

Vacuum ultraviolet and photoelectron spectra of fluoro-chloro derivatives of methane

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The photoelectron and vacuum ultraviolet absorption spectra (200–120 nm) of CF_3Cl , CF_3Br , CF_2HCl , CFH_2Cl , CFHCl_2 , CF_2Cl_2 , and CFCl_3 are reported and discussed. The lowest ionization potentials belong to the chlorine or bromine lone pair orbitals, the next highest ones to the bonding orbitals of mainly C–Cl or C–Br character. In the absorption spectra the lowest frequency bands are due to weak valence-shell type transitions. At higher frequencies we find much stronger Rydberg type bands related to the first ionization potential. All absorption bands up to $84\,000\text{ cm}^{-1}$ depart from chlorine or bromine lone pair orbitals. Some of the bands exhibit vibrational fine structure. An increase in the number of the fluorine atoms causes a shift to either higher or lower energies of the ionization potentials belonging to orbitals of mainly C–H or C–Cl character according to the cases while the lone pair ionization potentials and the absorption spectra shift to higher energies in all cases.

INTRODUCTION

In the present paper we are dealing with the vacuum ultraviolet (vuv) spectra from 200 to 120 nm and the He I photoelectron (PE) spectra of the following mixed halogenated methane derivatives: CF_3Cl , CF_3Br , CF_2HCl , CFH_2Cl , CFHCl_2 , CF_2Cl_2 , and CFCl_3 . These molecules are of great interest since they enable us to follow the changes that occur in the electronic structure and transitions of methane and the halogen lone pairs as a function of substitution and to gain knowledge on their excited states and ions. They are also of great practical importance since they are widely used in industry: actually they are fluorocarbon—13, 13-B-1, 22, 31, 21, 12, and 11 in the above order. The photochemical reactions of these compounds could not be understood without a knowledge of their spectra. They might be important from the point of view of their ecology.

The most important features of the electronic spectrum of methane were interpreted by Mulliken as long ago as 1935.¹ He based his reasoning on the united atom approximation. Under T_d symmetry, omitting the carbon 1s orbital, the following configuration is obtained for the ground state:

$$[sa_1]^2[pf_2]^6\ ^1A_1,$$

where a_1 and f_2 are the usual group theoretical symbols. In the photoelectron spectrum the broad band corresponding to ionization from the triply degenerate orbital covers the range from 12.7 to about 16.0 eV.² The large splittings observed in this band can only be understood by invoking the Jahn–Teller theorem.³ The second ionization potential (sa_1) lies at much higher energies, about 23 eV.⁴ Recent quantum chemical calculations^{5–10} give the same order for the molecular orbitals of methane.

The first electronic transition of methane yields a broad band at about 128 nm. It is readily interpreted as a $3s \leftarrow (pf_2)$ Rydberg transition in the united atom

language or as a $\sigma^* \leftarrow \sigma$ type transition in minimal basis molecular orbital language. In both cases the transition is $^1F_2 \leftarrow ^1A_1$ and allowed.

The orbitals “occupied” by the bonding electrons in the halogenated methane derivatives can be derived from the methane orbitals. In addition, we have to consider the orbitals occupied by the lone pairs of electrons of the halogens.

EXPERIMENTAL

The ultraviolet absorption spectra from 200 to 120 nm were measured on a 1 m model 225 McPherson monochromator mounted with a 1200 lines/mm grating, using a hydrogen discharge tube as the lightsource, EMI-6256-S photomultiplier tubes, a McPherson model 665 double beam attachment, and photoelectric recording. More details were given in previous publications from this laboratory.^{11,12} The photoelectron spectra were taken with a Perkin–Elmer PS-16 spectrometer having an He I source. The instrument was calibrated with the argon lines and spectra known from the literature. The pressures of our samples were of the order of 10 torr for the weakest (longest wavelength) bands of the vuv spectra; of the order of 0.2–0.5 torr for the strong absorption bands and 0.1 for the photoelectron bands. In Figs. 1–19 the vuv spectra are given in molar extinction coefficients against wave numbers, the PE spectra in counts sec^{-1} against electron volts. All spectra were measured in the vapor phase. The ionization potentials quoted in the text are vertical values.

Our samples were obtained from E. I. DuPont de Nemours and Company of Wilmington, Delaware. We checked their purity by gas chromatography using a 20 ft column containing Chromosorb-W with 30% of KEL-F oil no. 3 as adsorbent. For CF_3Br we used a column $\frac{1}{4}$ in. \times 3 m, Porapak Q, 80–100 mesh. The purity of our samples was 99.8% in all cases.

TABLE I. Comparison of the I.P. (electron volts) of CH_3Cl , CHF_3 , and CF_3Cl .^a

CH_3Cl			CHF_3			CF_3Cl		
$\bar{\text{Cl}}$	11.3	<i>e</i>	C-H	14.8	<i>a</i> ₁	$\bar{\text{Cl}}$	13.0	<i>e</i>
C-Cl	14.4	<i>a</i> ₁	$\bar{\text{F}}$	15.5	<i>a</i> ₂	C-Cl	15.0	<i>a</i> ₁
CH_3	15.4	<i>e</i>	$\text{CF}_3-\bar{\text{F}}$	16.2	<i>e</i>	$\bar{\text{F}}$	15.55	<i>a</i> ₂
			$\bar{\text{F}}$	17.2	<i>e</i>	$\text{CF}_3-\bar{\text{F}}$	16.5	<i>e</i>
						$\bar{\text{F}}$	17.4	<i>e</i>

^a The data for CH_3Cl are from Ref. 3 and for CHF_3 from Ref. 14.

INTERPRETATION OF THE SPECTRA

CF_3Cl and CF_3Br

The photoelectron spectrum of CF_3Cl is given in Fig. 1.

It is interesting to compare it with those of CH_3Cl and CHF_3 ¹³ (Table I). The order of the orbitals in CH_3Cl is well established. The lowest ionization potential (11.3 eV) corresponds to the doubly degenerate chlorine lone pair orbital, the second one (about 14.4 eV) to the (σa_1) C-Cl orbital and the third one (about 15.4 eV) to the doubly degenerate π type CH_3 orbital. (In this paper we often use expressions like "C-Cl orbital" or " CH_3 orbital," etc. These are convenient expressions for designating a molecular orbital that has a large electronic charge density in the given bond or group but it does not imply any idea of localization in that bond or group. Lone pair orbitals of halogens will be designated as $\bar{\text{F}}$, $\bar{\text{Cl}}$, $\bar{\text{Br}}$. The symbol (C-Cl)* stands for an excited valence shell type orbital anti-bonding in the C-Cl link.) For CHF_3 we have both the photoelectron spectra^{14,15} and an *ab initio* calculation by Brundle, Robin, and Basch.¹⁴ The lowest ionization potential (I.P.) must come from the (σa_1) CH orbital (about 14.8 eV). The order of the C-F bonding and F lone pair orbitals is a more delicate matter. The six lone pair atomic orbitals of the three fluorine atoms combine to yield *a*₁, *a*₂, *e*, and *e* molecular orbitals. According to the calculations of Brundle, Robin, and Basch,¹⁴ *a*₂ has the lowest ionization potential, followed by an *e* orbital of mixed lone-pair bonding character and an *e* orbital which is more purely nonbonding.

According to the above we expect the following order

in CF_3Cl : Cl lone pair, C-Cl, F lone pair (*a*₂), degenerate CF_3 bonding (πe), degenerate F lone pair (*e*). We see that the frontier orbital, which is occupied by the chlorine lone pair, is stabilized by about 1.7 eV (Table I) with respect to CH_3Cl due to the replacement of the hydrogens by fluorine atoms. The C-Cl orbital undergoes a lesser change being stabilized by about 0.6 eV. The difference between the C-H IP in CHF_3 and the C-Cl IP in CF_3Cl is slight.

The PE spectrum of CF_3Br (Fig. 2) is very similar to the spectrum of CF_3Cl except that the first I.P. (12.0 eV) is shifted to lower energies by about 1 eV and the second one (the C-Br) by about 0.8 to 14.2 eV. These expected changes confirm the assignment of these bands for both molecules. The three following I.P.'s are very nearly the same in CHF_3 , CF_3Cl , and CF_3Br showing little influence of the fourth atom on the bonding and lone pair orbitals involving the fluorines. Splittings due to spin-orbit coupling of the order of 0.3 eV¹⁶ are expected in the case of CF_3Br . We actually found that the 12.0 eV band contains two strongly overlapping components but the band is broad and we cannot clearly separate them.

According to the foregoing the ultraviolet spectra of CF_3Cl and CF_3Br (200 to 120 nm, at least) are expected to be due to transitions starting from the Cl or Br lone pair orbitals. Spin-orbital splittings are expected to be slight in the case of CF_3Cl (less than 0.1 eV) and non-observable under the given experimental conditions. Russell-Saunders coupling can be taken approximately valid for this molecule. On the other hand, spin-orbital

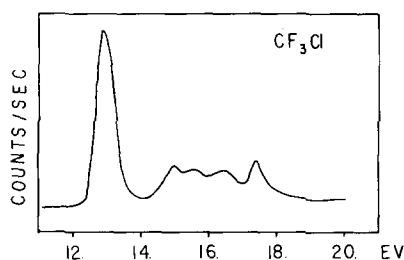


FIG. 1. The photoelectron spectrum of CF_3Cl .

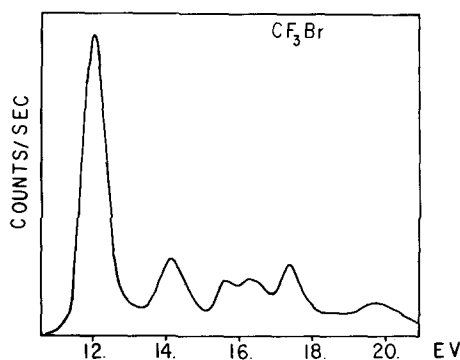


FIG. 2. The photoelectron spectrum of CF_3Br .

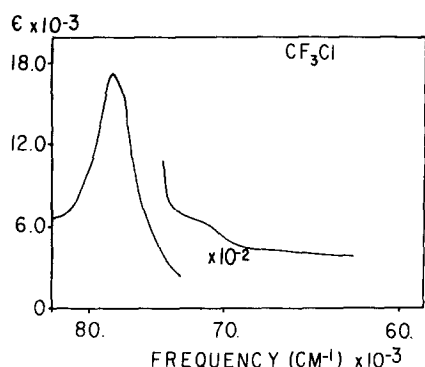


FIG. 3. The vacuum ultraviolet absorption spectrum of CF_3Cl . The ϵ values of the lowest frequency band are multiplied by 100.

splittings should be observable in the case of CF_3Br and ($\Omega \cdot \Omega$) coupling should apply.

The spectrum of CF_3Cl is given in Fig. 3. Only two bands are clearly distinguished. Both are diffuse and structureless. A weak and broad band is centered at $71\,500\text{ cm}^{-1}$ (ϵ_{max} about 60) and a much stronger band is found at $78\,100\text{ cm}^{-1}$ (ϵ_{max} about 17 000).

The spectra of the methylhalides were examined by Price¹⁷ and by Zobel and Duncan¹⁸ and a detailed summary was given by Herzberg.¹⁹

Taking into account the large hypsochromic shift due to the replacement of the hydrogens by fluorines we can assign the weak band at $71\,500\text{ cm}^{-1}$ to Herzberg's $^1\tilde{A} \leftarrow ^1X$ band. Singlet-triplet transitions in CF_3Cl must be very weak and unobservable under the pressures used. Zobel and Duncan¹⁸ took the spectra of a number of chlorine containing methane derivatives and, in all cases, found a band at about $57\,000\text{ cm}^{-1}$. They assigned it to a transition from the chlorine lone pair orbital of the ground state to a valence-shell type orbital antibonding in the C-Cl bond. Since our attempts to integrate this band into a Rydberg series remained unsuccessful, we adopt this assignment. The strong band at $78\,100\text{ cm}^{-1}$ is readily interpreted as the first member of an ns type Rydberg series with a quantum defect of 0.92. It is $(3sa_1) \leftarrow (e)^3$ or $^1E \leftarrow ^1A_1$ under C_{3v} symmetry and allowed. It corresponds to Herzberg's \tilde{C} band for CH_3Cl that is an excitation

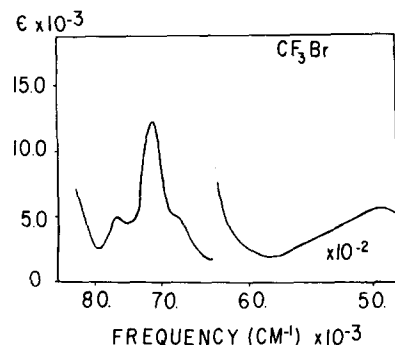


FIG. 4. The vacuum ultraviolet spectrum of CF_3Br . The ϵ values of the lowest frequency band are multiplied by 100.

from the chlorine lone pair orbital to an $3s$ Rydberg orbital.

The higher members of this series as well as other Rydberg series are expected to lie beyond 1200 Å , the limit of the measurements reported here.

In the ultraviolet spectrum of CF_3Br (Fig. 4) we find a broad and weak band with a maximum at $48\,850\text{ cm}^{-1}$ (ϵ_{max} about 60), which according to the preceding argument we assign to a transition leading from the bromine lone pair orbital to a valence-shell type orbital antibonding in the C-Br bond. We found no clear indication of spin-orbital coupling effects on *this* band.

At higher frequencies we can distinguish at least three bands: a strong shoulder at $67\,900\text{ cm}^{-1}$, an intense band at $70\,500$ ($\epsilon_{\text{max}} \approx 12\,500$) and a weaker but well pronounced band at $76\,900\text{ cm}^{-1}$. Clearly, the main band must be due to a $(3sa_1) \leftarrow (e)^3$ type excitation in complete analogy with CF_3Cl . The location of this band reflects well the expected bathochromic shift upon

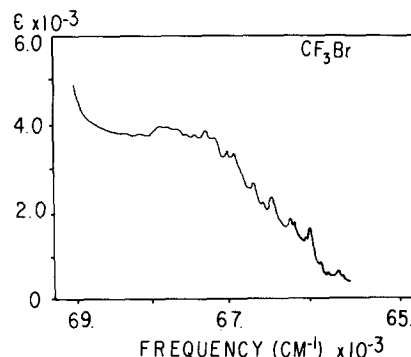


FIG. 5. The vibrational fine structure of the $67\,900\text{ cm}^{-1}$ (max) band of CF_3Br .

replacement of the chlorine by bromine and the hypsochromic shift occurred upon replacing the hydrogens by fluorines (cf. Ref. 20). The band observed at $67\,900$, absent in CF_3Cl , is separated by about 2700 cm^{-1} from the strong band. This fits in well with the spin-orbit splitting observed for the ionization potentials in the case of CH_3Br^3 . The problem of spin-orbit coupling in this type of molecule is discussed in detail by Herzberg.²¹

In case of strong coupling two E type excited states originate from the $E_{3/2}$ state of the ion and $E + A_1 + A_2$ from $E_{1/2}$. Evidence was found for the three E states in the case of CH_3I .²² The case of CF_3Br is likely to be a case of moderate coupling. The resulting states are the same but we can still speak of singlet-singlet and singlet-triplet transitions in a first approximation. Thus we can assign the strong band at $70\,500\text{ cm}^{-1}$ to the $(3sa_1) \leftarrow (e)^3$ singlet-singlet transition. (It would become the E state originating from $E_{1/2}$ in case of strong coupling.) The transitions of mainly singlet-triplet character must then be contained in the weak band at $67\,900\text{ cm}^{-1}$. Then both the $70\,500$ and $67\,900\text{ cm}^{-1}$ bands are accounted for as being due to transitions

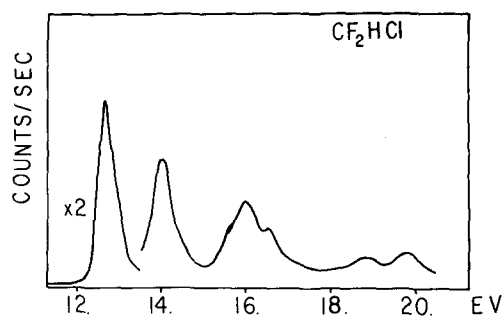
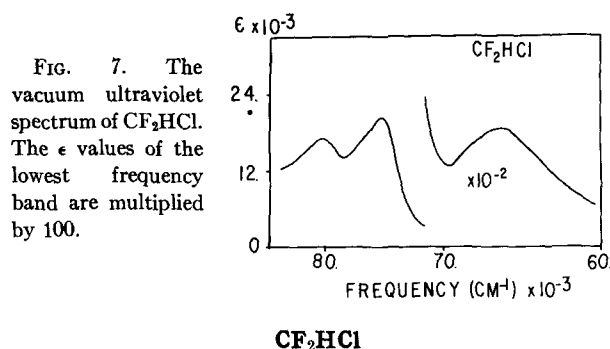
TABLE II. Vibrations in the fine structure of the 67 900 cm^{-1} band of CF_3Br .

Observed frequencies (cm^{-1})	Vibrations, excited state (cm^{-1})	Vibrations, ground state (cm^{-1})	Assignment
65 506	
65 746	240	348	ν_4
65 980	474		$2\nu_4$
66 207	701		$3\nu_4$
66 270	760	761	ν_3
66 449	943	1085	ν_1
66 680	1174		$\nu_1 + \nu_4$
66 916	1410		$\nu_1 + 2\nu_4$
67 019	1509		$2\nu_3$
67 145	1640		$\nu_1 + 3\nu_4$
67 268	1758		$2\nu_3 + \nu_4$
67 362	1852		$2\nu_1$
67 567	2061		$2\nu_1 + \nu_4$
67 828	2318		$3\nu_3$

from the bromine lone pair orbital to a 3s Rydberg state with spin-orbit splitting.

The band at 76 900 cm^{-1} can be assigned to the first member of a p type Rydberg series converging also to the lowest ionization potential although its quantum defect (0.6) is somewhat too high. A strong band follows at higher frequencies but its maximum lies beyond the high frequency limit of our measurements.

The 67 900 cm^{-1} band has vibrational fine structure. Figure 5 shows this structure obtained with a slit of 30 μ and a recording speed of 10 $\text{\AA}/\text{min}$. It can be interpreted in terms of three totally symmetrical vibrations of the excited state: 240, 760, and 960 cm^{-1} whose ground state values are 348, 761, and 1085 cm^{-1} . The latter are from Plyler and Acquista²³ who assigned them to the symmetrical CF deformation, C-Br stretching and symmetrical C-F stretching modes, respectively. Dunn and Herzberg²² interpreted the vibrational fine structure of the analogous band in the spectrum of CF_3I in the same way (see Ref. 19, p. 163). Our assignments are given in Table II.

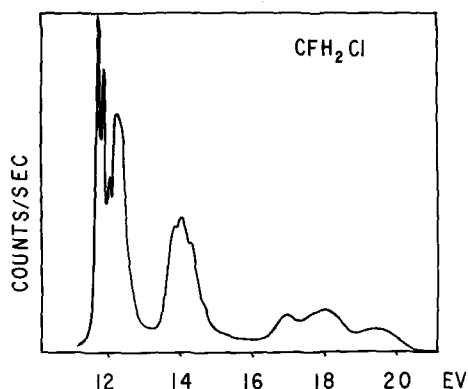
FIG. 6. The photoelectron spectrum of CF_2HCl .

The photoelectron spectrum is shown in Fig. 6. CF_2HCl can only have C_s symmetry. The chlorine lone pair orbital, which was e under C_{3v} symmetry, splits into $a' + a''$ where a' is symmetrical and a'' is anti-symmetrical with respect to the plane. The splitting is expected to be slight, however. Actually, we find one band in the PE spectrum, having its maximum at 12.6 eV, about 0.4 lower than in CF_3Cl . The band is asymmetrical, however, and it probably contains both bands resulting from the splitting.

The second I.P. should correspond to the bonding electrons in the C-H or C-Cl bonds. The (σa_1) and (πe) orbitals of CH_3Cl or CF_3Cl of which (σa_1) corresponded to the C-Cl bond become a' and $a' + a''$ under C_s symmetry. The CF bonding electrons will occupy the high energy a' orbital [which was $(s a_1)$ in methane with an IP at about 23 eV] and the a'' orbital so that two a' remain for C-H and C-Cl.

In CH_3Cl the band at 14.4 eV was assigned¹³ to the C-Cl orbital on the basis of the observed vibrational intervals. In CF_3Cl the PE band at 15.0 eV must be the C-Cl band (see above). One might then expect to find it between these two values for CF_2HCl but it is actually at 14.0, the next band being a shoulder at 15.4 eV. The C-H and C-Cl orbitals are probably highly mixed, the orbital related to 14.0 eV having more C-Cl and the one related to 15.4 eV more C-H character. Their mean value, about 14.7, is actually between 14.4 (CH_3Cl) and 15.0 eV (CF_3Cl).

At higher energies in the PE spectrum of CF_2HCl we

FIG. 8. The photoelectron spectrum of CFH_2Cl .

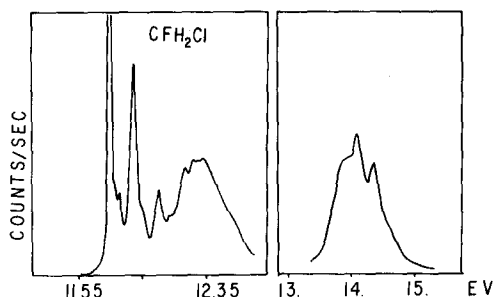


FIG. 9. The fine structure of the three lowest photoelectron bands of CFH_2Cl .

find a complex band with maximum at 15.9 eV and shoulders at about 15.4 and 16.4 eV. Beyond these we find weaker bands at 18.7 and 19.7 eV. Since the chlorine 3s orbital is not expected to come in below 21 eV these bands must be due to the a' and a'' C-F bonding orbitals and to the four fluorine lone pair combinations, two of which are a' and two a'' . We can only refer to the order obtained by Brundle, Robin, and Basch¹⁴ in their calculations on CH_2F_2 . Thus the complex band between 15 and 16 eV must contain the higher of the (C-H)-(C-Cl) orbitals, the bonding C-F orbital of lower I.P., and the fluorine lone pair of lowest I.P. (a'' , which was a_2 for CH_2F_2) while the bands observed at 18–20 eV can be assigned to the remaining fluorine lone pair orbitals and the C-F orbital of higher I.P.

In the ultraviolet spectrum (Fig. 7) of CF_2HCl we can distinguish three broad bands. The one of lowest frequency is at $66\,200\text{ cm}^{-1}$ with an $\epsilon_{\text{max}} = 120$. We assign it in the same way as in CF_3Cl that is, to $(\text{C}-\text{Cl}^* \leftarrow \text{Cl})$.

The strong band at $74\,500\text{ cm}^{-1}$ can be interpreted as $3s \leftarrow \bar{\text{Cl}}$ with a quantum defect of about 0.9. The band at $80\,650\text{ cm}^{-1}$ could be $3p \leftarrow \bar{\text{Cl}}$ although the quantum defect of about 0.6 again seems to be too high.

CFH_2Cl

The photoelectron spectrum is shown in Fig. 8. The lowest energy bands exhibit partly resolved fine struc-

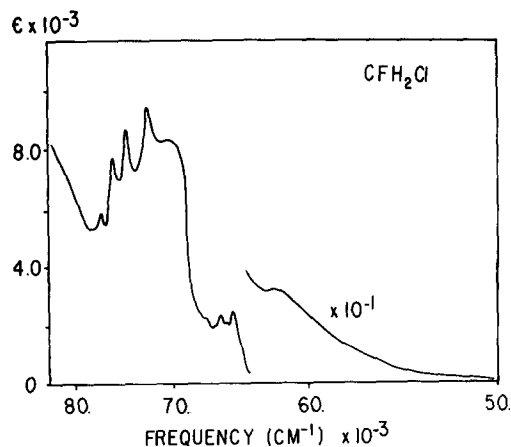


FIG. 10. The vacuum ultraviolet spectrum of CFH_2Cl .

ture. There are three well defined bands at 11.74, 11.89, and 12.03 eV. Their mutual separation, about 1200 cm^{-1} , is likely to correspond to the CH_2 bending frequency of the ion obtained through ionization from the chlorine lone pair orbital (Fig. 9). 11.74 is the adiabatic value while the vertical I.P. could be given the approximate value of 11.9 eV. The remaining fine structure could be due to C-Cl modes. The value 11.74 is intermediate between the respective first I.P. of CH_2Cl_2 (11.31 eV) and CH_2F_2 (12.74 eV).²⁴ The second band of CFH_2Cl is centered at about 12.3 eV and also has some (poorly resolved) fine structure. The assignment of this band is not so obvious. Since the molecule has only C_s symmetry the lone pair orbital is non-degenerate and there must be two such levels, both of which may have some bonding character. The question then is if the perturbation by the rest of the molecule can be sufficient to explain the observed relatively large splitting (0.4 eV). As we have seen, for CF_2HCl we find only one apparent peak but the band

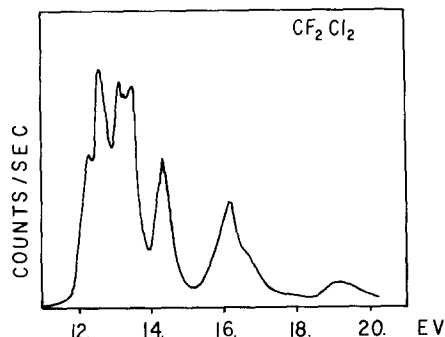


FIG. 11. The photoelectron spectrum of CF_2Cl_2 .

is broad and has shoulders and could well contain two I.P.'s. In CH_2Cl_2 ³ both observed bands (11.31 and 12.18, adiabatic values) appear to be double. If we have a look at CF_2Cl_2 (see below) we find the expected four bands well resolved. It seems then that the fluorine atoms exert a stronger perturbation on the Cl lone pairs than the hydrogens. We assign the 12.3 eV band to the second chlorine lone pair I.P.

The only alternative assignment would be the lower of the two (mainly) CH I.P.'s. This is very unlikely, however. In CH_2Cl_2 ³ there is no peak in the photoelectron spectrum between the higher chlorine lone pair I.P. (12.18) and 15.05 eV, which is in all probability actually the lower C-Cl band, and the lower C-H I.P. is closer to 16 eV. On the other hand, in CH_2F_2 the two CH I.P.'s are at 12.74 and 15.58 eV. Thus we see that the fluorines push the CH I.P.'s to lower energies than their values in the respective chlorine compounds. In view of this, a low I.P. like 12.3 eV is very unlikely to belong to an orbital of CH character, in a molecule containing only one fluorine atom.

In the 14 eV region we see a complex band. The

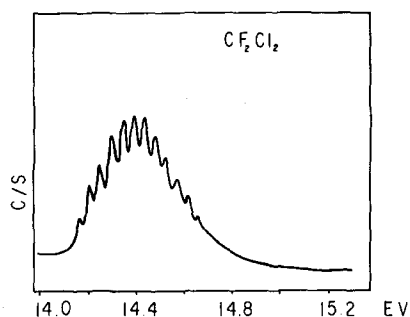


FIG. 12. The vibrational fine structure of the 14.4 eV band in the photoelectron spectrum of CF_2Cl_2 .

broad low energy wing (about 13.85 eV) has the right energy (cf. CH_3Cl) to be the I.P. of the C-Cl bonding electrons. The peaks at 14.1, 14.35, and 14.6 eV could then belong to the lower CH I.P. The interval between these is of the order of 2000 cm^{-1} . This is too high for either a CH deformation or a C-F stretching mode. It could belong to a CH stretching mode but this should be confirmed by measuring the spectrum of the deuterated molecule.

The higher CH I.P. could belong to the band observed at 16.85 eV while the remaining two peaks could correspond to the fluorine lone pair and bonding orbitals (18.0 and 19.5 eV).

The ultraviolet spectrum (Fig. 10) of CFH_2Cl is more similar to that of CH_3Cl ⁸ than to those of the other fluorocarbons. At low frequencies (maximum at $62\,500\text{ cm}^{-1}$) we find the usual weak band ($\epsilon \sim 250$), which we again assign to a $(\text{C-Cl})^* \leftarrow \text{Cl}$ transition. At higher frequencies we find a group of bands of which the strongest are at $65\,310$, $66\,400$, and $67\,590\text{ cm}^{-1}$. The vibrational interval is of the order of $1100\text{--}1200\text{ cm}^{-1}$, probably the CH_2 bending mode. Another frequency distinguished in this system is likely to be a C-Cl mode. Since these frequencies are similar to those which we found on the first photoelectron band and since the quantum defect with respect to this I.P. is 0.99, we assign it to a transition from the lower chlorine lone pair orbital to a $3s$ Rydberg orbital.

The following intense band (maximum at $71\,120\text{ cm}^{-1}$) has a quantum defect of 0.99 with respect to

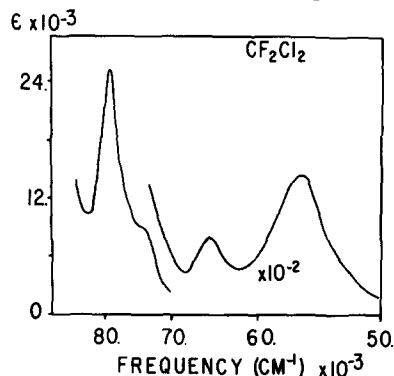


FIG. 13. The vacuum ultraviolet spectrum of CF_2Cl_2 . The ϵ values of the lowest frequency bands are multiplied by 100.

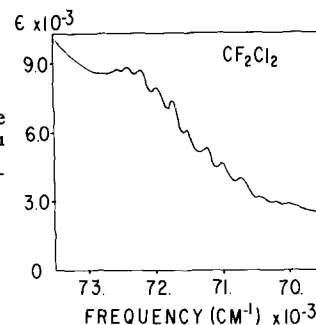


FIG. 14. The vibrational fine structure in the $74\,000\text{ cm}^{-1}$ shoulder in the vacuum ultraviolet spectrum of CF_2Cl_2 .

the *higher* chlorine lone pair I.P. (12.3 eV) and we therefore assign it to the $3s$ Rydberg for the 12.3 eV I.P. The band cannot be related to the first I.P. with any reasonable value for the quantum defect (neither s or p).

The well defined peaks that follow at higher frequencies can be assigned to p type Rydberg levels with respect to the first I.P. The peaks are at $72\,780$, $74\,850$, $76\,130$, and $77\,350\text{ cm}^{-1}$. The last three are separated by an interval of about 1200 cm^{-1} , which could again be the CH_2 bending mode. The first one is at 2000 cm^{-1} from the second one and it is doubtful whether it belongs to the same electronic transition. Knowledge of the spectra of the deuterated molecule and other related molecules could help to elucidate this problem and we prefer to reserve further discussion for after this has been done.

CF_2Cl_2

The photoelectron spectrum is shown in Fig. 11. Under C_{2v} symmetry the chlorine lone pair orbitals combine to four molecular orbitals: $a_1 + a_2 + b_1 + b_2$. These are readily assigned to the bands at 12.3, 12.6, 13.2, and 13.5 eV. (Two weaker peaks are distinguished at the high energy side of the 13.2 band (to perhaps 500 and 1000 cm^{-1}), which are probably due to partly resolved vibrational fine structure.) They are shifted to higher frequencies by about 1 eV with respect to CH_2Cl_2 .³ The two following bands can be assigned to the two bonding MO of mainly C-Cl character (b_2 and a_1). These are the band at 14.4 eV and the shoulder at about 16.0 eV. The former band has well developed vibrational fine structure and must correspond to a stable state of the ion. The main vibrational interval is 385 cm^{-1} , which is

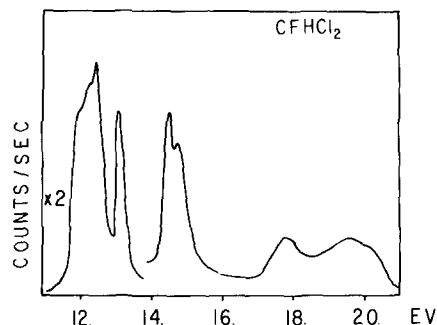


FIG. 15. The photoelectron spectrum of CFHCl_2 .

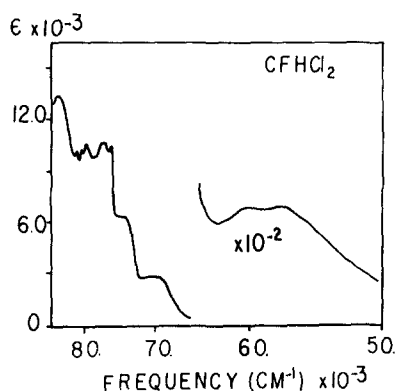


FIG. 16. The vacuum ultraviolet spectrum of CFHCl_2 . The ϵ values of the lowest frequency bands are multiplied by 100.

likely to correspond to a C-Cl deformation mode. (Fig. 12).

At higher frequencies we expect bands due to the two orbitals bonding in the C-F bonds (b_1 and a_2) and to the fluorine lone pairs ($a_1 + a_2 + b_1 + b_2$). What we actually find is a peak at 16.3 eV, with a shoulder at about 16.5 eV, and a broad band at about 19.0 eV. They probably all contain more than one overlapping band.

The ultraviolet spectrum of CF_2Cl_2 is given in Fig. 13. This spectrum has already been studied by Zobel and Duncan¹⁸ and by Stokes and Duncan.²⁵ We are giving it a modified interpretation based on the ionization potentials that became known more recently.

At about $56\,460\text{ cm}^{-1}$ we find a band that is somewhat broader and more intense than the corresponding band in the monochloroderivatives. This band was interpreted as a $(\text{C-Cl})^* \leftarrow \text{Cl}$ transition. Now, we have two close lying I.P. (12.3 and 12.6), separated by only about 2000 cm^{-1} and the observed band might well receive contributions from transitions departing from both. At $65\,400\text{ cm}^{-1}$ we find a weaker but broad band with a pronounced shoulder. It is similar to the $56\,460\text{ cm}^{-1}$ band in that it cannot be integrated into any Rydberg series. It could again correspond to transitions from the 13.2 and 13.5 eV lone pair levels to relatively small C-Cl antibonding orbitals.

At higher frequencies we find a shoulder at about $74\,000$, which is superimposed onto the wing of the strong band at $79\,100\text{ cm}^{-1}$.

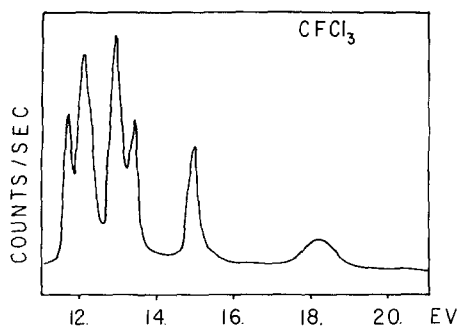


FIG. 17. The photoelectron spectrum of CFCl_3 .

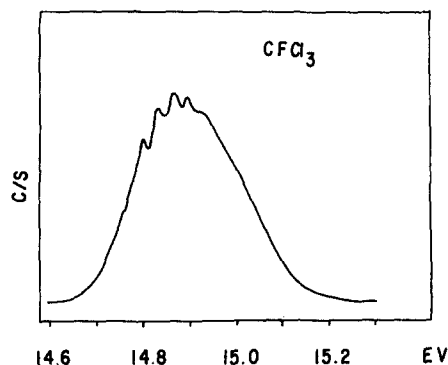


FIG. 18. The vibrational fine structure of the 15.0 eV photoelectron band of CFCl_3 .

The shoulder has vibrational fine structure with an interval of about 260 cm^{-1} , already noted by Zobel and Duncan.¹⁸ It is likely to correspond to a CCl deformation mode (Fig. 14).

The shoulder at $74\,000$ and the band at $79\,100\text{ cm}^{-1}$ have quantum defects of 0.91 and 0.85, respectively, and can be assigned to $3s \leftarrow \text{Cl}$ transitions with the I.P.'s at 12.3 and 12.6 eV.

CFHCl_2

In the photoelectron spectrum (Fig. 15) the four bands due to the chlorine lone pairs are distinguished although only two of them give well defined peaks. Their approximate values are 12.0, 12.2, 12.5, and 13.1, slightly lower than in CF_2Cl_2 . We assigned a band at 14.4 eV to the lower of the two C-Cl orbitals in CF_2Cl_2 . In CFHCl_2 this band moved to 14.6 eV. There is another band nearby at 14.8 eV, which is probably linked to an orbital of mixed (C-H)-(C-Cl) character. Again we find that the presence of the fluorines destabilizes the C-Cl orbitals. The first C-Cl band is above 15.0 eV in CH_2Cl_2 .^{3,15} The well defined band at 16.0 eV in CF_2Cl_2 and its high frequency shoulder are absent in CFHCl_2 . This and their presence in CF_2HCl shows that at least two fluorine atoms are needed to produce them. In CFHCl_2 the bands at 17.8, 19.5, and 20.0 eV could correspond to the C-F bonding orbital and to the two fluorine lone pairs. The energies of the latter could be split under C_s symmetry.

In the ultraviolet spectrum (Fig. 16) we find a diffuse

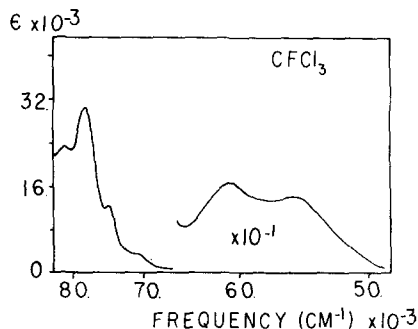


FIG. 19. The vacuum ultraviolet spectrum of CFCl_3 . The ϵ values of the two lowest frequency bands are multiplied by 100.

TABLE III. The lowest (Cl lone pair and C-Cl type) ionization potentials of chloro-fluoro-methanes and the ultraviolet transitions departing from the former.

	Cl lone pair I.P. (eV)	Lowest C-Cl I.P. (eV)	Cl lone pair to antibonding C-Cl orbital valence-shell transitions (cm ⁻¹)	Cl lone pair to 3s Rydberg transitions (cm ⁻¹)
CF ₃ Cl	13.0	15.0	71 500	78 100
CF ₂ HCl	12.6	14.0	66 200	74 500
CF ₂ Cl ₂	12.3 12.6 13.2 13.5	14.4	56 460-65 400	74 000 shoulder 79 100
CFCHCl ₂	12.0 12.2 12.5 13.1	14.6	57 500-60 600	70 000-82 000
CFCI ₃	11.9 12.2 13.0 13.5	15.0	54 000-60 500	70 000-82 000
CF ₃ Br	12.0	14.2	48 850	67 900 shoulder 70 500 76 900

region with ill defined peaks at 57 500 and 60 600 cm⁻¹. As before we assign these two transitions from the Cl lone pair orbitals to orbitals antibonding in the C-Cl. Starting at about 70 000 cm⁻¹ we find four bands. These can be assigned to 3s←Cl̄ transitions with quantum defects between 1.0 and 0.9 corresponding to the Cl lone pair ionization potentials. Some of them exhibit incompletely resolved vibrational fine structure. These bands are similar to those found in CF₂Cl₂ but only two are seen in the latter up to the limit of our measurements.

CFCI₃

The lone pairs give four MO under C_{3v} symmetry: $a_1 + a_2 + e + e$. We actually find four well resolved bands in the PE spectrum (Fig. 17) (11.9, 12.2, 13.0, and 13.5 eV). They underwent a moderate hypsochromic shift with respect to chloroform (about 0.4 eV). The usual intensity argument suggests that the more intense 12.2 and 13.0 eV bands correspond to the e levels.

The next band is evidently the (πe) C-Cl bonding level. It is at 15.0 eV shifted to lower energies by about 1 eV with respect to chloroform. The band has fine structure with an interval of 260 cm⁻¹, which is likely to be a CCl deformation vibration of the ion (Fig. 18).

We find one more PE band at 18.2 eV. The (σa_1)

C-F orbital and the fluorine lone pairs are expected to contribute to it.

The ultraviolet spectrum (Fig. 19) is similar to the spectrum of CF₂Cl₂ except that in this case the lower frequency (54 000 cm⁻¹) band is weaker than the one at 60 500 cm⁻¹. These are again probably the (C-Cl)*←Cl̄ transitions. Beyond 70 000 cm⁻¹ we find three or four transitions just as in CF₂Cl₂ or CFHCl₂, which we again assign to the 3s←Cl̄.

DISCUSSION AND CONCLUSIONS

In all fluoro-chloro substituted methanes the lowest ionization potentials are connected with the chlorine lone-pair electrons. They have values between 11.9 and 13.5 eV in the cases we examined. As expected on group theoretical grounds one such I.P. is found when the molecule contains one chlorine and four when it contains two or three chlorines (Table III). They tend to have higher values when the number of fluorines increases. The next lowest I.P.'s correspond to the mainly C-Cl bonding orbitals (13.5 to 15.0 eV).

All electronic transitions up to 120 nm (or 84 000 cm⁻¹) depart from the chlorine lone pair orbitals (Table III). The longest wavelength transitions are of the valence-shell type and weak. Their peak frequencies follow the trend in the values of the chlorine lone

pair I.P.'s. When there are more than one such I.P.'s there are more than one electronic transitions of this type. Above 70 000 cm^{-1} we find strong Rydberg bands departing also from the chlorine lone pair orbitals and having 3s orbitals for the excited electron. Again we obtain more than one band when the molecule has more than one chlorine lone pair I.P.

For CF_3Br the lowest I.P. and electronic transitions are at lower frequencies. Splittings due to spin-orbit coupling are clearly observed.

Vibrational fine structure was observed in the highest C-Cl type I.P. of CF_2Cl_2 and CFCl_3 as well as in the 67 900 cm^{-1} band of CF_3Br (one of the 3s) and in the 74 000 cm^{-1} (one of the 3s) bands of CF_2Cl_2 , indicating stable excited states.

For molecules containing one chlorine atom the lone pair I.P.'s are highest with the maximum number of fluorines in the molecules and so are the corresponding absorption bands. The photochemical reactivity of these molecules in going toward lower frequencies is expected to increase in the series $\text{CF}_3\text{Cl} \rightarrow \text{CF}_2\text{HCl} \rightarrow$

$\text{CFH}_2\text{Cl} \rightarrow \text{CH}_3\text{Cl}$. The same is expected when the number of chlorine atoms is increased or a chlorine is replaced by a bromine. The first singlet-singlet excited states lead to an orbital antibonding in the C-Cl link and are therefore expected to liberate chlorine atoms in their excited states. In the Rydberg states that follow at higher frequencies the molecules will likely behave in a way similar to the molecular ion.

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