The σ* molecular orbitals of perfluoroalkanes as studied by inner-shell electron energy loss and electron transmission spectroscopies

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This paper is dedicated to Professor Charles A. McDowell on the occassion of his seventieth birthday

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Absolute oscillator strength spectra in the C 1*s* (280–340 eV) and F 1*s* (680–740 eV) regions of the perfluoro-*n*-alkanes from C_2 to C_6 and perfluorocycloalkanes from C_3 to C_6 have been determined from inner-shell electron energy loss spectra recorded under electric-dipole scattering conditions. The spectral features are interpreted in terms of spatially localized transitions terminating at orbitals of predominantly σ*(C—F) and σ*(C—C) character. When compared to the spectra of the perfluoro-*n*-alkanes, both the C 1*s* and F 1*s* spectra of the perfluorocycloalkanes exhibit additional low-lying bands which are assigned to transitions terminating at σ*(C—C) orbitals which are shifted to low energy by the combination of the strain of cyclization and the inductive effect of the fluorination. The electron transmission spectra of selected perfluorocycloalkanes (which provide information on their anion states) show as well that the electron affinities of the cyclic systems are substantially lower than those of the corresponding perfluoro-*n*-alkanes, again as a result of a low-lying σ* orbital in the cyclic species. Quantum chemical calculations of the alkane and perfluoroalkane ground-state orbital structures support the experimental results. The localized character of the inner-shell excitations, indicated by the constancy of both term values and oscillator strengths with increasing chain length, contrasts with the more delocalized character of the states accessed in ultraviolet excitation or negative ion formation.

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Utilisant les spectres de pertes d'énergie électronique des couches internes enregistrés dans des conditions de diffraction du dipôle électrique, on a déterminé les spectres de force absolute de l'oscillateur des régions C 1*s* (280 à 340 eV) et F 1*s* (680 à 740 eV) des perfluoro-*n*-alcanes (C_2 à C_6) et des perfluorocycloalcanes (C_3 à C_6). On interprète les caractéristiques spectrales en fonction de transitions qui sont localisées dans l'espace et qui se terminent avec les orbitales possédant des caractéres σ*(C—F) et σ*(C—C) prédominants. Lorsqu'on les compare aux spectres des perfluoro-*n*-alcanes, les spectres tant C 1*s* que F 1*s* des perfluorocycloalcanes présentent de faibles bandes additionnelles que l'on a attribuées à des transitions se terminant au niveau des orbitales σ*(C—C) qui sont déplacées vers les basses énergies par une combinaison de tensions de cycle et d'effet inductif des fluors. De plus, les spectres de transminnion électronique des ions négatifs de perfluorocycloalcanes choisis montrent que les affinitiés électroniques des systèmes cycliques sont beaucoup plus faibles que celles des perfluoro-*n*-alcanes correspondants; ces résultats sont encore une fois expliqués par la présence d'orbitales σ* basses dans les systèmes cycliques. Des calculs de chimie quantique effectués sur les structures des orbitales des états donsamentaux d'alcanes et de perfluorocycloalcanes sont en accord avec les résultats expérimentaux. Le caractère localisé des excitations de couches internes, tel qu'indiqué par la constance de chacun des termes des valeurs ainsi que des forces d'oscillation avec une augmentation de la longueur de la chaîne, est en opposition avec le caractère plus délocalisé des états atteints par les excitations ultraviolettes ou par la formation d'ions négatifs.
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1. Introduction

The fate of electronic transitions terminating at σ* MO's in the outer-shell (5–50 eV) and inner-shell (50–1000 eV) spectra of large organic molecules remains very much an open question. At first sight, the problem would seem to be that the transitions to σ* are rather high lying, and so are difficult to identify either because they fall among the clutter of transitions to Rydberg (R) orbitals or because they are autoionized in the ionization continua. However, the problem is more complex, for there is a very real possibility that a particular valence (V) σ* MO is mixed more or less with the R MO's of the same symmetry so that its valence identity becomes clouded; in extreme cases a σ* MO can dissolve in the Ryberg sea to such an extent as to lose its valence character completely (1, 2). Though valence transitions to σ* in the ionization continuum do appear as shape resonances (3, 4) and cannot be confused with transitions to R orbitals, assignment still can be ambiguous here as well, for other phenomena such as two-electron excitation, shake-up, and EXAFS interference also can contribute structure in this region (5). Finally, because the nature of the transitions to σ* MO's in the outer-shell and inner-shell spectra of the same molecule may be quite different, conclusions about σ* MO's reached in one type of study would not necessarily apply to the other.

In the present work, we have studied the inner-shell excitation energies and oscillator strength distributions of a series of perfluoro-*n*-alkanes (C_2—C_6) and perfluorocycloalkanes (C_3—C_6) as well as perfluoroneopentane. For certain of these compounds, we also have determined the negative-ion electron transmission spectra and performed *ab initio* ground state calculations. In our discussion of the spectral results, we address the following questions: (*1*) What are the energies and

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relative R/V characters of the σ* MO's accessed in the inner-shell and negative-ion spectroscopies of the perfluoroalkanes? (2) To what extent are σ* orbitals stabilized by perfluorination and/or ring strain? (3) Are the inner-shell and negative-ion excitations terminating at σ* in the perfluoroalkanes localized or delocalized?

Identification of transitions terminating at σ* is most readily approached through the study of inner-shell spectra, for in this case though the terminating MO manifold may be complex, at least the originating inner-shell MO manifold is simpler than the occupied valence MO manifold involved in outer-shell excitations. In addition, because of the smaller number of configurations of similar core-excitation energies, a one-electron orbital model is expected to be more applicable to inner-shell than to outer-shell excitation. Given the inner-shell ionization potential, usually from X-ray photoelectron spectroscopy, one knows that the corresponding R excitations will fall in a certain region below this limit (1). The energy difference between the ionization potential and the corresponding discrete excitation is called the term value. Term values for R states are usually between 0 and 5 eV. On the other hand, transitions to σ* orbitals can occur over a much wider spectral range; in this case, term values as large as 14 eV (F_2) and as small as −22 eV (C_2H_2) have been reported (4).

Recently it has been shown that the term value of a $1s \rightarrow \sigma^*$(A—B) transition can be estimated from empirical considerations of the atomic numbers of atoms A and B involved in forming the σ* MO and the A–B internuclear distance (3, 4). This correlation assumes that the σ* MO reached in an inner-shell excitation is strongly localized in the region of a localized core hole, even in systems of large size containing several equivalent and adjacent bonds. The localization of the $1s \rightarrow V(\sigma^*)$ excitation could arise from a local character of the σ* orbital and/or spatial localization of the core hole.

In the case where inner-shell excitations to σ* and R orbitals are nearly degenerate, term value arguments are less compelling and the question arises as to the separate existence of near-degenerate R and V levels (1, 2). Although the answer to this is ambiguous in many cases, clear evidence for the coexistence of distinct V and R levels in the same spectrum has been presented for F_2O (6).

In addition to the term-value criteria, there are a number of effects that can assist in the determination of the relative R/V character of a particular spectroscopic feature. First, in the condensed phase, transitions to R levels are generally broadened significantly and shifted to higher energies so as to make the transitions effectively disappear (1, 7). In contrast, the transitions to V states persist virtually unchanged in a condensed phase. Second, there is a well-known upper limit to the oscillator strength of transitions to R states (1), whereas many transitions to V states have oscillator strengths which exceed the R limit. Third, the transition energies and oscillator strengths exhibit systematic variations through a homologous series of molecules which may help to distinguish transitions to R states from those to V states.

In a specific class of molecules, it has been found that σ* MO's can lie so low that their identification is not comprised by problems of congestion or orbital mixing. Thus, if a molecule has a bond between atoms A and B which has a strength of 60 kcal/mol or less, then the σ–σ* splitting will be abnormally small and the σ*(A—B) MO will be relatively low lying, as will inner-shell transitions such as A $1s \rightarrow \sigma^*$(A—B) and outer-shell transitions such as B $2p \rightarrow \sigma^*$(A—B). This lowering of the inner-shell and outer-shell energies for excitations to σ* has been called the weak-bond effect (2, 6).

In addition to the questions listed above, we also raise the question as to whether an *overall* molecular strain energy which weakens several bonds simultaneously also can result in a small σ–σ* split. If so, then such strained systems also will show unambiguous low-lying excitations to σ* with unusually large term values. In this regard, it is pertinent to note that C $1s \rightarrow \sigma^*$ transitions at lower-than-expected energies already have been observed in the spectra of cyclopropane and cyclobutane (8).

The opportunities for observing transitions to low-lying σ* MO's may be heightened yet again by perfluorinating the strained cyclic hydrocarbons. This could arise both from the introduction of strain energy due to F—F repulsions (9), and from the fact that fluorination of a molecule acts to lower both σ and σ* MO's due to the strong inductive effect of the F atom (6, 10). That the perfluoroalkanes may prove to be a rich hunting ground for low-lying transitions to σ* MO's was mentioned earlier following a comparison of the vacuum ultraviolet (VUV) spectra of alkanes and their perfluoro derivatives (1); related ideas can be found in discussions of the inner-shell spectra of the fluoromethane (1, 11–13) and chloromethane series (14).

In hydrocarbons consisting of several C—C bonds, the C $1s$ AO's on equivalent sites form a narrow band of width *ca.* 0.01 eV. It is generally believed that because of the narrow bandwidth, mobility of the $1s$ hole is so low that the originating orbital in the core-excited state can be localized at a single atomic site during the very short lifetime of the hole state (15–18). However, see the work of Schwartz *et al.* (19) for possible exceptions to this point of view. There clearly is a question at present as to the degree of localization of the core hole in the core excited states of molecules having the excited atoms in equivalent sites. Related aspects to this problem are the degree of delocalization of the σ* MO's populated in the core states, and the fact that the degree of delocalization of the optical orbital may differ depending upon the spectroscopy by which it is examined (20). That is, the potential experienced by the optical electron in a ($1s$, σ*) hole-localized excited state in the X-ray region of a given molecule is quite different from that appropriate to a delocalized (σ, σ*) state in the VUV excitation of that molecule. In these situations, the σ* MO's may be quite different both in spatial extent and term value.

The presence of low-lying, strain-induced σ* MO's in the perfluorocycloalkanes could be revealed not only in the inner-shell spectra but in their negative-ion spectra as well (21). Though the potential experienced by an electron in a σ* orbital is very different in the case of a negative-ion and inner-shell excitation in a neutral molecule, this avenue was felt to be worth exploring in spite of the possible differences. Inner-shell and negative-ion comparisons of this type have been found useful in studying the unoccupied orbitals of the fluorobenzenes (10) and fluoroethylenes (6).

In the present work, we have measured the negative-ion transmission spectra of the perfluoro-*n*-alkanes and the corresponding perfluorocycloalkanes. These results are compared with virtual-orbital calculations of the successive electron affinities of the linear and cyclic perfluoroalkanes. Negative-ion resonances in saturated molecules may involve not only σ* resonances, but Feshbach resonances as well, in which two electrons occupy a single R orbital. For purposes of assigning

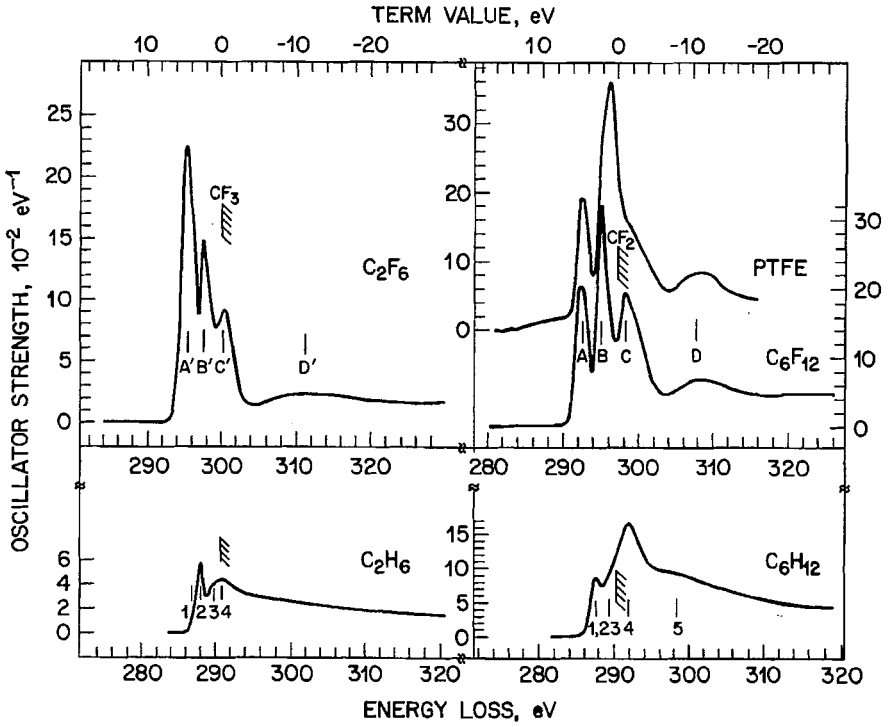

FIG. 1. Comparison of the oscillator strength spectra of C_2H_6 and C_6H_{12} with those of C_2F_6 and C_6F_{12}, as derived from energy-loss spectra recorded with 2.5 keV final electron energy, 2° scattering angle and 0.6 eV FWHM resolution. The spectra have been shifted so as to bring the C 1*s* ionization potentials into alignment. Also shown is the optical spectrum of PTFE, as recently reported by Ohta *et al.* (32), plotted on the same absolute energy scale as that of C_6F_{12}.

the negative-ion resonances, the strategy used here is to first assign the Feshbach resonances, using the well-known energy criteria for such excitations (1, 20, 22), and then assume that the remaining resonances involve occupation of the σ* MO's.

In this paper, we consider successively the C 1*s* spectra of the linear and branched perfluoroalkanes (sect. III) and compare these with the C 1*s* spectra of the cyclic perfluoroalkanes (sect. IV). Similar comparisons are drawn for the F 1*s* spectra of the same series of compounds (sect. V). The ordering of the virtual orbitals and their R/V characters as derived from these spectra are then compared with the conclusions deduced from the negative-ion spectra, as supported by *ab initio* calculations (sect. VI). These comparisons lead to a discussion of excitation localization/delocalization in these spectra (sect. VII).

II. Experimental

The C 1*s* and F 1*s* inner-shell spectra of the perfluoro-*n*-alkanes from C_2F_6 to C_6F_{14}, perfluoroneopentane, and the cyclic compounds from C_3F_6 to C_6F_{12} were recorded by electron energy loss spectroscopy using the McMaster inner-shell electron energy loss (ISEEL) spectrometer. Operating under conditions chosen to accentuate electric-dipole transitions (2.5 keV final electron energy and scattering angles less than 2°), a resolution of 0.6 eV FWHM was achieved. Further details of the spectrometer and operating procedures are presented elsewhere (3, 23). Each of the perfluoroalkanes was a commercial product except for perfluorocyclopropane, perfluorocyclopentane, and perfluoroneopentane which were gifts from Professor J. L. Adcock. Sample purity within the spectrometer cell was monitored mass spectrometrically and the energy loss spectra calibrated by the addition of appropriate gases of known transition energies. In all cases, the energy loss spectra reported here have had the underlying continuum intensity subtracted and have been converted to approximate absolute oscillator strength distributions (±20%) using corrections for kinematic effects and normalization to calculated atomic 1*s* photoionization oscillator strengths (24).

Negative-ion resonance energies were determined using an electron transmission spectrometer operating in the derivative mode. The technique is described in ref. 21. Negative-ion spectra were determined for selected members of both the linear and cyclic perfluoroalkanes, as well as for certain alkanes.

III. Inner-shell spectra of perfluoro-*n*-alkanes

The discrete transitions below the C 1*s* ionization potentials in the inner-shell spectra of the alkanes are of mixed R/V character (3, 8, 25). Since the general effect of fluorination is to accentuate the V character of the lower excitations, we must expect to see much stronger R/V mixing in the perfluoroalkanes or even low-lying transitions to relatively pure σ* MO's. In the latter case, the V levels may rest among the R levels or even precede them. Indeed, it is clear from earlier work (1, 12, 13, 26–30) that the C 1*s* spectrum of CF_4 involves comingling of transitions to both R MO's and to V σ*(C—F) levels. However, there is no *a priori* way of knowing how this will be reflected in the perfluoroalkane spectra.

Because the separation between the C 1*s*(CF_2) and C 1*s*(CF_3) ionization potentials is nearly 2 eV (31) in the perfluoro-*n*-alkanes, one has two partially overlapped inner-shell spectra and difficulties therefrom for perfluoro-*n*-alkanes larger than C_2F_6. In this case, it is best to first focus on a molecule containing only CF_3 groups (CF_3CF_3) and a molecule containing only CF_2 groups [$(CF_2)_6$], and then to apply this information toward interpreting the spectrum of $CF_3(CF_2)_xCF_3$, x = 1–4, which can be considered as a mixture of more or less weakly interacting CF_3 and CF_2 chromophores. The spectra of the molecular pair C_2H_6 and C_2F_6 and the pair C_6H_{12} and C_6F_{12} are

TABLE 1. Transition energies (E, eV), term values (TV, eV) and proposed assignments for features in the C 1*s* spectra of the perfluoro-*n*-alkanes

	C_2F_6		C_3F_8		*n*-C_4F_{10}		*n*-C_5F_{12}		*n*-C_6F_{14}		Assignment[b]	
Band[a]	E	TV	E	TV	E	TV	E	TV	E	TV	C 1*s*(CF_2)	C 1*s*(CF_3)
A			293.0	4.7	292.8	4.9	292.7	5.0	292.7	5.0	σ^*(C—F)$_\sigma$	
A'	295.4	4.5	295.3	4.4	295.4	4.3	295.2	4.5	295.3	4.4		σ^*(C—F)$_\pi$
B			295.3	2.4	295.4	2.3	295.2	2.5	295.3	2.4	σ^*(C—F)$_\sigma$	
B'	297.7	2.1	297.6	2.1	297.5	2.2	297.3	2.4	297.3	2.4		σ^*(C—F)$_\sigma$
IP			297.74	—	297.7[c]	—	297.7[c]	—	297.7[c]	—		
IP'	299.85	—	299.74	—	299.7[c]	—	299.7[c]	—	299.7[c]	—		
C			298.5	−0.8	298.9	−1.2	298.8	−1.1	298.6	−0.9	σ^*(C—C)	
C'	300.5	−0.7	300.8	−1.1	300.8	−1.1	302	−2.3	301	−1.3		σ^*(C—C)
D,*D'*	311	−11	311	−11	309	−11	308	−11	308	−11	Shape resonance or delayed onset	

[a]The unprimed bands originate at CF_2 groups whereas the primed bands originate at CF_3.

[b]Rydberg excitations to *3s*, *3p*, *4p*, etc. will fall at energies below the ionization potentials. However, they are either overlapped or mixed with the excitations to σ* and do not appear as discrete features in these spectra.

[c]Ionization potentials assumed equal to those of C_3F_8 (31).

presented on common term value and oscillator strength scales (Fig. 1) to facilitate interpretation of the mixed chromophore systems. The spectrum of another possible CF_2 prototype, polytetrafluoroethylene (PTFE) $(CF_2)_x$ taken from the work of Ohta *et al.* (32) also appears in this figure.

III.1. The CF_3 spectrum

We consider CF_3CF_3 to be the prototypical CF_3 chromophore. This molecule has a spectrum in the C 1*s* region, Fig. 1 and Table 1, which not only is deeper by about 8 eV than that of CH_3CH_3, but also has a dramatically different oscillator strength distribution. Based on term values, analogy can be made between band *A'* of C_2F_6 (295.4 eV, 4.50 eV term value) and band 1 of C_2H_6 (286.9 eV, 3.69 eV term value) (25). In C_2H_6, this band has been assigned as terminating at a mixed $3s/\sigma^*$ MO with predominantly R character (1, 25). The increased term values of the transitions to $3s/\sigma^*$ upon fluorination of a wide variety of systems is well known (1, 2). What is more interesting here is that in C_2H_6 the C $1s \rightarrow 3s/\sigma^*$ transition is relatively weak and seems to be following the quasiatomic propensity rule forbidding $1s \rightarrow 3s$ transitions, whereas what appears to be the corresponding transition in C_2F_6 has more than 10 times the oscillator strength and is the most prominent band in the spectrum! Since the most intense Rydberg transitions in VUV spectroscopy have oscillator strengths of only 0.08 per degree of degeneracy (1) and R transitions in the inner-shell region will be much weaker still, both the 0.15 oscillator strength of the *A'* band of C_2F_6 and the increased term value indicate that the F atoms of C_2F_6 are strongly perturbing the $3s/\sigma^*$ orbital, acting to make it increasingly valence shell. In light of this, it follows that the 295.4 eV feature of C_2F_6 (band *A'*) can be considered as predominantly C $1s \rightarrow \sigma^*$(C—F). The spectral intensification and change of character from $3s/\sigma^*$-(C—H) to σ^*(C—F) on going from C_2H_6 to C_2F_6 has its parallels, for these changes also are observed on going from C_2H_4 to C_2F_4 (22, 24) and throughout the fluoromethane series (1, 12, 13, 26, 29).

Band *B'* of C_2F_6 with a term value of 2.09 eV has its counterpart in C_2H_6 (band 2), thought to be mixed $1s \rightarrow 3p$ and $1s \rightarrow \sigma^*$(C—H) (25, 33) with a term value of 2.70 eV. In this case, band *B'* has an oscillator strength which is threefold larger than that of band 2 in C_2H_6. Note that the observed increase of the *A'* term value, decrease of the *B'* term value and intensification of both transitions in C_2F_6 all follow naturally from a strong mixing of *3s* and *3p* orbitals among themselves along with further strong mixing with σ* V orbitals. See sect. III.2 for further discussion of excitations to σ*(C—F) in the CF_3 group.

The assignment of both *A'* and *B'* as transitions terminating at σ*(C—F) is consistent with the bond length/term value correlation (4) which predicts a term value of 2.3 eV for the 1.326 Å C—F bond length in C_2F_6. This predicted value lies between the term values observed for features *A'* (4.5 eV) and *B'* (2.1 eV). Although the splitting of the σ*(C—F) intensity into two peaks contradicts the bond-localized excitation assumption of the bond length correlation, this splitting (2.4 eV) is relatively small and the two observed lines straddle the predicted C $1s \rightarrow$ σ*(C—F) position. More dramatic examples of this type of deviation from the most simple implementation of the bond length correlation have been noted in the σ*(C—C) resonances of benzene and the fluorobenzenes (10), as well as the σ*(C—O) resonances of CO_2 (5).

Band *C'* of C_2F_6 (300.5 eV, 0.7 eV beyond the ionization potential) has its counterpart in C_2H_6 as band 4 (290.8 eV, 0.2 eV beyond the ionization potential). As in the CH_4/C_2H_6 comparison (3, 25), we see on comparing the CF_4 (26–30) and C_2F_6 (Fig. 1 and Table 1) inner-shell spectra, that the *C'* shape resonance of C_2F_6 does not appear in CF_4 and so must terminate at σ*(C—C). The doubling of the C $1s \rightarrow$σ*(C—C) oscillator strength upon perfluorinating C_2H_6 can be rationalized in terms of the potential barrier localization of the σ*(C—C) orbital (34).

In C_2F_6, band *D'* can be assigned as either an unusually strong first EXAFS feature or alternatively, feature *D'* may represent the energy at which the C 1*s* photoelectron energy exceeds the height of the potential barrier associated with the large number of electronegative F atoms in this molecule (34). Within the framework of group-localized core excitations, the *D'* excitation energy is much too large to terminate at σ*(C—C) or σ*(C—F) (4). In the potential barrier interpretation, the spectral feature of interest is not the *D'* maximum, but rather the depressed C 1*s* continuum intensity between 302 and 310 eV which reaches a minimum value of 0.01 eV^{-1} at 305 eV compared to a value of 0.03 eV^{-1} at an equivalent photoelectron energy in C_2H_6 (Fig. 1). A strong suppression of the C 1*s*

TABLE 2. Oscillator strengths ($\times 10^{-2}$) for discrete and continuum regions in the C 1s spectra of the perfluoroalkanes and selected alkanes

Species	A^a	σ^{*b}	f(disc)^c	f/x^d	f''(cont)$/x^e$	f'(cont)^f	f'/x^g	f/f'
CF_4			36	36	5.7	25	25	1.4
C_2F_6			80	40	8.5	60	30	1.3
C_3F_8	12		107	36	8.2	82	27	1.3
C_4F_{10}	22		125	31	8.2	103	26	1.2
C_5F_{12}	27		135	27	7.6	118	24	1.1
C_6F_{14}	29		154	25	7.7	136	23	1.1
C_3F_6	7	7	84	26	7.7	68	23	1.2
C_4F_8	9	12	111	28	8.1	89	22	1.2
C_5F_{10}	14	15	139	28	7.4	119	24	1.3
C_6F_{12}	10^h	30^h	154	26	8.2	143	24	1.1
C_2H_6			14	7	11.7	61	31	0.23
C_6H_{12}			34	5.7	13.0	210	35	0.16
C_6H_{14}			36	6.1	10.7	179	30	0.20

[a]Oscillator strength for C 1s(CF_2) → σ*(C—F), feature A, derived from curve fitting.
[b]Oscillator strength for C 1s(CF_2) → σ*(C—C) derived from curve fitting.
[c]Oscillator strength summed from threshold to the C 1s ionization potential.
[d]Oscillator strength in the discrete region on a per-carbon-atom basis.
[e]f'' is the oscillator strength summed from 4 eV beyond the ionization potential to 12 eV beyond that point, on a per-carbon-atom basis.
[f]f' is the oscillator strength summed from the C 1s ionization potential to a point 25 eV beyond the IP.
[g]Oscillator strength in the continuum region (0–25 eV relative to the ionization potential) on a per-carbon-atom basis.
[h]This division of the total oscillator strength of the structured first band of C_6F_{12} (0.40) is derived from curve fitting.

near-continuum intensity of CF_4 relative to that in CH_4 was found in recent quantitative optical studies (29). If one follows the continuum intensity backward from high energy loss to the ionization potential, the slow rise in continuum begins to fall off approximately at the maximum of the apparent peak. If this is interpreted as the energy at which a potential barrier begins to depress the ionization cross section, then one arrives at an estimate of approximately 11 eV for the height of the centrifugal barrier in C_2F_8. It is interesting that this estimate is slightly greater than the estimate of 8 eV for the centrifugal barrier in C_2F_4 reached using slightly different arguments (24). That the potential barrier becomes larger as the number of electronegative F atoms surrounding the central C atom increases is intuitively acceptable. The depressed continuum intensity between 302 and 310 eV is found not only in C_2F_6 but also throughout all of the perfluoroalkanes. This is shown in Table 2, which compares on a per-C-atom basis the near-continuum intensity (from −4 to −12 eV term value) for all of the compounds studied in this work with those of the representative alkanes C_2H_6, C_6H_{12}, and C_6H_{14}.

Based on the above considerations, and with due allowance for the effects of fluorination on term values (1) and relative intensities (34), it is concluded that the A' and B' transitions of C_2F_6 are superficially related to those of C_2H_6 labelled 1 and 2 in Fig. 1, but whereas those of the latter are largely R in character, those of C_2F_6 are largely V. Shape resonances which closely resemble one another in energy and width are seen in C_2F_6 (band C') and C_2H_6 (band 4); both terminate at σ*(C—C).

III.2. The CF_2 spectrum

We use perfluorocyclohexane $(CF_2)_6$ as a model of the CF_2 inner-shell spectrum and compare its spectrum with that of $(CH_2)_6$ in Fig. 1. As an alkane is lengthened, the term values for the excitations to $3s/\sigma^*$ and to $3p/\sigma^*$ orbitals converge upon one another at *ca.* 2.6 eV (1, 25). Accordingly, in C_6H_{12} (8), the transitions from C 1s to $3s/\sigma^*$ and $3p/\sigma^*$ no longer can be resolved, and instead form a single sharp feature (bands 1 and 2) with a term value of 2.60 eV. This coincidence is not expected in C_6F_{12}, for a large $3s/\sigma^*$–$3p/\sigma^*$ splitting (2–4 eV) often is observed in heavily fluorinated molecules. Indeed, the lowest two sharp bands (A and B) in the inner-shell spectrum of C_6F_{12} have term values of 4.8 and 2.11 eV, in the range characteristic of R transitions terminating at 3s and 3p orbitals, respectively. However, as with the bands of C_2F_6, these bands of C_6F_{12} when compared to those of C_6H_{12} are seen to have the greatly increased oscillator strengths more characteristic of valence transitions. The V bands in $(CF_2)_6$ are sufficiently broad that the C 1s → 4p transition (band 3 of the alkanes) does not appear. The dominance of C 1s → σ*(C—F) and the relative weakness of C 1s → R transitions also is consistent with the potential barrier model for core excitation in perfluoro compounds (34). Features C (C 1s → σ*(C—C)) and D appear in C_6F_{12} with term values close to those observed in C_2F_6. Feature C in C_6F_{12} has a high-energy shoulder and is broadened with respect to that in C_2F_6, consistent with contributions from several overlapping C 1s → σ*(C—C) transitions in this region, as noted as well for the transitions to σ*(C—C) in the longer alkanes.

If one considers the peak heights or oscillator strengths of bands A/A' and B/B' in C_6F_{12}/C_2F_6, one finds that, per carbon atom, the sum of the A' and B' oscillator strengths of C_2F_6 is roughly twice that of the A and B bands of C_6F_{12}, Table 2. This is somewhat larger than but similar to the relative numbers of C—F bonds in the CF_3 and CF_2 groups, for which C_2F_6 and C_6F_{12} are taken as prototypes. The oscillator strength per carbon atom of bands B and B' are approximately the same in the two species, whereas that for band A' in C_2F_6 is 2–3 times greater

than that for band A in C_6F_{12}. If one considers a local C_{2v} symmetry for the CF_2 group and local C_{3v} symmetry for the CF_3 group, the oscillator strengths then suggest that peaks B and B' correspond to C $1s$ excitations to the nondegenerate local σ^*(C—F) MO in both cases (a_1 in CF_3; a_1 or b_1 in CF_2). On the other hand, peaks A and A' then correspond to C $1s$ excitations to σ^*(C—F) levels of e symmetry in CF_3 groups but b_1 or a_1 symmetry in CF_2 groups. Thus in C $1s(CF_3)$ spectra, we label the A' band as $\sigma^*(C—F)_\pi$ and the B' band as $\sigma^*(C—F)_\sigma$. It should be noted that in this assignment scheme for CF_3, the A' and B' bands do not necessarily have the same symmetries as the $3s$ and $3p$ R orbitals, and so we are not dealing with the intensification of R transitions by mixing with V transitions, but rather with the overlapping of intense V transitions upon R transitions. It also should be noted that there is not necessarily a general one-to-one relationship between relative degeneracies and relative intensities. However, such a relationship is not unexpected when orbitals of similar character are involved.

Further support for a $\sigma^*(C—F)_\pi$ below $\sigma^*(C—F)_\sigma$ ordering of the CF_3 group orbitals in the C $1s$ excitation spectrum is found in the *ab initio* calculations for CF_3H and CF_2H_2 reported by Snyder and Basch (35). The C $1s$ spectra of CF_3H (14) and C_2F_6 are very similar except that the C_2F_6 spectral intensities are twice as large and there is additional intensity at the C $1s$ ionization potential associated with the C $1s \rightarrow \sigma^*$(C—C) promotion in C_2F_6. In the CF_3H ground state, a nondegenerate MO of σ^*(C—F) character ($8a_1$) is calculated to lie 1.8 eV above a degenerate pair of $\sigma^*(C–F)_\pi$ orbitals (*11*, *12e*), in agreement with the $\sigma^*(C—F)_\pi$ below $\sigma^*(C—F)_\sigma$ ordering we assign for C_2F_6 on the basis of intensities.

Similarly, the discrete portion of the C $1s$ spectrum of CF_2H_2 resembles that of C_6F_{12}, although additional sharp structures associated with C $1s \rightarrow \sigma^*$(C—H) transitions are observed in CF_2H_2, the second σ^*(C—F) feature is much weaker, and the C $1s \rightarrow \sigma^*$(C—C) transition is absent. This provides further justification for our use of these compounds to model the C $1s(CF_3)$ and C $1s(CF_2)$ excitations in perfluoro-*n*-alkanes.

The ground-state virtual orbital eigenfunctions of CF_3H and CF_2H_2 calculated by Snyder and Basch (35) also can be used to estimate the relative intensities of C $1s(CF_3) \rightarrow \sigma^*$(C—F) and C $1s(CF_2) \rightarrow \sigma^*$(C–F) transitions and thus to provide further support for our spectral interpretation. In the absence of strong distortions by the core hole, the intensity of C $1s$ (F $1s$) excitations to a virtual orbital are expected to be proportional to the squares of the C $2p$ (F $2p$) atomic orbital coefficients on the core excited atom. This approach has been used recently to compare calculated and experimentally derived spatial distributions of the π^*(C—O) orbital in substituted carbonyls (36). According to the double-zeta GTO calculations (35), the ratio of the squared coefficients in the $\sigma^*_\pi/\sigma^*_\sigma$ orbitals of CF_3H is 1.5 (using the diffuse component) and 1.0 (using the compact component) (35), while the ratios of the squared C $2p$ coefficients in the first two virtual orbitals in CF_2H_2 are 0.8 (diffuse) and 1.2 (compact). Thus the ground state calculation suggests that the C $1s(CF_3) \rightarrow \sigma^*(C—F)_\pi$ transition should be more intense than the C $1s(CF_3) \rightarrow \sigma^*(C—F)_\sigma$ transition while the two C $1s(CF_2) \rightarrow \sigma^*$(C—F) excitations should be of similar magnitude. This is consistent with our interpretation of the virtual orbital ordering in C_2F_6 since the ratio of the areas of the first two peaks in the C $1s$ spectra is 2.7 in C_2F_6 and 0.7 in C_6F_{12}.

Further support for a $\sigma^*(C—F)_\pi$ below $\sigma^*(C—F)_\sigma$ ordering of the CF_3 group orbitals in the C $1s$ excitation spectrum is found in the *ab initio* calculation for C_2F_6 (see sect. VI). In this, we find the lowest virtual orbital to be C—F antibonding with overall e_u symmetry in the molecular point group; this corresponds to $\sigma^*(C–F)_\pi$. The virtual orbital corresponding to $\sigma^*(C–F)_\sigma$ is a_{2u} in the molecular point group, an orbital which is 2.92 eV higher in energy.

III.3. Condensed phase spectra

It is generally acknowledged (1, 7) that R states are very susceptible to perturbation by adjacent molecules in a condensed phase, whereas valence excitations are much less so. The R excitations of a solute molecule in a condensed phase of low electron mobility generally are shifted to higher energies and broadened so greatly as to make the transitions effectively disappear, whereas a valence transition to σ^* in the same molecule will suffer a much weaker perturbation, shifting slightly to lower energy. It is of great interest to use this difference to further illuminate the R/V characters of the inner-shell excitations in perfluoroalkanes. Possible problems which one might encounter using this approach are the effect due to a matrix/solvent of high electron mobility (rare gases, metal surfaces, matrices/solvents of near spherical symmetry, etc.) and the deperturbation which might be wrought by the matrix/solvent on a transition which in the gas phase is of mixed R/V character (37).

The electron yield spectrum of a thin film of PTFE recorded by Ohta *et al.* (32) using synchrotron radiation is plotted in Fig. 1 for comparison with that of C_6F_{12} in the vapor phase. A very similar spectrum of PTFE has been recorded by Fink *et al.* using inelastic electron scattering (38). There is a remarkably close correspondence between the bands of the $(CF_2)_x$ and $(CF_2)_6$ systems in spite of the fact that one of them is in the vapor phase and the other is a solid of low electron mobility. One argues from this that since the spectra of $(CF_2)_x$ and $(CF_2)_6$ are in one-to-one correspondence and since all of the observed bands of PTFE are necessarily valence, that all of the resolvable features of C_6F_{12} also are predominantly valence shell. It follows as well that since we are taking C_6F_{12} as prototypical of the CF_2 group excitation spectrum, all of the excitations attributed to the CF_2 group in whatever molecule are also strongly valence shell.

As with the PTFE/C_6F_{12} pair, comparison of the C $1s$ spectra of the analogous pair polyethylene (PE)/C_6H_{12} also shows a remarkably close correspondence of excitations (33). Further, these spectra bear close resemblance to those of the much smaller vapor phase *n*-alkanes (C_2H_6–C_6H_{14}). In the case of PE, polarization studies have been performed on the oriented material, leading to confirmation of the assignments of the two lowest energy features as valence excitations terminating at σ^*(C—H) and σ^*(C—C) MO's, respectively (32, 33). By analogy with the situation in PE, the B and C bands of oriented PTFE (292.7 and 296.0 eV), Fig. 1, should be polarized respectively perpendicular and parallel to the C—C direction.

III.4. The spectra of $CF_3(CF_2)_xCF_3$

It appears from the work quoted above that the inner-shell excitations in the CF_2 and CF_3 groups are very much localized. Working further in this approximation, one expects in zeroth order that the C $1s$ inner-shell spectrum of a perfluoro-*n*-alkane will be the sum of the spectra of its constituent CF_2 and CF_3 groups. Deviations from this may be due to inter-group interactions which spread the excitation over two or more CF_x groups. Thus, within the localization model, consideration of the C_2F_6 and C_6F_{12}/PTFE spectra leads to certain expectations

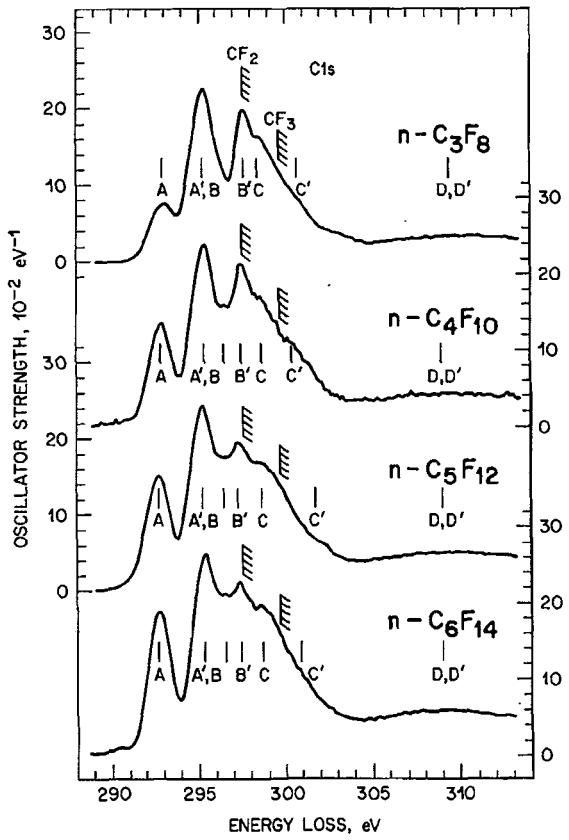

FIG. 2. Oscillator strength spectra of the perfluoro-*n*-alkanes in the C 1*s* region as derived from energy loss spectra (for details, see caption to Fig. 1). Inner-shell ionization potentials are shown by hatched areas. The unprimed transitions originate at CF_2 groups whereas the primed transitions originate at CF_3 groups.

in regard the spectra of perfluoro-*n*-alkanes: (*1*) On the term value scale, essentially the same spectral pattern is observed for CF_2 and CF_3 groups, although the relative intensities of the component transitions differ for the CF_2 and CF_3 chromophores. Thus the same transitions to σ*(C—F) and σ*(C—C) considered in sects. III.1 and III.2 will dominate the discrete structure of the perfluoro-*n*-alkane C 1*s* spectra, but with oscillator strengths proportional to the numbers of CF_2 and CF_3 groups in the molecule. (*2*) Spectra originating at CF_2 and CF_3 groups will be offset by the difference in the ionization potentials of these groups, typically 1.2–1.8 eV. Although the *A*/*B* and *A*′/*B*′ features are well separated in the spectrum of each chromophore, confusion may arise because their splitting in the perfluoro-*n*-alkanes will very nearly equal the splitting of the CF_2 and CF_3 ionization potentials. This leads to unavoidable coincidences of bands, e.g., the C 1*s*(CF_3) → σ* *A*′ transitions will be accidentally degenerate (or nearly so) with C 1*s*(CF_2) → σ* *B* transitions in all perfluoro-*n*-alkanes larger than C_2F_6. The characteristic relative intensities of bands *A* and *B* in the CF_2 and *A*′ and *B*′ in the CF_3 group spectra may assist in resolving this overlap.

Spectral analysis of the perfluoro-*n*-alkanes as a sum of CF_2 and CF_3 group excitations originating at C 1*s* is summarized in Table 1 and in Fig. 2; one sees a facile resolution of the spectra provided one accepts the unresolved coincidence of the *A*′ and *B* transitions in the C_3F_8–C_6F_{14} series. The (C 1*s*, σ*) term values of the lowest excitations increase very slowly with the size of the molecule, being 4.5 eV in C_2F_6 and reaching only 5.0 eV in C_6F_{14}. The term values for excitations originating at C 1*s*(CF_3) appear systematically smaller than those of the corresponding transitions originating at C 1*s*(CF_2). As expected from the localization model, the spectra of the perfluoro-*n*-alkanes can be interpreted as combinations of the spectra of the CF_2 and CF_3 groups. Only the transitions to σ* levels are seen. To some extent, this situation may result from the rather limited resolution (0.6 eV) of the present spectra, so that weak but discrete R features may be revealed with higher resolution studies. However, we expect them to be weaker and/or more congested than in CF_4 since the R structure in CF_4 is detected by our present apparatus.

The dramatic differences in the oscillator strength distributions for C 1*s* excitation in the perfluoro-*n*-alkanes as compared to the *n*-alkanes is emphasized by comparing the ratio of the sum of the discrete oscillator strengths to that obtained by integrating from the ionization potential to a point 25 eV beyond, Table 2. It is interesting to note that whereas the ratio of discrete to continuum oscillator strength values is 1.2 ± 0.1 for all of the perfluoro-*n*-alkanes (including CF_4), it is significantly lower for the *n*-alkanes (0.20 ± 0.05). It is clear as well that the oscillator strengths in the discrete regions of the C 1*s* spectra of the perfluoro-*n*-alkanes are many times larger than those in the corresponding *n*-alkanes, and much larger than expected solely from Rydberg excitations. This supports our interpretation of the discrete features in the perfluoro-*n*-alkanes as excitations to virtual orbitals of predominantly valence character. This also is consistent with the potential barrier model (34) since the intensities of transitions to inner-shell valence type orbitals are expected to be enhanced strongly in the core excitation spectrum of an atom surrounded by many highly electronegative atoms.

Our simplified view of the inner-shell spectra of the perfluoro-*n*-alkanes as sums of the CF_2 and CF_3 group excitations predicts that the intensity of a band such as *A* should scale linearly with the number of CF_2 groups in the molecule. In fact, if the C 1*s* spectra of C_2F_6 and C_6F_{12} are truly good models for the perfluoro-*n*-alkane spectra, then the oscillator strength of the *A* peak in a given $CF_3(CF_2)_xCF_3$ species should be predictable from the oscillator strength of the *A* peak in C_6F_{12}, scaled by $x/6$. As shown in Table 2, the oscillator strength of the first peak does increase systematically with x, but is almost twice as large as that predicted from C_6F_{12}. Our comparison of the C 1*s* oscillator strengths among these molecules must be treated with caution. The extrapolation of the background was made from a relatively short pre-edge region in some cases, and in all species the continuum intensity is very small relative to that of the discrete structure. Both factors contribute to the uncertainty in our determination of the C 1*s* continuum intensity at 25 eV beyond the ionization potential and thus to the estimated 20% uncertainty in the oscillator strength for peak A. If our results are confirmed by more precise measurements, it would appear that C_6F_{12} is not a perfect model for the C 1*s*(CF_2) excitations in the perfluoro-*n*-alkanes.

In our intensity analysis of band *A* in the perfluoro-*n*-alkanes, we have assumed that all of band *A* in C_6F_{12} corresponds to a transition to σ*(C—F). However, closer examination of this feature and comparison with the spectra of other perfluorocycloalkanes strongly suggest that there is a second transition to this band which terminates at σ*(C—C) and is common to all perfluorocycloalkanes (see sect. IV). In this regard, the spectrum of PTFE might be a better model for the perfluoro-*n*-alkanes than C_6F_{12}, especially if intensity information were available on it. Caution is therefore needed in applying an

independent-systems model to inner-shell spectra. Although this approach has worked well in the past (chloroethane (14) and methyl formate (39)), in the present case quantitative problems appear when comparing expectations with experiment. In view of the near degeneracy of the σ*(C—F) MO's within the CF_2 and CF_3 groups, mixing of these levels is not unexpected, and in part may be the reason behind the inconsistency between the observed and the predicted scaling of the *A*-band oscillator strengths with increasing numbers of CF_2 groups.

We similarly expect the peak at *ca.* 295 eV in the perfluoro-*n*-alkanes to grow in intensity with increasing chain length according to our assignment of it as overlapping *A'* and *B* transitions. However, the peak intensity of this feature is relatively constant at *ca.* 0.25 eV^{-1} in all species, contrary to the approximate doubling expected on going from C_3F_6 to C_6F_{12}. This suggests that the *A'* and *B* transitions possibly are not exactly aligned, but rather displaced so that the feature broadens rather than heightens as the chain length increases. This broadening is evident in Fig. 2, particularly on the high energy side.

III.5. Branched isomers

It is known from previous work (25) that there is little or no difference between the inner-shell spectra of the isomers *n*-pentane and neopentane, the reason being that at the present level of resolution there is no difference between the spectra of CH_2 and CH_3 groups. Because this is not true for CF_2 and CF_3 groups, it is anticipated that there will be significant differences between the C 1*s* spectrum of perfluoro-*n*-pentane and that of its isomer perfluoroneopentane since the latter contains no CF_2 groups. On the other hand, both contain CF_3 groups which should add their characteristic pattern to both spectra. There should be smaller differences in the F 1*s* spectra of these isomeric pentanes (see sect. V.2). The C 1*s* spectra of the two compounds appear in Figs. 2 and 3 and are summarized in Tables 1 and 3. Though C 1*s* ionization potentials are not known for $C(CF_3)_4$, the X-ray photoelectron spectra of other molecules (31) suggest ionization potentials of 293 eV for C 1*s*(C) and 300 eV for C 1*s*(CF_3). These reasonable values for the C 1*s* ionization potentials in turn result in quite reasonable term values for the observed transitions, Table 3.

The C 1*s* spectra of the C_5F_{12} isomers are similar in that they both show the *A'*, *B'*, *C'*, *D'* patterns of bands which correspond to transitions originating at the CF_3 groups. On the other hand, the four bands of perfluoro-*n*-pentane corresponding to transitions originating at the CF_2 groups (*A*, *B*, *C*, *D*) are replaced in perfluoroneopentane by only two relatively weak bands, *A* and *D*, which must originate at the central C atom of that molecule. The dominance of CF_3 group excitations in perfluoroneopentane leads to a remarkable similarity between its C 1*s* spectrum and that of C_2F_6 (Fig. 3), in spite of their very different symmetries. This similarity is reasonable if the C 1*s* holes are localized in the core excited states of each molecule, resulting in an effective C_{3v} symmetry at the core hole in each case.

Band *D* of $C(CF_3)_4$ originating at the central C atom has been assigned to a shape resonance or a delayed onset continuum feature, analogous to that discussed previously (see sect. III.1). The *A* band, while appearing relatively weak in the $C(CF_3)_4$ spectrum nonetheless has an oscillator strength of 0.095; though its term value of 2.6 eV is appropriate for a Rydberg upper state, the oscillator strength is too large for such an assignment. Thus the transition in question is assigned as C 1*s*(C) → σ*(C—F)$_\pi$.

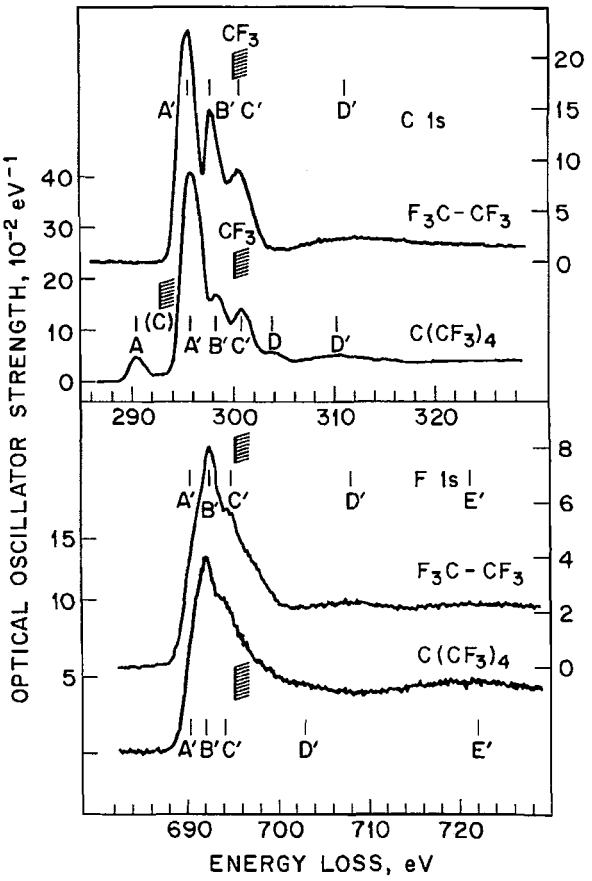

FIG. 3. Comparison of the oscillator strength spectra of C_2F_6 and $C(CF_3)_4$ in the C 1*s* (*upper panel*) and F 1*s* regions (*lower panel*). Primed and unprimed transitions originate with the CF_3 and C groups, respectively.

The term values of the C 1*s*(CF_3) → σ*(C—F)$_\pi$ and C 1*s*(CF_3) → σ*(C—F)$_\sigma$ transitions are 4.5 and 2.1 eV in C_2F_6 and 4.3 and 1.9 eV in $C(CF_3)_4$, respectively. The assignment of band *A* to C 1*s*(C) → σ*(C—F)$_\pi$ thus may seem strange based on the relatively low term value of 2.6 eV. However, it recently has been observed for a few well-defined cases (6) that transitions to highly localized molecular orbitals from the inner shells of atoms which are one atom removed from the localized bond show a decrease of 1–4 eV in their term value as compared to those in which the excitation involves a hole on an atom within the localized bond. A similar reduction of the term value also can be observed for valence excitations to the same σ* orbital. For example, inner-shell transitions to the local σ*(O—F) orbital of CF_3OF have term values of 11.1 and 11.0 eV in the O 1*s* and F 1*s*(OF) spectra, and are the dominant features of the spectra (6). Here the originating orbital has strong overlap with the terminating orbital and is highly localized. However, the C 1*s* → σ*(O—F) transition has a term value of only 7.0 eV and its oscillator strength is reduced by a factor of approximately 6 compared to the transition terminating at the same orbital in the O 1*s* and F 1*s*(OF) spectra. Similar discrepancies in term values and intensities also have been reported for inner-shell transitions to π* orbitals from local and distant sites in various carbonyls (36) and the fluoroethylenes (24).

The phenomenon of widely differing term values for transitions to a highly localized orbital when originating at atoms

TABLE 3. Transition energies (E, eV), term values (TV, eV), and proposed assignments for features in the C 1*s* and F 1*s* spectra of perfluoroneopentane

	Band	E	TV (C)	TV (CF_3)	Assignment (C)	Assignment (CF_3)
C 1*s*						
	A	290.4	2.6		$\sigma^*(C—F)_\sigma$	
	A'	295.7[a]		4.3		$\sigma^*(C—F)_\pi$
	B'	298.1		1.9		$\sigma^*(C—F)_\sigma$
	IP(C)[b]	293				
	IP'(CF_3)[b]	300				
	C'	300.7		−0.7		$\sigma^*(C—C)$
	D	303.8	−11		Shape resonance or delayed onset	
	D'	310		−10		σ^*
F 1*s*						
	A'	690		4.5	σ^*	
	B'	692.0[c]		2.4	$\sigma^*(C—F)$	
	C'	694.0		0.4	$\sigma^*(C—C)$	
	IP(*F*)[b]	694.45		—		
	D'	703		−9	Shape resonance or delayed onset	
	E'	722		−27	EXAFS	

[a]Calibrated as 8.33 (5) eV above the C 1*s* → 1π* band of CO.
[b]Ionization potentials estimated by comparison with known values (31) of related compounds, i.e., $CF_3C{=}CSF_5$ (292.5); CF_3CH_3 (292.1); $CF_3C{\equiv}CCF_3$ (292.7); $CF_3C{\equiv}CH$ (292.2); CF_3CF_3 (299.8 eV).
[c]Calibrated as 157.8 (1) eV above the O 1*s* → 1π* band of CO.

which are distant rather than close to that orbital can be rationalized in terms of an energy penalty which must be paid when significant charge transfer is involved in the excitation.

IV. Low-lying σ* MO's in perfluorocycloalkanes

To this point, there is no evidence in the inner-shell spectra of the perfluoro-*n*-alkanes for a distinct transition to σ* which lies below the normal Rydberg region, although there is evidence for intense C 1*s* → σ* transitions overlapping the R transitions and most likely mixing with them. However, the C 1*s* excitations in several perfluorocycloalkanes, Fig. 4 and Table 4, are distinctly different from those of their linear counterparts in this regard, Fig. 2. Consider perfluorocyclopropane C_3F_6, as an example. The lowest-energy band in the C 1*s* spectrum of C_3F_6, Fig. 4 and Table 4, has a very large term value of 6.1 eV. Inasmuch as the lowest energy band of the corresponding linear system C_3F_8 has a term value of only 4.7 eV, Table 1, it is clear that the first band in the C 1*s* spectrum of C_3F_6 is unusually low lying due to the cyclization. We conclude that it is an additional transition to a σ* valence MO lying below those of C_3F_8 in the 293–300 eV region, with an enhanced term value due to molecular strain.

The C 1*s* → σ* transition is a prominent low-lying feature in the inner-shell spectrum of cyclopropane (8). According to X-α (8) and SCF-MO calculations (40), the lowest σ* MO in cyclopropane is a_2', an MO which is strictly C—C antibonding and has no C—H contribution whatsoever. Presumably, the additional band which is so low lying in C_3F_6 is a C 1*s* → a_2' σ*(C—C) transition. On the other hand, a virtual orbital calculation of C_3F_6 (sect. VII) shows that the a_2'(C—C) level is only second lowest, with a_2' σ*(C—F) being lower by *ca.* 1.2 eV.

The next band in the C 1*s* spectrum of C_3F_6 has a term value of 4.4 eV and so is assignable as C 1*s* → σ*(C—F), i.e., on the basis of its term value it corresponds to the *A* band for C 1*s* (CF_2) excitation. The *B*-band transition in C_3F_6 falls at 294.1 eV with a term value of 3.1 eV. This term value is unexpectedly high for a *B* band (Table 1), however, the upward shift of this spectral feature relative to its position in the perfluoro-*n*-alkanes may be a consequence of σ*(C—C) mixing with σ*(C—F).

The assignment of the lowest band of C_3F_6 to a transition to σ*(C—C) follows from the very high strain energy of 54 kcal/mol estimated for this molecule (9). In this regard, it is interesting then that Liebman *et al.* (9), have estimated the strain energy in perfluorocyclobutane, C_4F_8, as 14.5-18 kcal/mol, this being due in part to F—F repulsions. We argue that bond strain can be a significant factor in a four-membered ring such as C_4F_8, and as with C_3F_6, again may lead to a transition to a low-lying σ*(C—C) MO.

The *A* band in C_4F_8 at 293.1 eV (C 1*s* → σ*(C—F), 4.2 eV term value) is preceded by a prominent band which has a term value of 6.0 eV, Fig. 5. This term value is much larger than that expected for a transition to σ*(C—F) (Table 1), and thus the transition is assigned as terminating at a σ*(C—C) valence orbital which is shifted down due to molecular strain. The abnormal nature of the lowest excitation from C 1*s* in C_4F_8 (Table 4) is obvious when compared to the C 1*s* spectrum of C_4H_8 and the other cycloalkanes (8). Similarly, there is no complement of the low-lying σ* band of C_4F_8 to be found in C_4F_{10}. The narrow shape resonance at 302 eV in C_4F_8, Fig. 4, having a term value of −4.6 eV also is unique when compared with the spectra of the perfluoro-*n*-alkanes, and again suggests that there is something unusual going on in the σ* manifold of this compound.

Though the idea that molecular strain can lead to a low-lying transition to σ*(C—C) is an attractive one in view of the support

TABLE 4. Transition energies (E, eV), term values (TV, eV), and proposed assignments for features in the C 1*s* spectra of the cyclic perfluoroalkanes

	C_3F_6		C_4F_8		C_5F_{10}		C_6F_{12}		
Band	E	TV	E	TV	E	TV	E	TV	Assignment
σ*	291.1	6.1	291.2	6.0	291.7	5.5	292.2	5.0	σ*(C—C)
A	292.8	4.4	293.1	4.2	293.2	4.0	293.2	4.0	σ*(C—F)
B	294.1	3.1	295.0	2.3	295.1	2.1	295.1	2.1	σ*(C—F)
4	295.0	2.2	296.3	1.0	296.4	0.8	—	—	
IP	297.2[a]	—	297.2	—	297.2[a]	—	297.2[a]	—	
C	298	−0.8	297.4	−0.2	299	−2	298.3	−1.1	σ*(C—C)
6	—	—	301.9	−4.6			300.1	−2.9	σ*
D	309	−12	310	−13	309	−12	308.2	−11	EXAFS

[a]Taken as equal to that of C_4F_8 (31).

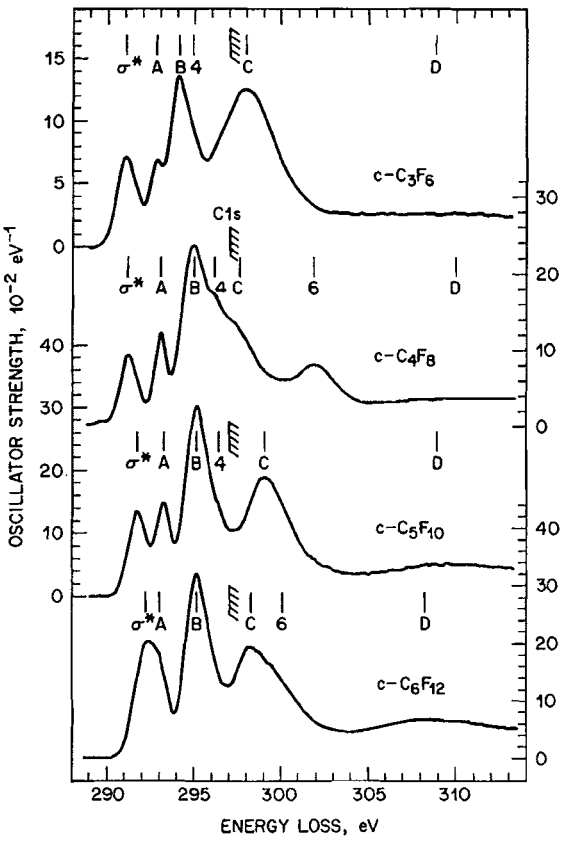

FIG. 4. Oscillator strength spectra of the perfluoro-*n*-alkanes in the C 1*s* region.

it receives from the C 1*s* spectra of C_3F_6, C_3H_6 (8) and C_4F_8, note too that the strain energy in C_4H_8 is 6 kcal/mol *higher* than in C_4F_8, yet there is no prominent, low-lying transition to σ*(C—C) in its inner-shell spectrum (8). Perhaps the low-lying position of the σ*(C—C) MO in C_4F_8 is due in part to its mixing with the low-lying σ*(C—F) levels. Note that an empirical analysis of the outer-shell spectrum of C_4H_8 (1) did lead to the suggestion of a valence excitation to σ* preceding the lowest R transition.

To this point, the role of strain in lowering σ* seems reasonable, with low-lying σ*(C—C) MO's appearing in the strained molecules C_3F_6 and C_4F_8, but not in the open chain relatives C_3F_8 and C_4F_{10}, nor apparently in C_6F_{12}. Though there is no data on molecular strain in C_5F_{10}, data on C_5H_{10} (41) shows it to be almost strain-free. Thus for C_5F_{10}, one might expect a C 1*s* spectrum much like that of C_6F_{12}. How surprising then to see, Fig. 6, that C_5F_{10} also shows a low-lying transition to σ*(C—C)!

The presence of an "extra" low-lying band in the spectra of the perfluorocycloalkanes is graphically illustrated in Figs. 5 and 6, where the C 1*s* spectra of the corresponding cyclic and linear perfluoroalkanes are compared on the basis of energy and intensity. One sees clearly from these comparisons that the lowest energy feature in the C_3, C_4, and C_5 linear compounds correspond to the second lowest in the cyclic compounds. The term values of the lowest bands in the cyclic systems, Table 4, are far too large for excitations to σ*(C—F) MO's, and so must terminate at σ*(C—C). A careful examination of the "C 1*s* → σ*(C—F)" transition of C_6F_{12} (Fig. 4) at 292.4 eV in fact shows that it too consists of two strongly overlapped transitions, the lower one of which is presumably a transition to σ*(C—C). With this feature in place, one sees a monotonic trend of the (C 1*s*, σ*(C—C)) term value from 6.1 to 4.8 eV as the ring strain decreases from C_3F_6 to C_6F_{12}.

It is at first sight anomalous that C_5F_{10} and C_6F_{12} would show low-lying excitations to σ*(C—C) due to strain (Fig. 6) when the C_5H_{10} and C_6H_{12} rings have strain energies of only 6.2 and 0.0 kcal/mol, respectively (41). However, it must be remembered that this argument neglects the F—F repulsions undoubtedly present in the perfluoro derivatives. The possibility that the σ*(C—C) level is low-lying in the perfluorocycloalkanes because the C 1*s* and σ* levels are delocalized around the rings leads to the expectation that, all other factors being equal, the (C 1*s*, σ*) term value will be largest in C_6F_{12} and smallest in C_2F_6, whereas the opposite is observed. The persistence of a low-lying σ*(C—C) level up to C_6F_{12} in the perfluorocycloalkanes may be due to mixing with low-lying σ*(C—F) levels (symmetry allowing) which amplifies the strain shift.

One can imagine that the $(CF_2)_x$ ring is formed by removing a CF_2 group from $(CF_2)_{x+1}$ and rejoining the terminal CF_2 groups. If this exercise is performed on perfluorocyclopropane, the result is tetrafluoroethylene, which we take for our purposes as a two-membered ring. In this two-membered ring, the MO conventionally taken as the "π" MO is the one that closes the ring; this MO is here relabelled σ′, while its antibonding counterpart (π*) is relabelled σ′*. Of course, the "two-membered ring" is extremely strained and so will have an unusually small σ′−σ′*

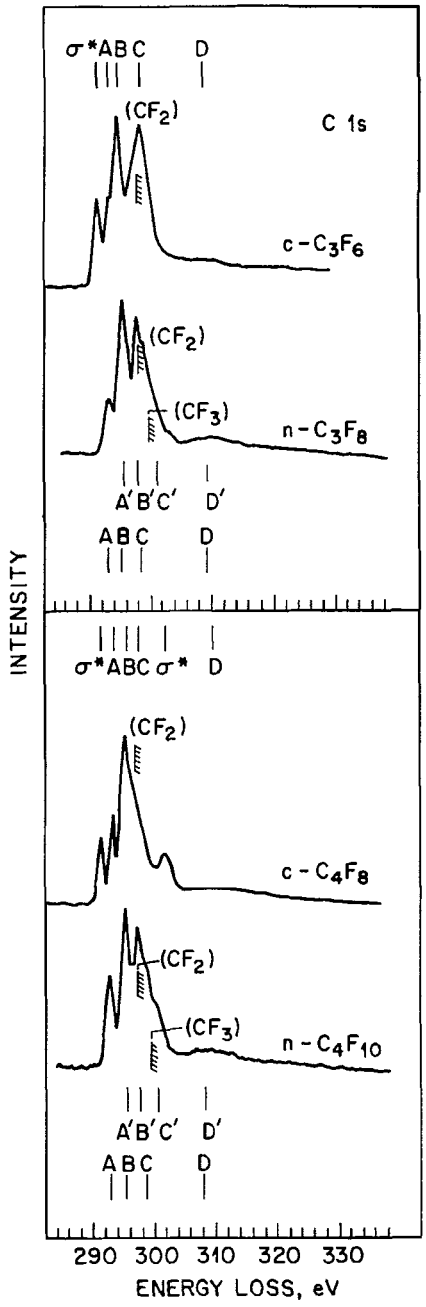

FIG. 5. Comparison of the C 1*s* spectra of the C_3 and C_4 perfluorocycloalkanes with those of corresponding perfluoro-*n*-alkanes.

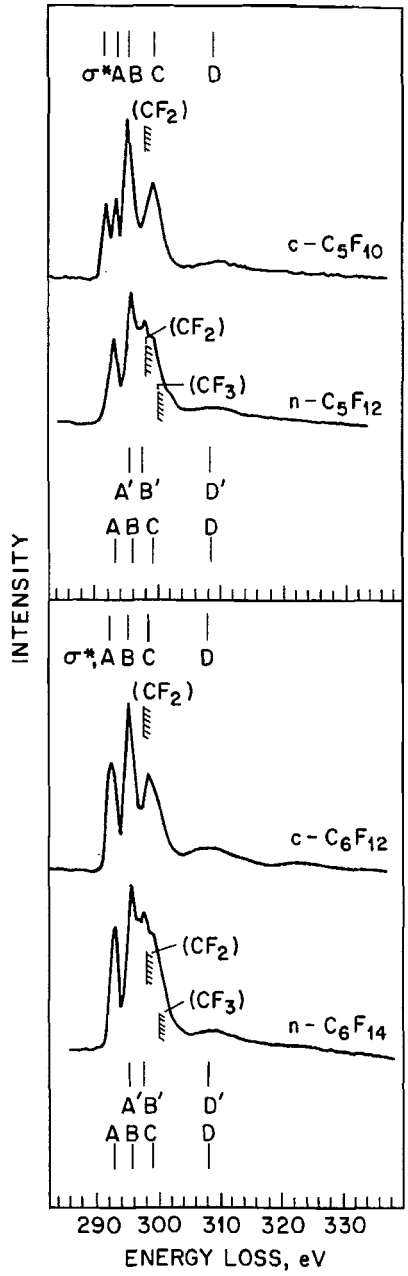

FIG. 6. Comparison of the C 1*s* spectra of the C_5 and C_6 perfluorocycloalkanes with those of the corresponding perfluoro-*n*-alkanes.

split. As anticipated from this, the C $1s \rightarrow \sigma'^*$ excitation of tetrafluoroethylene (conventionally written as C $1s \rightarrow \pi^*$) falls well below the lowest Rydberg excitation, having a term value of 6.47 eV (24). In this brief discussion, it is not our aim to propose a new nomenclature for olefins in which π/π^* and σ/σ^* are interchanged, but rather to show how the inner-shell spectra of unsaturates can be related to those of saturated compounds by virtue of the high strain in the former when considered as "cyclic" systems. If C_2F_4 is added to the list of strained perfluorocycloalkanes, then the term value trend for the C $1s \rightarrow \sigma^*$(C—C) transition stretches monotonically from 6.47 to 4.8 eV.

V. F 1*s* spectra of the perfluoroalkanes

Although not as well structured as those from C 1*s*, the F 1*s* spectra of the perfluoroalkanes also are of use when investigating low-lying transitions to σ^*. Note however, that ionization from F 1*s* in CF_4 is unusually broad (FWHM *ca.* 1.5 eV) due to dissociation of the F $1s^{-1}$ molecular ion (15). The strongly dissociative nature of F $1s^{-1}$ states is easily understood within the $Z + 1$ equivalent core model whereby the F 1*s* ionized atom is replaced by a Ne atom. This dissociation leads to very broad features in the F 1*s* inner-shell spectra of all of the perfluoroalkanes. In a previous study of the F 1*s* spectra of the

fluoromethanes, the first broad bands below the F 1*s* ionization potentials were assigned as terminating at antibonding V levels (42).

*V.1. The perfluoro-*n*-alkanes*

Our experience from earlier work on perfluorinated systems (10, 22, 24, 43) is that many of the transitions appearing in the C 1*s* spectra also appear in the F 1*s* spectra, though with poorer resolution and often with somewhat smaller term values. This is the case as well in the perfluoroalkanes. The F 1*s* spectra of the perfluoro-*n*-alkanes are plotted in Fig. 7, in comparison with those of the perfluorocycloalkanes. The spectral energies, term values and assignments are tabulated in Tables 3, 5, and 6. The poorly resolved character of the F 1*s* spectra is due not only to the large linewidths of the transitions to dissociative excited states (15), but also to the fact that the F 1*s*(CF_3) and F 1*s*(CF_2) ionization potentials are separated by only 1.5 eV (assuming that the measured ionization potentials of C_3F_8 (31) apply as well to the higher members of the perfluoro-*n*-alkanes series). Nonetheless, certain aspects of the F 1*s* spectra are clear:

(*1*) In the case of C_2F_6 (see Fig. 3), the F 1*s*(CF_3) → σ*(C—F) *A′* band is expected to have a term value of *ca.* 4.3–5.0 eV, which fits for the barely perceptible shoulder at 690 eV having a 5.3 eV term value. In C_3F_8 the *A′* shoulder is more easily seen (689.9 eV) and is probably at 690–691 eV in the F 1*s* spectra of the other compounds in this series. Note too, there is an F 1*s*(CF_2) ionization in the C_3F_8–C_6F_{14} series which is *ca.* 1.5 eV lower than that from F 1*s*(CF_3), yet there are no signs whatever of the F 1*s*(CF_2) → σ*(C—F) transitions! Since we are confident where these missing transitions should appear, we are led to conclude that the F 1*s*(CF_2) → σ*(C–F) *A* band transitions are unusually weak. The 689.9 eV band of C_3F_8 is predominantly F 1*s*(CF_3) → σ*(C—F). As in the C 1*s* spectra, there is nothing in the F 1*s* spectra of the perfluoro-*n*-alkanes to suggest a distinct σ* MO lying below the R levels.

(*2*) Although the F 1*s* → σ* *A* and *A′* transitions appear to be strongly electric-dipole forbidden, the F 1*s* → σ* transitions *B* and *B′* should be strongly dipole allowed and thus the spectra should show two intense bands separate by *ca.* 1.5 eV, the difference of F 1*s* (CF_2) and F 1*s*(CF_3) ionization potentials. Indeed, the first two intense peaks in the F 1*s* spectra of C_3F_8 to C_6F_{14} are separated by *ca.* 1.5 eV.

(*3*) What appear to be high-energy shape resonances in the F 1*s* spectra of the perfluoro-*n*-alkanes from CF_4 to C_6F_{14} (features *D* and *D′*) have term values of *ca.* −14 eV, and seem to parallel those observed in the C 1*s* spectra with nearly the same term values (−11 eV). However, EXAFS or delayed continuum onset assignments also are possibilities here. The minima between *C* and *D* in the F 1*s* spectra are much less pronounced than the corresponding minima in the C 1*s* spectra. This is consistent with a potential barrier, delayed continuum onset interpretation of band *D*, since the F atoms are on the periphery of the molecule and thus should experience a smaller barrier.

(*4*) There are peaks in the F 1*s* spectra at 694–695 eV (*C′*) which are just at the F 1*s*(CF_3) ionization potential. It seems likely that these are F 1*s*(CF_2) → σ*(C—C) shape resonances corresponding to band *C*, *C′* in the C 1*s* spectra.

(*5*) A very broad feature (*E*, *E′*) has a term value of *ca.* −28 eV in CF_4 to C_6F_{14}, and does not appear in any of the C 1*s* spectra. This is likely to be an EXAFS oscillation associated with backscattering from an F atom bonded to the same C atom as that to which the core-excited F atom is attached.

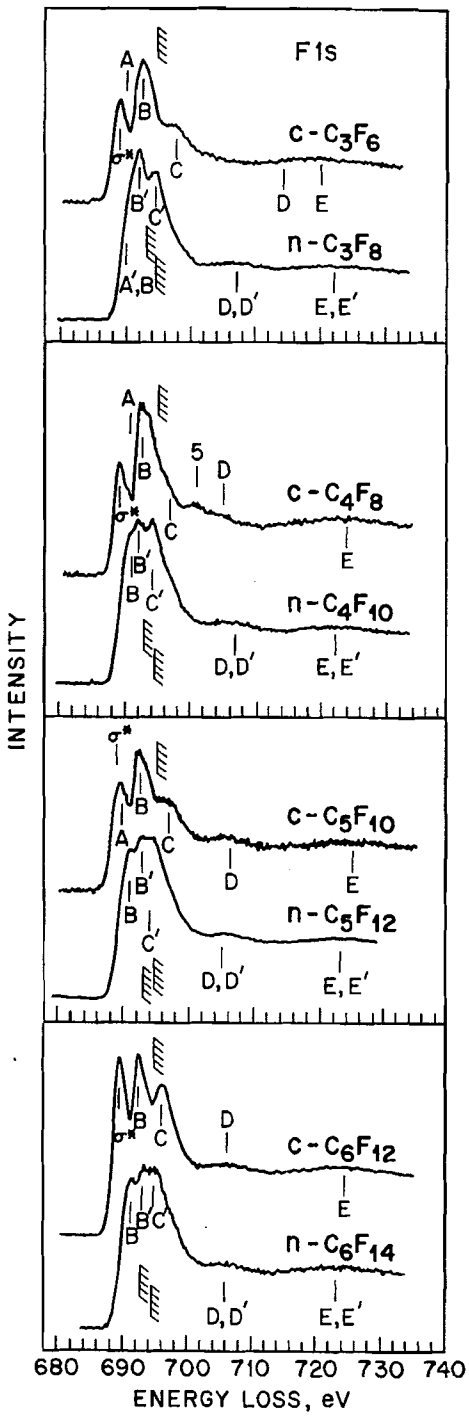

FIG. 7. Oscillator strength spectra of the perfluoro-*n*-alkanes and perfluorocycloalkanes in the F 1*s* region as derived from energy-loss spectra. Inner-shell ionization potentials are shown by hatched areas. The unprimed transitions originate at CF_2 groups whereas the primed transitions originate at CF_3 groups.

V.2. Branched perfluoroalkanes

Even more than with the C 1*s* spectra, the F 1*s* spectra of C_2F_6 and $C(CF_3)_4$ show a remarkable match, Fig. 3 and Tables 3 and 4. This close similarity arises not only because all of the F atoms in the two molecules are in CF_3 groups and thus are spectroscopically equivalent at our resolution, but also because of the apparent localization of the excitations to the CF_3 groups. This

TABLE 5 Transition energies (E, eV), term values (TV, eV), and proposed assignments for features in the F 1*s* spectra of the perfluoro-*n*-alkanes

	C_2F_6		C_3F_8		*n*-C_4F_{10}		*n*-C_5F_{12}		*n*-C_6F_{14}		Assignment	
Band[a]	E	TV	E	TV	E	TV	E	TV	E	TV	F 1*s*(CF_2)	F 1*s*(CF_3)
A'	690	5.3	689.9	4.7								σ^*(C—F)$_\pi$
B			689.9	3.1	691	2.1	691.0	2.1	691.3	1.8	σ^*(C—F)	
B'	692.7	2.6	692.0	2.6	692.2	2.4	692.7	1.9	693.3	1.3		σ^*(C—F)$_\sigma$
C'	694.7	0.6	694.4	0.2	694.3	0.3	694	0.6	694.9	−0.3		σ^*(C—C)
IP(CF_2)	—	—	693.07	—	693.1[b]	—	693.1[b]	—	693.1[b]	—		
IP'(CF_3)	695.33	—	694.61	—	694.6[b]	—	694.6[b]	—	694.6	—		
D,D'	708	−13	707	−13	706	−11	705	−10	706	−11	Shape resonance or delayed onset	
E,E'	721	−26	722	−28	722	−27	723	−28	723	−28	EXAFS	

[a]The unprimed bands originate at CF_2 groups whereas the primed bands originate at CF_3.
[b]Ionization potentials assumed to be equal to those of C_3F_8 (31).

TABLE 6. Transition energies (E, eV), term values (TV, eV), and proposed assignments for features in the F 1*s* spectra of the cyclic perfluoroalkanes

	C_3F_6		C_4F_8		C_5F_{10}		C_6F_{12}		
Band	E	TV	E	TV	E	TV	E	TV	Assignment
σ^*	689.2	5.9	689.5	5.6	689.4	5.7	—	—	σ^*(C—C)
A	690	5.1	690.8	4.3	690	5.1	689.8	5.3	σ^*(C—F)
B	692.8	2.3	693.2	1.9	692.4	2.7	692.7	2.4	σ^*(C—F)
IP	695.1[a]	—	695.1	—	695.1[a]	—	695.1[a]	—	
C	698.2	−3.1	697.0	−1.9	696.7	−1.6	696.3	−1.2	σ^*(C—C)
5			701	−6			—	—	
D	704	−9	705	−10	706	−11	706	−11	Shape resonance or delayed onset
E	720	−25	724	−29	725	−30	724	−29	EXAFS

[a]Taken as equal to that of C_4F_8 (31).

similarity includes not only spectral shape and peak positions but also intensities. The region below the F 1*s* ionization potential in $C(CF_3)_4$ has an integrated oscillator strength which is 1.7 times that of the corresponding region in C_2F_6, in reasonable agreement with the ratio of 2.0 between the number of F atoms in the two molecules. Indeed, on a per-F-atom basis, the oscillator strength in the discrete region of the F 1*s* spectra is remarkably constant, having a value of 0.53 (5) when averaged over all perfluoro species studied.

One dramatic difference between the F 1*s* spectra of C_2F_6 and $C(CF_3)_4$ is that band *D'* around 705 eV is not detected in $C(CF_3)_4$. This suggests that *D'*, a feature common to all of the perfluoroalkane F 1*s* spectra, may be a shape resonance or the first EXAFS oscillation associated with backscattering from an F atom on an adjacent C atom. These types of F—F distances do not exist in $C(CF_3)_4$. The presence of band *E'* with similar intensities in both C_2F_6 and $C(CF_3)_4$ is consistent with an EXAFS oscillation associated with backscattering from an F atom bonded to the same C atom as that to which the core-excited F atom is attached.

V.3. Perfluorocycloalkanes

The anomalous behavior of the C 1*s* spectra of the perfluorocycloalkanes (when compared with the linear species) persists in the F 1*s* spectra. Figure 7 compares the F 1*s* spectra of the cyclic and linear systems. One sees similar features in each case except for the addition of low-lying transitions to σ^*(C—C) orbitals in the cyclic species. The (F 1*s*, σ^*) term values, Table 6, are esentially the same as those for the C 1*s* → σ^* bands, Table 4. The observation of the low-lying excitations to σ^*(C—C) in the F 1*s* spectra suggest that there is considerable interaction between the σ^*(C—C) and σ^*(C—F) orbitals on a single center. This implies that the MO induced to be so low-lying by strain and the inductive effect has both C—C and C—F antibonding character and is thus somewhat delocalized on its center.

VI. Negative-ion resonances

We now attempt to apply the lessons learned from the inner-shell excitation spectra of the alkanes and perfluoroalkanes in the 280–740 eV region to the interpretation of their negative-ion spectra in the 0–8 eV region. The thread connecting these two very different spectroscopies is a set of virtual orbitals assumed to be common to the transitions in each.

The electron affinities of selected perfluoroalkanes were determined by the electron transmission (ETS) technique (21), with results as shown in Fig. 8 for the linear species and in Table 7 for both linear and cyclic species. These data in some cases differ substantially from those of Christophorou *et al.* (44–46), who used the less direct technique of dissociative electron attachment (DEA) for determining the energetics of negative-ion formation. One major difference between ETS and DEA is that corresponding peaks generally appear at lower energy in

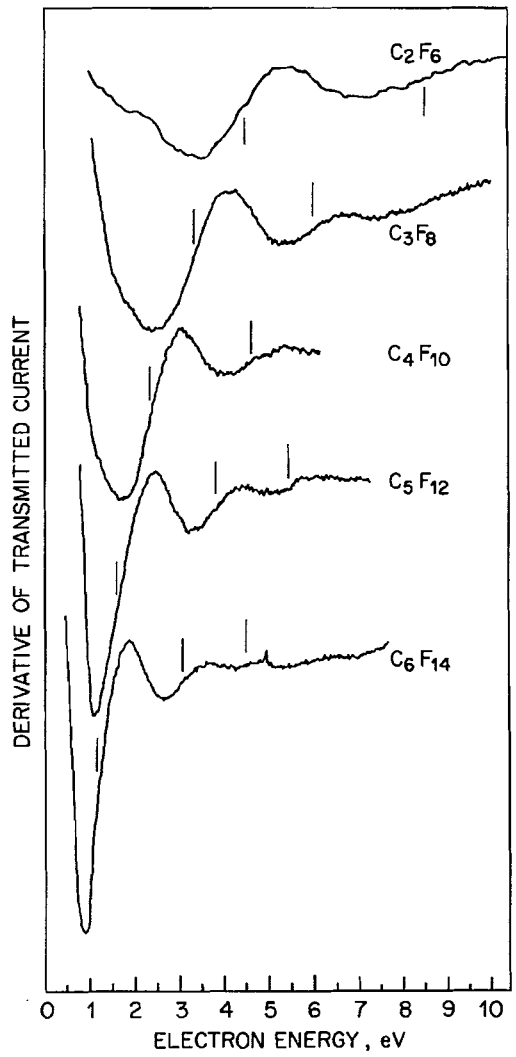

FIG. 8. Electron transmission spectra of the perfluorinated ethane, propane, *n*-butane, *n*-pentane, and *n*-hexane. Negative-ion resonance energies are indicated by the vertical bars.

DEA than in ETS because the attachment process is dissociative and so the survival probability of the anion decreases as the resonance energy increases from one end of the band to the other.

In each of the perfluoroalkanes investigated, two or more negative-ion resonances were observed. Since the target molecules are saturated, the negative ions must result either from electron capture into σ^* MO's or by formation of Feshbach resonances. In the latter, the incident electron excites a bound electron into an R orbital and is itself captured in an R orbital. Usually, but not always, the two electrons occupy the same R orbital. In the case where the R orbital in question is the $3s$ MO, it is known that the Feshbach resonance energy is very nearly 0.5 eV below the corresponding R excitation to $3s$ in the neutral molecule (1, 10, 22). That is to say, the $^1(\phi_i, 3s)$ R state has an electron affinity of +0.5 eV in forming the $^2(\phi_i, 3s^2)$ negative ion.

Referring to the uppermost valence ionization potentials in the perfluoro-*n*-alkanes as determined by photoelectron spectroscopy (1), one sees that the term values of the lowest transitions to $3s$ fall in the range 3.71–4.42 eV in the series CF_4 to C_6F_{14}. The corresponding transition energies to the $3s$ MO's are in the range 12.48–8.33 eV, thus placing the lowest possible Feshbach resonances for these compounds in the 12.0–7.8 eV range. For the *n*-alkanes CH_4 to C_6H_{14}, the corresponding limit below which negative-ion Feshbach resonances will not form is 9.2–7.2 eV. Any negative-ion states observed below these ranges necessarily must involve the occupation of σ^* MO's rather than R orbitals. If the qualitative conclusions of the inner-shell spectroscopic study carry over to the negative ions, then the σ^* resonances in the perfluoro-*n*-alkanes should lie considerably below those of the corresponding *n*-alkanes, and the σ^* negative ions should be particularly low lying in the highly strained perfluorocycloalkanes.

Negative-ion energies as determined by the electron transmission technique are summarized in Table 7. One sees that the negative-ion energies of the perfluoro-*n*-alkanes decrease as the size of the molecule increases. However, the incremental effect of each CF_2 group is diminished as the molecular chain is lengthened. All of the observed resonances are well below the region in which the lowest Feshbach resonances are expected, and so terminate at σ^*. Such behavior of the σ^* resonances is just that expected for delocalized σ^* valence MO's of large bandwidth, uncomplicated by the presence of R orbitals. Indeed, R MO's are irrelevant to the discussion of the binding of an electron to a neutral molecule because the electron does not experience a $-1/r$ potential. Unlike the electron transmission spectra of the perfluorinated alkanes, those of methane and *n*-hexane (47) provide no evidence of σ^* anion states below 6 eV. Thus the electron transmission spectra clearly show the strong stabilization of certain alkane σ^* MO's upon fluorination.

The lowest energy feature in the electron transmission spectrum of C_3F_6 occurs 1.27 eV above the ground state of the neutral molecule and is presumably due to the formation of the ground-state anion. Thus the lowest anion state of C_3F_6 is 2.17 eV more stable than that of acyclic C_3F_8. The electron transmission spectrum of C_3F_6 also shows structure due to anion states at 5.7 and 7.2 eV.

The electron transmission spectra of C_4F_8 and C_6F_{12} do not show structures due to anion formation below 3.7 eV. However, for each of these two compounds there is a feature just above the beam zero, the position of which varies with the retarding voltage. Experience shows that this often occurs when there is an anion state energetically slightly below the ground state of the neutral molecule. If the lowest anion states of these two molecules are indeed bound, this would imply that the ground-state anion of the cyclic C_4F_8 molecule is at least 2.37 eV more stable than that of the corresponding acyclic C_4F_{10}, and that the ground-state anion of the cyclic system C_6F_{12} is at least 1.20 eV more stable than that of acyclic C_6F_{14}. That the energy differences between the ground-state anions of the cyclic and acyclic compounds could be this large is clear from the above-mentioned results for the C_3 species. In light of the results discussed above for the inner-shell spectra, it is surprising that the drop in the electron affinity on going from C_4F_{10} to C_4F_8 is greater than that on going from C_3F_8 to C_3F_6. Perhaps this is due to the fact that the σ^* orbitals involved in the inner-shell spectra are localized while those in the electron transmission spectra are delocalized.

To aid in the assignments of the temporary-anion states, we have performed HF calculations on the ground states of the neutral molecules. In these calculations, the STO-3G basis set was employed and the geometries were fully optimized at the HF level. The virtual orbitals from these calculations are uniformly too high by about 9 eV as compared to the experimental electron

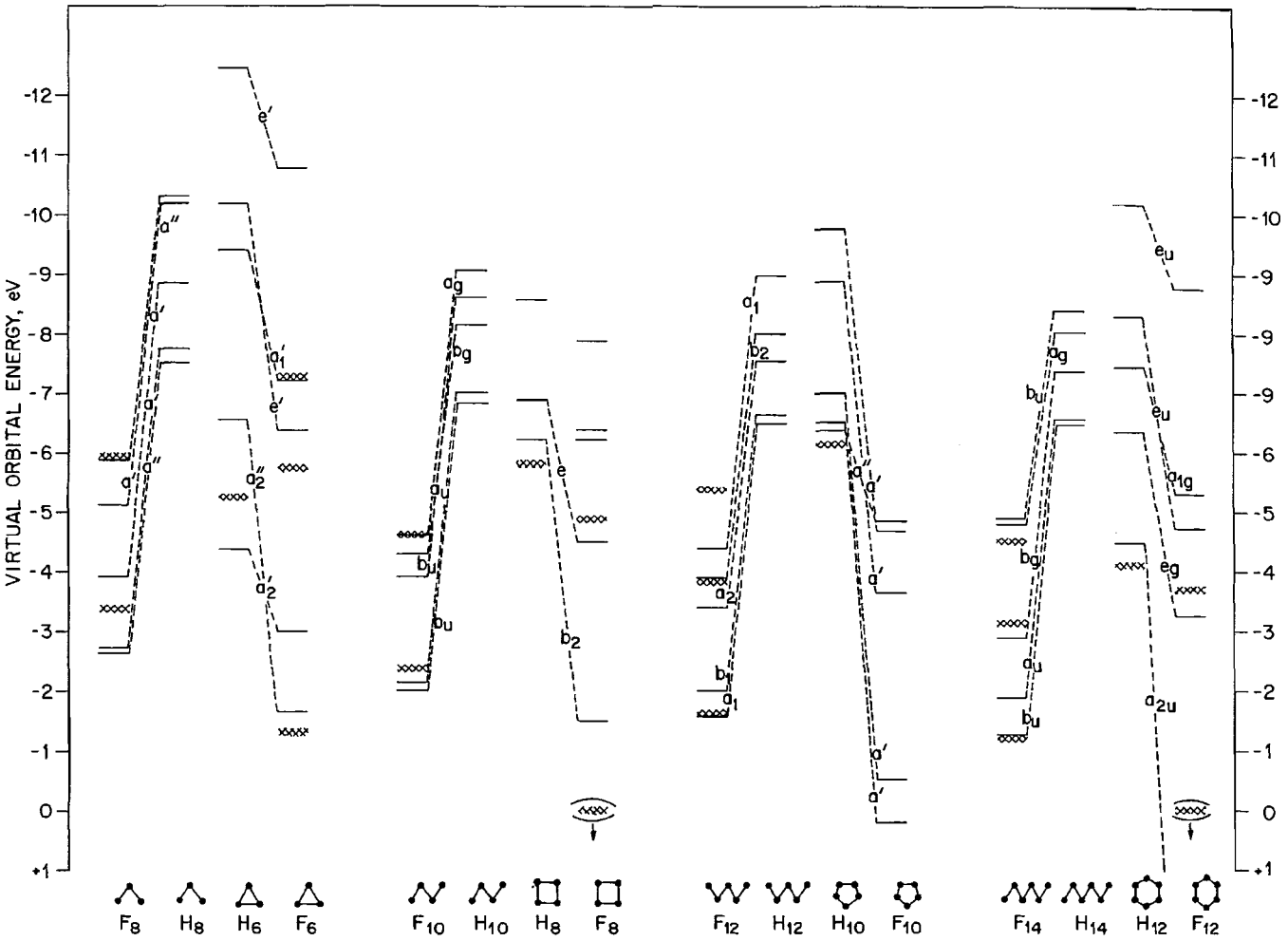

FIG. 9. Correlation of the computed virtual orbital energies of the linear and cyclic alkanes and perfluoroalkanes. All of the calculated energies have been shifted downward by 9 eV to improve agreement with experiment. The cross-hatched lines represent measured electron transmission resonance energies, with those in vertical parentheses being at energies greater than 0.0 eV, but otherwise of unknown magnitude.

affinities, and this quantity has been subtracted from the calculated eigenvalues. We note that this approach is quite crude, however more rigorous calculations would require introduction of continuum states for electron-molecule scattering, which is not yet practical for molecules of the complexity studied here.

One sees in Table 7 and Fig. 9 that the virtual MO approximation, naive though it is, does quite well in assigning the negative-ion features. In the perfluoro-*n*-alkanes series, the lowest resonance is observed to drop monotonically from 4.6 eV in C_2F_6 to 1.2 eV in C_6F_{14}, a trend which is semiquantitatively mirrored by the lowest predicted ngative-ion energies, which drop from 5.4 to 1.25 eV in the same series. The virtual MO calculations also predict that the lowest resonances in the perfluorocycloalkanes C_3F_6 and C_6F_{12} will be substantially below those of the corresponding perfluoro-*n*-alkanes, as observed. However, these calculations predict similar energies for the lowest anion states of C_4F_8 and C_4F_{10}, in contrast to the experimental evidence.

We also have performed calculations on selected hydrocarbons and the results are compared in Fig. 9 and Table 7 with the electron transmission results found in the literature (47, 48). In the *n*-alkane series C_2H_6 to C_6H_{14}, the lowest negative-ion resonance is predicted to drop by 2.39 eV, paralleling the drop of 2.49 eV observed for the corresponding perfluoro-*n*-alkanes. However, there is an almost uniform offset of 5 eV between the lowest anion energies in the two series of compounds, which would appear to be due to an inductive effect of the F atom.

As our electron transmission spectra of CH_4 and *n*-C_6H_{14} did not provide evidence for σ^* states below 6 eV, we presume that the transmission spectra of the intermediate *n*-alkanes also lack low-energy features due to anion formation. According to the calculations, Table 6, the lowest σ^* anion states in CH_4 through C_6H_{14} should fall between 6.5 and 7.0 eV above the neutral molecule ground states. Although this is indeed quite high in energy, it is interesting to observe that a peak due to anion formation shows clearly at 6.4 eV in the transmission spectrum of C_5H_{10} (this work). There are several factors which could cause the resonance in a cyclic system such as C_5H_{10} to be more visible than in the *n*-alkanes. First, the partial wave expansions of the lowest σ^* MO's of cyclic compounds are expected to contain greater contributions from high l values than are those of linear compounds. Second, at room temperature a significant

TABLE 7. Observed and calculated TNI energies (eV) in alkanes and their perfluoro derivatives

Molecule	Observed resonance energies	Calculated virtual orbital energies[a]
CF_4	$(-7.3)^b$	$-6.30(a_1)$; $-6.37\ (t_2)$
C_2F_6	$-4.60; -8.86; (-4.0)^b$	$-3.73(e_u)$; $-4.24(a_{2u})$; $-6.65(a_{2u})$
C_3F_8[c]	$-3.34; -6.00; (-2.55)^b$	$-2.61(a'')$; $-2.71(a')$; $-3.93(a')$
C_4F_{10}	$-2.37; -4.63; (-1.95)^b$	$-1.99(b_u)$; $-2.15(a_u)$; $-3.90(b_u)$
C_5F_{12}	$-1.64; -3.82; -5.40; (-1.55)^b$	$-1.57(a_1)$; $-1.97(b_1)$; $-3.37(a_2)$
C_6F_{14}	$-1.20; -3.10; -4.50; (-1.20)^b$	$-1.24(b_u)$; $-1.87(a_u)$; $-2.85(b_g)$
C_3F_6	$-1.27; -5.74; -7.25$	$-1.66(a''_2)$; $-3.02(a'_2)$; $-6.40(e')$
C_4F_8	>0; -4.91	$-1.47(b_2)$; $-4.48(e)$; $-6.21(a_1)$
C_5F_{10}	—	$0.21(a')$; $-0.50(a')$; $-3.66(a')$
C_6F_{12}	>0; -3.70	$4.44(a_{2u})$; $-3.22(e_g)$; $-4.71(a_{1g})$
CH_4	<-6	$-10.33(t_2)$; $-11.30(a_1)$
C_2H_6	—	$-8.84(e_u)$; $-9.70(a_{2u})$; $-11.05(a_{1g})$
C_3H_8[c]	—	$-7.55(a'')$; $-7.75(a')$; $-8.84(a')$
C_4H_{10}	—	$-6.84(b_u)$; $-7.01(a_u)$; $-8.17(b_g)$
C_5H_{12}	-6.1[d]	$-6.50(a_1)$; $-6.61(b_1)$; $-7.57(a_2)$
C_6H_{14}	<-6	$-6.45(b_u)$; $-6.49(a_u)$; $-7.40(b_g)$
C_3H_6	-5.29[e]	$-4.34(a'_2)$; $-6.57(a''_2)$
C_4H_8	-5.80	$-6.19(b_2)$; $-6.87(e)$; $-8.57(a_2)$
C_5H_{10}	-6.14	$-6.34(a'')$; $-6.50(a')$; $-6.97(a')$
C_6H_{12}	-4.11[e]	$-4.46(a_{2u})$; $-6.36(e_g)$; $-7.44(e_u)$

[a]Calculated values increased by 9.0 eV.
[b]Experimental values from Christophorou *et al.* (44–46).
[c]Calculated in C_s geometry.
[d]Experimental values for *n*-pentane are not available, however, a resonance energy of −6.14 eV is reported for neopentane (48).
[e]Experimental values from Howard and Staley (47).

fraction of the molecules in the vapor phase of an *n*-alkane will have geometries considerably removed from that of the lowest energy conformation. This will tend to broaden the electron-transmission peaks of alkanes, both due to the thermal motion and due to the fact that the empty σ* MO will tend to have more *s* wave character in the higher energy conformer. In general, resonance lifetimes are expected to decrease with symmetry lowering and with the accompanying increase in importance of low-*l* partial waves. If the resonance lifetimes become too short, the resonances are difficult to detect in the total scattering cross sections. The observation by Giordan and Moore (48) of a relatively sharp resonance in neopentane is compatible with the rules stated above.

A far more substantial difference between hydrocarbon and perfluorocarbon is seen in the cyclic compounds, where the lowest negative-ion resonance energy in the $(CF_2)_x$ series decreases monotonically with increasing x, whereas for the $(CH_2)_x$ compounds the trend is strongly upward for $x = 3$ to $x = 5$ and then downward at $x = 6$, as calculated.

Though the virtual orbital calculations would seem to give a satisfactory simulation of the observed negative-ion resonance energies in the perfluoroalkanes, a look at the wavefunctions raises some questions. The delocalized virtual orbital wavefunctions are inappropriate to a discussion of the localized inner-shell excitations (sect. VII), but may be better suited to a discussion of negative-ion states. Note however, Fig. 9, that on cyclizing C_3F_8 to C_3F_6, the virtual orbital which is predicted to be stabilized is the LUMO a'_2. This orbital is σ*(C—F)$_\pi$ rather than σ*(C—C) as deduced from the inner-shell spectra. More sophisticated calculations on inner-shell excitation and negative-ion formation are needed to clarify some of the band assignments.

VII. Core hole and optical σ* orbitals; localization versus band formation

The two electron impact techniques used in this paper (inelastic electron scattering and electron transmission) were chosen because each should yield a clear picture of the role of σ* MO's in the virtual orbital manifolds of the perfluoroalkanes. However, we find that in the inner-shell spectra of unstrained systems, the excitations to σ* MO's have very nearly constant energies irrespective of the molecular size (Tables 1 and 5), whereas when studied by electron transmission, the σ* MO's have energies which decrease substantially with increasing molecular size (Table 7). Only in the strained molecules C_4F_8 and C_6F_{12} do the two techniques agree in placing a σ* MO at anomalously low energy. Yet a third technique, that of VUV spectroscopy (1), suggests that the σ* MO's in the perfluoro-*n*-alkanes descend with increased molecular size, in support of the trend displayed by the electron transmission spectra.

In order to rationalize the apparent contradiction between the trends in the inelastic electron impact and electron transmission data in regard to the behavior of σ* MO's in the perfluoroalkanes, one must recognize that the σ* MO's in the excited states of the two spectroscopies are very different. In the case of the σ* negative ions, the σ* MO is a global one, spanning the length of the molecule and having an orbital energy which decreases particle-in-a-box-like with increasing molecule size. In contrast, the energies for inner-shell excitations to the same σ* MO are very weakly dependent upon molecular size, suggesting to us that the 1*s* hole in the inner-shell excited states is localized which in turn localize the σ* MO. There is at the same time evidence in the inner-shell spectra for mixing of the σ*(C—C) and σ*(C—F) bond orbitals; we suggest that this only occurs

between such bond orbitals bonded to a common center, thus preserving the local character of the excitation.

It is relevant here to note the close similarity of the number of bands, their intensities and separations for the excitations to σ*(C—C) and σ*(C—F) in the perfluoroalkanes and in PTFE. The saturation of electronic band formation at relatively short chain lengths is consistent with the effective localization of the excitation during the lifetime of the core hole. Just such a conclusion was reached as well in regard the ($1s$, π*) localization in unsaturated hydrocarbons of increasing length (22). Paralleling the situation in the perfluoroalkanes, the spectra of the short-chain alkanes closely resemble those of PE, which again is understandable in terms of localized excitations to ($1s$, V) states (33). In addition, Hutson and Ramaker (49) conclude on the basis of comparisons of calculated and experimental Auger spectra that the (C $1s$, σ*(C—C)) states in PE are appreciable localized. Although in these two cases we argue from saturation of band formation with chain length in favor of localized core hole excited states, it should be noted that the width of the occupied C $2p$ band of the alkanes is essentially constant above C_4H_{10} (50), yet the $2p$ orbitals are generally considered to be delocalized. Thus there are aspects to this problem yet to be understood.

VIII. Summary[3]

In summary, our interpretation of the inner-shell and negative-ion spectra of the perfluoroalkanes lead to the following qualitative picture of their σ* MO structures. In these species, the σ* levels are inherently lower and the inner-shell transitions to them more intense than in the corresponding alkanes; in the perfluoro-*n*-alkanes the lowest σ* MO has dominant (C—F) character. This valence character is confirmed by the lack of spectural perturbation observed on going into a condensed phase. On cyclizing the perfluoro-*n*-alkanes, a σ*(C—C) MO appears at yet lower energies. Its very large term value is related to molecular strain in the cyclic compounds. The uniquely low energy of the σ*(C—C) MO in the perfluorocycloalkanes is qualitatively confirmed by negative-ion spectroscopy and *ab initio* calculations, as is the relative stabilization of σ*(C—F) MO's in relation to σ*(C—H). However, the differences among inner-shell, negative-ion and VUV spectral shifts with chain length suggest that the core hole excited states are far more localized whereas the negative-ion states span the entire molecule.

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[3]NOTE ADDED IN PROOF: In this work and in earlier work as well (22), it was concluded on the basis of experiment that fluorination strongly increases the valence character of what are otherwise Rydberg upper levels. Just such an effect has recently been reported in theoretical calculations on the fluoroethylene series (51).

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