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Photoreactions of Small Organic Molecules V.

Absorption-, Photoion- and Resonancephotoelectron-Spectra of CF_3Cl, CF_2Cl_2, $CFCl_3$ in the Energy Range 10-25 eV

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The absorption spectra, photoion spectra, and resonance photoelectron spectra of CF_3Cl, CF_2Cl_2, *and* $CFCl_3$ *have been measured in the energy range from 9 eV to 25 eV. - Absolute cross sections of absorption are given. The stability of the parent ions decreases with increasing symmetry of the parent molecules. The fragment ions have been analyzed. Besides photocations, atomic chlorine and fluorine, fluoride and chloride are formed. The decay mechanisms are discussed, spectra are influenced by autoionization. The resonance photoelectron spectra reveal some new ionization potentials at high excitation energies.*

Es wurden die Absorptions-, Photoionen- und Resonanzphotoelektronenspektren von CF_3Cl, CF_2Cl_2 *und* $CFCl_3$ *im Energiebereich von 9 - 25 eV gemessen. - Für die Absorptionsspektren werden absolute Wirkungsquerschnitte angegeben. Die Stabilität der Molekülionen nimmt mit steigender Symmetrie der neutralen Moleküle ab. Die Fragementionen wurden analysiert; neben verschiedenen Photokationen, atomarem Chlor und Fluor werden Fluorid und Chlorid gebildet. Die Zerfallsmechanismen werden diskutiert, der Einfluß von Autoionisation auf die Spektren kann nachgewiesen werden. Die Resonanzphotoelektronenspektren zeigen einige bisher nicht beobachtete Ionisierungspotentiale bei hohen Anregungsenergien.*

Introduction

Recently the role of halogenated methanes in the photochemistry of the upper atmosphere has come under discussion. Molina and Rowland[1] stated that halomethanes diffusing into the upper atmosphere destroy the ozone layer via a Cl-O-reaction chain with chlorine atoms produced by photolysis of the halomethanes. Considering the importance of the ozone layer as a UV-radiation shield and the strongly increasing production of fluorinated and chlorinated alkanes, investigation of their photoreactions is of considerable interest. In this paper we will extend the discussion to an energy range where photoionization and formation of fragment ions play an important role. One feature of interest is the instability of the molecular ions of CF_4 and CCl_4. In fact, CF_4^+ and CCl_4^+ have not been observed in photoionization or electron impact experiments.[2-6] Somewhat contradictory to this observation is the interpretation of photoelectron spectra by means of stable molecular ion configurations. This problem was discussed by Kaufman et al.[7]

Only a few publications exist on excitation and ionization of fluoro-chloromethanes in the VUV region.[8] There is some evidence from older electron impact measurements that molecular ions of the mixed fluoro-chloro-methanes do not decay completely.[9]

In order to get more knowledge about the above-cited phenomena and to discuss the ionic fragmentation processes in a wide energy range (9-24 eV) we recorded the absorption-, photoion- and resonance photoelectron spectra of CF_3Cl, CF_2Cl_2, and $CFCl_3$. In our experiments we used the advantages of synchrotron radiation,[11] which are especially remarkable in the measurement of absorption spectra. Formerly published absorption spectra[8] suffer from discontinuities caused by insufficiencies of the light source used (HeI-continuum).

Ionic states may be reached not only by direct ionization, but also indirectly by radiationless transitions such as autoionization and predissociation. These processes influence the shape of photoion spectra. The identification and localization of these processes is possible by comparison of the mass selected photoion spectra with absorption spectra and total ion spectra.

Experimental set up

The experimental equipment was described in previous work.[12,13] It consists mainly of a 1.1 m VUV monochromator in a modified Wadsworth mounting. As light source we used the 7.5 GeV electron accelerator DESY in Hamburg. In the energy range 8.5 - 25 eV the optimal wavelength resolution is about 1 Å. Behind the exit slit of the monochromator a multipurpose reaction chamber is mounted which can be equipped alternatively with a gas absorption cell, a quadrupole mass filter and a zero energy electron filter.[14,15] For a more detailed description see reference 12. Absorption spectra were taken with a optimal wavelength resolution of about 1.5 Å, all the other spectra were recorded with 2 Å resolution. The accuracy of the wavelength scale was better than ±1 Å. Absorption spectra were recorded with a gas pressure of some 10^{-2} Torr, photoion and resonance photoelectron spectra only needed some 10^{-4} Torr. During measurements the pressure was kept constant within 5 %. The substances were supplied by Hoechst AG. Their purity was controlled by mass spectrometry. No further purification was performed. The impurities were mainly restricted to water (ca. 1 %) and should have no considerable influence on the experimental results.

Results

Absorption spectra and total photoionization.

In Figs. 1-3 the VUV spectra in the energy range 9-24 eV and the total photoionization spectra of CF_3Cl, CF_2Cl_2 and $CFCl_3$ are shown. Determination of absolute absorption cross sections is difficult, because a windowless gas absorption cell and a Pirani type pressure gauge were used. Nevertheless, our relative absorption cross sections can be fitted to absolute values taken with the Ne-resonance lines at about 16.75 eV (740 Å)[16]. At that energy none of the spectra reveals sharp structure, so a normalization of our spectra to that value will not suffer from inaccuracy due to restricted energy resolution. At very low or very high energies second order as well as scattered light of the monochromator must be taken into account. Thus an estimated uncertaincy of our normalized absorption cross sections of as much as 20 % must be considered. In the case of CF_2Cl_2 an absorption cross section value of 80.3 Mbn at 1014 Å (12.23 eV) is cited in the literature.[17] This value is 13 % lower than that taken from our spectrum. In a previous paper Sandorfy et al.[8] published VUV-spectra of chloro-fluoro-methanes. The absolute extinction coefficients reported there are considerably lower than our values; especially in the energy range from 15-20 eV discrepancies up to an order of magnitude appear.

(Table 1)

Total photoionization spectra (Fig. 1-3) were recorded running the qudrupole mass filter in the total ion collection mode. Neglecting ion pair production from the molecules, in the energy range considered the spectra should correspond immediately to the total photoionization cross sections.

Absolute ionization quantum yields at 740 Å (16.75 eV) for CF_3Cl, CF_2Cl_2, and $CFCl_3$ are given in the literature.[16] From photoionization measurements of the chloro-fluoro-methanes only ionization potentials have been reported.[18] None of the ionization spectra reveals a stepwise threshold function. The determination of appearance potentials by measuring the ionization current may suffer from restricted sensitivity. This would explain the differences between values given in this work and earlier investigations.[18]

Mass selected photoion spectra

In Figs. 4-6 the photoion spectra of CF_3Cl, CF_2Cl_2 and $CFCl_3$ are shown together with the corresponding part of the absorption spectra. The main criterion for the selection of the ions was sufficient intensity. For instance lack of intensity was the reason that no photoion spectrum of $CFCl_3^+$ was recorded, yet we were able to detect this ion using the higher intensity of the monochromator's direct image. Determination of the relative ion intensities is somewhat difficult since the transmission function of the mass filter is strongly influenced by the mass peak resolution used. To get reliable relative intensities, mass spectra excited by 20.4 eV photons where recorded with minimum mass resolution. The relative intensities of the molecular ions and their fragments are summarized in Table 2 together with the corresponding appearance potentials.

(Table 2)

Table 3 contains the heats of formation used for the calculation of appearance potentials.

(Table 3)

Negative ions

The production of fluoride and chloride from CF_3Cl, CF_2Cl_2, and $CFCl_3$ could be proved by means of the high intensity of the monochromator's direct image. Only in the case of CF_2Cl_2 we were able to record a photoion spectrum of these anions (Fig. 7). The shape of the ion yield curve of both ions corresponds surprisingly well with the total photoionization spectrum. The same phenomena has been observed in H^- production from ethane.[19] This process was interpreted as electron capture by atomic hydrogen.

No negative ions could be collected in our experiments at lower excitation energies than the appearance potential of the molecular ions, although electron impact work[10,20] on CF_3Cl, CF_2Cl_2, $CFCl_3$ reports the existence of F^- ions. The photon flux of our monochromator becomes very small at energies below 10 eV, therefore the search for anions suffered from low intensity there.

Resonance photoelectron spectra

The photoelectron spectra shown in Figs. 8-10 were recorded by collecting zero or nearly zero energy electrons while varying the energy of the incident photon beam. The resonant excitation of the different ionic states is characteristic of this resonance[14] or threshold photoelectron[15] spectroscopy. Advantages of this technique are the constant transmission, the accurate energy scale given by the monochromator's wavelength setting, and the suppression of angular distribution effects of the electrons. A summary of the data taken from our spectra is given in Table 4.

(Table 4)

Discussion

Absorption and total photoionization spectra

The absorption spectra of CF_3Cl, CF_2Cl_2 and $CFCl_3$ (Figs. 1-3) are divided in two regions. At lower excitation energies a few outstanding but relatively broad peaks are observed, whereas at higher excitation energies the spectrum is a relatively flat curve. Although one expects several Rydberg transitions due to the excitation of halogen lone pair electrons, there is only doubtful indication of such series. Sandorfy et al.[8] connect the low energy absorption peaks with the first members of different Rydberg series converging to different ionization potentials. It is impossible to find higher members of a series. The absence of any higher members is obvious especially in the spectrum of $CFCl_3$. Similar results have been observed in spectra of alkyl halides[22] but no explanation for the missing higher Rydberg transitions was given.

CF_3Cl

In the lower energy range up to about 16 eV the spectrum (Fig. 1) reveals some prominent maxima, which had been assigned to Rydberg transitions in earlier work[8]. At higher energies there are some weak, but clearly resolved maxima, that have not been observed before. The resonance photoelectron spectrum of this compound indicates two ionization potentials at 20.1 eV and 21.0 eV, unknown until now. Thus the maxima cited above may come from partial overlapping of unresolved Rydberg transitions, converging to these ionization potentials. Detailed assignment of this structure is the subject of present studies and will be published later.

CF_2Cl_2

The comparison of the spectrum (Fig. 2) with that of Sandorfy et al.[8] shows fairly good agreement. Only in the regions from 11-12.5 eV and 16-24 eV, we found some new structure. Interpretation of the rather flat maximum at 19 eV is somewhat ambiguous since a higher ionization potential (20 eV) has been found now and a similar situation as described before appears.

$CFCl_3$

There is a fairly good agreement between our spectrum (Fig. 3) and previous work.[8] As in the case of CF_3Cl and CF_2Cl_2, Sandorfy's spectrum consists of individually recorded parts. Therefore some discontinuity is recognized in the region from 11-13 eV. Here we find two clearly resolved maxima at 11.28 eV and 12.05 eV.

Total photoionization spectra.

The photoionization spectra (Figs. 1-3) consist of relatively flat ascending background continua that are influenced by intense structure due to autoionization. In the total photoionization curves of $CFCl_3$ and CF_3Cl this structure corresponds directly to that found in the respective absorption spectra. However, in the case of CF_2Cl_2 there is a small maximum at 13.6 eV, which cannot be related to a maximum in the absorption spectrum. This peak is caused by direct ionization. Its considerable intensity was predicted from photoelectron spectroscopy[8] and is confirmed by means of the resonance photoelectron spectrum (Fig. 9).

Mass selected photoionization.

Influences due to autoionization of neutral states must be considered in the spectra of the molecular ion and its fragments as well as in the total photoionization curves mentioned above. These spectra result primarily from molecular ion states with stable or dissociative potential energy surfaces.

Substances like the halogenated hydrocarbons discussed here tend to fragment partly via predissociation of stable ionic states. This causes the characteristic ascent of the fragment ion yield.

On the other side, the extremely low intensity of the molecular ion current (Table 2) must be related to instability of their electronic configurations. In the case of CF_4 and CCl_4 this fact is somewhat contradictionary to the assignment of the photoelectron peaks to stable ion configurations[8,21] predicted from theoretical calculations. Some authors[7] have overcome this problem by assuming that in a frist step the molecule dissociates and then the CF_3 or CCl_3 radials are ionized subsequently. The first peak in the PES must then be related to ionization of these radicals. Our results show that at least in the case of CF_2Cl_2 and CF_3Cl, the steep ascent of the molecular ion yield at the ionization potential is sharply interrupted by the onset of the first fragmentation process. Therefore the instability of the molecular ion must be attributed to predissociation of the primary stable ion configuration. Because the photoelectron peaks result from fast direct ionization they will not be affected by the subsequent ion dissociation.

Investigations on fragmentation processes of CF_3Cl[9] and CF_4[5] show that release of kinetic energy to fragment ions is considerable. Because of similar instability in the fragmentation of CF_3Cl, CF_2Cl_2, and $CFCl_3$, fragments with kinetic energy are produced with high probability already at the threshold. Thus a direct calculation of thermodynamic data from experimental ionization potentials seems to be ambiguous in many cases. Furthermore there is some spread among the data given for standard enthalpies of formation of the corresponding neutral species.[23] This handicaps the following discussion of the fragmentation processes.

CF_3Cl (Fig. 4)

CF_3Cl^+

As mentioned above the increase of molecular ion yield is interrupted immediately above the adiabatic ionization potential by the appearance of the most probable fragmentation reaction. The CF_3^+ is produced by predissociation of molecular ions. As a result of the small energy gap between the ionization potential and the appearance potential of CF_3^+ a very low intensity of the molecular ion peak is observed. From I = 12.45 eV, which is in good agreement with the value given by Noutary[2] (I = 12.43 eV), and ΔH_f (CF_3Cl) = -169.2 kcal/mol we calculate ΔH_f (CF_3Cl^+) = 117.9 kcal/mol.

CF_3^+

The most probable fragmentation process involves cleavage of the C-Cl-bond. In agreement with Noutary's value (12.57 eV) in this measurement the appearance potential is found to be 12.55 eV. A reliable experimental value for the ionization potential of CF_3 is available[25] (I(CF_3) = 9.17 eV). Taking $\Delta H_f(CF_3)$ = -112.5 kcal/mol and $\Delta H_f(CF_3Cl)$ = -169.2 kcal/mol we calculate the appearance potential of the reaction

$$CF_3Cl + h\nu \rightarrow CF_3^+ + Cl + e^- \qquad (1)$$

to be 12.89 eV. Generally experimental values are expected to be higher than calculated thresholds, because the amount of excess energy in the products of fragementation is unknown. We suppose that this deviation results from an uncertain $\Delta H_f(CF_3)$ value. As the amount of excess energy in our experiment was not measured, we omit values for $\Delta H_f(CF_3^+)$.

CF_2Cl^+

The onset region of the CF_2Cl^+ spectrum is typical of a direct fragmentation process. Between 17 eV and 21 eV the spectrum is also influenced by autoionization. Determination of the appearance potential suffers from the flat onset behaviour, therefore the value of 14.25 eV given here has a limited accuracy. The heat of formation of CF_2Cl^+ evaluated under these restrictions is 140.6 kcal/mol.

CF_2^+

As in the case of CF_2Cl^+ the formation of CF_2^+ ions is a direct fragmentation process. The small shoulder at about 20 eV results from autoionization effects. Calculations based on A_p = 18.85 eV lead to $\Delta H_f(CF_2^+)$ = 217.5 kcal/mol. The relatively high value of the appearance potential is a strong indication that the CF_2^+ ions are produced according to the following reaction:

$$CF_3Cl + h\nu \rightarrow CF_2^+ + F + Cl + e^- \qquad (2)$$

CF^+

As the CF^+ yield is very low we confine ourselves to quoting the appearance potential (Table 2).

CF_2Cl_2 (Fig. 5)

$CF_2Cl_2^+$

The molecular ion $CF_2Cl_2^+$ is much more stable than CF_3Cl^+. The predominant maximum in the molecular ion curve between threshold and about 14 eV has its origin in autoionization effects. However, there is no direct correlation between the structure in the molecular ion curve and the absorption spectrum. This phenomenon results from superposition of autoionization and direct ionization. There is a very small energetic difference between the various ionization potentials and the autoionizing neutral states in this region (Table 1 and 4). Based on $\Delta H_f(CF_2Cl_2) = -117.5$ kcal/mol and $I(CF_2Cl_2) = 11.75$ eV we calculate $\Delta H_f(CF_2Cl_2^+) = 153.5$ kcal/mol.

CF_2Cl^+

The cleavage of a C-Cl bond (eq. 3)

$$CF_2Cl_2 + h\nu \rightarrow CF_2Cl^+ + Cl + e^- \tag{3}$$

is the most probable process observed. The heat of formation $\Delta H_f(CF_2Cl^+)$ calculated with aid of the experimental appearance potential (12.10 eV) and data from the literature[23] (Table 3) is found to be 132.45 kcal/mol, a value which agrees fairly well with the corresponding value established from the C-F fragmentation in CF_3Cl.

$CFCl_2^+$

The shape of this ion yield curve reminds one of that of CF_2Cl^+ from CF_3Cl. The fragment ion is predominantly the product of a direct process. The $A_p(CFCl_2^+) = 14.15$ eV gives a $\Delta H_f(CFCl_2^+) = 189.9$ kcal/mol.

CF_2^+

The appearance potential of CF_2^+ from CF_2Cl_2 is 17.22 eV. Presuming the reaction

$$CF_2Cl_2 + h\nu \rightarrow CF_2^+ + 2\ Cl + e^- \tag{4}$$

we calculate $\Delta H_f(CF_2^+) = 221.4$ kcal/mol. This value agrees with $\Delta H_f(CF_2^+) = 217.5$ kcal/mol calculated from the decay of CF_3Cl. Furthermore Hildenbrand[24] recently reported the ionization potential of CF_2 to be 11.54 eV. Taking $\Delta H_f(CF_2) = -43.5$ kcal/mol a value of $\Delta H_f(CF_2^+)$ = 222.6 results. This means obviously that no excess energy is involved in the CF_2^+ formation from CF_2Cl_2 or from CF_3Cl.

CF^+

Different fragmentation processes may yield CF^+. Indeed the spectrum has an unique structure, two appearance potentials at 17.65 eV and 20.20 eV are recognized. The production of CF^+ according to the reaction

$$CF_2Cl_2 + h\nu \rightarrow CF^+ + Cl_2 + F + e^- \qquad (5)$$

requires the lowest threshold energy. Using data from Table 3 we calculate $A_p(CF^+) = 17.84$ eV. From the comparison of experimental and calculated appearance potential we conclude that practically no excess energy is involved in this process near threshold.

The calculated appearance potential for the process

$$CF_2Cl_2 + h\nu \rightarrow CF^+ + 2Cl + F + e^- \qquad (6)$$

is 20.33 eV, it is in good agreement with the experimental value. Thus no excess energy is involved in this fragmentation process either.

$CFCl_3$ (Fig. 6)

$CFCl_3^+$

The ion yield of $CFCl_3^+$ is extremely small, therefore no photoion spectrum could be taken.

The instability of this molecular ion reminds one of that of CF_3Cl^+. Considering the stability of the ions CF_4^+, CCl_4^+, $CFCl_3^+$, CF_3Cl^+, and $CF_2Cl_2^+$ it seems that the stability increases with decreasing symmetry and that the influence of the chemical properties of substituents is less important.

$CFCl_2^+$

This ions produces the most intense signal. The response of the spectrum is apperently influenced by autoionization. With an A_p = 11.65 eV, $\Delta H_f(CFCl_3)$ = −69 kcal/mol according to

$$CFCl_3 + h\nu \rightarrow CFCl_2^+ + Cl + e^- \qquad (7)$$

$\Delta H_f(CFCl_2^+)$ is 170.6 kcal/mol. This value is considerably smaller than that found from fragmentation of CF_2Cl_2 (189.9 kcal/mol). The difference indicates that at least in the case of $CFCl_2^+$ formation from CF_2Cl_2 a considerable amount of excess energy is involved.

CCl_3^+

The formation of CCl_3^+ is influenced by autoionization. The appearance potential (13.50 eV) reveals $\Delta H_f(CCl_3^+)$ = 223.45 kcal/mol. Werner et al.[4] report $\Delta H_f(CCl_3^+)$ = 208.8 kcal/mol from the reaction

$$CCl_4 + h\nu \rightarrow CCl_3^+ + Cl + e^- \qquad (8)$$

We suppose that the difference is due to kinetic energy of the fragments.

CCl_2^+, $CFCl^+$

CCl_2^+ and $CFCl^+$ are mainly formed by a direct fragmentation process. Literature data[23] for $\Delta H_f(CCl_2^+)$ spread from 347 - 370 kcal/mol. Based on the reaction

$$CFCl_3 + h\nu \rightarrow CCl_2^+ + FCl + e^- \qquad (9)$$

we calculate $\Delta H_f(CCl_2^+)$ = 335.4 kcal/mol using the appearance potential of CCl_2^+ = 17.0 eV. Therefore the formation according to equation (9) seems the most probable.

From $A_p(CFCl^+)$ = 16.0 eV we get $\Delta H_f(CFCl^+)$ = 300 kcal/mol based on the fragmentation reaction:

$$CFCl_3 + h\nu \rightarrow CFCl^+ + Cl_2 \tag{10}$$

$\Delta H_f(CFCl^+)$ values calculated from electron impact data[23] are only slightly higher (309 kcal/mol and 336 kcal/mol).

CCl^+, CF^+

The lack of reliable reference data prevents one from specifying the correct fragmentation process for the formation of CCl^+. (A_p = 20.5 eV).

For the formation of CF^+ two appearance potentials can be given, according to the formation of this ion from $CFCl_3$ in the reactions:

$$CFCl_3 + h\nu \rightarrow CF^+ + Cl_2 + Cl + e^- \tag{11}$$

$$CFCl_3 + h\nu \rightarrow CF^+ + 3Cl + e^- \tag{12}$$

It is somewhat difficult to take the correct appearance potential connected with the first reaction ($A_p \approx$ 15.7 eV) because the ion yield curve shows a very flat ascent in this region. From the more reliable appearance potential of reaction (12) A_p = 18.35 eV we get $\Delta H_f(CF^+)$ = 267 kcal/mol. This value is in agreement with the $\Delta H_f(CF^+)$ given in Table 3.

A common feature of photodissociation of the halogenated hydrocarbons under question is the copious production of chlorine atoms as neutral products in addition to the different photocations. This result seems important in view of recent publications[1] concerning the decomposition of ozone in the upper atmosphere via a Cl-O reaction chain.

Negative Ions

Formation of the photoanions chloride and fluoride was detected as products of the photodecomposition of $CFCl_3$, CF_3Cl, CF_2Cl_2. Only in the case of CF_2Cl_2 was the production of these anions sufficient to record photoion spectra of the anions.

It is an outstanding feature of the photoanion curves that their shape is very similar to that of the total photoionization curve of CF_2Cl_2 (Fig. 7). Furthermore F^- and Cl^- exhibit the same appearance potential which agree with the ionization potential of CF_2Cl_2. Thus ion pair formation as the origin of anions can be excluded. We propose a two stage process for the formation of anions. It is well known that chlorine atoms result from irradiation according to the equation[26]

$$CF_2Cl_2 + h\nu \rightarrow CF_2Cl + Cl. \qquad (13)$$

As soon as the energy of the photons is sufficient to produce $CF_2Cl_2^+$ (this means $I(CF_2Cl_2)$ is reached), the resulting photoelectrons are attached to chlorine atoms (eq. 15)

$$CF_2Cl_2 + h\nu \rightarrow CF_2Cl_2^+ + e^- \qquad (14)$$

$$Cl + e^- \rightarrow Cl^- \qquad (15)$$

In an analogous manner fluoride may be produced. Although the proposed mechanism explains the observed experimental results further experiments concerning the formation of anions will be done.

Resonance photoelectron spectra

In photoelectron spectroscopy the major problem is to assign the measured maxima of electron yield to ionization potentials from different molecular orbitals. The intensity and line shape of the peaks indicate the character of the molecular orbital involved in the ionization process. Because of the instability of the molecular ions in the PE-spectra (He-I) of

CF_3Cl, CF_2Cl_2 and $CFCl_3$[8,21] almost no vibrational structure on the photoelectron bands has been observed. Contrary to these spectra the resonance-photoelectron spectra reported here show a considerable difference among the shape and intensity ratios of the bands. The main factors that may cause these differences are: Firstly, constant collection efficiency with no angle and energy dependence of the analyzer and the excitation of ionic states partly via autoionization. Secondly, different ionization cross sections for threshold and He-I-excitation (21.2 eV). The influence of autoionization may be interpreted by comparison of the absorption and the photoionization spectra (Figs. 1-3). In Table 4 the ionization potentials and the relative intensities of bands have been compared with previous work.[8,21]

The resonance photoelectron spectrum of CF_3Cl reveals bands at 20.1 eV and 21.2 eV which where not observed before. Sandorfy et al. expected ionic states higher than 17.4 eV from VUV-measurements. Also in the spectrum of CF_2Cl_2 a shoulder in the 19.2 eV band indicates an ionic state not observed previously. We suppose that these highly energetic states involve fluorine lone pair electrons.

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Literature

1. M.J. Molina and F.S. Rowland, Nature 249, 810 (1974)
   Federal Council for Science and Technology ICAS-Report 18a-FY 75, Mai 1975
2. C.J. Noutary, J.Res.Nat. Bureau Stand. 72A, 479 (1968)
3. T.A. Walter, C. Lifshitz, W.A. Chupka, and J. Berkowitz, J.Chem.Phys. 51, 3531 (1969)
4. A.S. Werner, B.P. Tsai, and T. Baer, J.Chem.Phys. 60, 3650 (1974)
5. R. Frey, Thesis Freiburg 1974
6. J.H.D. Eland, Photoelectron Spectroscopy, Butterworths London 1974, p. 184 ff
7. J.J. Kaufman, E. Kerman, and W.S. Koski, Int. J. of Quantum Chem. 4, 391 (1971)
8. J. Doucet, P. Sauvageau, and C. Sandorfy, J.Chem.Phys. 58, 3708 (1973)
   R. Gilbert, P. Sauvageau, and C. Sandorfy, ibid. 60, 4820 (1974)
9. V.H. Dibeler, R.M. Reese, and F.L. Mohler, J.Res.Nat. Bureau Stand. 57, 113 (1956)
10. R.K. Curran, J.Chem.Phys. 34, 2007 (1961)
11. R. Haensel and C. Kunz, Z. Angew. Physik 23, 276 (1967)
12. H.W. Jochims, W. Lohr, and H. Baumgärtel, Ber. Bunsenges. phys. Chem. in press
13. D. Reinke, R. Kräßig, and H. Baumgärtel, Z. Naturforschung 28a, 1021 (1973)
14. T. Baer, W.B. Peatman, and E.W. Schlag, Chem.Phys.Lett. 4, 243 (1969)
15. D. Villarejo, R.R. Herm, and M.G. Inghram, J.Chem. 46, 4995 (1967)
16. R.E. Rebbert and P. Ausloos, J.Res.Nat. Bureau Stand. 75A, 481 (1971)
17. R.H. Huebner, D.L. Bushnell, R.J. Celotta, S.R. Mielczarek, and C.E. Kuyatt, to be published
18. K. Watanabe, T. Nakayama, and J. Mottl, J.Quant. Spectroscop. Rad. Transfer 2, 369 (1962)
19. W.A. Chupka and J. Berkowitz, J.Chem.Phys. 47, 2921 (1967)

20. R.M. Reese, V.H. Dibeler, and F.L. Mohler, J.Res.Nat. Bureau Stand. 57, 367 (1956)

21. F.T. Chau and C.A. McDowell, J.Electron. Spec. 6, 357 (1975)

22. M.B. Robin: Higher Excited States of Polyatomic Molecules, Academic Press, New York 1974

23. a) D.R. Stull and H. Prophet, JANAF-Tables, Nat. Bureau of Stand. NSRDS-NBS 37, Washington 1971,
    JANAF Thermochemical Tables, 1974 Supplement J.Phys.Chem.Ref. Data 3, 385 (1974)

    b) J.L. Franklich, J.G. Dillard, H.M. Rosenstock, J.T. Herron, K. Draxl, and F.H. Field, Nat. Bureau Stand. NSRDS-NBS 26, Washington 1969

    c) J.D. Cox and G. Pilcher: Thermochemistry of Organic and Organometallic Compounds, Academic Press, London 1970

24. D.L. Hildenbrand, Chem.Phys.Lett. 30, 32 (1975)

25. C. Lifshitz and W.A. Chupka, J.Chem.Phys. 47, 3439 (1967)

26. R. Milstein and F.S. Rowland, J.Chem.Phys. to be published

Table 1: Absorption maxima of CF_3Cl, CF_2Cl_2 and $CFCl_3$ in the energy range from 9 - 25 eV

CF_3Cl		CF_2Cl_2		$CFCl_3$	
(eV)	10^{-18} (cm^2)	(eV)	10^{-18} (cm^2)	(eV)	10^{-18} (cm^2)
9.60	43	9.80	121	9.30	45
10.60	18	10.50	80	9.78	163
11.51	74	10.80	100	10.12	112
13.31	86	11.24	100	10.50	137
14.76	58	11.50	99	10.65	108
16.27	85	11.80	98	11.15	102
17.33	88	12.10	103	11.28	110
18.25	91	12.75	110	11.50	118
18.7	93	12.90	112	12.05	122
19.5	91	14.7	117	12.60	134
		16.5	119	12.85	132
		19.2	126	13.60	155
				15.0	180
				16.7	168
				20.0	155

Table 2: Photoionization and Photofragmentation data of CF_3Cl, CF_2Cl_2, and $CFCl_3$

	Ion	A_p(exp.) (eV)	rel. Intensity	reaction
CF_3Cl	CF_3Cl^+	12.45	1	$CF_3Cl + h\nu \rightarrow CF_3Cl^+ + e^-$
	CF_3^+	12.55	40	$CF_3Cl + h\nu \rightarrow CF_3^+ + Cl + e^-$
	CF_2Cl^+	14.25	20	$CF_3Cl + h\nu \rightarrow CF_2Cl^+ + F + e^-$
	CF_2^+	18.85	4	$CF_3Cl + h\nu \rightarrow CF_2^+ + F + Cl + e^-$
	CF^+	20.20	2	--------
CF_2Cl_2	$CF_2Cl_2^+$	11.75	2	$CF_2Cl_2 + h\nu \rightarrow CF_2Cl_2^+ + e^-$
	CF_2Cl^+	12.10	10	$CF_2Cl_2 + h\nu \rightarrow CF_2Cl^+ + Cl + e^-$
	$CFCl_2^+$	14.15	1	$CF_2Cl_2 + h\nu \rightarrow CFCl_2^+ + F + e^-$
	CF_2^+	17.22	2	$CF_2Cl_2 + h\nu \rightarrow CF_2^+ + 2Cl + e^-$
	CF^+	17.65	{ 1	$CF_2Cl_2 + h\nu \rightarrow CF^+ + F + Cl_2 + e^-$
	CF^+	20.20		$CF_2Cl_2 + h\nu \rightarrow CF^+ + F + 2Cl + e^-$
$CFCl_3$	$CFCl_3^+$	-	-	---------
	$CFCl_2^+$	11.65	80	$CFCl_3 + h\nu \rightarrow CFCl_2^+ + Cl + e^-$
	CCl_3^+	13.50	2	$CFCl_3 + h\nu \rightarrow CCl_3^+ + F + e^-$
	$CClF^+$	16.0	20	$CFCl_3 + h\nu \rightarrow CClF^+ + Cl_2 + e^-$
	CCl_2^+	17.0	6	$CFCl_3 + h\nu \rightarrow CCl_2^+ + FCl + e^-$
	CCl^+	20.5	1	----------
	CF^+	15.7	{ 2	$CFCl_3 + h\nu \rightarrow CF^+ + Cl_2 + Cl + e^-$
	CF^+	18.35		$CFCl_3 + h\nu \rightarrow CF^+ + 3Cl + e^-$

Table 3: Summary of literature data used for the thermodynamical calculations

Compound	ΔH_f^{298} (kcal/mol)
CF_3Cl	-169.2[23a]
CF_2Cl_2	-117.5[23a]
$CFCl_3$	- 69.0[23a]
CF_3	-112.4[23a]
CF_2	- 43.5[23a]
FCl	- 12.36[23c]
Cl_2	0[23c]
F	18.88[23b]
Cl	29.1[23b]
CF^+	274.7[23a]

Table 4: Photoelectron spectroscopic data of CF$_3$Cl, CF$_2$Cl$_2$ and CFCl$_3$

CF$_3$Cl

RPES (this work)

IP(eV)	relative abundance	IP (eV)		relative abundance		assignment	
13.15	10	13.0[8]		10[8]		e $\overline{\text{Cl}}$[8]	
15.0	3	15.0		2.5		a_1 C-Cl	
15.55	3	15.55		2.5		a_2 $\overline{\text{F}}$	
16.6	8	16.5		2.5		e CF$_3$-F	
17.5	6	17.4		3		e F	
20.1	2						
21.2	4						
CF$_2$Cl$_2$							
12.55	10	12.3[8]		10[8]		$\overline{\text{Cl}}$[8]	
12.50	13	12.6		15		$\overline{\text{Cl}}$	
13.20	13	13.2		14		$\overline{\text{Cl}}$	
13.50	15	13.5		14		$\overline{\text{Cl}}$	
14.35	11	14.4		10		C-Cl	
16.25	11	16.0		7		C-Cl	
19.20	8	19.0		1.5			
20.0	6						
CFCl$_3$							
11.85	10	11.9[8]	11.77[21]	10[8]	10[21]	a_1[8]	$1a_2$[21]
12.30	14	12.2	12.16	14	13.5	e	5e''
13.0	18	13.0	12.95	15	13.5	e $\overline{\text{Cl}}$	4e'
13.5	19	13.5	13.46	9	12	a_2	$5a_1$
15.0	17	15.0	15.04	8	12	πe C-Cl	3e'
18.3	9	18.2	18.44	2	11		$4a_1$

Figure Captions

Fig. 1: Absorption spectrum and total photoionization yield of CF_3Cl

Fig. 2: Absorption spectrum and total photoionization yield of CF_2Cl_2

Fig. 3: Absorption spectrum and total photoionization yield of $CFCl_3$

Fig. 4: Absorption and mass selected photoion spectra of CF_3Cl

Fig. 5: Absorption and mass selected photoion spectra of CF_2Cl_2

Fig. 6: Absorption and mass selected photoion spectra of $CFCl_3$

Fig. 7 Total photoionization yield and photoion spectra of chloride and fluoride from CF_2Cl_2

Fig. 8: Resonance photoelectron spectrum of CF_3Cl

Fig. 9: Resonance photoelectron spectrum of CF_2Cl_2

Fig. 10: Resonance photoelectron spectrum of $CFCl_3$

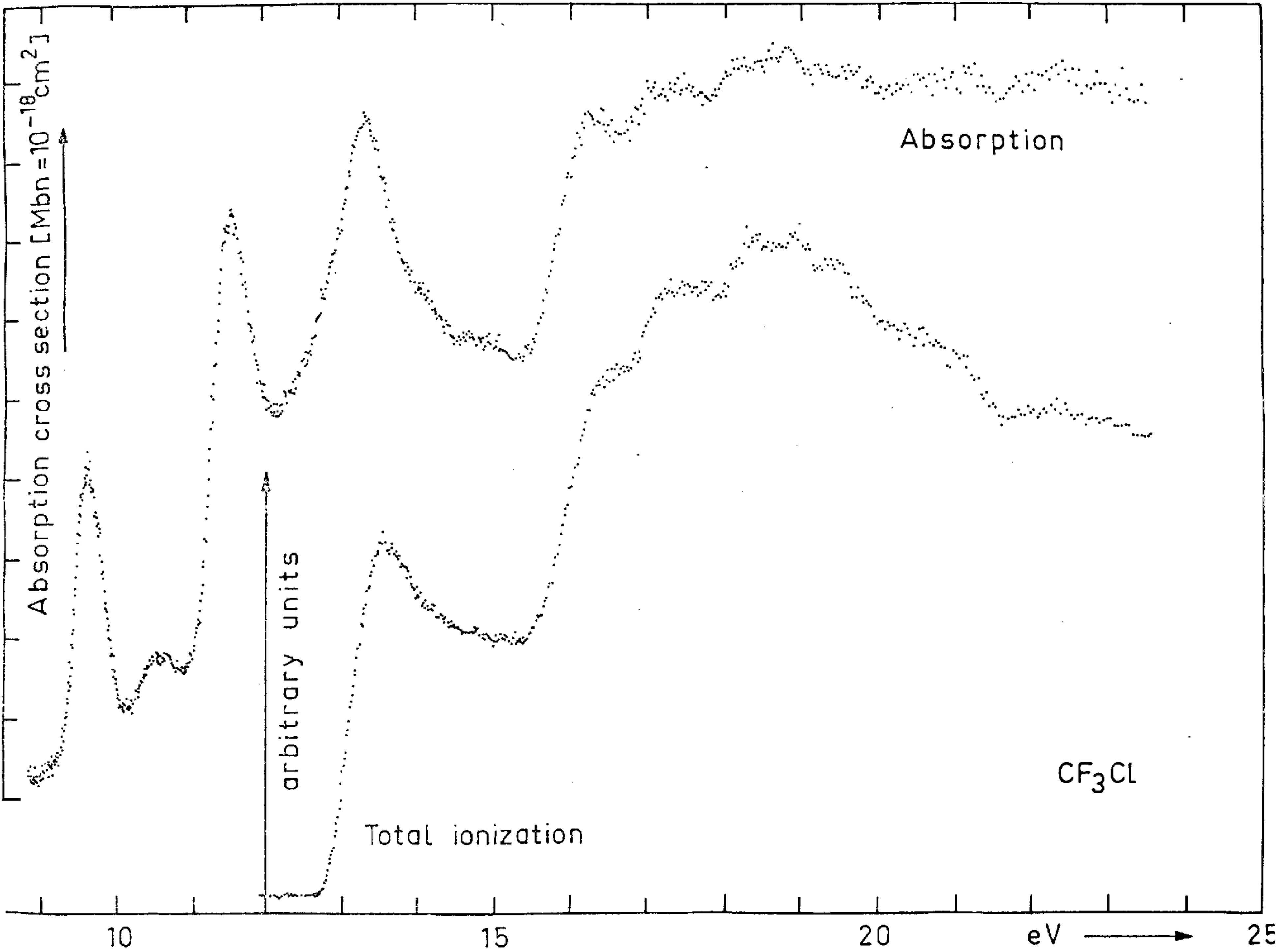
90
80
70
60
50
40
30
20
10
0
Absorption cross section [Mbn = 10^{-18}cm^2]
arbitrary units
Absorption
Total ionization
CF_3Cl
10
15
20
eV
25

Fig. 1

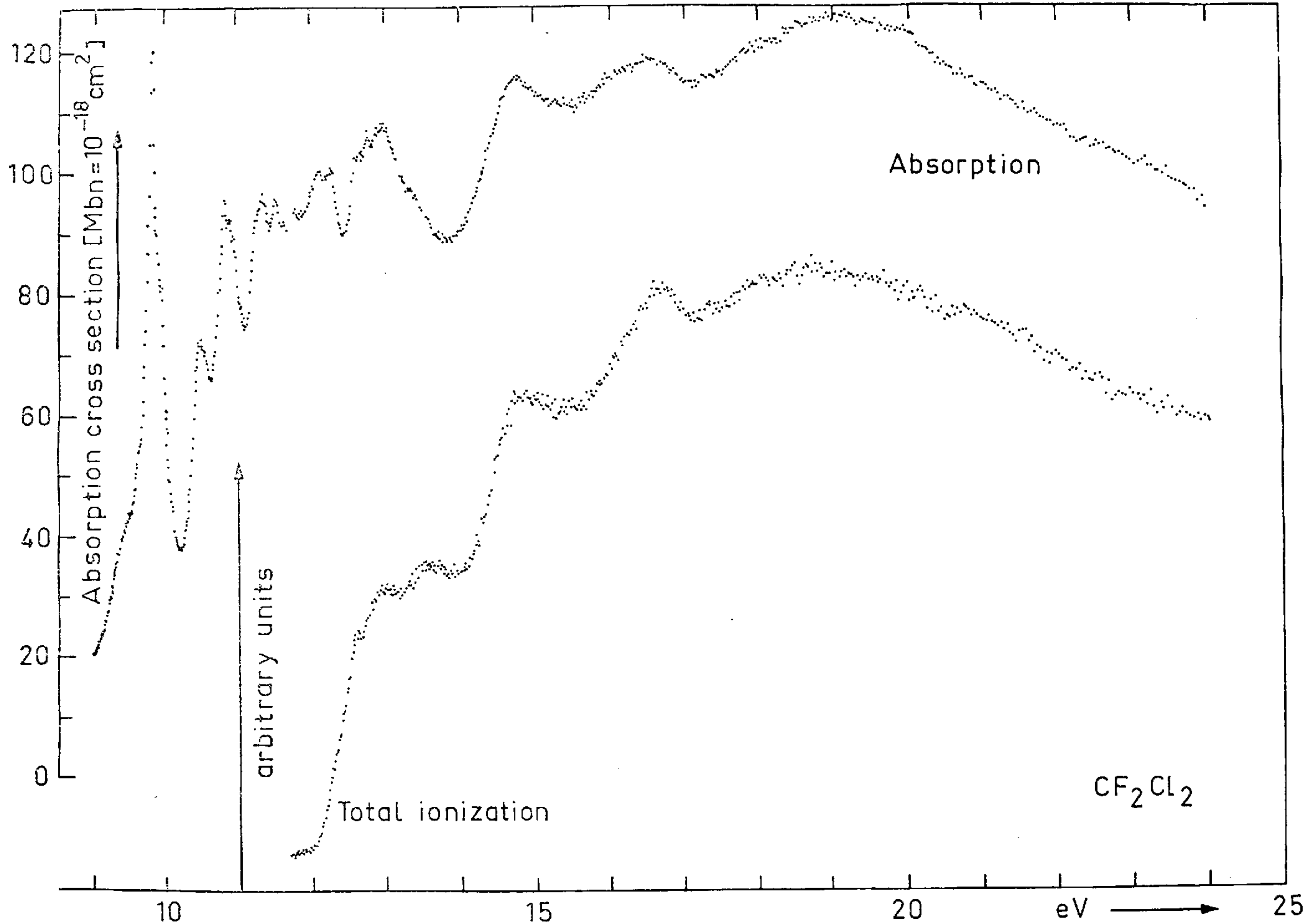
120
100
80
60
40
20
0
Absorption cross section [Mbn=10^{-18}cm^2]
arbitrary units
Absorption
Total ionization
CF_2Cl_2
10
15
20
25
eV

Fig. 2

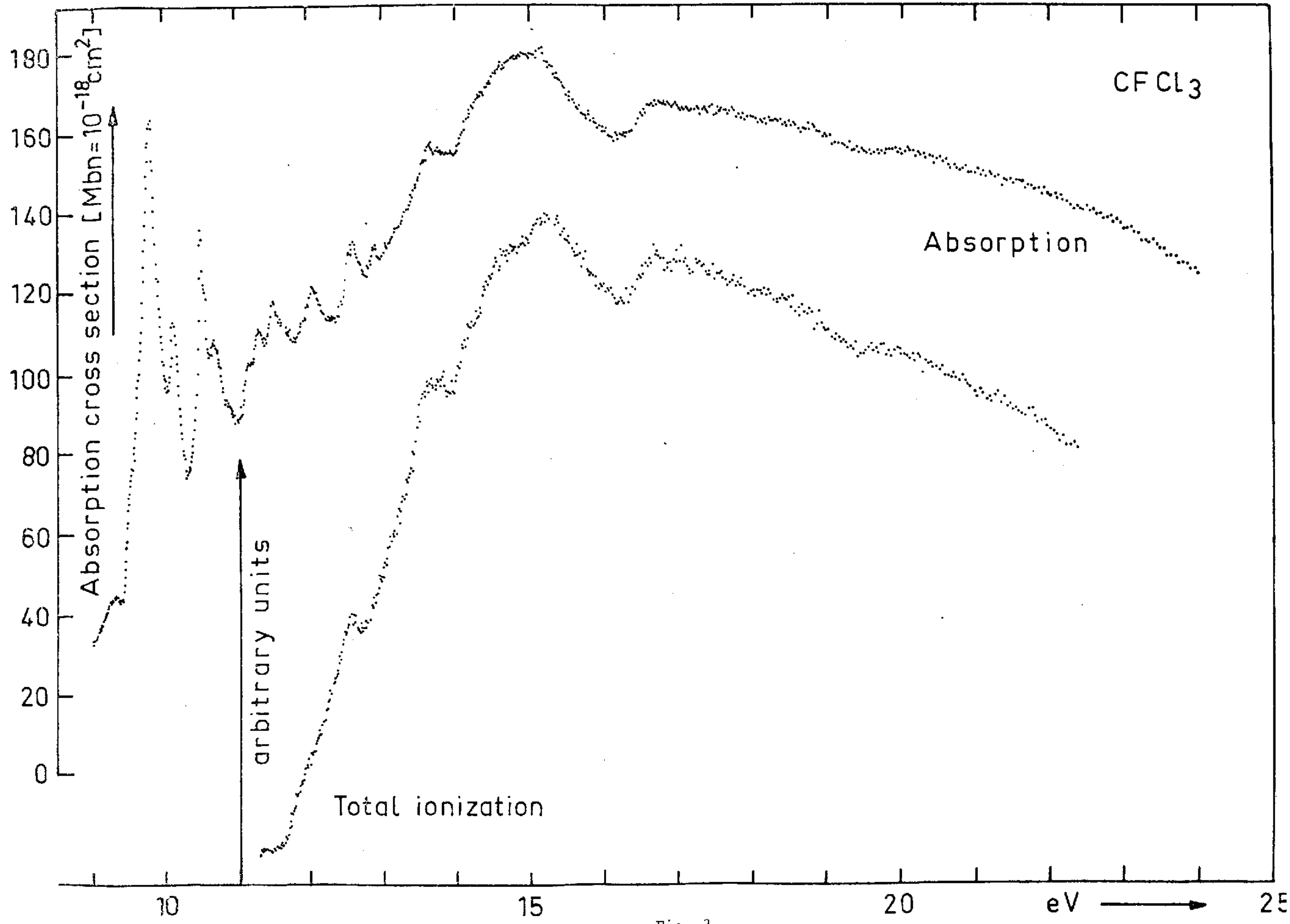
CFCl3
Absorption
Total ionization
Absorption cross section [Mbn=10^-18 cm^2]
arbitrary units
180
160
140
120
100
80
60
40
20
0
10
15
20
25
eV

Fig. 3

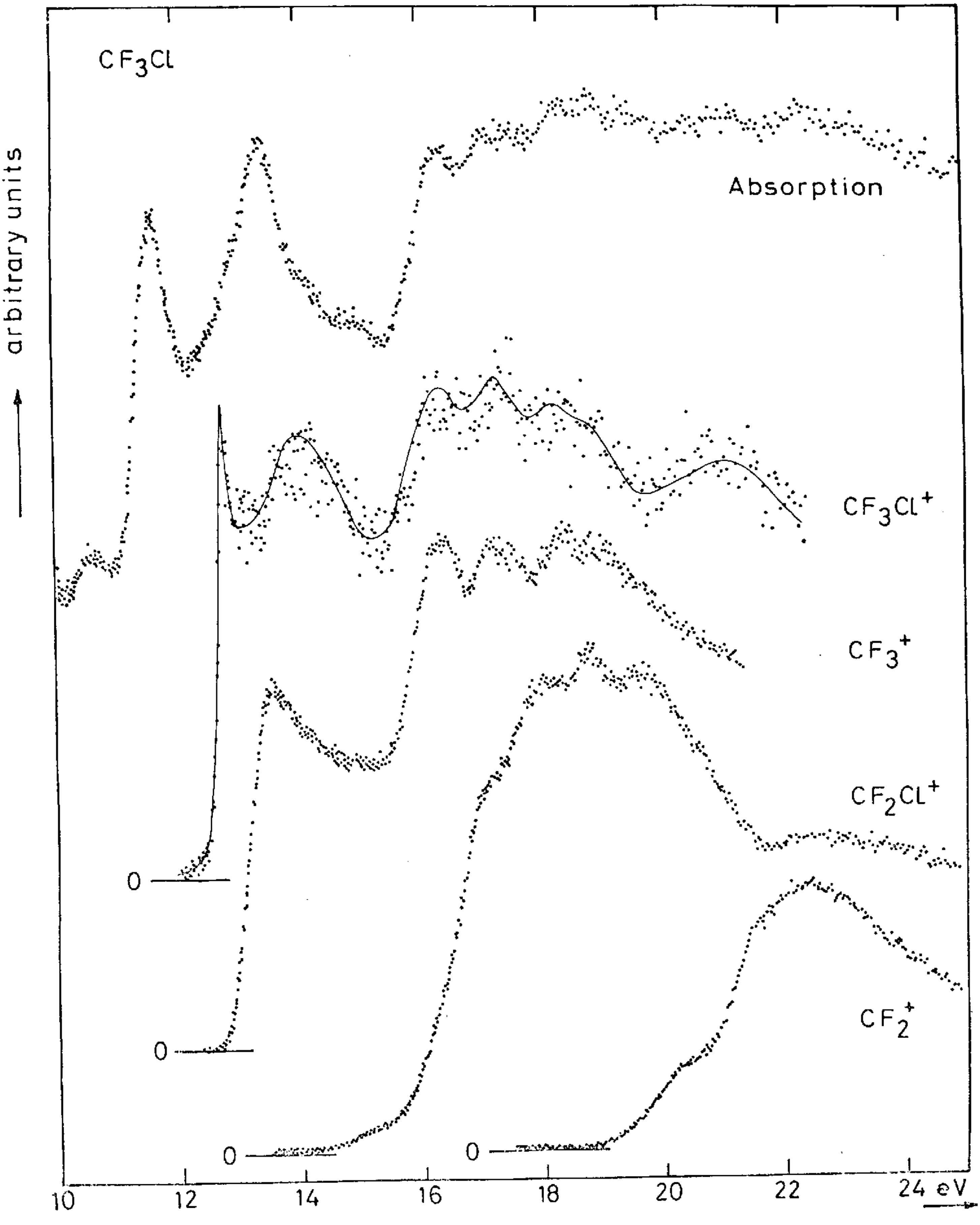
CF$_3$Cl
arbitrary units
Absorption
CF$_3$Cl$^+$
CF$_3^+$
CF$_2$Cl$^+$
CF$_2^+$
0
0
0
0
10
12
14
16
18
20
22
24 eV

Fig. 4

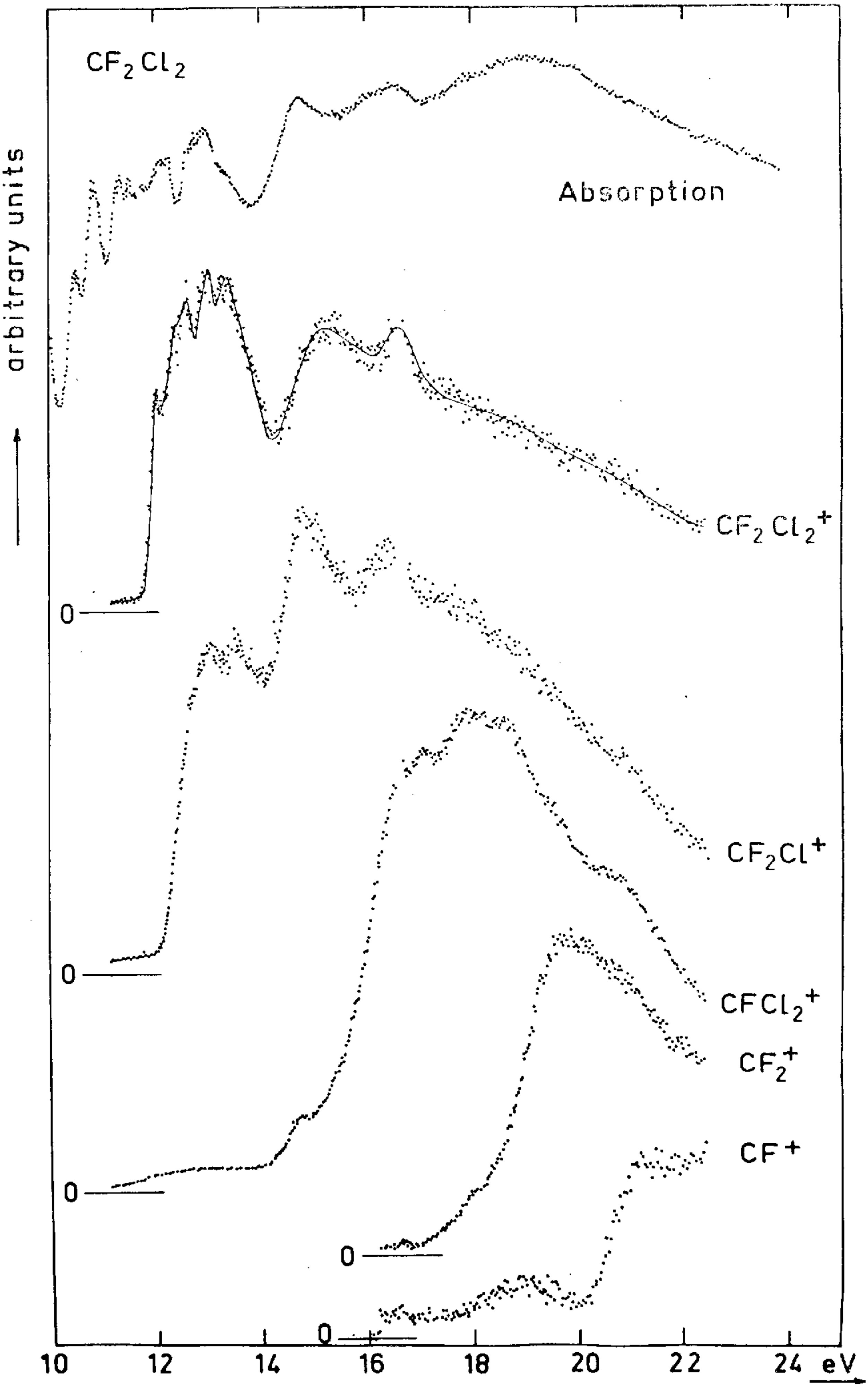
CF₂Cl₂
Absorption
arbitrary units
CF₂Cl₂⁺
CF₂Cl⁺
CFCl₂⁺
CF₂⁺
CF⁺
0
0
0
0
0
10
12
14
16
18
20
22
24
eV

Fig. 5

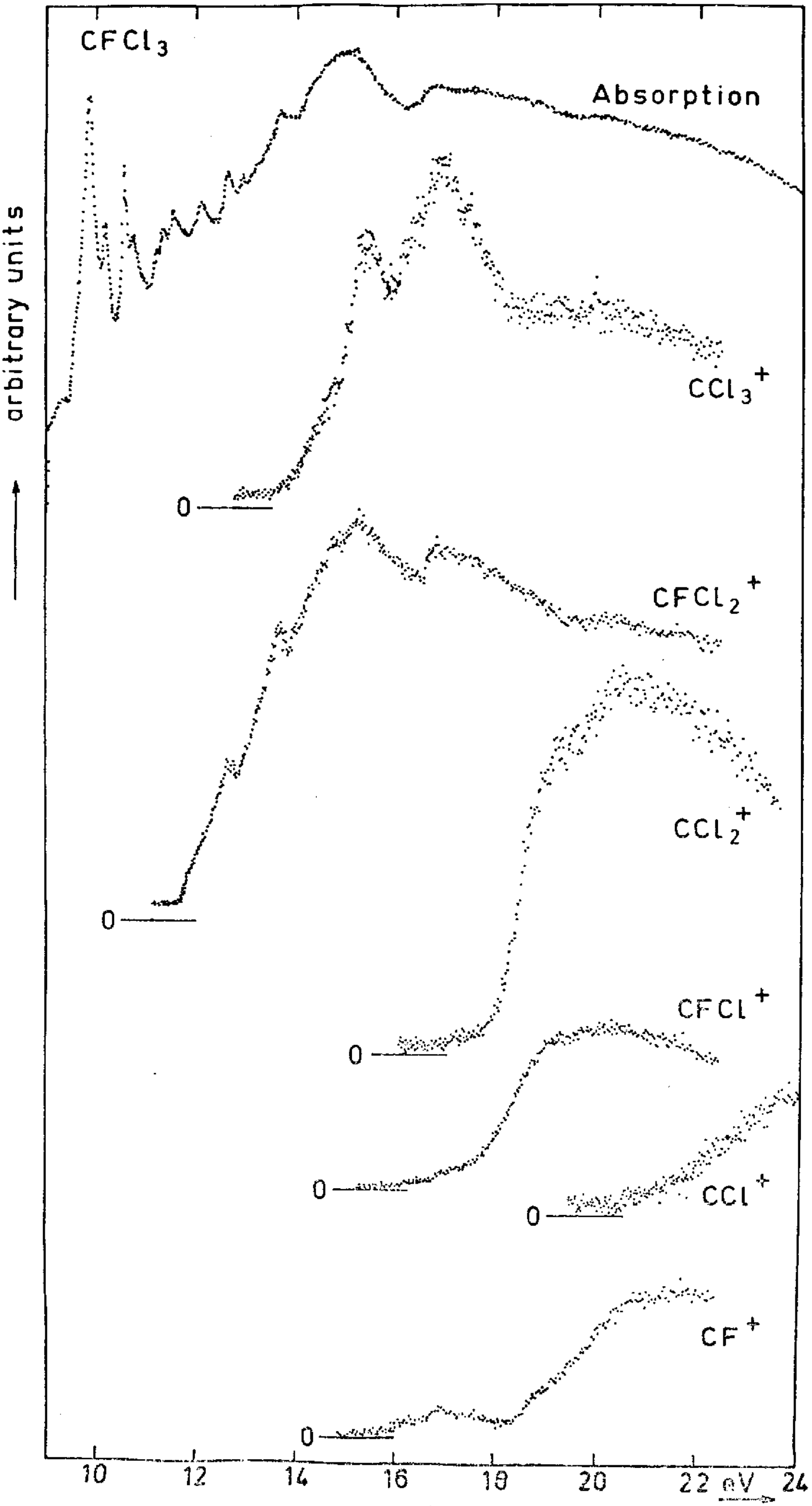
CFCl$_3$
Absorption
CCl_3^+
$CFCl_2^+$
CCl_2^+
$CFCl^+$
CCl^+
CF^+
arbitrary units
0
0
0
0
0
0
10
12
14
16
18
20
22
eV
24

Fig. 6

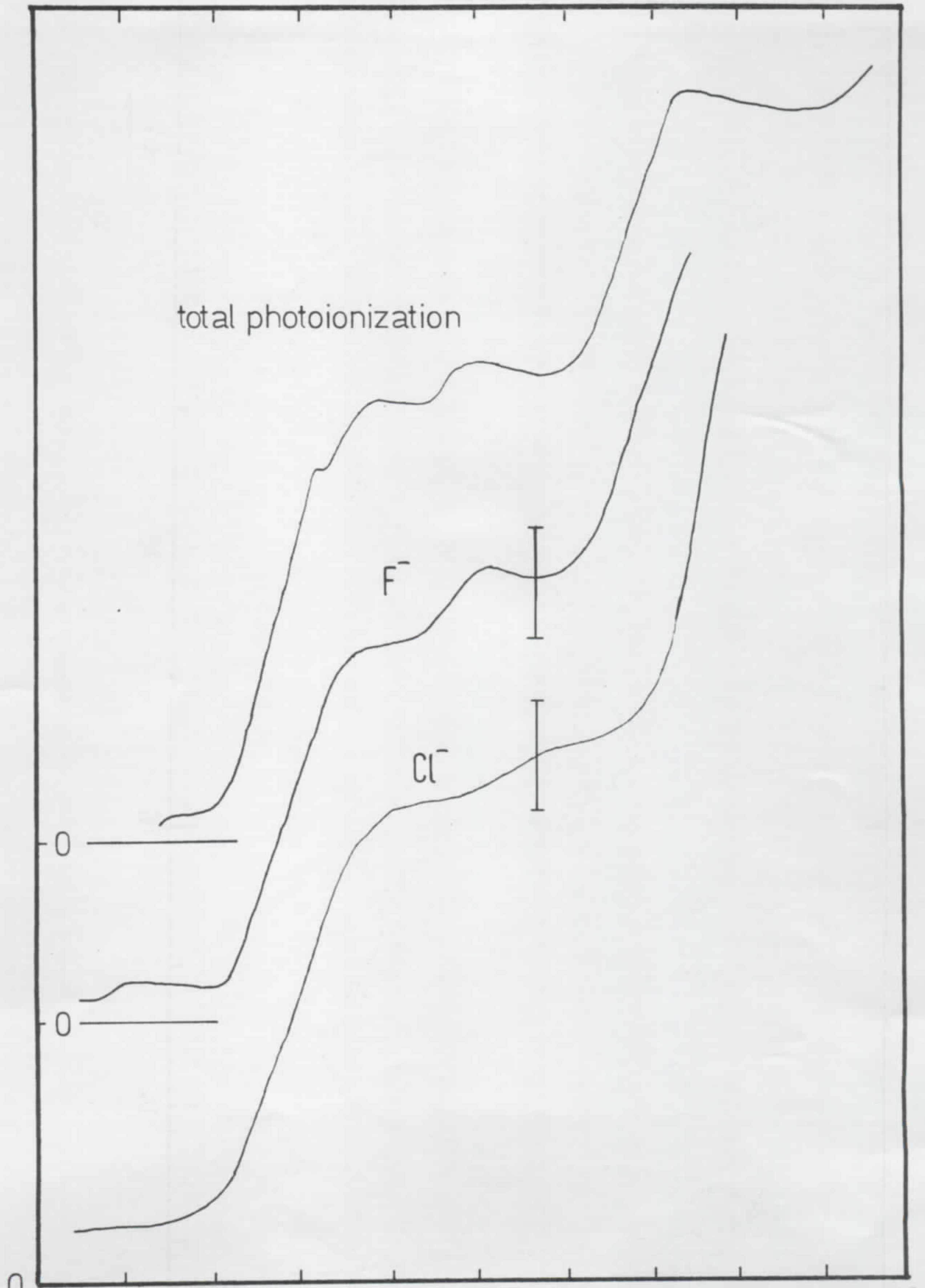

Fig. 7

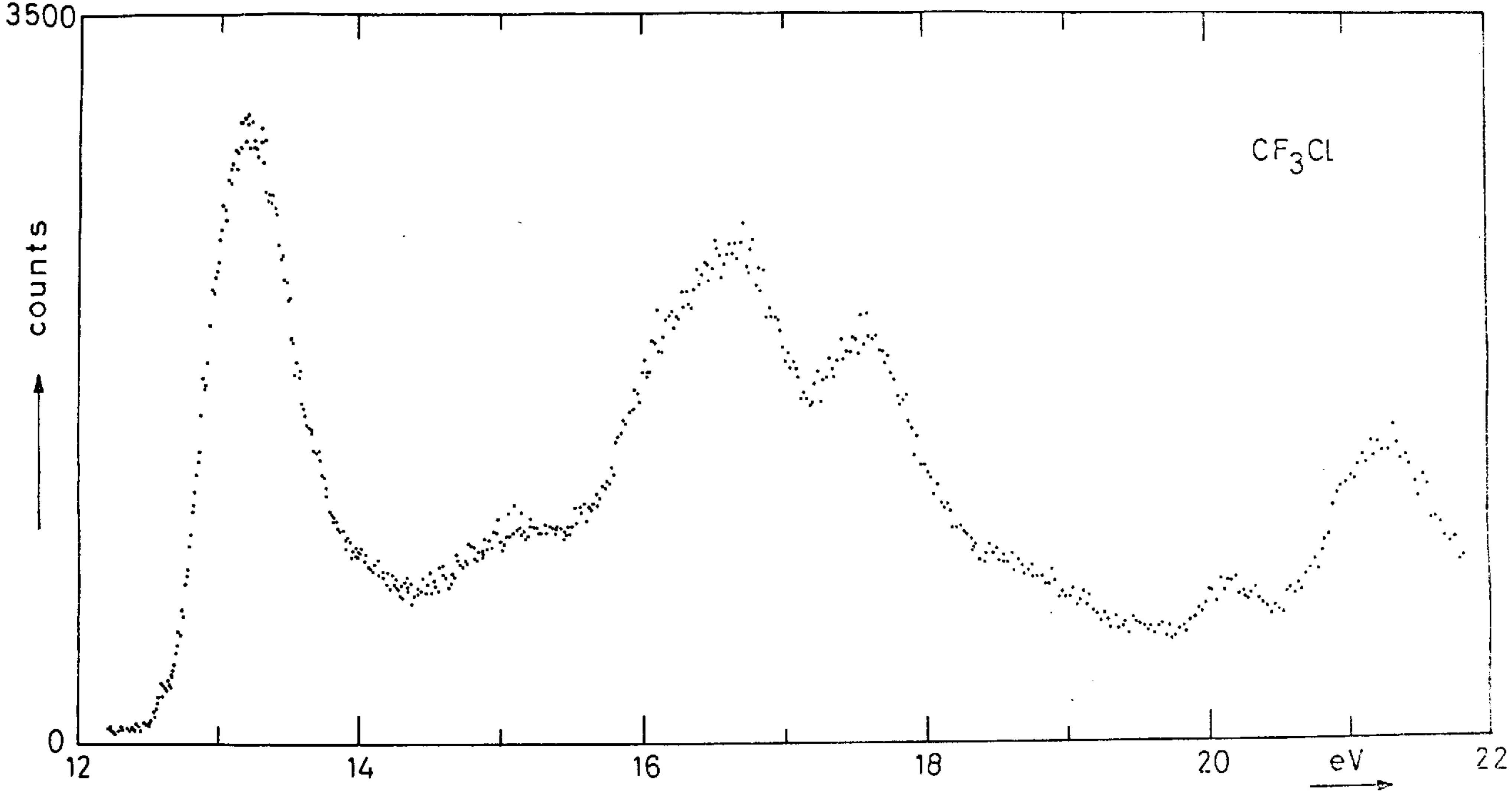

Fig.8

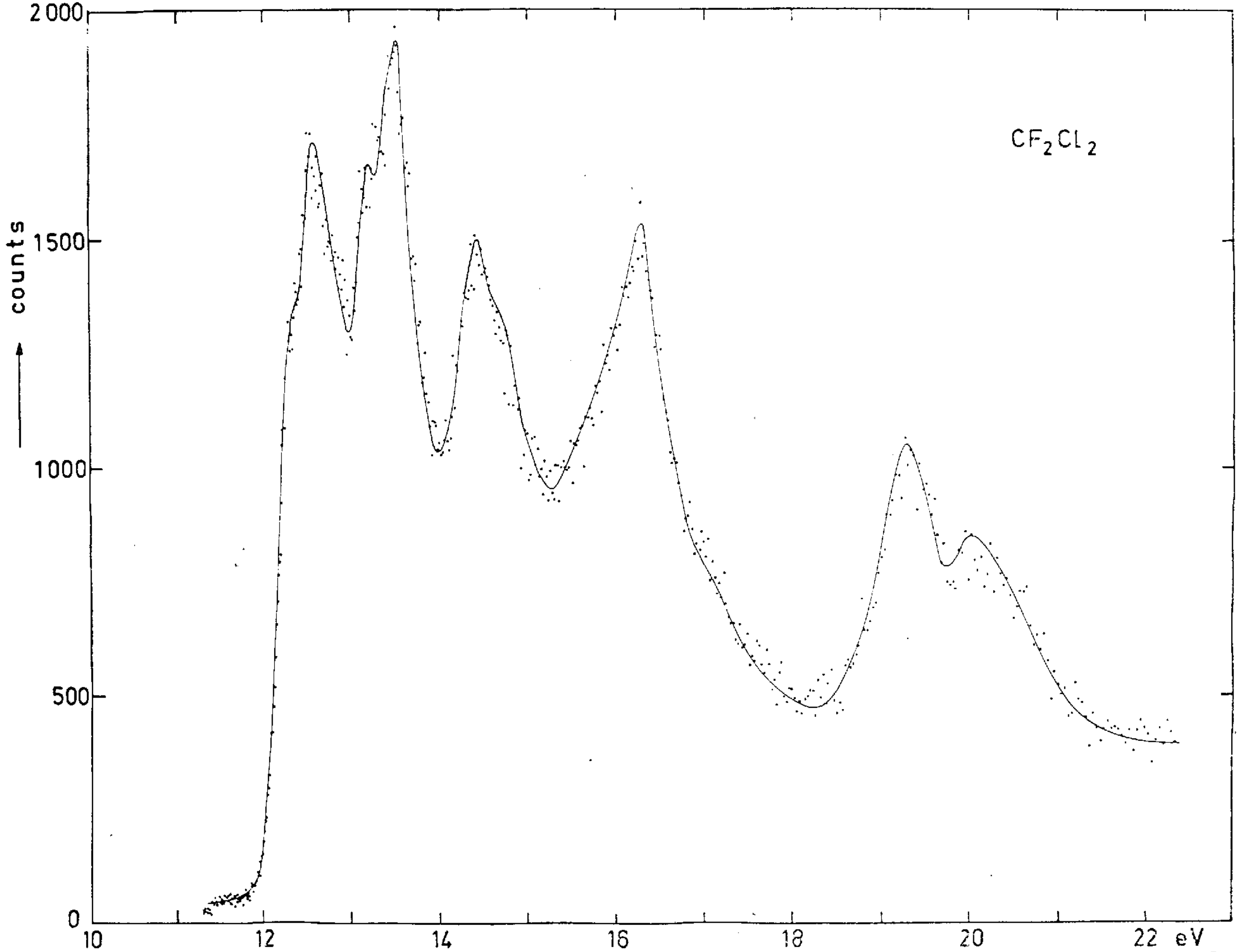

Fig. 9

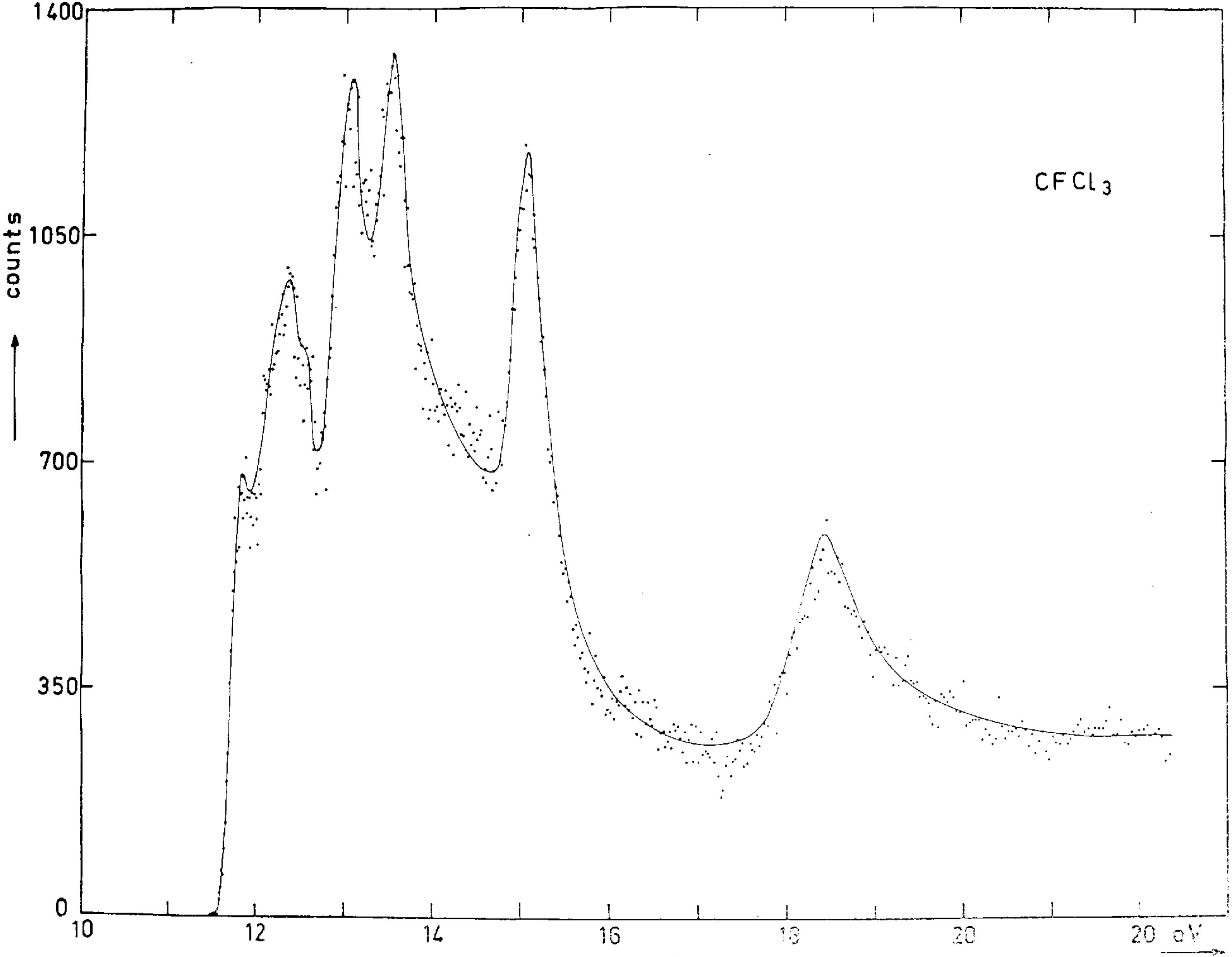

Fig. 10