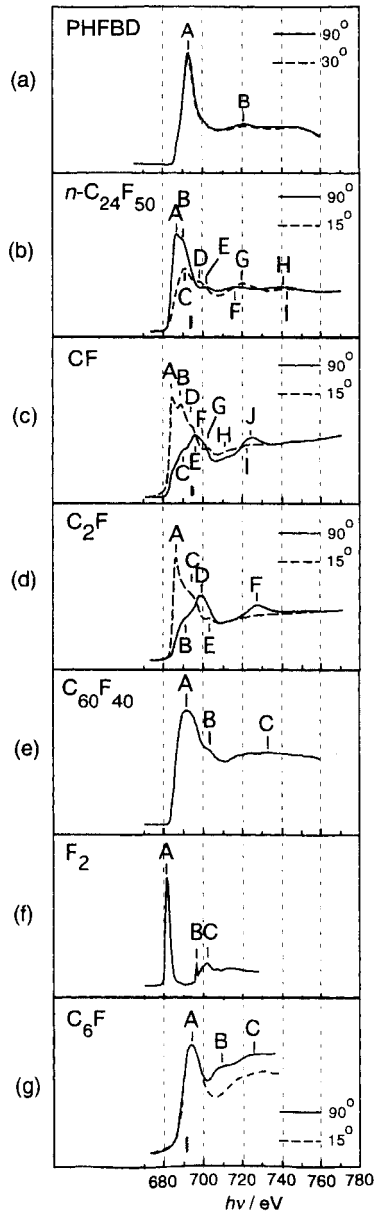

FIGURE 10 Fluorine K-edge NEXAFS spectra of various C-F systems and a related compound. (a) poly(hexafluoro-1.3-butadiene) (PHFBD) $[C(CF_3)=C(CF_3)]_n$, (b) n-$C_{24}F_{50}$, [13] (c) CF, (d) C_2F, (e) $C_{60}F_{40}$, [16], (f) F_2, and (g) C_6F. The spectra at normal incidence (NI; $\theta = 90°$) and grazing incidence (GI; $\theta = 15°$ except for PHFBD, where $\theta = 30°$) are indicated by drawn-out and broken lines, respectively

many fine structures with significant polarization dependence. It is evident that they cannot be readily interpreted in the simple picture of localized σ^* excitation in a CF bond. Although there have been trials of interpreting these features based on molecular orbital calculations[36] or band calculations, [41] more detailed interpretation based on explicit calculations of σ^* excitations taking account of the core hole effect[17,42] will be necessary for a reliable analysis. Since many of these final states are above the vacuum level, scattering theory rather than molecular-orbital type calculation may be required. [17]

The spectra of PHFBD (**Fig. 10(a)**) and fluorinated fullerenes (**Fig. 10 (e)**) show little polarization dependence. This is reasonable in view of the complex structure of the specimen and the lack of uniaxial orientation of CF bonds in the CF_3 group. For both cases, the spectrum is characterized by a single peak, but the peak width is larger for $C_{60}F_{40}$ than for PHFBD. In PHFBD, the F atom is connected to the 1-dimensional polyacetylene chain through a C atom, while it is directly connected to the 2-dimensionally connected carbon network in fluorinated fullerenes. Thus the final states accessible for the core electron in the Fls orbital will be more delocalized and wide in energy in the fluorinated fullerenes than in PHFBD. Actually the peak width for the fluorinated fullerene is similar to the average of the polarized spectra of CF and C_2F, where the F atom is also connected to a 2-dimensionally extended carbon network. The width for *n*-$C_{24}F_{50}$ (**Fig. 10(b)**) is between those for PHFBD and fluorinated fullerenes. This is reasonable since F atom is directly connected to a 1-dimensionally extended carbon main chain.

Finally, we will discuss the spectra of C_6F (**Fig. 10(g)**). The significant difference from the spectrum of F_2 in **Fig. 10(f)** immediately excludes the molecular form of F_2 for the F atoms in C_6F. Also the spectra show little polarization dependence. If the F atoms in C_6F are covalently bonded to the C atoms, the spectrum should show significant polarization dependence as seen in CF and C_2F. The absence of polarization dependence strongly suggests that the F atoms are in the atomic state, either in the neutral form or as an ion. This is consistent with the picture that F atoms are in an ionic or semi-ionic state in C_6F. [4,6]

CONCLUDING REMARKS

In this paper, we have reported on the new experimental results about two classes of C+F systems, *i.e.* PHFBD and fluorinated graphites, using high-energy spectroscopies, *i.e.* UPS, vacuum-UV optical spectroscopy, and NEXAFS spectroscopy. The results are compared and discussed together with the results for other C+F systems: perfluoroalkanes and fluorinated fullerenes. The electronic struc-

tures of these systems could be understood in a rather unified way in terms of (1) the degree of π- and σ-conjugation, (2) inductive effect of F and CF_3 substituents, and (3) the conformational change due to the steric hindrance in the molecule.

As for the newly studied systems, PHFBD is characterized by the largest ionization energy known to date for an organic solid with double bonds. The origin of this large value was ascribed to the small conjugation due to steric hindrance and the large inductive effect of the CF_3 group. Also its electronic excitation energy is large, reflecting the localized nature of the double bonds. Although extensive studies of fluorinated graphites were not performed, the NEXAFS studies for CF and C_2F showed rich structures with significant polarization dependence. The observed spectra could be reasonably well interpreted with the spectra of *n*-$C_{24}F_{50}$ and related systems. The NEXAFS of the C_6F showed that the F atoms in C_6F are neither in the F_2 form nor covalently bonded to the carbon atoms.

These results, together with the already reported results for perfluoroalkanes and fluorinated fullerenes, reveal how much variety of electronic structure can be realized by structures formed by using carbon and fluorine. In view of the increasing demand for materials of low dielectric compounds and electronic materials with unique electronic properties for organic electronic devices, these data will serve as a guide for designing such materials.

Finally we note that we recently succeeded in observing the intrachain energy-band dispersion relation for *n*-$C_{24}F_{50}$ by angle-resolved UPS studies of oriented specimen. [15] The unoccupied electronic structures of this compound was also studied using electron transmission spectroscopy, and the results will be reported in combination with theoretical studies in near future.

Acknowledgements

The authors dedicate this article to late Professor E. A. Silinsh, for commemorating his outstanding contribution to the elucidation of the electronic structure and related subjects about organic molecular solids. We kept contact with him for more than 25 years, and his warm and sincere character always impressed us.

He was all the time kind and helpful, and respectful to the truth of nature. It was in particular a pity for us that he passed away just after accepting our invitation for a stay with us in Japan. This work was supported in part by the Grant-in-Aid from the Ministry of Education, Science, Sports, and Culture of Japan (Nos. 07CE2004, 10440205, and 10141602). The measurements using synchrotron radiation were carried out under the approval of Program Advisory Comittees of KEK-PF and UVSOR. We are also grateful to Prof. A. Yagishita

and Y. Kitajima of Photon Factory and Prof. M. Kamada and Dr. S. Tanaka of UVSOR for their kind support at the measurements using synchrotron radiation.

References

1. A. Nagai, S. Nishimura, A. Takahashi, A. Mukoh, T. Narita, T. Hagiwara, and H. Hamana, *J. Polym. Sci., C* **28**, 373 (1990).
2. S. Nishimura, A. Nagai, A. Takahashi, T. Narita, T. Hagiwara, and H. Hamana, *Macromolecules* **25**, 1648 (1992).
3. S. Nishimura, A. Nagai, A. Takahashi, T. Narita, T. Hagiwara, and H. Hamana, *Polymer* **35**, 3474- (1994).
4. M. Dresselhaus, M. Endo, and J.-P. Issi, in *Fluorine-Carbon and Fluoride-Carbon Materials: Chemistry, Physics, and Applications*, edited by T. Nakajima (Marcel-Dekker, New York, 1995), pp. 95–186.
5. N. Watanabe, T. Nakajima, and H. Touhara, *Graphite Fluorides* (Elsevier, Amsterdam, 1988).
6. S. Suganuma, T. Mizu, H. Sakagoshi, K. Momoto, F. Okino, and H. Touhara, *TANSO* (in English), 266 (1993).
7. H. Selig, C. Lifshitz, T. Peres, J. E. Fischer, A. R. McGhie, W. J. Romanow, J. P. McCauley Jr., and A.B. Smith III, *J. Am. Chem. Soc.* **113**, 5475 (1991).
8. A. A. Tuinman, P. Mukherjee, J. L. Adcock, R. L. Hettich, and R. N. Compton, *J. Phys. Chem.* **96**, 7584 (1992).
9. K. Kniaz, K. Fisher, H. Selig, G. B. M. Vaughan, W. J. Romanow, D. M. Cox, S. K. Choudhury, J. P. McCauiey, R. M. Strongin, and I. Smith, A. B., *J. Am. Chem. Soc.* **115**, 6060 (1993).
10. N. Liu, H. Touhara, F. Okino, S. Kawasaki, and Y. Nakacho, *J. Electrochem. Soc.* **143**, 2267 (1996).
11. K. Seki, H. Tanaka, T. Ohta, and Aoki, *Phys. Scr.* **41**, 167 (1990).
12. T. Ohta, K. Seki, T. Yokoyama, I. Morisada, and K. Edamatsu, *Phys. Scr.* **41**, 150 (1990).
13. K. Nagayama, R. Mitsumoto, T. Araki, Y. Ouchi, and K. Seki, *Physica* **B208/209**, 419 (1995).
14. K. Nagayama, T. Miyamae, R. Mitsumoto, H. Ishii, Y. Ouchi, and K. Seki, *J. Electron Spectrosc. Relat. Phenom* **78**, 407 (1996).
15. T. Miyamae, S. Hasegawa, D. Yoshimura, H. Ishii, N. Ueno, and K. Seki, *J. Chem. Phys.* **112**, 3333 (2000).
16. R. Mitsumoto, T. Araki, E. Ito, Y. Ouchi, K. Seki, K. Kikuchi, Y. Achiba, H. Kurosaki, T. Sonoda, H. Kobayashi, O. V. Boltalina, V. K. Pavlovich, L. N. Sidorov, Y. Hattori, N. Liu, S. Yajima, S. Kawasaki, F. Okino, and H. Touhara, *J. Phys. Chem. A* **102**, 552 (1998).
17. J. Stoehr, *NEXAFS Spectroscopy*(Springer, Berlin, 1992).
18. R. C. Eden, *Rev. Sci. Instrum.* **41**, 252 (1970).
19. T. Mitani, H. Mori, S. Suga, T. Koda, S. Shin, K. Inoue, I. Nakada, and H. Kanzaki, *J. Phys. Soc. Jpn.* **47**, 679 (1979).
20. T. Kanetake, K. Ishikawa, T. Koda, Y. Tokura, and K. Takeda, *Appl. Phys. Lett.* **51**, 1957 (1987).
21. R. K. Ahrenkiel, *J. Opt. Soc. Am.* **61**, 1651 (1973).
22. L. G. Bulusheva, A. V. Okotrub, and O. V. Boltalina, *J. Phys. Chem.* **103**, 9921 (1999).
23. K. Seki, T. Furuyama, T. Kawasumi, Y. Sakurai, H. Ishii, K. Kajikawa, Y. Ouchi, and T. Masuda, *J. Phys. Chem. B* **101**, 9165 (1997).
24. M. B. Robin, *Higher Excited States of Polyatomic Molecules* (Academic Press, New York, 1975).
25. G. G. Furin, A. V. Zibarev, L. N. Mazalov, and V. D. Yumatov, *Elektronnaya struktura ftororganicheskikh soedinenii* (Nauka, Novosibirsk, 1988).
26. L. E. Lyons, *J. Chem. Soc.*, 5001 (1957).
27. E. A. Silinsh and V. Capek, *Organic Molecular Crystals- Interaction, Localization, and Transport Phenomena* (AIP Press, New York, 1994).
28. N. Sato, K. Seki, and H. Inokuchi. *J. Chem. Soc., Faraday Trans. 2* **77**, 1621 (1981).
29. C. R. Brundle, M. B. Robin, and N. A. Kuebler, *J. Am. Chem. Soc.* **94**, 1466 (1972).
30. C. R. Brundle, M. B. Robin, K. Kuebler, and H. Basch, *J. Am. Chem. Soc.* **94**, 1466 (1972).
31. E. Heilbronner, J. Wirz, and R. I. Soulen, *Helv. Chim. Acta* **67**, 47 (1984).

32. S. J. W. Price and H. J. Sapiano, *Can. J. Chem.* **57**, 685 (1979).
33. J. Tanaka. C. Tanaka, T. Miyamae, K. Kamiya, M. Shimizu, M. Oku, K. Seki, J. Tsukamoto, S. Hasegawa, and H. Inokuchi, *Synth. Met.* **55**, 121 (1993).
34. D. L. Lichtenberger, K. W. Nebesny, C. D. Ray, D. R. Huffman, and L. D. Lamb, *Chem. Phys. Lett.* **176**, 203 (1991).
35. M. S. Dresselhaus, G. Dresselhaus, and P. C. Eklund, *Science of Fullerenes and Carbon Nanotubes* (Academic Press, San Diego, 1996).
36. I. Ishii, R. McLaren, A. P. Hitchcock, K. D. Jordan, Y. Choi, and M. B. Robin, *Can. J. Chem.* **66**, 2104 (1988).
37. C. Jin, R. L Hettich, R. N. Compton, A. Tuinman, A. Derecskei-Kovacs, D. S. Marynick, and B. I. Dunlap, *Phys. Rev. Lett.* **73**, 2821 (1994).
38. K. Edamatsu, Y. Takata, T. Yokoyama, K. Seki, M. Tohnan, T. Okada, and T. Ohta, *Jpn. J. Appl. Phys., Part 1* **30**, 1073 (1991).
39. K. Nagayama, M. Sei, R. Mitsumoto, E. Ito, T. Araki, H. Ishii, Y. Ouchi, K. Seki, and K. Kondo, *J. Electron Spectrosc. Relat. Phenom* **78**, 375 (1996).
40. A. P. Hitchcock and C. E. Brion, *J. Phys.* **A14**, 4399 (1981).
41. C. Ziegler, T. Schedel-Niedrig, G. Beamson, D. T. Clark. W. R. Salaneck, H. Sotobayashi, and A. M. Bradshaw, *Langmuir* **10**, 4399 (1994).
42. H. Oji, R. Mitsumoto, E. Ito, H. Ishii, Y. Ouchi, K. Seki, T. Yokoyama, T. Ohta, and N. Kosugi, *J. Chem. Phys.* **109**, 10409 (1998).
43. M. B. Robin, G. N. Taylor, N. A. Kuebler, and R. D. Bach, *J. Org. Chem.* **38**, 1049 (1973).
44. G. Bieri and L. Asbrink, *J. Electron Spectrosc. Rel. Phenom.* **20**, 149 (1980).
45. J. Tanaka, M. Tanaka, H. Fujimoto, M. Shimizu, N. Sato, and H. Inokuchi, *J. Phys.* **C3**, 279 (1983).
46. M. B. Robin, *Higher Excited States of Polyatomic Molecules* (Academic Press, New York, 1974).