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 CF₃Cl, CF₃Br, CF₂HCl, CF₂Cl₂, CF₂BrCl, CF₂Br₂, CF₂BrCl₂, CF₂ClBr, CF₂Cl₂Br, CF₂Cl₂Br₂, and CFCl₃ 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 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: CF₃Cl, CF₃Br, CF₂HCl, CF₂Cl₂, CF₂BrCl, CF₂Br₂, CF₂ClBr, CF₂Cl₂Br, and CFCl₃. 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. 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:

$$[3s_{a_1}]^2[3p_{f_2}]^6 1A_1,$$

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. The large splittings observed in this band can only be understood by invoking the Jahn–Teller theorem. The second ionization potential $(3s_{a_1})$ lies at much higher energies, about 23 eV. Recent quantum chemical calculations 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 $3s^*\rightarrow(p f_2)$ Rydberg transition in the united atom language or as a $\sigma^*\rightarrow\sigma$ type transition in minimal basis molecular orbital language. In both cases the transition is $1P_D\rightarrow1A_1$ 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, a McPherson model 665 double beam attachment, and photoelectric recording. More details were given in previous publications from this laboratory. 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 CF₃Br we used a column \( \frac{3}{4} \) in. × 3 m, Porapak Q, 80–100 mesh. The purity of our samples was 99.8% in all cases.
SPECTRA OF DERIVATIVES OF METHANE

TABLE I. Comparison of the I.P. (electron volts) of CH₃Cl, CHF₃, and CF₃Cl.

<table>
<thead>
<tr>
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<th>CH₃Cl</th>
<th>CHF₃</th>
<th>CF₃Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>11.3</td>
<td>Cl</td>
<td>13.0</td>
</tr>
<tr>
<td>C-Cl</td>
<td>14.4</td>
<td>F</td>
<td>15.5</td>
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<tr>
<td>CH₃</td>
<td>15.4</td>
<td>CF₃-F</td>
<td>16.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>F</td>
<td>17.2</td>
</tr>
</tbody>
</table>

*The data for CH₃Cl are from Ref. 3 and for CHF₃ from Ref. 14.

INTERPRETATION OF THE SPECTRA

CF₃Cl and CF₃Br

The photoelectron spectrum of CF₃Cl is given in Fig. 1.

It is interesting to compare it with those of CH₃Cl and CHF₃ (Table I). The order of the orbitals in CH₃Cl 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 (σ al) C-Cl orbital and the third one (about 15.4 eV) to the doubly degenerate type CH₃ orbital.

(In this paper we often use expressions like “C-Cl orbital” or “CH₃ 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 F, Cl, Br. The symbol (C-Cl) stands for an excited valence shell type orbital antibonding in the C-Cl link.) For CHF₃ we have both the photoelectron spectra and an ab initio calculation by Brundle, Robin, and Basch. The lowest ionization potential (I.P.) must come from the (σ al) C-Cl 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 σ₂, σ₃, e, and e molecular orbitals. According to the calculations of Brundle, Robin, and Basch, 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 CF₃Cl: Cl lone pair, C-Cl, F lone pair (σ₃), degenerate CF₃ bonding (π), 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 CH₃Cl 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 CHF₃ and the C-Cl IP in CF₃Cl is slight.

The PE spectrum of CF₃Br (Fig. 2) is very similar to the spectrum of CF₃Cl 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 CHF₃, CF₃Cl, and CF₃Br 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 eV are expected in the case of CF₃Br. 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 CF₃Cl and CF₃Br (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 CF₃Cl (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
splittings should be observable in the case of CF$_3$Br and
(\Omega\cdot\Omega) coupling should apply.

The spectrum of CF$_3$Cl 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 cm$^{-1}$ ($\epsilon_{\text{max}}$ about 60) and a much stronger band
is found at 78 100 cm$^{-1}$ ($\epsilon_{\text{max}}$ about 17 000).

The spectra of the methylhalides were examined by
Price\textsuperscript{17} and by Zobel and Duncan\textsuperscript{18} and a detailed
summary was given by Herzberg.\textsuperscript{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 cm$^{-1}$ to Herz­
berg's $^1\Delta_e \rightarrow ^1\Sigma_g$ band. Singlet–triplet transitions in CF$_3$Cl
must be very weak and unobservable under the pres­
ures used. Zobel and Duncan\textsuperscript{18} took the spectra of a
number of chlorine containing methane derivatives and,
in all cases, found a band at about 57 000 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–Br bond. Since our at­
tempts to integrate this band into a Rydberg series
remained unsuccessful, we adopt this assignment. The
strong band at 78 100 cm$^{-1}$ is readily interpreted as
the first member of an $ns$ type Rydberg series with a
quantum defect of 0.92. It is $(3sa_1)\rightarrow (e)^3$ or $^1E \rightarrow ^1A_1$
under $C_3v$ symmetry and allowed. It corresponds to
Herzberg's $C$ band for CH$_3$Cl that is an excitation
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$_3$Br (Fig. 4) we
find a broad and weak band with a maximum at 48 850
cm$^{-1}$ ($\epsilon_{\text{max}}$ 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 cm$^{-1}$, an
intense band at 70 500 ($\epsilon_{\text{max}} \approx 12 300$) and a weaker but
well pronounced band at 76 900 cm$^{-1}$. Clearly, the main
band must be due to a $(3sa_1)\rightarrow (e)^3$ type excitation in
complete analogy with CF$_3$Cl. The location of this
band reflects well the expected bathochromic shift upon
replacement of the chlorine by bromine and the hypo­
chromic shift occurred upon replacing the hydrogens by
fluorines (cf. Ref. 20). The band observed at 67 900,
absent in CF$_3$Cl, 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$_3$Br\textsuperscript{4}. The problem of spin-orbit coupling in
this type of molecule is discussed in detail by Herzberg.\textsuperscript{21}

In case of strong coupling two $E$ type excited states
originate from the $E_{\Delta_2}$ state of the ion and $E+A_1+A_2$
from $E_{\Pi_2}$. Evidence was found for the three $E$ states in the
case of CH$_3$F.\textsuperscript{22} The case of CF$_3$Br 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 cm$^{-1}$ to the
$(3sa_1)\rightarrow (e)^3$ singlet–singlet transition. (It would become
the $E$ state originating from $E_{\Delta_2}$ in case of strong
coupling.) The transitions of mainly singlet–triplet
character must then be contained in the weak band at
67 900 cm$^{-1}$. Then both the 70 500 and 67 900 cm$^{-1}$
bands are accounted for as being due to transitions.
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 $\rho$ 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 $\mu$ and a recording speed of 10 Å/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 Acquista $^{23}$ who assigned them to the symmetrical CF deformation, C–Br stretching and symmetrical C–F stretching modes, respectively. Dunn and Herzberg $^{22}$ interpreted the vibrational fine structure of the analogous band in the spectrum of CF$_3$I in the same way (see Ref. 19, p. 163). Our assignments are given in Table II.

Table II. Vibrations in the fine structure of the 67,900 cm$^{-1}$ band of CF$_3$Br.

<table>
<thead>
<tr>
<th>Observed frequencies (cm$^{-1}$)</th>
<th>Vibrations, excited state (cm$^{-1}$)</th>
<th>Vibrations, ground state (cm$^{-1}$)</th>
<th>Assignment</th>
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<td>66.916</td>
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<tr>
<td>67.828</td>
<td>2318</td>
<td>$3p_3$</td>
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</table>

The photoelectron spectrum is shown in Fig. 6. CF$_3$HCl can only have $C_s$ symmetry. The chlorine lone pair orbital, which was $e$ under $C_{2v}$ 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$_3$Cl. The band is asymmetrical, however, and it probably contains both bands resulting from the splitting.

The second IP. should correspond to the bonding electrons in the C–H or C–Cl bonds. The ($o_1$) and ($\pi e$) orbitals of CH$_3$Cl or CF$_3$Cl of which ($o_1$) 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 ($o_1$) 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$_3$Cl the band at 14.4 eV was assigned$^{13}$ to the C–Cl orbital on the basis of the observed vibrational intervals. In CF$_3$Cl 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$_3$HCl 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$_3$Cl) and 15.0 eV (CF$_3$Cl).

At higher energies in the PE spectrum of CF$_3$HCl we
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.

The orbitals and to the four fluorine lone pair combinations, 3s, two of which are orbitals and to the four fluorine lone pair combinations, 3s, two of which are 

FIG. 9. The fine structure of the three lowest photoelectron bands of CF₃Cl.

The strong band at 74 500 cm⁻¹ can be interpreted as 3s—Cl with a quantum defect of about 0.9. The band at 80 650 cm⁻¹ could be 3p—Cl although the quantum defect of about 0.6 again seems to be too high.

**CF₃Cl**

The photoelectron spectrum is shown in Fig. 8. The lowest energy bands exhibit partly resolved fine structure. 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 CH₂ 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 CH₃Cl (11.31 eV) and CH₂F₂ (12.74 eV). The second band of CF₃Cl 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 C₃ᵥ 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 CF₂HCl we find only one apparent peak but the band is broad and has shoulders and could well contain two I.P.’s. In CH₂Cl₂ both observed bands (11.31 and 12.18, adiabatic values) appear to be double. If we have a look at CF₂Cl₂ (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 CH₂Cl₂ 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 CH₂F₂ 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. 10.** The vacuum ultraviolet spectrum of CF₃Cl.

**FIG. 11.** The photoelectron spectrum of CF₂Cl₂.
The vibrational fine structure of the 14.4 eV band in the photoelectron spectrum of CF₂Cl₂.

The ultraviolet spectrum (Fig. 10) of CF₂Cl₂ is more similar to that of CH₃Cl than to those of the other fluorocarbons. At low frequencies (maximum at 62 500 cm⁻¹) we find the usual weak band (ε~250), which we again assign to a (C-Cl)⁻→Cl transition. At higher frequencies we find a group of bands of which the strongest are at 65 310, 66 400, and 67 590 cm⁻¹. The vibrational interval is of the order of 1100–1200 cm⁻¹, probably the CH₂ 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 cm⁻¹) has a quantum defect of 0.99 with respect to 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 cm⁻¹. The last three are separated by an interval of about 1200 cm⁻¹, which could again be the CH₂ 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.

**CF₂Cl₂**

The photoelectron spectrum is shown in Fig. 11. Under C₂ᵥ symmetry the chlorine lone pair orbitals combine to four molecular orbitals: a₁+a₄+b₁+b₂. 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 CH₂Cl₂. The two following bands can be assigned to the two bonding MO of mainly C–Cl character (b₂ and a₁). 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
likely to correspond to a C–Cl deformation mode.

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$_2$Cl$_2$ is given in Fig. 13. This spectrum has already been studied by Zobel and Duncan$^{18}$ and by Stokes and Duncan. We are giving it a modified interpretation based on the ionization potentials that became known more recently.

At about 56,460 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 (C–Cl)$^*$$\rightarrow$Cl transition. Now, we have two close lying I.P. (12.3 and 12.6), separated by only about 2000 cm$^{-1}$ and the observed band might well receive contributions from transitions departing from both. At 65,400 cm$^{-1}$ we find a weaker but broad band with a pronounced shoulder. It is similar to the 56,460 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 cm$^{-1}$.

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 cm$^{-1}$ have quantum defects of 0.91 and 0.85, respectively, and can be assigned to 3$s^−$Cl transitions with the I.P.'s at 12.3 and 12.6 eV.
The lowest (Cl lone pair and C-Cl type) ionization potentials of chloro-fluoro-methanes and the ultraviolet transitions departing from the former.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Cl lone pair I.P. (eV)</th>
<th>Lowest C-Cl I.P. (eV)</th>
<th>Cl lone pair to antibonding C-Cl orbital valence-shell transitions (cm⁻¹)</th>
<th>Cl lone pair to 3s Rydberg transitions (cm⁻¹)</th>
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<tbody>
<tr>
<td>CF₂Cl</td>
<td>13.0</td>
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</tbody>
</table>

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)*-Cl 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→Cl.

**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\(_2\)Br 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\(_2\)Cl\(_2\) and CFCI\(_2\) as well as in the 67,900 cm\(^{-1}\) band of CF\(_2\)Br (one of the 3s) and in the 74,000 cm\(^{-1}\) (one of the 3s) bands of CF\(_2\)Cl\(_2\), 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 CF\(_3\)Cl$\rightarrow$CF\(_2\)HCl$\rightarrow$CF\(_2\)Cl.$\rightarrow$CFHCl$\rightarrow$CH\(_3\)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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13Reference 3, pp. 215 and 221.
21Reference 19, p. 338.
22T. M. Dunn and G. Herzberg, cited in Ref. 17, p. 528.
24Reference 3, pp. 234.