RIVISTA DEL NUOVO CIMENTO Vol. 24, N. 4 2001

One century of experiments on electron-atom and molecule scattering: A critical review of integral cross-sections

III. – Hydrocarbons and halides

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(ricevuto il 22 Gennaio 2001)

1. – Introduction

Electron scattering on less common molecular species both of industrial and atmospheric interest, like halocarbons or halosilanes, have been studied for the first time in recent years. The present paper (part III) is a continuation of the review of cross-sections (CS) for atomic and diatomic molecules, part I (Zecca, Karwasz and Brusa 1996) and polyatomic molecules including HCl, part II (Karwasz, Brusa and Zecca 2001). The present paper deals with hydrocarbons (apart from CH_4 discussed in part II) and halides, including substituted hydrocarbons, substituted silanes (SiF_4 and so on) and hexafluorides (SF_6, WF_6, UF_6).

As in part II, some targets, like more complex organic molecules, for which little experimental work exists, are grouped in sections where it seemed to be most appropriate. In this manner, the reader will find a few comments and references on CH_3OH in subsect. **3**˙3, "Methyl halides"; on BCl_3 in subsect. **3**˙5 entitled "Trihalides (NF_3 and others)"; on C_6H_5Cl and C_6F_5Cl in subsect. **3**˙7 "Hexafluorobenzene (C_6F_6)" and so on.

The review focuses on integral cross-sections, in particular on total cross-sections (TCS). Differential elastic cross-sections or integral cross-sections for electron attachment are present for some targets, where we have found these data significant for the physics of scattering. In figures presenting integral CS, the same energy span of 7 decades is maintained, in order to facilitate the comparisons. In targets, like CCl_4, for which the CS (usually electron attachment CS) measurements extend below 1 meV, the energy scale was additionally expanded. In other gases, like SiF_4, where TCS were measured in a limited energy range only, the E scale is reduced. In these cases the format of the drawings is changed, in order to stress the difference with the adopted standard.

Numerous "specialized" reviews have been dedicated to the detailed study of previous experimental and theoretical papers regarding integral and differential cross-sections on a limited number of targets (very often a single gas). Tawara *et al.* (1992) reviewed cross-sections for hydrocarbons. Christophorou *et al.* (1997a, b) reviewed extensively total, integral and differential cross-sections for CHF_3 and CF_2Cl_2, Christophorou and Olthoff (1998a, b) have made the same work for C_2F_6 and C_3F_8, respectively. Large progress has also been achieved in theoretical treatment of electron-complex targets scattering, see for example Gulley and Buckman (1999) and Gianturco and Lucchese (1998) for benzene.

A sort of "reader's guide" has been published in the Introduction sections of part I and part II of the review. The scope of this guide is to help the user in reading the paper. The reader of the present work is referred to the Introduction of part II. There, he can find information regarding:

- numerical tables
- organization and layout of the figures
- organization of the reference lists
- special terminology
- experimental errors
- the methods used by us for the analysis of differential and vibrational cross-section data
- units.

The reference list of this subsection also includes a number of general references to review papers (Shimamura (1989), van de Burgt *et al.* (1989), Kauppila and Stein (1990), Hayashi (1992), Inokuti (1994), Smith and Španel (1994), Chutjian *et al.* (1996), Christophorou and Olthoff (1998a, b, 1999), Kimura *et al.* (2000).

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2. – Hydrocarbons

Electron scattering on hydrocarbons was studied in relatively few laboratories. Saturated hydrocarbons (alkanes) show similar features in TCS and for this reason will be presented in a single subsection (**2**˙3). Cross-sections for unsaturated hydrocarbons, like acetylene (subsect. **2**˙1) and benzene (subsect. **2**˙2), show a wider variety of resonant structures, mainly in the total and vibrational excitation channels. An example of alkenes (ethene) is included in the "linear hydrocarbons" subsection (**2**˙3). In subsect. **2**˙3 the reader will also find a comprehensive list of measurements on hydrocarbons in general.

2˙1. *Acetylene (*C_2H_2*).* – The acetylene molecule is isoelectronic with N_2 and CO and it triggers a continuous theoretical interest. In particular, numerous calculations (Tossell 1985, Krumbach *et al.* 1989, Szmytkowski 1989, Khurana and Jain 1992, Jain 1993, Gianturco and Stoecklin 1994, Venkatnathan and Mishra 1998) predicted a shape $^2\Pi_g$ resonance in analogy to the low-energy shape resonances in N_2 and CO, see figs. 21 and 25 in part I. Integral cross-sections for C_2H_2 are shown in fig. 1.

Total cross-sections. The first measurements of TCS by Brüche date to 1929 and cover the 1–40 eV energy range. Normalized TCS have been obtained by Sueoka and Mori (1989) between 0.7 and 400 eV; absolute TCS by Xing *et al.* (1994) between 400 eV and 2600 eV. The TCS shows a peak of $35.8 \cdot 10^{-20}$ m^2 at 2.5 eV and another bump with a maximum of $24.4 \cdot 10^{-20}$ m^2 at 7.5 eV (Sueoka and Mori 1989). Dressler and Allan (1987) measured the relative TCS in the 0.05–5 eV energy range. In fig. 1 we report their data normalized to the experiment of Sueoka and Mori (1989) at 2.5 eV: the two TCS curves coincide in the overlapping energy range.

In the 3–40 eV energy range the data of Sueoka and Mori (1989) are, on the average, 10% lower than those of Brüche (1929) and at 400 eV they are lower than the data of Xing *et al.* (1994) by the same amount. Below 2 eV the data of Sueoka and Mori are higher than the measurements of Brüche (1929); the use of a longitudinal magnetic field in Sueoka's and Mori apparatus can cause such an effect. The TCS of Sueoka and Mori (1989) are lower than the elastic CS calculation of Jain (1993) at the position of the maximum (2.5 eV) and than the theoretical elastic CS of Gianturco and Stoecklin (1994) in the whole 2–50 eV energy range.

At high energies the measurements of Xing *et al.* (1994) agree well with the optical model of Jain and Baluja (1992) and with the additivity rule of Jiang *et al.* (1995). Between 400 eV and 2600 eV the C_2H_2 TCS is by 20–25% higher than both the N_2 and CO total cross-sections (Xing *et al.* 1995).

Elastic cross-sections. Relative DCS at 10°–150° angular, 10–225 eV energy, ranges were reported by Hughes and McMillen (1933); DCS in the 0°–130° angular and 100–1000 eV energy ranges, normalized to the independent-atoms model, were given by Fink *et al.* (1975); differential and integral CS at 5–100 eV, normalized by the relative flow method, were obtained by Khakoo *et al.* (1993). Absolute DCS at a single energy 2.0 eV, 10°–105° angles were determined by Kochem *et al.* (1985). The DCS of Khakoo *et al.* agree well in shape with the relative measurements of Hughes and McMillen, except at small scattering angles. The values of DCS at 100 eV given by Fink *et al.* (1975) and Khakoo *et al.* differ roughly by a factor of two at 30°–130° scattering angles. At 100 eV the DCS obtained by the three groups (Fink *et al.*, Khakoo *et al.*, Hughes and McMillen) and normalized at 90° to the measurements of Khakoo *et al.* (1993), diverge for scattering angles below 15°. This discrepancy is probably due to the worsening of the angular resolution in the three apparatuses, respectively.

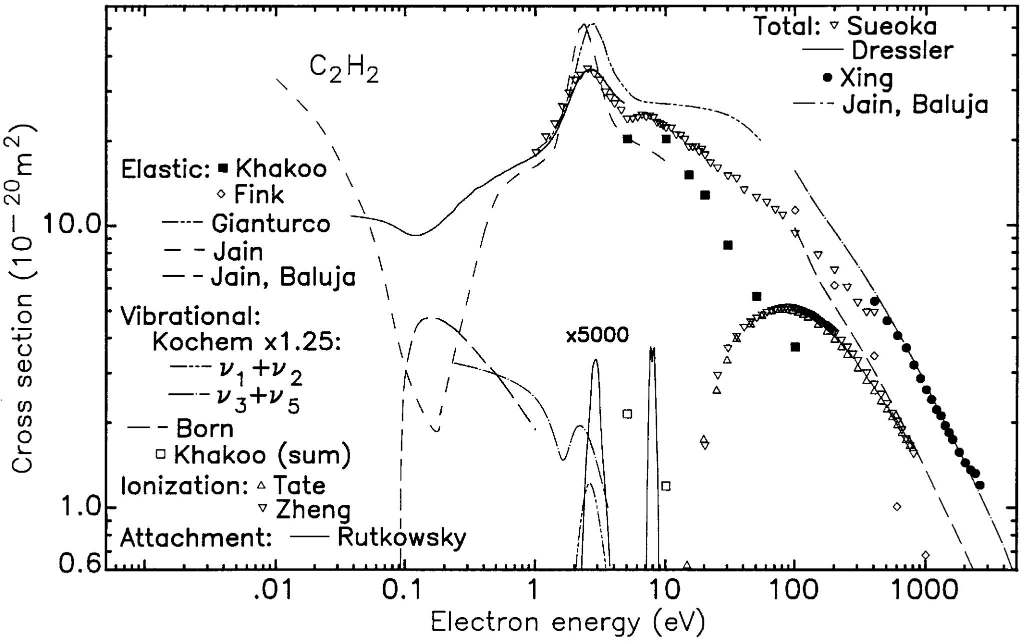

Fig. 1. – Integral cross-sections for electron scattering on C_2H_2. *Total*: normalized data of Sueoka and Mori (1989); relative data of Dressler and Allan (1987) normalized to Sueoka and Mori at 2.5 eV; absolute of Xing *et al.* (1995); optical model of Jain and Baluja (1992). *Elastic*: absolute of Khakoo *et al.* (1993); Fink *et al.* (1975) normalized to the independent-atoms model and presently integrated (±15% error); Jain (1993) and Jain and Baluja (1992), theoretical; Gianturco and Stoecklin (1994) theoretical. *Vibrational*: Kochem *et al.* (1985), multiplied by a factor of 1.25, see text; Khakoo *et al.* (1993), summed; Born approximation for ν_3 and ν_5 (eq. (15) in part I). *Ionization*: Tate and Smith (1932); Zheng and Srivastava (1996); data of Djurić *et al.* (1996), Gaudin and Hagemann (1967), Tian and Vidal (1998) and a single, 75 eV point of Lampe *et al.* (1957) are not shown as practically overlapping with the other data. *Dissociative attachment*: Rutkowsky *et al.* (1980), energy scale corrected by +0.3 eV according to the calibration of Dressler and Allan (1987).

The integral elastic CS of Khakoo *et al.* (1993) shows the same value of $20.3 \cdot 10^{-20}$ m^2 at 5 and 10 eV, then it descends monotonically with energy. This fall is faster than the one predicted by the low-energy calculation of Gianturco and Stoecklin (1994). The integral elastic CS obtained from the DCS of Fink *et al.* (1975) in the present work (±15% integration and extrapolation uncertainty) are compatible at 100 eV and 200 eV with the calculations of Lee *et al.* (1990), not shown in the figure, and with those of Jain and Baluja (1982) within 10% . Between 400 eV and 600 eV the integral values obtained from the DCS of Fink *et al.* fall rapidly with energy, faster than the $1/E$ dependence. We suppose some error in their normalization to the independent-atoms model (Fink *et al.* 1975).

Low-energy calculations (Jain 1993) predict a Ramsauer minimum at about 0.15 eV. Measurements of the 90° elastic DCS at low energies (Kochem *et al.* 1985) show a fall up to the energy of 0.1 eV. Probably the elastic CS rises again at energies lower than 0.1 eV, as is indicated by the transmission experiment of Dressler and Allan (1987), see fig. 1. At 2 eV the DCS in C_2H_2 (Kochem *et al.*) resembles that in N_2 at 2.2 eV, see fig. 23 in part I; this similarity could indicate scattering via a resonant state.

Swarm measurements. Drift velocities at 300–370 K were measured by Bowman and Gordon (1967). According to this work the momentum transfer CS falls from $100 \cdot 10^{-20}$ m^2 at 0.02 eV to about $20 \cdot 10^{-20}$ m^2 at 0.06 eV. This result disagrees with the analysis of Duncan and Walker (1972) who derived momentum transfer CS rising monotonically from $9.5 \cdot 10^{-20}$ m^2 at 0.01 eV to about $2.5 \cdot 10^{-20}$ m^2 at 1.0 eV.

Vibrational. Five fundamental vibrational modes are possible for acetylene. Due to the close spacing between vibrational levels, the experiments (Kochem *et al.* 1985, Khakoo *et al.* 1993) could not resolve the ν_1 (symmetric C-H stretching, 418 meV energy loss) from the ν_3 (asymmetric stretching, 409 meV) modes and the ν_4 (symmetric bending, 73 meV) from the ν_5 (asymmetric bending, 91 meV) modes. At 0.6 eV collision energy and 10° scattering angle, the excitation of the infrared-active ν_3, $(\nu_4 + \nu_5)$ and ν_5 modes only was observed (Kochem *et al.* 1985). For the ν_5 mode, the excitation functions in the near-threshold region can be well described by the Born approximation. At 2.6 eV the Born approximation reproduces well the low-angle ν_5 DCS but underestimates its values above 30°. For the $\nu_3 + \nu_1$ modes the Born approximation underestimates the experimental DCS even at 1.6 eV. The maximum of the low-energy vibrational CS as presently calculated (see eq. (15) in part I) from the Born approximation for ν_3 and ν_5 modes is rather high, $4.7 \cdot 10^{-20}$ m^2 ; its position coincides with the minimum in the elastic CS as calculated by Jain (1993).

At 2.6 eV the DCS for the $\nu_3 + \nu_1$ modes and for the ν_2 (symmetric C≡C stretching, 245 meV) mode show a *d*-wave–like shape (Kochem *et al.* 1985), similar to the vibrational excitation DCS in N_2 at 2.1 eV, see fig. 24 in part I. At 2.6 eV the branching ratio for the five modes (from ν_1 to ν_5) is 1:6:2:1:8. A 25% underestimation of the experimental absolute values (Kochem *et al.* 1985), as indicated by the comparison with the Born approximation, could be caused by the normalization procedure. To take into account this possible underestimation, in fig. 1 we present the integral CS of Kochem *et al.* multiplied by a factor of 1.25.

An enhancement of the ν_2 symmetric stretch mode with some quanta of the ν_4 bending mode was observed at 1.8 eV (Andrić and Hall 1988). It can be explained in terms of scattering via the $^2\Pi_g$ shape resonance. More overtones were observed at 1.8 eV than in the maximum of the resonance at 2.5 eV. Measurements of Andrić and Hall (1988) and of Khakoo *et al.* (1993) also evidenced a rise of the $\nu_1 + \nu_3$ vibrational CS at 6 eV, pointing out to the existence of another resonant state at this energy.

Electronic excitation at 25 eV and 35 eV, 10°–80° scattering angles range was studied by Trajmar *et al.* (1968, 1970). DCS for the $\tilde{C}\ ^1\Pi_u$ (8.16 eV energy loss for $\nu_2' = 0$) and the $\tilde{D}$ (9.26 eV energy loss for $\nu_2' = 0$) states are both of similar intensity at 25 eV and 35 eV, with the $\tilde{C}$ state being sightly more forward-centered. DCS for the broad $\tilde{B}$, 7.2 eV energy loss band are by one order of magnitude smaller. DCS for $\tilde{a}$ and $\tilde{b}$ (5.2 eV and 6.1 eV energy loss, respectively) triplet states rise between 10° and 80° scattering angles. The relative values for all these states rise by a factor of two, roughly from 25 eV to 35 eV, apart from the $\tilde{a}$-state DCS which rises by a factor of four (Trajmar *et al.* 1970).

Lassettre *et al.* (1968) reported energy loss spectra at 40 eV and 50 eV collision energy, 0° and 10° scattering angles. Energy loss spectra in the region of valence electronic excitations were examined also by Dance and Walker (1973), van Veen and Plantenga (1976), Wilden *et al.* (1977, 1980), Hammond *et al.* (1987), Dressler and Allan (1987) and de Souza and de Souza (1988); in the region of the core-excitation by Tronc *et al.* (1979). Assignments of observed states were done by Dressler and Allan (1987). Forward-angle electron scattering was studied by Cooper *et al.* (1988, 1995) for the 6–180 eV energy loss. Photoabsorption CS below the ionization threshold reaches a maximum value of $0.33 \cdot 10^{-22}$ m^2 at 9.5 eV (Cooper *et al.* 1988).

Optical emission from dissociated fragments (40–200 nm wavelength range) was measured by Pang *et al.* (1987) at 20–400 eV collision energy. The atomic hydrogen Lyman-α emission intensity at 100 eV in C_2H_2 is 30% lower than in CH_4. Emission spectra in the 415–440 nm range due to the $A\ ^2\Delta \rightarrow X^2\Pi$ de-excitation of the CH radical at 17–100 eV impact energies were studied by Tokeshi *et al.* (1996).

Ionization. An excellent agreement exists between the early (Tate and Smith 1932, Gaudin and Hagemann 1967) and recent (Zheng and Srivastava 1996, Tian and Vidal 1998, Kurepa *et al.* 1991, Djurić *et al.* 1996) ionization CS measurements. The semiempirical model (Hwang *et al.* 1996) reproduces well the experimental data. In fig. 1 we report the data of Tate and Smith (1932) and of Zheng and Srivastava (1996) only.

The ionization CS in C_2H_2 at 100 eV is by as much as 70% higher than the ionization CS for the isolectronic molecules CO and N_2 (Tate and Smith 1932). This difference still amounts to 40% at 750 eV. Dissociative ionization in C_2H_2 is rather small at 100 eV: 67% of the ionization yield is constituted by parent $C_2H_2^+$ ions. The C_2H^+, H^+, CH^+, C_2^+ and C^+ yield is 14%, 8.2%, 5.5%, 4.0%, 1.3%, respectively (Zheng and Srivastava 1996, Tate *et al.* 1935).

Dissociative attachment has been studied in several works (see Dressler and Allan 1987 and references therein). A large maximum for the C_2H^- yield occurs at 2.9 eV (Dressler and Allan 1987). At 8 eV another broad C_2H^- band and several ovarlapping C_2^- bands with vibrational structures are visible (Dressler and Allan 1987). Rutkowsky *et al.* (1980) reported $6\text{–}7 \cdot 10^{-24}$ m^2 peak values both at 2.5 and 7.5–8 eV energies. The position of the first peak in the paper of Rutkowsky *et al.* seems to be shifted by −0.3 eV, compared to the value of Dressler and Allan (1987). As these latter authors performed a detailed calibration of the energy scale using the O^- peak formation from CO at 9.62 eV, in fig. 1 we have shifted the spectrum of Rutkowsky *et al.* (1980) by +0.3 eV.

Resonances. A shape resonance of the $^2\Pi_g$ (π^*) type at 2.6 eV has been observed in the trapped electron measurements of Dance and Walker (1973), van Veen and Plantenga (1976), in the dissociative attachment CS (Dressler and Allan 1987) and in the vibrational excitation (Kochem *et al.* 1985, Andrić and Hall 1988). In TCS this resonance manifests itself as a structureless peak, similar to the one observed in CO, see fig. 25 in part I.

At 6 eV a core excited-resonance, analogous to that at 8 eV in N_2, of the Σ_g symmetry and due to the $s\sigma$ partial-wave scattering has been seen in the vibrational CS (Andrić and Hall 1988). Dressler and Allan (1987) observed four additional Feshbach resonances in the dissociative attachment CS between 7.5 eV and 9.5 eV. These states were also observed in the transmission spectra (van Veen and Plantenga 1976) and in threshold electrons spectra (Hammond *et al.* 1987). The configurations of these states have been discussed by Andrić and Hall (1988).

Sum check indicates a rather good consistency between the elastic cross-sections of Khakoo *et al.* (1993) up to 100 eV, the ionization data of Tate and Smith (1932) and the total values of Sueoka and Mori (1989), see Table I. The difference (20%) between the total and summed values in the 15 eV–50 eV energy range is probably due to the electronic excitation part. At 400 eV the sum of Fink's *et al.* elastic and Tate and Smith's ionization CS is 10% higher than the TCS of Xing *et al.* (1995); at 1000 eV this sum is 40% lower. This confirms the possibility of errors in the normalization procedure of elastic CS of Fink *et al.* (1975).

Table I. – *Integral cross-sections for electron scattering on acetylene (in* 10^{-20} m^2 *units).*

Energy	Elastic	Vibrational	Ionization	Summed	Total
5.0	20.3 K	2.1 K		22.4	23.7 S
10.0	20.3 K	1.2 K		21.5	22.1 S
15.0	15.1 K		0.75 T	15.9	18.9 S
20	12.8 K		1.8 T	14.6	17.7 S
30	8.5 K		3.4 T	11.9	14.9 S
50	5.6 K		4.7 T	10.3	12.5 S
100	3.7 K		5.0 T	8.7	9.3 S
	11.3 F				
200	6.1 F		4.0 T	10.1	6.9 S
400	3.4 F		2.6 T	6.0	4.9 S
					5.38 X
600	1.0 F		2.0 T	3.0	4.06 X
1000	0.68 F		1.18 H	1.86	2.61 X

F - Fink *et al.* (1975) presently integrated (±15% error)
H - Hwang *et al.* (1996) semiempirical values
K - Khakoo *et al.* (1993)
S - Sueoka and Mori (1989)
T - Tate and Smith (1932)
X - Xing *et al.* (1995)

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2˙2. *Benzene (*C_6H_6*).* – Benzene molecule has been the subject of intensive studies by electron transmission spectroscopy. However, only few CS measurements were reported. Integral cross-sections for C_6H_6 are shown in fig. 2.

Total cross-sections were measured by Holst and Holtsmark (1931) at collision energies between 0.5 eV and 25 eV using a low-energy Ramsauer technique. Sueoka (1988) has determined normalized TCS between 1 eV and 400 eV in a linear-transmission apparatus with longitudinal magnetic field. Możejko *et al.* (1996) reported absolute TCS in a linear apparatus with cylindrical spectrometer (Gdansk laboratory) at 0.6–250 eV and in a modified Ramsauer set-up (Trento laboratory) at 90–3500 eV. Very low-energy absolute TCS between 35 meV and 2 eV in C_6H_6, C_6H_5D and C_6D_6 were studied by Gulley *et al.* (1998); using a strong axial magnetic field they also measured the "backward" scattering CS down to 10 meV. Gulley *et al.* used two apparatuses, both of them based on a synchrotron-radiation electron source, at Daresbury (UK) and Århus (Denmark). As stated by Gulley *et al.* (1998) only negligible differences appeared between the spectra from the two laboratories.

TCS from the two low-energy experiments (Sueoka 1988, Możejko *et al.* 1996) agree well in shape. The data of Sueoka are somewhat lower, probably due to the normalization

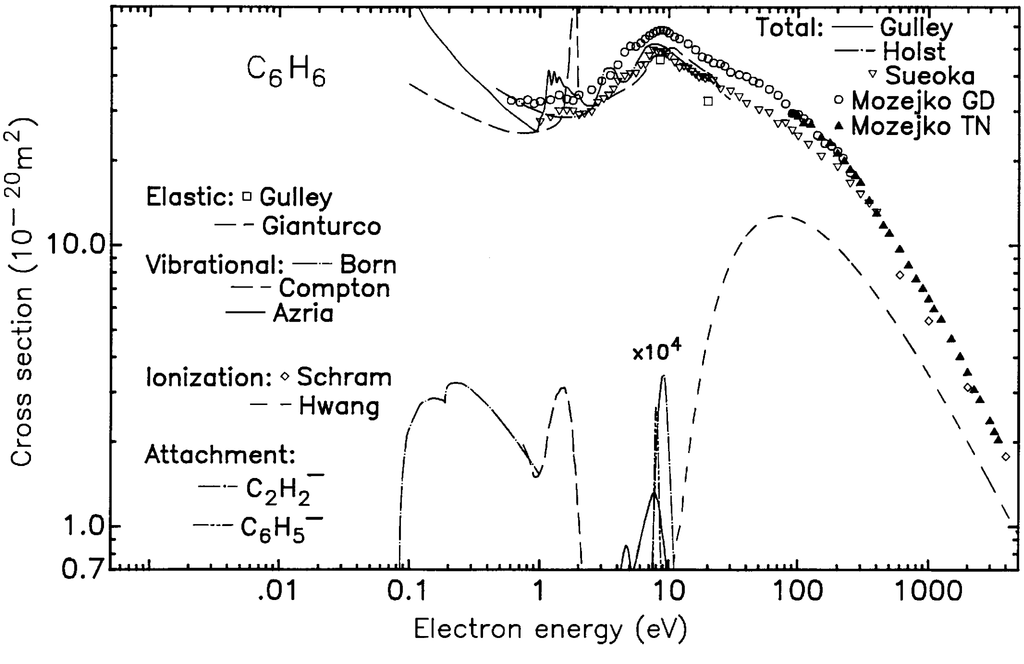

Fig. 2. – Integral cross-sections for electron scattering on C_6H_6 (in 10^{-20} m^2 units). *Total:* Możejko GD, low-energy data (Gdansk laboratory) from Możejko *et al.* (1996); Możejko TN, intermediate-energy data (Trento laboratory) from Możejko *et al.* (1996), absolute; Sueoka (1988), normalized; Holst and Holtsmark (1931), absolute; Gulley *et al.* (1998), "total scattering", absolute. *Elastic:* Gulley and Buckman (1999a), absolute; Gianturco and Lucchese (1998), calculation. *Vibrational:* Born approximation (eq. (15) in part I); Compton *et al.* (1968) and Azria and Schulz (1975) are shown only for illustration purposes, see text. *Ionization:* Schram *et al.* (1966); Hwang *et al.* (1999), semiempirical. *Dissociative attachment:* Fenzlaff and Illenberger (1984), $C_2H_2^-$ and $C_6H_5^-$ yields in arbitrary units, see text.

procedure. The TCS in C_6H_6 exhibits a broad maximum, as in alkanes, centered near 8.5 eV and reaching a value of $58 \cdot 10^{-20}$ m^2 (Możejko *et al.* 1996). On the low-energy side of this maximum a shoulder structure at about 4–5 eV was seen both by Sueoka (1988) and Możejko *et al.* (1996). The data of Holst and Holtsmark do not show this shoulder but exhibit a well-distinct maximum centered between 3 and 4 eV. Electron transmission experiments (Sanche and Schulz 1973, Mathur and Hasted 1976, Burrow *et al.* 1987) indicated the presence of a $^2B_{2g}$ resonant state at 4.82 eV (Burrow *et al.* 1987).

At 1.4–1.5 eV another, weak maximum was seen in TCS by Możejko *et al.* (1996) and by Sueoka (1998). Gulley *et al.* (1998) observed, instead, a weakly modulated, vibrational-like structure in TCS, starting at 1.17 eV and with 0.115 eV spacing. Numerous transmission-current measurements (see below) localized an $^2E_{2u}$ resonance in this energy range.

Swarm experiments. Christophorou *et al.* (1966) measured drift velocities relative to C_2H_4 at thermal energies. Approximating the momentum transfer CS by an $E^{-1/2}$ functional dependence they derived a momentum transfer CS a factor of nine higher in C_6H_6 than in C_3H_8. High values of CS ($50 \cdot 10^{-20}$ m^2 at 0.1 eV) were confirmed also by Mechlińska-Drewko (1980) in her $D_T\ /\mu$ measurements.

Studies of Rydberg atoms quenching in C_6H_6 were performed by Uematsu *et al.* (1984) and Popple *et al.* (1993). In experiments with potassium atoms prepared in intermediate ($n \cong 30$, where n is the principal quantum number) Rydberg states very low ($\cong 3 \cdot 10^{-8}$ cm^3 s^{-1}) rate constants were observed, for collisions leading to state-changing of potassium (Popple *et al.* 1993). Instead, high rates were observed for formation of associated $KC_6H_6^+$ ions at low collisional velocities. This indicates an effective transfer of collisional energy to internal energy of the $KC_6H_6^{+\,*}$ complex. Such a complex may be subsequently stabilized by energy transfer to the Rydberg electron.

Elastic cross-sections at 8.5, 10 and 20 eV have been reported by Gulley and Buckman (1999a,b). The integral elastic CS at 8.5 eV is 50% higher than at 20 eV. The DCS at energy of the TCS maximum (8.5 eV) shows a rather unusual angular shape, with an almost flat minimum between 60°–120° and a quick rise below 60° (see fig. 6 subsect. **2**.3). At 20 eV the DCS shows a more visible *d*-wave like pattern. Experimental DCS at 8–20 eV (Gulley and Buckman 1999a,b) agree in shape with the calculations of Gianturco and Lucchese (1998), which indicate the trapping of an incoming electron by the $l = 6$ partial-wave potential barrier. Both the experiment (Allan 1989) and the theory (Gianturco and Lucchese, 1998) pointed out the existence of a broad shape resonance in the region of elastic (and total) CS maximum (8.5 eV), due to the capture of an incoming electron to the $^2(e_{1u}\sigma^*)$ molecular orbital.

Calculated integral elastic CS (Gianturco and Lucchese 1998) follow very well the shape of TCS as measured by Sueoka (1988). However, the peak calculated at 1.82 eV is much narrower than the weak maximum seen in TCS measurements (Sueoka 1988, Możejko *et al.* 1996). This is probably due to neglecting the nuclear motion in the calculations. (The same effect is visible, for example, in fixed-nuclei calculations for CS_2, see fig. 21 in part II.) Both the 1.82 eV peak and the broad maximum calculated at about 10 eV (Gianturco and Lucchese 1998) are shifted to slightly higher energies with respect to the features observed in experimental TCS (Sueoka 1988, Możejko *et al.* 1996).

Vibrational excitation. Benzene possesses 30 normal vibrational modes but only 20 fundamental frequencies. Herzberg's labelling for the modes, used for example by Wong and Schulz (1975), Cheung and Bishop (1982), differs from Wilson's notation, currently in use (see, for example, Iachello and Oss 1993). We use below Herzberg's labelling, giving reference to the symmetry group. Among the possible vibrational modes only few are efficiently excited in electron collisions (Larkin and Hasted 1972, Wong and Schulz 1975). At 1.18 eV collision energy, *i.e.* in the region of the first shape resonance, the modes involving C-C bond are excited (Wong and Schulz 1975): the ν_2 (C-C symmetric stretch, A_{1g} symmetry), the ν_{16} (C-C in-plane bending, E_{2g}) and the ν_{20} (C-C out-of-plane bending, E_{2u}) modes and their harmonics. The DCS measured at 25°–100° for the ν_2 mode in this energy region show an angular distribution characteristic for the $f\delta$ partial-wave scattering, with a clear minimum near 40° and the second minimum at 90° somewhat washed out (Wong and Schulz 1975).

DCS for the infrared active mode ν_4 (C-H out-of-plane bending, A_{2u}) descend with angle and show a strong peak in the forward direction; the excitation decreases monotonically with energy without structures in the resonance regions (Wong and Schulz 1975). In the region of the 4.8 eV resonance, only the excitations of ν_7 (C-H out-of-plane bending, B_{2g} symmetry group) and ν_1 (C-H symmetric stretch, A_{1g}) modes are enhanced (Wong and Schulz 1975). The energy dependence of the DCS at 60° for the ν_7 mode show another large maximum centered at 8.0 eV (Azria and Schulz 1975).

We are not aware of absolute measurements of integral CS for vibrational excitation in benzene. In order to give a very approximate picture of the vibrational excitation CS, in fig. 2 we have reported: the vibrational excitation for the infrared active (ν_4, ν_{12}, ν_{13}, ν_{14}) modes as evaluated with the Born approximation (eq. (15) in part I) with transient dipole moments from Bishop and Cheung (1982); the threshold-electron spectrum of Compton *et al.* (1968) normalized at 1 eV to Born evaluation; the ν_1 DCS at 60° of Azria and Schulz (1975) normalized to the Compton *et al.*'s data at 3.5 eV.

Electronic excitation. We are not aware of CS for electronic excitation in C_6H_6. Energy loss spectra were collected at 300 eV collision energy by Skerbele and Lassettre (1965), at 40–100 eV by Lassettre *et al.* (1968), at 13.6 and 20 eV by Doering (1969), at 12.7–40 eV by Doering (1977), at 25–75 eV by Frueholz *et al.* (1977, 1979), at 10 and 100 eV by Wilden and Comer (1980). In particular, the first three triplet states $^3B_{1u}$, $^3E_{1u}$, $^3B_{2u}$ with energy loss in the 3.53–5.79 eV were studied by Wilden and Comer (1980) with energy resolution allowing to separate vibronic modes. The oscillator strength for the $1\ ^1B_{2u} \rightarrow \tilde{X}^1A_{1g}$ transition (4.79 eV excitation threshold, see Frueholz *et al.*, 1979) at 400 and 500 eV collision energy was measured by Klump and Lassettre (1977).

Spectra of trapped electrons in the electronic excitation energy region were collected by the SF_6 scavenger technique (Compton *et al.* 1968, Hubin-Franskin and Collin 1970) and the retarding-field method (Brongersma *et al.* 1969, van Veen and Plantenga 1975). Brongersma *et al.* (1969) at 1.6 eV above the excitation thresholds, reported CS values of $1.5 \cdot 10^{-20}$ m^2 and $3.2 \cdot 10^{-20}$ m^2 for the 4.7 eV ($^1B_{2u} + {}^3E_{1u}$ excitations) and 6.9 eV ($^1E_{1u}$ state) energy loss processes, respectively. Electron momentum spectroscopy for valence shells was performed by Samardzic *et al.* (1993).

Optical emission. Low-resolution (10 nm) fluorescence excitation functions in the 250–400 nm wavelength range the metastables yield and the optical emission spectra in the 220–520 nm wavelength range were reported for 2–300 eV collision energies by Smyth *et al.* (1974a, b, c, respectively). The fluorescence spectrum for the symmetry forbidden vibronic levels of the $^1B_{2u}$ state was studied by Kawazumi *et al.* (1984). Emission in the 185–900 nm wavelength region from H, C and CH fragments was studied by Beenakker and de Heer (1974). Cross-sections at 100 eV collision energy for the emission from dissociated fragments (Balmer H_β line and the CH radical $A\ ^2\Delta \rightarrow X\ \ ^2\Pi$ transition) amount to $0.68 \cdot 10^{-22}$ m^2 and $0.34 \cdot 10^{-22}$ m^2, respectively (Beenakker and de Heer 1974). The CS for the emission from the C_6H_6 transition $^1B_{2u} \rightarrow X^1A_{1g}$ exhibits a threshold peak (Beenakker *et al.* 1974b) and amounts to $0.21 \cdot 10^{-22}$ m^2 at 100 eV (Beenakker *et al.* 1974a).

Ionization. We are only aware of measurements of Schram *et al.* (1966) in the 0.6–12 keV energy range. These data are significantly higher than the results of a semiempirical model of Hwang *et al.* (1996). According to the two sets of data, the ionization CS at 1000 eV would contribute for 54% (Hwang *et al.* 1996) or for 83% (Schram *et al.* 1966) to the TCS. As a comparison we recall that the ionization CS in methane (Nishimura and Tawara 1994) is 63% of the TCS (Zecca *et al.* 1992) at 1000 eV.

Dissociative attachment. There are few measurements in C_6H_6. Azria and Schulz (1975) reported a large dissociative attachment peak of 2.2 eV FWHM centered at 8.0 eV, with a value of about $2.6 \cdot 10^{-24}$ m^2. This peak resembles the dissociative attachment in CH_4, see fig. 1 in part II. Fenzlaff and Illenberger (1984) measured relative yields for the formation of the $C_2H_2^-$, centered at 8 eV and for the $C_6H_5^-$, centered at about 9 eV. In fig. 2 we have normalized the $C_2H_2^-$ peak of Fenzlaff and Illenberger to the value of Azria and Schulz at 8.0 eV. The attachment of low-energy (< 1 eV) electrons in C_6H_6 mixtures with N_2 and Ar was studied by Christophorou and Goans (1974).

Resonances. The C_6H_6 molecule exhibits an interesting pattern of resonant states. Allan (1989) observed three resonant enhancements in the excitation functions for the $2\nu_1$ and $3\nu_2$ vibrational modes: at about 1.2, 4.8 and 8 eV (see also Ben Arfa and Tronc 1990). The lowest, $C_6H_6^-$ ($^2E_{2u}$) state was seen in electron transmission spectra (Boness *et al.* 1967, Larkin and Hasted 1972, Sanche and Schulz 1973, Nenner and Schulz 1975, Mathur and Hasted 1976, Burrow *et al.* 1976, Fesenko and Iogansen 1977, Frazier *et al.* 1978, Burrow *et al.* 1987) and in threshold electrons spectra (Compton *et al.* 1968). The vibrational structure observed in transmitted current, with an offset at 1.15 eV and the first spacing of 123 meV, resembles that for excitation of the totally symmetric breathing vibrational mode of the C_6 ring in C_6H_6 molecule (Sanche and Schulz 1973, Mathur and Hasted 1976). A similar vibrational structure has also been observed in the recent TCS measurements performed with 8 meV energy resolution (Gulley *et al.* 1998). Calculations (Gallup 1986, Gianturco and Lucchese 1998) indicate that the 1.1 eV resonance occurs via capture of one electron ($l = 3$ partial wave in the entrance and $l = 0$ at the exit channel) into the doubly degenerate c_{2u} (π^*) antibonding orbital located over the C-C bonds.

The next, $C_6H_6^-$ ($^2B_{2g}$) short-lived, temporary negative ion state manifests itself in electron transmission measurements as a structureless minimum (Sanche and Schulz 1973, Nenner and Schulz 1975, Mathur and Hasted 1976, Burrow *et al.* 1976), centered at 4.8–4.9 eV. This state was also observed in threshold electrons spectra (Compton *et al.* 1868, van Veen and Plantenga 1975). Trapping of one electron (the l=4 incoming partial wave) to the π^*-orbital has been proposed as a mechanism for the formation of this temporary negative-ion state (Gallup 1986, Gianturco and Lucchese 1998). As stated by Gallup (1986), since the $l = 4$ partial wave peaks far from the center of the molecule, the C-H (ν_7) rather than C-C (ν_1) deformations are responsible for the vibrational spectrum (Wong and Schulz 1975).

A short-lived resonance was observed in transmission spectra (Mathur and Hasted 1976) at about the energy of the TCS maximum. This resonance gives rise to an unusual shape of DCS at 8.5 eV (Gulley and Buckman 1999a) compared to other hydrocarbons. It was discussed theoretically by (Gianturco and Lucchese 1998). A broad enhancement of the ν_1 vibrational mode was observed close to this energy (Azria and Schulz 1975).

A number of additional resonant states was observed in transmission spectra on solid benzene (Sanche 1979); only a few of these structures were confirmed in threshold-excitation experiments (Compton *et al.* 1968, van Veen and Plantenga 1975). K-shell resonances in C_6H_6 were observed by inner-shell energy loss spectra (Horsley *et al.* 1985).

Sum check. A reasonable agreement exists between the elastic CS of Gulley and Buckman (1999a) and total CS of Możejko *et al.* (1996). At 8.5 eV the TCS is higher than the elastic integral CS by $12 \cdot 10^{-20}$ m^2. Brongersma *et al.* (1969) obtained an electron excitation CS for three states of about $5 \cdot 10^{-20}$ m^2 at 8.5 eV. A part of the remaining difference between TCS and (elastic + electronic) excitation CS comes from the vibrational excitation, enhanced in this energy region. At 20 eV the sum of elastic (Gulley and Buckman 1999a) and ionization (Hwang *et al.* 1996) CS is $37 \cdot 10^{-20}$ m^2 *vs.* TCS determinations of $45.9 \cdot 10^{-20}$ m^2 by Możejko *et al.* (1996) and $39.3 \cdot 10^{-20}$ m^2 by Sueoka (1988).

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2·3. *Linear hydrocarbons (*C_2H_4*,* C_2H_6*,* C_3H_8*).* – In many cases cross-sections for several hydrocarbons were presented in the same paper; therefore also in the present work we will group them together. Table II contains a list of significant experiments in which integral CS for electron scattering on hydrocarbons (excluding those performed only for CH_4, C_2H_2 or C_6H_6) have been measured. Integral CS for ethene C_2H_4, ethane C_2H_6, propane C_3H_8 are shown in figs. 3, 4 and 5, respectively. As far as possible, we will discuss also the results on other hydrocarbons in this chapter. A set of total and partial CS for C_2H_6 was given, among others, by Shishikura *et al.* (1997) and for several hydrocarbons by Hayashi (1992).

Total cross-sections. TCS were measured by Brüche in 1929-1930 in a Ramsauer-like apparatus covering the 0.2–50 eV energy range; by Sueoka and Mori (1986) both for electrons and positrons in a linear configuration using a longitudinal magnetic field; by Floeder *et al.* (1985) in a linear set-up with a weak longitudinal magnetic field; by Szmytkowski and Krzysztofowicz (1995) in an electrostatic spectrometer; by Nishimura and Tawara (1991) in a linear electrostatic set-up; by Lunt *et al.* (1994) in two experiments using synchrotron radiation as electron source. TCS of Nishimura and Tawara (1991) are about 5% systematically higher than the measurements of Floeder *et al.* (1985),

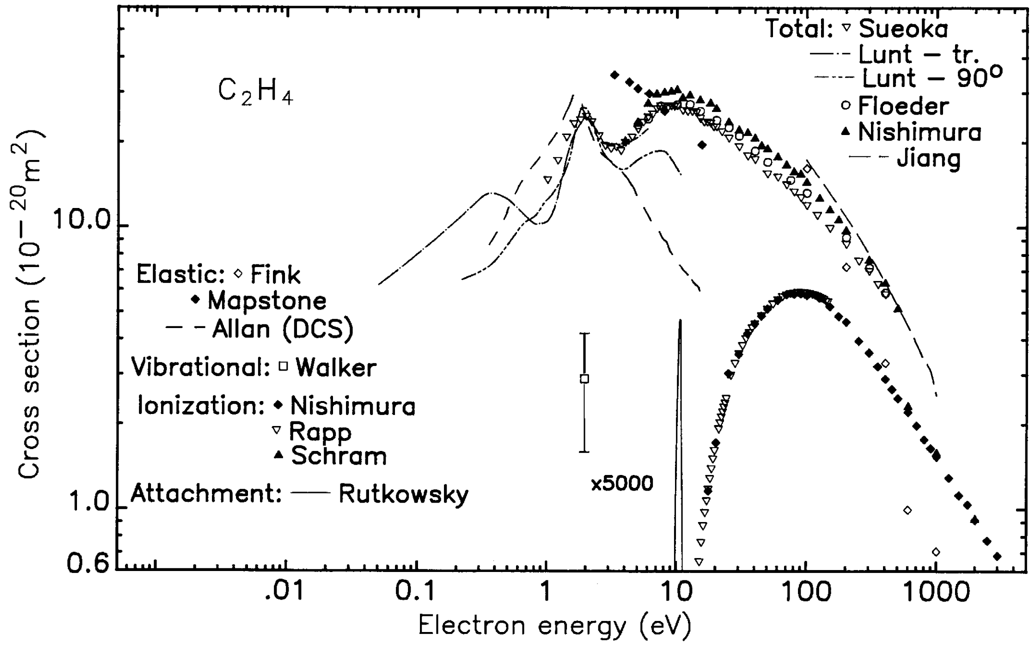

Fig. 3. – Integral cross-sections for electron scattering on ethene (C_2H_4). *Total*: Floeder *et al.* (1985) absolute; Nishimura and Tawara (1991) absolute; Sueoka and Mori (1986) normalized; Lunt *et al.* (1994), relative scattering into 90° ± 30° and the transmission experiment, presently normalized to Sueoka and Mori at 2.0 eV; Jiang *et al.* (1995), optical model, shown only above 100 eV for clarity. *Elastic:* Mapstone and Newell (1992), integrated in the present work; Fink *et al.* (1975) normalized to independent-atoms theory, integrated in the present work; Allan (1994), 90° DCS multiplied by 4π. *Vibrational:* absolute of Walker *et al.* (1978) at 1.95 eV. *Ionization*: Nishimura and Tawara (1994); Rapp and Englander-Golden (1965); Schram *et al.* (1966). *Dissociative attachment:* Rutkowsky *et al.* (1980).

Table II. – *Important measurements of integral cross-sections for electron scattering on hydrocarbons (works on only* CH_4*,* C_2H_2 *and* C_6H_6 *are not included). Note that only the first authors are reported.*

Process	Authors	Gases	Energies (eV)
Total	Brüche (1929)	C_2H_2, C_2H_4	0.8–50
	Brüche (1930a)	CH_4, C_2H_6, C_3H_8, n-C_4H_{10}	0.8–50
	Brüche (1930b)	n-C_4H_{10}, iso-C_4H_{10}	0.2–50
	Floeder (1985)	CH_4, C_2H_4, C_2H_6, C_3H_8, C_3H_6, cyclo-C_3H_6, n-C_4H_{10}, iso-C_4H_{10}, 1-C_4H_8	5–400
	Nishimura (1991)	C_2H_4, C_2H_6, C_3H_6, cyclo-C_3H_6, C_3H_8	4–500
	Szmytkowski (1995)	C_2H_6	0.6–250
	Sueoka (1986)	CH_4, C_2H_4, C_2H_6	1–400
	Lunt (1994)	CH_4, C_2H_4, C_2H_6	0.05–11
	Lunt (1998)	CH_4, C_2H_6, C_3H_8, C_3H_6	0.01–0.18
	Tanaka (1999)	C_3H_8	0.8–600
	Sueoka (1999)	C_3H_6, C_5H_{10}, C_6H_{12}, C_8H_{16}	0.7–600
Elastic	Fink (1975)	C_2H_2, C_2H_4, C_2H_6	100–1000
	Tanaka (1988)	C_2H_6	2–100
	Boesten (1994), Tanaka (1999)	C_3H_8	2–100
	Curry (1985)	CH_4, C_2H_6	7.5–20
	Mapstone (1992)	CH_4, C_2H_4, C_2H_6	3–15
	Merz (1998)	C_2H_6	0.4–10
	Maji (1998)	CH_4, C_2H_4, C_2H_6	300–1300
Swarm	Bowman (1967)	CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_6, 1-C_4H_8	0.01–0.06
	Duncan (1972)	C_2H_2, C_2H_4	0.01–1
	Duncan (1974)	C_2H_6, C_3H_8, C_3H_6, cyclo-C_3H_6	0.01–1
	McCorkle (1978)	CH_4, C_2H_6, C_3H_8, C_4H_{10}, n-C_5H_{12}	0.02–0.3
	Gee (1983)	C_3H_6, cyclo-C_3H_6, C_3H_8, n-C_4H_{10}, iso-C_4H_{10}	0.01–0.3
	Gee (1992)	cyclo-C_6H_{12}, cis-$C_{10}H_{18}$, trans-$C_{10}H_{18}$	
	Floriano (1986)	CH_4, C_2H_6, C_3H_8, n-C_4H_{10}, n-C_5H_{12}, iso-C_4H_{10}, neo-C_5H_{12}, n-C_8H_{18}, n-$C_{10}H_{22}$	0.01–0.5
	Schmidt (1992)	CH_4, C_2H_4, C_2H_6, C_3H_8, cyclo-C_3H_6, C_3H_6	
	Shishikura (1997)	C_2H_6	
Vibrational	Boesten (1990)	C_2H_6	3–20
	Curry (1985)	CH_4, C_2H_6	7.5–20
	Mapstone (2000)	C_2H_4, C_2H_6	3.2–15.4
	Boesten (1994)	C_3H_8	7.5
Electronic	Lassettre (1964)	CH_4, C_2H_6, C_3H_8, C_2H_4, cyclo-C_6H_{12}	
	Ehrhardt (1965)	CH_4, C_3H_8, n-C_7H_{16}	70
	Lassettre (1968a)	C_2H_2, C_2H_4, C_2H_6	33–100
	Lassettre (1968b)	CH_4, C_2H_6, C_3H_8, C_4H_{10}	50–180
	Johnson (1979)	CH_4, C_2H_6, n-C_5H_{12}	30–250
	Kuppermann (1979)	C_2H_2, C_2H_4, C_3H_3, C_4H_5 (1-butyn, 1,3-butadien), C_6H_6	20–90
	Au (1993)	CH_4, C_2H_6, C_3H_8, C_4H_{10}, C_5H_{12}, C_6H_{14}, C_7H_{16}, C_8H_{18}	tr–200*

TABLE II. – *Continued.*

Process	Authors	Gases	Energies (eV)
Optical emission	Beenakker (1975)	CH_4, C_2H_2, C_2H_4, C_2H_6	100–5000
	Donohue (1977)	CH_4, C_2H_4, CH_3OH	0–2000
	Möhlmann (1977)	CH_4, … , C_8H_{18}	0–2000
	Tokeshi (1996)	C_2H_2, C_2H_4, C_2H_6	17–100
Ionization	Schram (1966)	CH_4, C_2H_4, C_2H_6, C_3H_6, cyclo-C_3H_6, C_3H_8, 1,3-C_4H_6, 1-C_4H_8, trans-2-C_4H_8, cis-2-C_4H_8, n-C_4H_{10}, iso-C_4H_{10}, n-C_5H_{12}, neo-C_5H_{12}, iso-C_5H_{12}, n-C_6H_{14}, C_6H_6	600–12000
	Rapp (1965)	C_2H_4	tr–145
	Nishimura (1994)	CH_4, C_2H_4, C_2H_6, C_3H_6, cyclo-C_3H_6, C_3H_8	tr–3000
	Chatham (1984)	CH_4, C_2H_6, SiH_4, Si_2H_6	15–400
	Duric (1991)	CH_4, C_2H_3, C_3H_8	tr–240
	Grill (1993a)	C_2H_6	tr–950
	Grill (1993b)	C_3H_8	tr–950
Attachment	Rutkowsky (1980)	CH_4, C_2H_6, C_3H_8, C_4H_{10}, C_2H_4, C_3H_6, iso-, trans-, 1-C_4H_8, 1,3-butadien, C_2H_2, C_3H_4, 1-C_4H_6	

* Energy loss
tr - Threshold

for all the hydrocarbons studied in common.

For C_2H_4 and C_2H_6 the TCS of Sueoka and Mori (1986) are 5% lower than the data of Floeder *et al.* in the whole energy range of overlap (4–400 eV). For C_2H_6 the results of Szmytkowski and Krzysztofowicz (1995) are placed between the data of Nishimura and Tawara (1991) and of Floeder *et al.* (1985). Note that the measurements of Nishimura and Tawara (1991) were performed with the best (extrapolated to zero) angular resolution. For C_3H_8 Sueoka and collaborators (Tanaka *et al.* 1999) have corrected the measured TCS for the angular resolution error. The data of Tanaka *et al.* agree very well in shape with other experiments (Nishimura and Tawara 1991, Floeder *et al.* 1985) but are somewhat higher (10% at 8 eV). This difference is opposite in sign with respect to that for C_2H_4 and C_2H_6 for which no correction was done (Sueoka and Mori 1986).

TCS for C_2H_4, C_2H_6 (and CH_4) at very low energies are made by Lunt *et al.* (1994) who performed measurements of scattering with $90° \pm 30°$ angles (Daresbury laboratory) and of the transmitted current (Orsay laboratory). To get absolute values of TCS, we have normalized the Orsay data to the measurements of Sueoka and Mori (1986) at 1 eV for C_2H_6 and at 2 eV for C_2H_4. According to Lunt *et al.*, the TCS in C_2H_6 exhibits a Ramsauer minimum at about 0.6 eV and rises monotonically up to 6 eV (for clarity only a low-energy part of data is presented in fig. 4). For C_2H_4 no such deep minimum was seen but an additional maximum at 2.0 eV attributed to the $^2B_{2g}$ resonant state was observed (Lunt *et al.* 1994, Sueoka and Mori 1986). A structure is also visible at about 0.4 eV in the transmission experiment (Orsay laboratory) but it is probably an experimental artifact, as it has not been observed in the measurements performed in the Daresbury laboratory (Lunt *et al.* 1994). In fig. 3 we present both the Orsay and

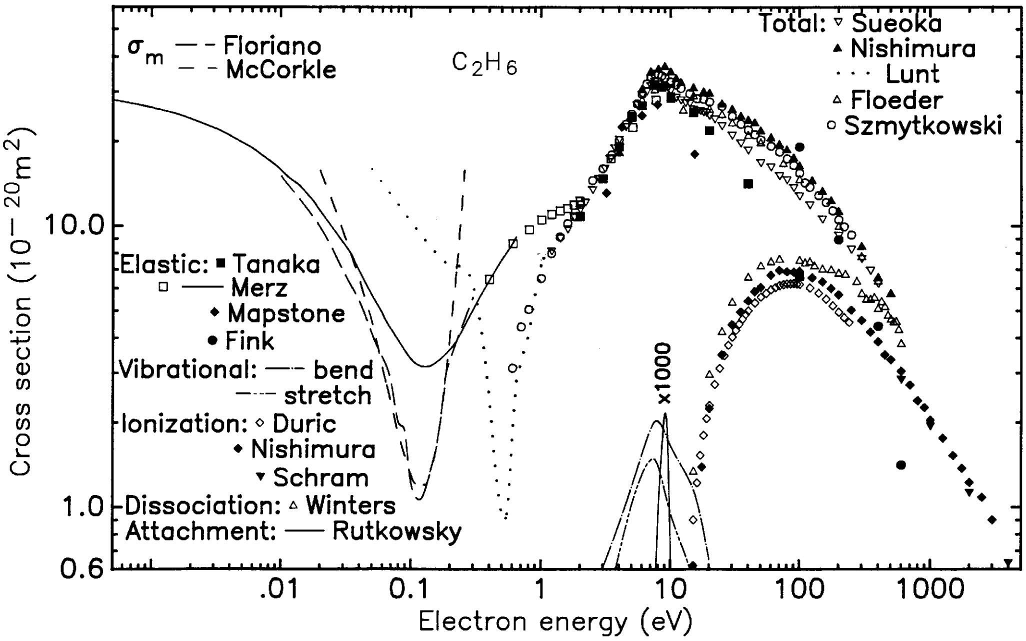

Fig. 4. – Integral cross-sections for electron scattering on ethane (C_2H_6). *Total:* Floeder *et al.* (1985) absolute; Nishimura and Tawara (1991) absolute; Sueoka and Mori (1986) normalized; Lunt *et al.* (1994) relative from transmission experiment, presently normalized; Szmytkowski and Krzysztofowicz (1995) absolute. *Elastic:* Tanaka *et al.* (1988) absolute; Mapstone and Newell (1992) normalized to theory and presently integrated; Merz and Linder (1998), measurements and semiempirical extrapolation; Fink *et al.* (1975) normalized to independent-atoms theory and presently integrated. *Momentum transfer:* Floriano *et al.* (1986), McCorkle *et al.* (1978). *Vibrational:* Boesten *et al.* (1990) absolute. *Ionization:* Duric *et al.* (1991); Nishimura and Tawara (1994); Schram *et al.* (1966); results of Grill *et al.* (1993b) practically coincide with those of Duric *et al.* (1991). *Dissociation:* Winters (1979). *Dissociative attachment:* Rutkowsky *et al.* (1980).

Daresbury results, for comparison. The more recent measurements of backscattering from the Orsay laboratory (Lunt *et al.* 1998) for C_2H_6 differ from previous measurements and are not reported in fig. 4.

As already noticed by Brüche (1930a), alkanes exhibit a maximum in the TCS at about the same energy, 7–8 eV. The absolute values of these maxima scale gradually, by a factor of two between CH_4 (Sueoka and Mori 1986) and C_3H_8 (Tanaka *et al.* 1999). Additionally, some shoulder structure (Nishimura and Tawara 1991, Floeder *et al.* 1985) is visible at 20–30 eV in light alkanes, C_2H_6, C_3H_8. For alkenes (C_2H_4, propene C_3H_6) and heavier alkanes (cyclo-propane C_3H_6, *n*-buthane C_4H_{10}, iso-butane C_4H_{10}, 1-butene C_4H_8) this shoulder is less visible (Floeder *et al.* 1985).

At energies above 20 eV the TCS for scattering on hydrocarbons rises with increasing the number of electrons. This dependence in the 100–400 eV energy (E) range has been parameterized by Floeder *et al.* (1985) as

$$\sigma^{\pm}(E) = aN_eE^{-1/2}\left[1 \pm b\exp[-cE]\right], \tag{1}$$

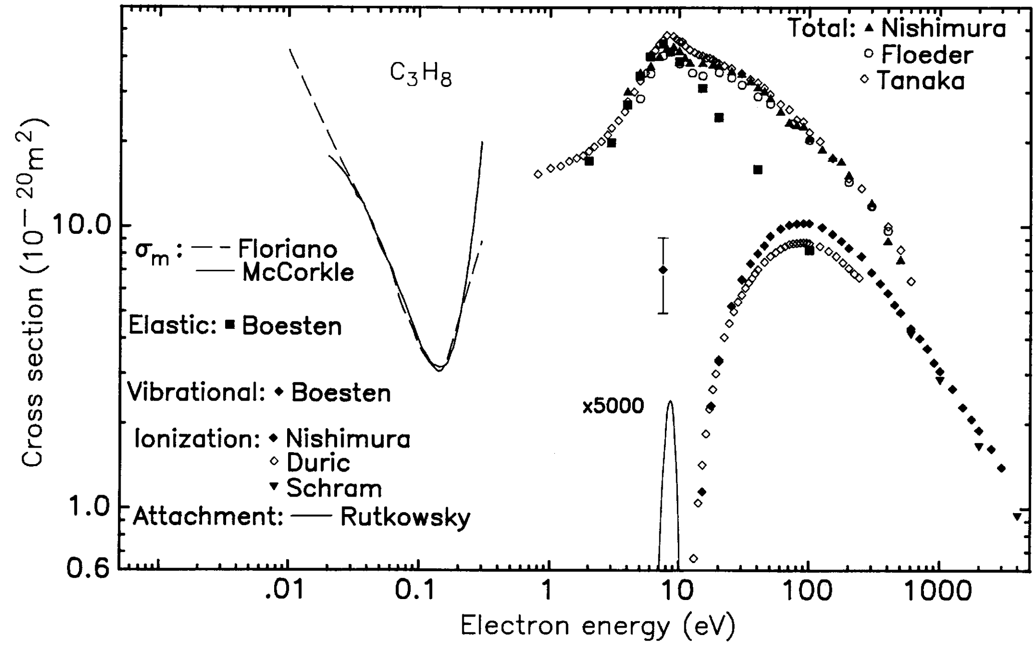

Fig. 5. – Integral cross-sections for electron scattering on propene (C_3H_8). *Total:* Floeder *et al.* (1985) absolute; Nishimura and Tawara (1991) absolute; Tanaka *et al.* (1999), absolute corrected for forward scattering. *Elastic:* absolute of Boesten *et al.* (1994). *Momentum transfer:* Floriano *et al.* (1986); McCorkle *et al.* (1978). *Vibrational:* absolute of Boesten *et al.* (1994) at 7.5 eV. *Ionization:* Duric *et al.* (1991); Nishimura and Tawara (1994); Schram *et al.* (1966); results of Grill *et al.* (1993b) practically coincide with those of Duric *et al.* (1991). *Dissociative attachment:* Rutkowsky *et al.* (1980).

where N_e is the total number of electrons in the target, signs + and − refer to positrons and electrons, respectively, and the parameters are $a = 7.2 \cdot 10^{-20}$ m^2 eV$^{-1/2}$, $b = 0.17$, $c = (333 \text{ eV})^{-1}$. On the other hand, Szmytkowski (1989) and Nishimura and Tawara (1991) argued that the TCS values in this energy range depend on the molecular polarizability. More measurements and in a larger energy range are needed to verify these models. Theoretical TCS for C_2H_4 were reported at 5–20 eV by Rescigno and Schneider (1992). The additivity rule was used by Jiang *et al.* (1995) at 10–1000 eV and Joshipura and Vinodkumar (1999) at 50–5000 eV to calculate molecular cross-sections starting from the atomic ones.

Elastic. Measurements on C_2H_4 were performed only by few groups (see table II for references). Mapstone and Newell (1992) have normalized their DCS at 8 eV and 15 eV to the theory of Winstead *et al.* (1991). The integral CS, obtained by integration of the DCS of Mapstone and Newell as performed in this work, agrees with the TCS (Floeder *et al.* 1985) at 8 eV. Below 8 eV, the integrated DCS of Mapstone and Newell increases with decreasing energy, in contrast to the TCS that decreases up to 2 eV. To get an agreement with the TCS values (Sueoka and Mori 1986) at lower energies, the relative data of Mapstone and Newell (1992) at 6.0, 5.0, 4.3 and 3.3 eV should be multiplied by 0.82, 0.72, 0.61 and 0.55, respectively. DCS in C_2H_4 at 3.3 eV and 8.0 eV (Mapstone and Newell 1992) are shown in fig. 6. Preliminary data of Suzuki *et al.* (1999) are quite

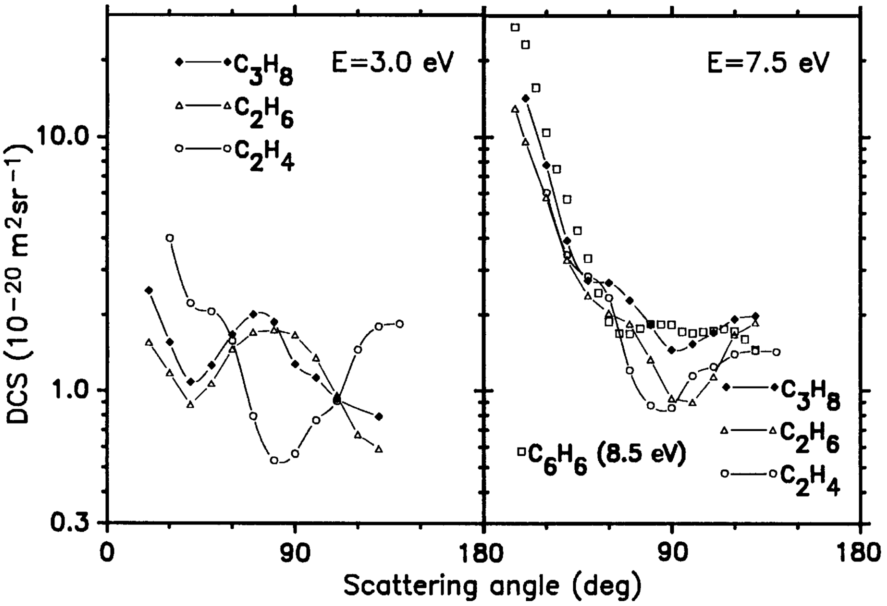

Fig. 6. – Differential cross-sections for elastic scattering of electrons on linear hydrocarbons and benzene. C_2H_4 (3.3 and 8.0 eV): Mapstone and Newell (1992), normalized to theory (Winstead *et al.* 1991) at 8 eV, 3.3 eV DCS renormalized (present work) to TCS (Sueoka and Mori 1986) by a factor 0.55. C_2H_6: Tanaka *et al.* (1988) absolute. C_3H_8: Boesten *et al.* (1994) absolute. C_6H_6: Gulley and Buckman (1999) at 8.5 eV.

different compared to the measurements of Mapstone and Newell (1992) below 5 eV but agree with them at 8 eV. Suzuki *et al.* reported DCS at 2 eV almost uniform in angle. DCS at 90° at 0.4–16 eV were also reported by Allan (1994). These data, differently from the "TCS" measurements of Lunt *et al.* (1994), do not exhibit a minimum at 1 eV but only a shoulder structure, similarly to in C_2H_6 (see figs. 3 and 4).

For C_2H_6 the most recent differential and integral CS in the 0.3–10 eV range were given by Merz and Linder (1998). These authors also extrapolated their integral CS to lower energies using two semiempirical methods: the phase shift analysis (see eq. (7) in part I) and the modified effective range theory (eq. (8) in part I). DCS in the limit of zero-energy change quickly with energy. Already at 0.15 eV the DCS exhibits a minimum at 90°, indicating a dominant *p*-wave scattering (Merz and Linder 1998). The *d*-wave scattering, somehow masked by other partial wave scattering, becomes distinguishable at impact energy of 2 eV (Tanaka *et al.* 1988, Merz and Linder 1998).

The Ramsauer minimum in C_2H_6 integral elastic CS, as obtained in the semiempirical analysis of elastic DCS measurements (Merz and Linder, 1998), in the transmission (Orsay) and in the 90° ± 30° scattering measurements of Lunt *et al.* (1994) and in the swarm experiments (McCorkle *et al.* 1978, Floriano *et al.* 1986), differ rather significantly, see fig. 4. However, these discrepancies can be somewhat apparent, as the physical quantities measured in these experiments are different and quick changes in DCS angular dependencies influence the integral cross-sections in different ways. Note that the integral elastic CS value at the Ramsauer minimum amounts to $3.0 \cdot 10^{-20}$ m^2 at 0.17 eV, three times more than the Ramsauer-Townsend minimum in momentum transfer CS,

$1.0 \cdot 10^{-20}$ m^2 at 0.1 eV, as evaluated by Merz and Linder (1998) and in agreement with McCorkle *et al.* (1978).

The C_2H_6 absolute elastic CS has also been measured at 2–100 eV, 15°–130° by Tanaka *et al.* (1988). Relative CS have been measured at 7.5–20 eV, 32°–142° by Curry *et al.* (1985) and at 3.3–15.5 eV, 30°–140° by Mapstone and Newell (1992). All these data agree reasonably well in the overlapping energy ranges. The integral elastic CS given by Tanaka *et al.* (1988) and those obtained in the present work by integration of the elastic data of Mapstone and Newell (1992) indicate a maximum of integral elastic CS at about 7–8 eV. The angular distribution at this energy is dominated by the f-partial wave scattering with some contribution from the p-wave (Tanaka *et al.* 1988). At 15 eV the normalized DCS of Mapstone and Newell are somewhat lower than the values of Tanaka *et al.* (1988).

C_2H_4, C_2H_6 (and CH_4) intermediate energy DCS have been measured by Fink *et al.* (1975) at 100–1000 eV, 0°–120° scattering angles and recently by Maji *et al.* (1998) at 300–1300 eV, 30°–120° scattering angles. Maji *et al.* (1998) have not compared directly their results to the earlier data. In C_2H_4 we have found, interpolating the data, that the DCS of Maji *et al.* at 300 eV agrees well with the measurements of Fink *et al.* (1975) at 130° but is underestimated by a factor of two at 30°. On the other hand, at 1000 eV the two data agree at 30° but at 130° the DCS of Maji *et al.* are lower by a factor of two. We note similar discrepancies for CH_4 (see subsect. **2**.1 in part II), comparing also to the most recent measurements (Iga *et al.* 2000). In C_2H_6 at 100 eV the DCS of Fink *et al.* (1975) normalized to the independent-atoms model are a factor 2–3 higher than the data of Tanaka *et al.* (1988). Consequently, also the integral CS obtained in the present work using the data of Fink *et al.* is higher both than the integral CS of Tanaka *et al.* (1988) and than the TCS of Floeder *et al.* (1985), see fig. 4. At high energies the integrated CS of Finch *et al.* fall quickly with energy; some error due to the normalization procedure of DCS (Finch *et al.* 1975) is not to be excluded.

C_3H_8 integral elastic CS (Boesten *et al.* 1994, Tanaka *et al.* 1999) exhibit a maximum at the same energy (7.5 eV) as in CH_4 and C_2H_6. In fig. 6 we compare the DCS for C_2H_6 and C_3H_8 at 3.0 and 7.5 eV (Tanaka *et al.* 1988, Boesten *et al.* 1994) and at 3.3 and 8.0 eV for C_2H_4 (Mapstone and Newell 1992). In the region of the total and elastic CS maxima all the three gases exhibit similar DCS angular distributions. However, these distributions are quite different from that in CH_4 at the same energy (compare fig. 3 in part II). At 3 eV the DCS for C_2H_6 (Tanaka *et al.* 1988) and C_3H_8 (Boesten *et al.* 1994) are almost equal for all angles and resemble the d-wave pattern. At about the same energy the C_2H_4 angular distribution (Mapstone and Newell 1992, normalized in the present work to the TCS, see before) is more complex than in C_2H_6, see fig. 6. This indicates the vicinity of a resonant state, visible in the TCS at 2 eV (Sueoka and Mori 1986).

Calculations of elastic scattering on hydrocarbons at low energies have been performed, among others, by Sun *et al.* (1992) and McCurdy (1992) for C_2H_6, by Winstead *et al.* (1991) for C_2H_4, C_2H_6, C_3H_8, Si_2H_6, by Brescansin *et al.* (1998) for C_2H_4.

Swarm measurements at 0.02–0.06 eV for several hydrocarbons (Bowman and Gordon 1967) indicate a rise of the momentum transfer CS in the limit of zero energy; however, the absolute values given by Bowman and Gordon have not been confirmed by more recent analyses. In C_2H_4 the analysis of Duncan and Walker (1972), not shown in fig. 3, indicates no Ramsauer-Townsend minimum down to 0.01 eV; their momentum transfer CS is almost constant ($5 \cdot 10^{-20}$ m^2) between 0.01 and 0.1 eV. Between 0.4 and 3.0 eV the momentum transfer CS of Duncan and Walker practically coincides with presently normalized 90° elastic DCS of Allan (1994). For C_2H_6 and C_3H_8 the momentum transfer CS of McCorkle *et al.* (1978) and Floriano *et al.* (1986) practically coincide, while the data of Duncan and Walker (1974) are somewhat shifted towards lower energies. The momentum transfer CS in C_2H_6 obtained by the modified effective range theory (see eq. (8) in part I) from elastic DCS measurements (Merz and Linder 1998), not shown in fig. 4, fall between the results of McCorkle *et al.* (1978) and Duncan and Walker (1974).

The recent measurements (Schmidt and Roncossek 1992) of drift velocities, longitudinal and transverse diffusion coefficients in light hydrocarbons at $0.02–14 \cdot 10^{-21}$ Vm^2 agree with previous data (McCorkle *et al.* 1978, Gee and Freeman 1980, 1983, Floriano *et al.* 1986) within ±5% , apart from the drift velocities in C_2H_6 where the discrepancy amounts to −15% for low reduced fields. Drift velocities for low ($< 2 \cdot 10^{-21}$ Vm^2) reduced fields were measured in 13 hydrocarbons from C_2H_4 to $C_{10}H_{22}$ by Christophorou *et al.* (1966), while characteristic energies for fields up to $50 \cdot 10^{-21}$ Vm^2 in n-C_5H_{12} to n-C_8H_{18} by Mechlińska-Drewko (1980). Christophorou *et al.* (1966) compared the low-energy hydrocarbon cross-sections to that in C_2H_4, approximating them with an $E^{-1/2}$ energy dependence. Mechlińska-Drewko derived CS in the 0.05–0.4 eV range: these CS agree well at the position of the Ramsauer-Townsend minimum with those of Floriano *et al.* (1986) but are underestimated at 0.4 eV. Recently, Shishikura *et al.* (1997) have measured the drift velocity and the longitudinal diffusion in C_2H_6 and its mixtures with Ar at $0.03–300 \cdot 10^{-21}$ Vm^2.

As noticed by Floriano *et al.* (1986), the Ramsauer-Townsend minimum occurs at the same energy (0.12 ± 0.01 eV) for all the chain alkanes from C_2H_6 to n-$C_{10}H_{22}$. The amplitude of the cross-section minima rises from about $1.2 \cdot 10^{-20}$ m^2 and $3.0 \cdot 10^{-20}$ m^2 for ethane and propane (Floriano *et al.* 1986, McCorkle *et al.* 1978), through $4.6 \cdot 10^{-20}$ m^2 and $5.8 \cdot 10^{-20}$ m^2 for butane and neopentane (McCorkle *et al.*) to about $16 \cdot 10^{-20}$ m^2 and $22 \cdot 10^{-20}$ m^2 for n-octane and n-decane, respectively (Floriano *et al.* 1986). The position of the minimum in the momentum transfer CS shifts to higher energies with the increase of the sphericity of the molecule: it occurs at 0.17 eV for i-butane, 0.22 eV for neo-pentane and 0.25 eV for methane (Floriano *et al.* 1986). The influence of the chain length on the electron mobility was studied by Gee *et al.* (1988). Electron scattering parameters in 14 hydrocarbons have been reviewed by Freeman and Armstrong (1985).

Scattering length. Large discrepancies exist among the different evaluations of the scattering length in hydrocarbons. Measurements of the pressure shift in perturbated molecular photoionization (Meyer *et al.* 1991) gave scattering lengths of $-2.34a_0$, $-3.33a_0$ and $-4.31a_0$ for CH_4, C_2H_6 and C_3H_8, respectively. Merz and Linder (1998) extrapolating their DCS measurements with the use of a modified effective range theory (see eq. (8) in part I) obtained a scattering length of $-3.00a_0$ in C_2H_6. Lunt *et al.* (1994) in C_2H_6 reported a scattering length of $-4.47a_0$ from their transmission data, of $-4.09a_0$ from the $90^\circ \pm 30^\circ$ experiment and of $-4.21a_0$ from the swarm data of McCorkle *et al.* (1978). In C_2H_4 Lunt *et al.* obtained a scattering length of $-11.7a_0$ extrapolating their data and of $-20.9a_0$ analyzing the momentum transfer CS of Bowman and Gordon (1969).

Vibrational excitation. The C_2H_4 vibrational excitation exhibits two peaks at about 1.8 eV and 7.5 eV (Walker *et al.* 1978). In the first region the dominating excited modes are totally symmetric ν_2 (C=C stretching) and ν_3 (C=C stretching with H-C-H bending). Both modes exhibit a d-wave–like angular distribution. At 1.95 eV the vibrational excitation amounts to about 10% of the TCS, with ν_2, ν_3 and 2 ν_3 CS equal to $1.4 \cdot 10^{-20}$ m^2, $1.1 \cdot 10^{-20}$ m^2 and $0.3 \cdot 10^{-20}$ m^2 (±40%), respectively (Walker *et al.* 1978). At 7.5 eV, apart from ν_2 and ν_3, the dominant mode is ν_1 (symmetric C-H stretching) and the DCS are isotropic. Allan (1994) reported the ν_2 absolute DCS at

1.95 eV: his data practically coincide with Walker *et al.*'s measurements. In fig. 3 the integral vibrational excitation of Walker *et al.* at 1.95 eV is shown.

In C_2H_6 (Boesten *et al.* 1990) and in C_3H_8 (Boesten *et al.* 1994) the vibrational excitation exhibits an enhancement around the energy corresponding to the maximum in the total and/or elastic CS, indicating a resonant process. The contribution from the vibrational channel to the TCS at the maximum position is higher for these two heavier hydrocarbons than for CH_4 (Szmytkowski and Krzysztofowicz 1995, Tanaka *et al.* 1999). It amounts to 10% and 15% for C_2H_6 and C_3H_8, respectively. For both C_2H_6 and C_3H_8, unresolved bending modes are excited with slightly (approximately 3:2) higher probability than stretching modes. In C_3H_8 a rise of the vibrational excitation of both bending and stretching modes has been observed at large (90° and 120°) scattering angles close to 2 eV (Boesten *et al.* 1994). This could be an indication of a low-energy resonant state.

Direct (non-resonant) vibrational excitation in C_2H_4 and C_2H_6 is rather weak. In particular, only little signal was observed at 1 eV from the most intense infrared active, ν_7 (out-of-plane bending) mode in C_2H_4 (Walker *et al.* 1978); in C_2H_6 only a slight rise was seen in 30° DCS towards 1 eV (Boesten *et al.* 1990). In C_2H_6, according to the Born approximation (eq. (15) in part I) with dipole transition moments from Bishop and Cheung (1982), the integral elastic CS is expected to reach a maximum of $0.5 \cdot 10^{-20}$ m^2 at 0.55 eV so it could be hardly visible in TCS. Low values of vibrational CS in the near-to-threshold region in C_2H_4 has also been observed in the transmission experiment of Lunt *et al.* (1994). Vibrational excitation DCS in C_2H_6 in the range 3.2–15.4 eV and in C_2H_4 at 8 eV and 15.5 eV have recently been reported by Mapstone *et al.* (2000).

Electronic excitation. C_2H_4 is the simplest system with C-C π bonding. For this reason electronic excitation in ethene was extensively studied in energy loss (Lassettre and Francis 1964, Ross and Lassettre 1966, Lassettre *et al.* 1968a, Trajmar *et al.* 1970, Kuppermann *et al.* 1979, Wilden and Comer 1980, Allan *et al.* 1994), trapped-electrons (Bowman and Miller 1965, Brongersma *et al.* 1969, Hubin-Franskin and Collin 1970, Verhaart and Brongersma 1980) and threshold electrons (Dance and Walker 1973, van Veen 1976) experiments. Energy loss spectra indicate the presence of the triplet at $\tilde{a}\ ^3B_{1u}$ state, observable as a broad maximum extending from 3.2 eV to about 6 eV. This structure is well separated from the next prominent feature, the $^1B_{1u}$ (π, π *) valence excited state centered around 7.5 eV. This last state overlaps with a number of sharp Rydberg transitions (Wilden and Comer 1980) and with a broad one (Vergaart and Brongersma 1980), presumably a valence transition in the 8–12 eV energy-loss range (Trajmar *et al.* 1970, Allan *et al.* 1994).

The $\tilde{a}\ ^3B_{1u}$ state of C_2H_4 has been extensively studied by Allan (1994). The rovibrationally integrated DCS at 90° reaches a maximum of $0.04 \cdot 10^{-20}$ m^2/sr at 7.0 eV. This value is somewhat lower than the theory of Rescigno and Schneider (1992). The DCS for this state exhibit an unusual, backward-peaked angular dependence, especially at higher collision energies (7.2 eV and 14.2 eV, Allan, 1994; 25 eV, Trajmar *et al.*, 1970). Measurements of Allan (1994) did not confirm the existence of a resonance in the at $\tilde{a}\ ^3B_{1u}$ excitation, as observed in the trapped-electron measurements (van Veen 1976) and as predicted theoretically at 5 eV (Rescigno and Schneider 1992).

Excitations in C_2H_4 to the Rydberg, 7.11 eV energy loss (for $\nu_2' = 0$), to the $\underline{E}$ (8.93 eV for $\nu_2' = 0$) and to the $\underline{C}$ (8.27 eV for $\nu_2' = 0$) states were studied by Trajmar *et al.* (1970). DCS for these states at 25 eV (collision energy) are forward centered and scale with respect to each other by a factor of five each. Assignment of Rydberg levels was done in electron energy loss studies (Wilden and Comer 1980) as well as in high-resolution photoabsorption experiments (Wu *et al.* 1991 and Chen and Wu 1999). However, the interpretation of the electronic spectrum in C_2H_4 is still controversial (compare Mulliken 1977, Ryu and Hudson 1995).

Forward electron scattering experiments in C_2H_4 were performed with a low-energy resolution (1 eV FWHM) by Ibuki *et al.* (1989) and with a high one (0.05 eV) by Cooper *et al.* (1995). Due to the narrowness of the energy loss lines, the values of maxima in the derived photoabsorption CS depend on the energy resolution. For this reason we quote only energy-integrated photoabsorption CS rather than absolute values in the maxima. The photoabsorption oscillator strength integrated over energy amounts to 0.423, 0.124 and 0.333 in the 6.3–8.79 eV, 8.79–9.45 eV and 9.45–10.99 eV bands, respectively (Cooper *et al.* 1995). Inner shell transitions in C_2H_4 (and C_2H_2) were studied by Tronc *et al.* (1979).

In C_2H_6, energy loss spectra were studied by Lassettre and Francis (1964) at 390 eV collision energy; by Ross and Lassettre (1966) at 150 eV; by Lassettre *et al.* (1968b) at 50–180 eV; by Johnson *et al.* (1979) at 30–250 eV; by Dillon *et al.* (1987) at 200 eV. No singlet-triplet transitions were observed for energy losses down to 4.5 eV (Lassettre *et al.* 1968b).

High-resolution forward-scattering energy loss spectra in C_2H_6 show three vibronic progressions centered at 9.4, 10.7 and 11.5 eV which are due to transitions from the $1e_g$ orbital to different Rydberg orbitals (Au *et al.* 1993). The first electronic transition $1e_g \rightarrow 3s$ with the onset at 7.9 eV (Johnson *et al.* 1979) is very weak. The photoionization CS for the first Rydberg band $1e_g \rightarrow 3p$ reaches its maximum of $0.3 \cdot 10^{-20}$ m^2 at 9.4 eV (Au *et al.* 1993).

For C_3H_8 we are aware of an extensive study of Ehrhardt *et al.* (1965) at 70 eV collision energy, 0–30 eV energy-loss and 0°–145° angular range. The energy loss spectrum at 6° shows a maximum at about 8–9 eV that amounts to 4/5 of the peak at 16 eV. Energy-loss spectra were also reported by Lassettre *et al.* (1968a) and Dillon *et al.* (1987). Electron excitation in forward scattering in C_3H_8 was studied by Au *et al.* (1993). The first peak in the photoabsorption CS, at 8.9 eV, amounts to $0.3 \cdot 10^{-20}$ m^2. Compared to C_2H_6, the CS peak in the photoionization range rises significantly, from $0.75 \cdot 10^{-20}$ m^2 to $1.2 \cdot 10^{-20}$ m^2 in C_2H_6 and C_3H_8, respectively (Au *et al.* 1993). Electron momentum spectroscopy in (e, $2e$) experiment was done by Pang *et al.* (1999) and Jia *et al.* (1999).

Optical emission from dissociated fragments in hydrocarbons was measured by Beenakker and de Heer (1975), Donohue *et al.* (1977), Möhlmann and de Heer (1977), Tokeshi *et al.* (1996). Emission CS for the Balmer H_α line (amounting to $3.1 \cdot 10^{-22}$ m^2 in CH_4) diminishes with the increasing of the number of carbon atoms in the molecule, from $2.5 \cdot 10^{-22}$ m^2 in C_2H_6 to $0.62 \cdot 10^{-22}$ m^2 in n-C_6H_{14} (Möhlmann and de Heer 1977). Emission from the $A\ ^2\Delta \rightarrow X\ ^2\Pi$ transition in the CH radical falls from $0.61 \cdot 10^{-22}$ m^2 to $0.2 \cdot 10^{-22}$ m^2 for the same series of molecules. Unsaturated hydrocarbons (C_2H_2, C_2H_4) show higher emission CS than C_2H_6; the difference is especially significant for the CH ($A \rightarrow X$) emission (Möhlmann and de Heer 1977). Vibrational states of the dissociated CH fragment were studied by Tokeshi *et al.* (1996).

Dissociation CS was measured in C_2H_6 at 15–600 eV by Winters (1979). The dissociation CS is somewhat higher than the total ionization CS. This is because the measurements of Winters include dissociation both due to electronic excitation and ionization. The sum check indicates that Winter's data are in a good agreement with the other CS.

Ionization. The recent measurements of ionization in hydrocarbons (Chatham *et al.* 1984, Duric *et al.* 1991, Grill *et al.* 1993a, b, Nishimura and Tawara 1994) agree quite well with earlier data (Rapp and Englander-Golden 1965, Schram *et al.* 1966).

Generally, the measurements of Nishimura and Tawara (1994) are higher than the other sets of data, but the difference does not exceed 15%. The semiempirical values of C_2H_6 ionization CS from the binary-encounter Bethe model by Hwang *et al.* (1996) agree within the experimental error bar with the measurements of Chatham *et al.* (1984), Duric *et al.* (1991) and Grill *et al.* (1993a) normalized to this latter at 100 eV, and are somewhat lower than those of Schram *et al.* (1966). In C_3H_8 the semiempirical model falls between the data of Duric *et al.* (1991) and Grill *et al.* (1993b) in the threshold region and coincides with these two sets and the results of Schram *et al.* (1996) above 100 eV. Only in C_2H_4 the model of Hwang *et al.* is lower than the experiment (Rapp and Englander-Golden 1965, Nishimura and Tawara 1994), by 20% in the maximum of the CS. The single-point measurements at 75 eV (Lampe *et al.* 1957) and at 70 eV (van Houte *et al.* 1992) disagree rather seriously with other experiments.

Both for C_2H_6 (Chatham *et al.* 1984) as well as for C_3H_8 (Grill *et al.* 1993b) the dissociative ionization dominates: parent ions $C_2H_6^+$ and $C_3H_8^+$ constitute 13% and 6.5%, respectively, of the total ionization CS at 100 eV. The $C_2H_4^+$ ion (50% of the yield) dominates in C_2H_6 ionization and the $C_2H_5^+$ ion (25%) in C_3H_8.

Dissociative attachment. Broad and weak peaks for the H^- production, centered at about 9.8, 9.5, 9.0 eV, were observed in C_2H_6, C_3H_8 and n-C_4H_{10}, respectively (Dorman 1966). More recently, Rutkowsky *et al.* (1980) reported dissociative attachment CS in the 0–12 eV energy range for as many as 14 hydrocarbons with one-to-four carbon atoms. CS for heavier hydrocarbons of this series are lower than that for CH_4, being of the order of 10^{-24} m^2. C_2H_4 and saturated hydrocarbons CH_4, C_2H_6, C_3H_8, C_4H_{10} show only one peak, shifting gradually from 10.5 eV to 8.5 eV. Alkenes and alkadienes develop also some low-energy peaks, depending not only on the overall chemical formula, but also on the isomeric structure (Rutkowsky *et al.* 1980).

Resonances. The peak in TCS for C_2H_4 at 1.8 eV (Sueoka and Mori 1986) corresponds to the $^2B_{2\mathrm{g}}$ shape resonance due to the capture of one electron to the π^* orbital (Walker *et al.* 1978, Gallup 1986). This resonance was seen as a structureless dip in the transmission spectra (Sanche and Schulz 1973, Burrow and Jordan 1975), in the vibrational excitation channel (Walker *et al.* 1978, Ben Arfa and Tronc 1990, Allan 1994). A peak at 7.5 eV in the vibrational DCS has been assigned (Allan 1994) to the $^2(\pi,\ \pi^{*2})\ ^2B_{3\mathrm{u}}$ core excited resonance, with a hole in the π-orbital and a double occupancy of the π^* orbital. This resonance was observed also in trapped-electrons experiments (Dance and Walker 1973, van Veen 1976) and in electron transmission spectra in the 6–8 eV energy range (Sanche and Schulz 1973). We are not aware of any confirmation of the weak structure seen at about 0.3 eV in transmission current by Boness *et al.* (1967) and in the Orsay transmission experiment (Lunt *et al.* 1994). Theoretical analysis of possible symmetries of the resonant states in C_2H_4 was performed by Gallup (1986) and Ben Arfa and Tronc (1990).

For the alkanes, CH_4, C_2H_6, C_3H_8 a broad maximum was observed in integral elastic CS (Boesten *et al.* 1994) and TCS at about 7.5 eV. In C_2H_6, on the basis of elastic angular distributions (Tanaka *et al.* 1988) and the vibrational excitation (Boesten *et al.* 1990) the existence of a short-lived resonant state has been postulated at this energy. Two possible symmetries are: $^2A_{2\mathrm{u}}$ corresponding to a temporary capture of the electron to the π^* valence orbital of the CH_3 group and $^2E_{\mathrm{u}}$ with the capture of the electron to the σ^*-orbital of the C-C valence bond (Boesten *et al.* 1990, Merz and Linder 1998). Shape resonances in C_2H_2, C_2H_4 and C_2H_6, as seen in carbon atom 1*s* photoionization, have been discussed recently by Kempgens *et al.* (1997). Temporary anion states of numerous polyatomic hydrocarbons were also reviewed by Jordan and Burrow (1987).

Sum check for C_2H_4 is not possible, at the moment. At low energies elastic CS

TABLE III. – *Integral cross-sections for electron scattering on ethane* (C_2H_6) *(in* 10^{-20} m^2 *units).*

Energy	Elastic	Vibrational	Ionization	Dissociation	Summed	Total
3.0	14.7 T	0.97 B			15.7	16.0 S
5.0	24.3 T	1.20 B			25.5	25.1 S
						24.6 NT
7.5	31.7 T	3.49 B			35.2	34.7 S
						30.6 F
10	28.8 T	2.60 B			31.4	32.5 S
						35.4 NT
15	25.3 T	1.71 B	0.62 N		27.6	28.9 S
			0.22 C	1.3 W	28.5	31.0 NT
20	21.8 T	0.88 B	2.24 N		24.9	27.6 S
			0.44 C	3.0 W	26.1	29.7 NT
40	14.1 T		5.41 N		19.4	21.9 S
			0.69 C	6.6 W	21.4	23.8 NT
100	6.6 T		6.89 N		13.5	15.4 S
			0.80 C	7.6 W	15.0	16.4 NT
						14.7 F

B - Boesten *et al.* (1990)
C - Chatham *et al.* (1984), non-dissociative part of ionization CS
F - Floeder *et al.* (1985), values in selected points are given only
N - Nishimura and Tawara (1994)
NT - Nishimura and Tawara (1991), read from figure
C - Szmytkowski and Krzysztofowicz (1995)
T - Tanaka *et al.* (1988)
W - Winters (1979), dissociation (neutral + ionization), read from figure

(Mapstone and Newell 1992, Allan 1994, Suzuki *et al.* 1999) and TCS (Sueoka and Mori 1986, Lunt *et al.* 1994) measurements and the theory (Winstead *et al.* 1992) are in serious disagreement. Ambiguities regard even the shape of the cross-section, see fig. 3. Serious discrepancies regard also high-energy CS: elastic (Fink *et al.* 1975, Maji *et al.* 1998) on one side and total (Sueoka and Mori 1986, Floeder *et al.* 1985, Nishimura and Tawara 1991) on the other.

For C_2H_6 the sum check, see Table III, would indicate a perfect (within 3%) agreement between summed elastic and vibrational cross-sections of Tanaka and co-workers and the total values of Szmytkowski and Krzysztofowicz (1995) up to the ionization threshold. This could be someway fortuitous, taking into account the experimental error bars: 30% for the integral vibrational CS (Boesten *et al.* 1990), 15–22% for the elastic CS (Tanaka *et al.* 1988) and 5% for the TCS. Between 15 eV and 100 eV the summed (with the ionization data of Nishimura and Tawara 1994) cross-sections are less than 10% smaller than the TCS; this amount could correspond to the electronic excitation. Electronic excitation CS can also be evaluated from the difference between the dissociation CS (Winters 1979) and the dissociative ionization CS (Chatham *et al.* 1984): such a difference amounts to

TABLE IV. – *Integral cross-sections for electron scattering on propane* (C_3H_8) *(in* 10^{-20} m^2 *units).*

Energy	Elastic	Vibrational	Ionization	Summed	Total
7.5	44.5 B	7.0 B		51.5	45.7 T 41.5 NT
10	38.4 B	5.2*		43.6	45.1 T 42.0 NT 37.7 F
15	30.9 B	3.5*	1.14 N	35.5	40.2 T 38.0 NT 34.2 F
20	24.3 B	1.6*	3.31 N	29.2	37.8 T 37.1 NT
40	15.9 B		8.0 N	23.9	32.3 T 31.1 NT
100	8.21 B		10.2 N	18.4	21.5 T 20.5 NT

* Rough extrapolation (present work) from excitation functions of Boesten *et al.* (1994)
B - Boesten *et al.* (1994), normalized to elastic CS
F - Floeder *et al.* (1985)
N - Nishimura and Tawara (1994)
NT - Nishimura and Tawara (1991), read from figure
T - Tanaka *et al.* (1999)

$1.8 \cdot 10^{-20}$ m^2 at 30 eV and $2.3 \cdot 10^{-20}$ m^2 at 100 eV. At 100 eV the sum of elastic (Tanaka *et al.* 1988), dissociation (Winters 1979) and non-dissociative ionization (Chatham *et al.* 1984) CS is in good agreement with the TCS value (Szmytkowski and Krzysztofowicz 1995).

Also for C_3H_8, see Table IV, the partial (Boesten *et al.* 1994, Nishimura and Tawara 1994) cross-sections sum pretty well to the total (forward-scattering corrected) CS (Tanaka *et al.* 1999). Some discrepancy exist at 7.5 eV where probably the integral elastic CS of Boesten *et al.* (1994) is overestimated. On the other hand the TCS of Floeder *et al.* at 10 eV and 15 eV are lower than other TCS results (Tanaka *et al.* 1999, Nishimura and Tawara 1991) and the summed value. At 100 eV the difference between the total (Tanaka *et al.* 1999) and elastic (Boesten *et al.* 1994) plus ionization (Nishimura and Tawara 1994) CS gives a rough estimate, $2.1 \cdot 10^{-20}$ m^2 of the electronic excitation CS. This values agrees with our estimate of the electronic excitation in C_2H_6 at the same energy (see above). Both for C_2H_4 (Chatham *et al.* 1984) and C_3H_8 (Grill *et al.* 1993b) ionization constitutes 40% of the TCS at 100 eV (Szmytkowski and Krzysztofowicz 1995 and Tanaka *et al.* 1999, respectively). Above 100 eV, it is not possible to perform the sum check in C_2H_6 and C_3H_8 due to the lack of reliable data.

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2˙4. *Fullerene (*C_{60}*).* – Fullerene discovery (Kroto *et al.* 1985, Krätschmer *et al.* 1990) triggered numerous experimental and theoretical investigations. In many aspects electron scattering on fullerene is atypical. This target attaches electrons with a very high CS in a few eV collision energy range. Lifetimes of the negatively charged complexes are very long. For this reason, almost no resonant vibrational excitation was observed for fullerenes in the gas phase (Elhamidi *et al.* 1997). We are not aware of TCS measurements in fullerene.

Elastic DCS in C_{60} in the 30°–90° angular and in the 1–12 eV energy ranges have been measured by Tanaka *et al.* (1994). There are big differences in the energy dependences of the DCS at specific angles: for 30° a single maximum of DCS is observed at 5 eV, for 50°, a minimum at 5 eV, a broad maximum at 8 eV and a rise towards 1 eV. At 9 eV three minima are observable in the 30°–90° angular range. A rough evaluation of the absolute DCS value of $410 \cdot 10^{-20}$ m^2/sr at 7 eV and 30° scattering angle could be subject to an error by a factor of 2 or 3 (Tanaka *et al.* 1994).

Elastic CS in C_{60} has been calculated by Gianturco *et al.* (1999) at 0–30 eV scattering energies. A number of resonant structures is visible in the integral CS. In the whole energy range examined the integral CS exceeds the value of $100 \cdot 10^{-20}$ m^2, showing a sharp peak of $180 \cdot 10^{-20}$ m^2 at 3 eV and a broad, structured maximum of about $160 \cdot 10^{-20}$ m^2 around 10 eV.

Vibrational excitation. Vibrational infrared frequencies in gas phase were found to be (Frum *et al.* 1991) 65.7, 71.1, 146 and 175 meV. The lowest Raman transition was observed at 34 meV (Bethune *et al.* 1991). Electron energy loss spectra obtained with 30 meV resolution show at 7 eV (30°, 50°) two peaks: a higher one in the 150 meV–200 meV region and a lower one in the 60 meV–110 meV (Tanaka *et al.* 1994).

Electronic excitation. The ground state of C_{60} is ^1A_g. Energy loss spectra for condensed phase were obtained, among others, by Gensterblum *et al.* (1991), Weaver *et al.* (1991), Lucas *et al.* (1992). Electron energy loss spectra in gas phase at 5° scattering angle, 50 and 100 eV collision energy were reported by Tanaka *et al.* (1994). They observed peaks at 2.2, 3.7, 4.8, 5.5. and 5.8 eV corresponding to one-electron $\pi \rightarrow \pi^*$ transition (Gensterblum *et al.* 1991). Tanaka *et al.* reported also some features at 5.8, 6.1, 6.3 and 6.5 eV superimposed on the 1 eV-wide π-electron plasmon (collective excitation) peak and a weak maximum at the 28.3 eV energy loss, attributed to the $\sigma + \pi$ plasmon excitation.

Bulliard *et al.* (1993) studied electron energy loss spectra with 60 meV resolution for the 1–10 eV energy loss and residual energies from 0.08 to 20 eV. They localized three distinct bands at 2.24, 3.77 and 4.88 eV and a large one at 6.1 eV. At low residual energies, where forbidden transitions are enhanced, they observed a rise of the 2.2 eV band, a sharp peak at 2.98 eV and some signal around 3.4 and 4.4. eV. A band peaking at 2.26 eV, being a superposition of triplet states and optically forbidden single states, was also observed in spectra with low residual energies by Abouaf *et al.* (1993). These authors, similarly to Bulliard *et al.*, observed a triplet character peak at 2.96 eV. In none of the energy-loss spectra for the C_{60} gas phase (Abouaf *et al.* 1993, Bulliard *et al.* 1993, Jaffke *et al.* 1994, Tanaka *et al.* 1994) the lowest $^3T_{2g}$ triplet state reported at 1.55 eV in solid film (Lezius *et al.* 1992) was found.

At 10 and 70 eV collision energy the DCS for all different energy loss processes between 2.3–7.3 eV are forward centered (Abouaf *et al.* 1993). At 70 eV, 4° scattering angle, the 1 ^1T_u, 3 ^1T_u, 6 ^1T_u energy loss peaks (3.03, 3.78, 4.84 eV) rise in amplitude; a possible peak for the 8 ^1T_u, excitation at 5.87 eV is hidden in the plasmon maximum.

Ionization. The total ionization CS (Düsner *et al.* 1995, Matt *et al.* 1996) rises quickly with energy (Tarnovsky *et al.* 1998) up to $33 \cdot 10^{-20}$ m^2 at 50 eV. The fall at high energies is unusually slow: $16 \cdot 10^{-20}$ m^2 at 1000 eV (Matt *et al.* 1996). The C_{60}^+ ion amounts to 75% of total ionization at 100 eV and almost 90% at 1000 eV. Fragment ions, with even number of atoms, down to C_{44}^+ were observed with diminishing intensities (Matt *et al.* 1996). In a more recent experiment, fragment ions down to C_4^+ were also observed (Muigg *et al.* 1998).

The high rate for multiple ionization in C_{60} is rather anomalous compared to other molecular targets: for example, the C_{60}^{2+} ion yield amounts to 30% of the C_{60}^+ one (Matt *et al.* 1996). In this respect, fullerene resembles noble gases. Also the small share of the dissociative ionization is anomalous (C_{58}^+ being 30 times less than the C_{60}^+ yield). The semiempirical model of Deutsch *et al.* (1996) disagrees with the experiment, giving a maximum value of ionization CS of almost $100 \cdot 10^{-20}$ m^2 and overestimating the high-energy (0.4–5.0 keV) experimental CS (Itoh *et al.* 1999) by a factor of two. The first determination of the ionization CS in C_{60}, $54 \cdot 10^{-20}$ m^2 at 38 eV (Sai Baba *et al.* 1992a), was higher than the recent measurements (Matt *et al.* 1996). Ionization of C_{70} was studied by Sai Baba *et al.* (1992b) and Matt *et al.* (1997).

Dissociative attachment in C_{60} is subject to intense investigations. It was measured by flowing afterglow method (Smith *et al.* 1993, Smith and Španěl 1996), Rydberg atoms quenching (Huang *et al.* 1995, Fink *et al.* 1995, Weber *et al.* 1996) and beam (Elhamidi *et al.* 1997) methods. Smith *et al.* reported a very small rate coefficient at 300 K rising to $3 \cdot 10^{-7}$ cm^3 s^{-1} at 4500 K. From these measurements an activation energy of 0.26 eV was deduced. Smith and Španěl (1996) argued that, in spite of the high attachment rate, similar to that in SF_6, the attachment mechanism in these two targets is essentially different: an s-wave capture in SF_6 and a p-wave capture (with a centrifugal barrier) in C_{60}. Jaffke *et al.* (1994) in a beam experiment obtained a similar value of the activation energy. They also showed quite complicated energy dependence of attachment CS between the threshold and 12 eV, with several maxima reaching about $100 \cdot 10^{-20}$ m^2. In another work of this group (Lezius *et al.* 1993) the zero-energy peak has been attributed to a nuclear-excited Feshbach resonance mechanism.

Quite different results, indicating a high electron attachment CS in C_{60} at zero energy, have been obtained in Rydberg-atoms quenching experiments (Huang *et al.* 1995, Finch *et al.* 1995, Weber *et al.* 1996) and in a high-resolution beam experiment (Elhamidi *et al.* 1997). These experiments indicate a rate coefficient of $2 \cdot 10^{-8}$ cm^3 s^{-1} (Weber *et al.* 1996) for the formation of the C_{60}^- anion at near-to-zero energies. Furthermore, this rate is independent of the quantum number of the Rydberg atom, indicating an s-wave character of the electron capture.

Elhamidi *et al.* (1997) located the maxima in attachment CS at 0.75, 1.20, 2.08, 2.74, 3.5, 4.27 and 5.35 eV and attributed them to long-lived resonant states; the first two of these states are shape resonances, the other states are understood as Feshbach resonances. The lifetimes of the C_{60}^- temporary anion falls exponentially with the incident electron energy, from 500 μs at 7 eV to 40 μs at 11 eV (Elhamidi *et al.* 1997). Studies of electron attachment to bigger fullerenes C_n, $n = 70$, 76, 84 (Abouaf *et al.* 1999), show that at the same electron energy the lifetime of metastable C_n^- anions rises exponentially with the number of carbon atoms in the molecule.

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3. – Halides

Many types of halides, mainly fluorides and chlorides (and among them mixed halides containing H, F and Cl atoms) were studied by electron scattering. In this section we follow the presentation order proposed for hydrides (and hydrocarbons). We start from five-atom molecules: chlorofluorocarbons (CF_4, CCl_4 and mixed), then methyl halides (CH_3X) and silicon tetrahalides (SiX_4). In subsect. **3**˙5 we discuss NF_3 and some similar molecules, in subsect. **3**˙6 fluorine-containing analogs of heavier hydrocarbons (C_2F_6, C_3F_8, C_6F_6). At the end, in subsects. **3**˙8 and **3**˙9 we review electron scattering cross-sections in SF_6 and its analogs.

Tetrahedral fluorides (CF_4, SiF_4) exhibit features in TCS similar to those observed in tetrahedral hydrides. One particularity of both groups of molecules is that a Ramsauer-Townsend minimum in the elastic and/or total CS is well visible. However, the presence of peripheral fluorine atoms in CF_4 and SiF_4 influences the resonant scattering differently. More marked differences regard also vibrational excitation, enhanced by substituting hydrogen atoms by fluorine ones.

3˙1. *Tetrafluoromethane (*CF_4*).* – The importance of CF_4 relies in the fact that this gas is the most frequently used for plasma etching and semiconductor passivation (Kastenmaier *et al.* 1996). For this reason, besides measurements of total and partial CS, very particular phenomena of electron scattering, like distribution of kinetic energies of dissociated fragments, have been studied in detail (Harland and Franklin 1974, Le Coat *et al.* 1994, Bruce *et al.* 1994). As a result of this recent interest, a set of quite congruent data have been established for CF_4. Cross-sections summaries, mostly oriented towards plasma modeling, were given by Hayashi (1987), Morgan (1992), Bordage *et al.* (1996); rather rough sets of momentum transfer CS have been published by Mašek *et al.* (1987) and Stefanov *et al.* (1988). Numerous works regard plasma modeling (Jauberteau *et al.* 1991, Gogolides *et al.* 1994).

Extensive reviews on CF_4 electron impact CS have recently been published by Bonham (1994) and Christophorou *et al.* (1996). We refer the reader to these works for detailed figures and tabulated presentation of partial CS and swarm parameters in CF_4 and its mixtures with other gases. In fig. 7 we report integral CS for CF_4; in fig. 13 (subsect. **3**˙2) we compare DCS for elastic scattering in CF_4, CF_3Cl and CF_2Cl_2.

Total cross-sections. Total absolute CS have been measured from 0.4 eV (Jones 1986, Szmytkowski *et al.* 1992) up to 4000 eV (Zecca *et al.* 1992). Relative measurements between 0.07 and 0.4 meV were obtained by Field *et al.* (1984). The agreement between the data of Jones and Szmytkowski *et al.* is very good at low energies. Between 20 and 120 eV the data of Szmytkowski *et al.* seem to be the most reliable. The data of Jones at 50 eV are underestimated by 7% (Jones 1986) due to scattering on exit orifices of the gas cell. In fig. 7 we report them corrected by an energy-dependent factor, varying smoothly from 1.01 at 10 eV to 1.07 at 50 eV. The data of Zecca below 120 eV can be overestimated due to beam instabilities. The remeasured data by Sueoka *et al.* (1994) are in better agreement with other experiments at low energies than the previous measurements from the same apparatus (Mori *et al.* 1985). However, above 30 eV the data of Sueoka *et al.* are somewhat lower than other results and seem to be slightly energy shifted. Such a shift is plausible in a time-of-flight apparatus, using a longitudinal guiding magnetic field.

In the experiment of Field *et al.* (1984) at Orsay laboratory, a synchrotron radiation electron source and a transmission geometry were used; the energy resolution of the

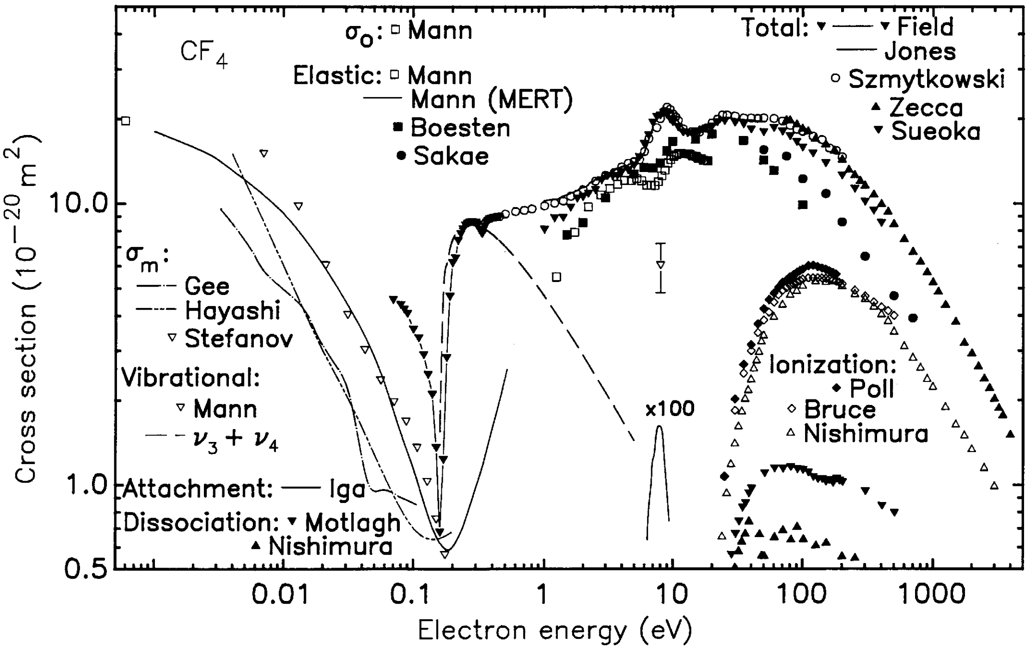

Fig. 7. – Integral cross-sections for electron scattering on CF$_4$ (in 10^{-20} m^2 units). *Total*: Field *et al.* (1984), normalized (this work) to Szmytkowski *et al.* (1992) at 0.4 eV; Szmytkowski *et al.* (1992); Jones (1986); Zecca *et al.* (1992); Sueoka *et al.* (1994). *Elastic:* Mann and Linder (1992a); Boesten *et al.* (1992); Sakae *et al.* (1989); MERT analysis of Mann and Linder (1992a) at low energies. *Momentum transfer:* Hayashi (1987); Stefanov *et al.* (1988); Gee and Freeman (1991). *Vibrational excitation:* Born approximation (eq. (15), part I), in general agreement with Mann and Linder (1992b) for ν_3 and ν_4 modes; at 8 eV, presently integrated DCS of Mann and Linder (1992b). *Ionization:* summed partial cross-sections of Poll *et al.* (1992); Bruce and Bonham (1993); Nishimura *et al.* (1999); semiempirical model of Kim and Rudd (1999) in Nishimura *et al.* (1999) and data from coincidence measurements (Bruce *et al.* 1994) not shown for clarity. *Dissociation into neutrals:* absolute of Motlagh and Moore (1998); Nishimura *et al.* (1999), semiempirical analysis; absolute of Mi and Bonham (1998) and of Nakano and Sugai (1992) not shown for clarity; total (ionization + neutrals) dissociation CS of Winters and Inokuti (1982), not shown for clarity, coincide above 50 eV with ionization CS (Bruce and Bonham 1993). *Dissociative attachment*: Iga *et al.* (1992), sum of CF$_3^-$ and F$^-$ signals.

apparatus was 40 meV. The relative measurements of Field *et al.* have been normalized (in this work) at 0.45 eV to the data of Szmytkowski *et al.* These data suggest the existence of a very narrow Ramsauer-Townsend minimum in TCS at 0.17 eV followed by a small bump at 0.27 eV. Note that this narrowness, similarly to the case of C$_6$H$_6$, could be an instrumental artifact.

Swarm experiments. Due to the above-mentioned practical importance of CF$_4$, the swarm parameters (electron mobility, characteristic energies) have recently been subjected to numerous measurements (Curtis *et al.* 1988, Hunter *et al.* 1988, Schmidt and Polenz 1988, Gee and Freeman 1991, Lisovskiy and Yegorenkov 1999) and semiempirical analysis (Mašek *et al.* 1987, Vasenkov 1999). The analysis of swarm results is difficult in the case of CF$_4$ due to the overlap between the maximum in the vibrational CS and the minimum in the elastic channel (see fig. 7).

In particular, Gee and Freeman (1991) and Hayashi (1987) reported a momentum transfer CS in the Ramsauer-Townsend minimum of about $1 \cdot 10^{-20}$ m^2, while Curtis *et al.* (not shown in the figure) one of $0.01 \cdot 10^{-20}$ m^2. Similarly, some discrepancies exist at very low energies (*e.g.*, 0.07 eV), where different data (of Gee and Freeman, Curtis *et al.*, Hayashi, Stefanov *et al.*) span from about $6 \cdot 10^{-20}$ m^2 to $15 \cdot 10^{-20}$ m^2, respectively.

Mann and Linder (1992a) used a modified effective range formalism (see part I, eq. (8)) to derive elastic and momentum transfer CS at low energies from their elastic differential CS measurements above 0.5 eV. Their momentum transfer CS at 0.1 eV is bounded by the results of Hayashi from the upper and Curtis *et al.* from the lower side. We note also that the early approximation of the momentum transfer CS at thermal energies from cyclotron resonance measurements (Tice and Kivelson 1967) by the $8/E$ function (in 10^{-20} m^2/meV units) was quite reliable, agreeing reasonably well both with Hayashi's and Mann and Linder's analysis.

Scattering length. Mann and Linder (1992a) by a modified effective range analysis derived a zero-energy cross-section σ_0 of $19.5 \cdot 10^{-20}$ m^2. This value is close to that in CH_4. We note also a good agreement in the determination of the Ramsauer-Townsend minimum between Mann and Linder's (1992a) analysis and the normalized TCS measurements of Field *et al.* (1984), see fig. 7. However, according to Hayashi (1987) and Morgan (1999), the zero-energy CS for CF_4 could be much bigger, exceeding the value of $60 \cdot 10^{-20}$ m^2.

Elastic cross-sections of Boesten *et al.* (1992) between 1.5 and 100 eV overlap very well (within 10%) in their low-energy limit with the measurements of Mann and Linder (1992a), normalized to Jones (1986). Both sets of data indicate a rapid fall of integral CS below 3 eV, pointing to the existence of a Ramsauer-Townsend minimum, predicted also theoretically (see, for example, Gianturco *et al.* 1996). Mann and Linder (1992a) extrapolated their experimental elastic CS towards zero energy using a modified effective range theory (part I, eq. (8)). According to this evaluation the Ramsauer-Townsend minimum amounts to $0.6 \cdot 10^{-20}$ m^2 at 0.185 eV.

At low energies we note a resonant dip in the integral elastic CS at 7 eV, just below the maximum in TCS. This dip, followed by a maximum, is visible both in Boesten's *et al.* and Mann and Linder's data. All recent theories, Huo (1988), Winstead *et al.* (1993), Gianturco *et al.* (1996), Natalense *et al.* (1995), Isaacs *et al.* (1998) reproduce sharp peaks in elastic integral CS but not such a dip structure. Note that none of these theories include vibrational excitation effects. Differential CS exhibit rapid changes in shape across the resonance, becoming forward peaked just at 10 eV (Mann and Linder 1992a).

At 100 eV the integral CS of Boesten *et al.* (1992) are 20% lower than the intermediate-energy measurements of Sakae *et al.* (1989). On the other hand, the discrepancy in differential CS for these two sets of data is, on the average, less than 10%. Therefore, the difference in the integral values derives probably from extrapolation and/or integration procedures. As Sakae *et al.* extended the DCS angular measurements down to 5°, their integrated values seem to be more reliable at 100 eV than the result of Boesten *et al.*

Tanaka *et al.* (1997) compared DCS at 15°–135° and 1.5, 30 and 100 eV in CF_4, CH_4 (and fluoromethanes CH_3F, CH_2F_2, CHF_3). At 1.5 eV, the CF_4 and CH_4 differential cross-sections are similar in shape; the absolute values in the two gases at 90° differ by a factor of two (compare also fig. 3 in part II and fig. 13 for 2 eV energy). At 100 eV the absolute DCS in CF_4 and CH_4 differ by a factor of four; DCS in CF_4 shows a more complex, interference-like pattern. Well-pronounced structures, due to interference (Raj 1991) and absorption (Khare *et al.* 1994) effects, are also visible in the intermediate energy DCS (Sakae *et al.* 1989). Meier *et al.* (1994) evidenced effects of multiple scattering in small-angle elastic DCS at 1 keV.

Vibrational excitation, differently than in CH_4, influences highly the TCS below 0.4 eV. Mann and Linder (1992b) and also Curtis *et al.* (1988) indicated the importance of the ν_3 (asymmetric stretch), optically allowed vibrational mode. Mann and Linder proved also a good agreement between excitation functions for infrared-active modes at different angles and the Born approximation, up to a few eV energy. Therefore, we applied the Born approximation (part I, eq. (15)) to the ν_3 excitation at low energies: the ν_3 cross-section amounts to about 70% of the TCS at 0.5 eV. We note however that vibrational-excitation CS for ν_3 and ν_4 (asymmetric deformation) modes as derived from swarm data by Curtis *et al.* would exceed Born values and exhibit near-to-threshold structures, similar to those observed experimentally, for example, in HCl (see subsect. **3**.5 in part II).

The ν_3 excitation function at 90° shows a large, structureless maximum centered at about 10 eV (Boesten *et al.* 1992). In the region of the maximum of TCS at 9 eV, the ν_3 vibrational excitation is the dominant channel for the resonant decay, with cross-section amounting to about $5 \cdot 10^{-20}$ m^2 (Mann and Linder 1992b, Boesten *et al.* 1992). Only the $2\nu_3$ and barely $3\nu_3$ overtones were observed at 8 eV, indicating a short lifetime of the resonant state (Boesten *et al.*). The overall vibrational excitation, as estimated roughly in the present work by integrating the angular spectra of Boesten *et al.* (in agreement with Mann and Linder 1992b), contributes to about 1/3 of the TCS at 8 eV, see a point with error bar in fig. 7.

Compared to CH_4, the vibrational excitation in CF_4 is more pronounced, both for direct (near-to-threshold) and resonant scattering, see fig. 7. This difference reflects the molecular structure, *i.e.* higher values of transient dipole moments for CF_4 than for CH_4 (Bishop and Cheung 1982).

Electronic excitation. Energy-loss spectra have been reported for valence excitations by Harshbarger and Lassettre (1973) and King and McConkey (1978) at 500 eV collision energy, by Kuroki *et al.* (1992) at 200 eV, by Verhaart *et al.* (1978) and Curtis and Walker (1989) at 11–17 eV in a trapped-electron experiment; for inner shell excitations by Tronc *et al.* (1979) at 1.5 keV collision energy and by Letardi *et al.* (1987) at a constant final energy of 1.5 keV. Absolute oscillator strength for valence excitations have been given by King and McConkey (1978) and Zhang *et al.* (1989) and for inner shells excitations by Zhang *et al.* (1992). Photoabsorption CS below the ionization threshold reaches a maximum of $0.24 \cdot 10^{-20}$ m^2 at 13.5 eV (Zhang *et al.* 1989). Detailed momentum spectroscopy for valence electrons was performed by Leung and Brion (1984). We are not aware of measurements of electronic excitation CS; an indirect evaluation can be done using dissociation CS (see below).

Optical emission in a form of a large band in the 200–500 nm wavelength region, attributed to different dissociated fragments in excited states, has been observed in numerous works (van Sprang *et al.* 1978, Aarts 1985, Blanks and Becker 1987, Müller *et al.* 1992 and reference therein). The absolute CS at 100 eV for the overall emission feature between 200 and 560 nm was evaluated as $0.45 \cdot 10^{-20}$ m^2 (Müller *et al.* 1992).

Absolute values for emission from fluorine atoms produced in collisional dissociation at 200 eV electron impact energy have been given by Becker and collaborators (Roque *et al.* 1991, Blanks *et al.* 1987): $0.8 \cdot 10^{-20}$ m^2 for emission at 95.5 and 97.5 nm due to transitions into the ground state $(2p^4 3s)\ ^{2,4}P \rightarrow (2p^5)\ ^2P^0$ and about $4.0 \cdot 10^{-20}$ m^2 for emission in the spectral range 620–780 nm, due to transitions from the $3p$ excited manifold $(2p^4 3p) \rightarrow (2p^4 3s)\ ^{2,4}P^2$. In the CS given for this first transition the cascading contribution has been subtracted (Roque *et al.* 1991). Emission due to inner-shell excitation was studied by Glans *et al.* (1994).

Ionization cross-sections of Bruce and Bonham (1993) superseding those of Ma *et al.* (1992) and Bruce *et al.* (1992) agree within a few percent with the re-measured (Poll *et al.* 1992) cross-sections from the Innsbruck group (Stephan *et al.* 1985). The semiempirical results of Kim and collaborators from a binary-encounter-Bethe model (Nishimura *et al.* 1999, Kim and Rudd 1999) coincide with the measurements of Poll *et al.* (1992) and Bruce *et al.* (1992), if multiple ionization is included in the model. Some discrepancies regard energies above 100 eV, see fig. 7.

The newest measurements (Nishimura *et al.* 1999) are about 20% lower in the maximum than those of Poll *et al.* The binary-encounter model agrees perfectly with Nishimura *et al.*'s measurements, if no multiple ionization is allowed. Nishimura *et al.* argued that the difference between the binary-encounter-Bethe models with and without multiple ionization accounts for the dissociation into neutrals.

Similarly to SiH_4, the ionization in CF_4 has a dissociative character: no parent CF_4^+ stable ion has been observed in electron scattering (Mi *et al.* 1996) neither in photoionization (Colding *et al.* 1991). Two excited states of CF_4^+ with lifetimes of 16 and 180 ns were observed in the optical emission experiment of van Sprang *et al.* (1978). CF_3^+ is the prevailing stable ion, amounting to 2/3 of the total ionization. Yields for production of other single charged ions (CF_2^+, CF^+, F^+, C^+) are one order of magnitude smaller (Bruce and Bonham 1993, Poll *et al.* 1992).

From optical emission measurements at 100 eV (Müller *et al.* 1992, Blanks and Becker 1987, van Sprang 1978) it follows that more than 15% of CF_3^+ ions are created in excited states. Also other debris fragments, like F atoms, are produced in excited states (van der Burgt 1991, Blanks *et al.* 1987) or with high recoil energies. About 6% of the ionization events leads to simultaneous production of two ions (Bruce *et al.* 1992, 1994).

Detailed sets of partial ionization, dissociation into neutrals and dissociative attachment CS were given by Bonham (1994).

Dissociation CS (dissociative ionization + neutrals) was measured by Winters and Inokuti (1982) up to 500 eV. Dissociation into neutrals can be evaluated from the difference between these measurements and the ionization CS. As numerous ionization CS determinations (Ma *et al.* 1991, Poll *et al.* 1992, Bruce and Bonham 1993) diverge above 200 eV, some indetermination regards also the dissociation CS. Dissociation into neutrals is an important scattering channel at energies below 100 eV. The difference between the data of Winters and Inokuti (1982) and those of Poll *et al.* (1992) amounts to $0.5 \cdot 10^{-20}$ m^2 at 30 eV.

Recently, several direct measurements of dissociation into neutrals have been performed. Nakano and Sugai (1992) and Sugai *et al.* (1995) studied selective ionization of radicals; Mi and Bonham (1998) measured DCS for scattered electrons in coincidence with ions; Motlagh and Moore (1998) used adsorption of radicals at tellurium surface. Bonham and Bruce (1992) in a semiempirical analysis reported $0.98 \cdot 10^{-20}$ m^2 at 80 eV. In direct measurements Mi and Bonham (1998) obtained $0.74 \cdot 10^{-20}$ m^2 at 35 eV. These values agree well with the determination of Motlagh and Moore and the recent analysis of Nishimura *et al.* (1999), see fig. 7. Bigger discrepancies exist above 100 eV.

The measurements of Sugai *et al.* (1995) indicate at 120 eV a dissociation-into-neutrals CS as low as $0.11 \cdot 10^{-20}$ m^2. According to these data the CF_3 radical is the dominating neutral fragment, exceeding both CF_2 and CF yields by almost two folds. Sugai *et al.* normalized their data using the ionization CS for radicals of Tarnovsky and Becker (1993). Nakano and Sugai (1992) using a different normalization, to the N_2 dissociation, reported higher CS, $0.73 \cdot 10^{-20}$ m^2 at 120 eV. This value is in good agreement with measurements of Motlagh and Moore (1998). On the other hand, the data of Nakano and Sugai seem to be underestimated below 100 eV, being much lower than the determination done by Winters and Inokuti (1982).

The recent analysis of Nishimura *et al.* (1999) using their ionization CS and measurements of Winters and Inokuti (1982) agrees very well in shape with the data of Motlagh and Moore (1998) but is lower by a factor of two, exactly. Dissociation into neutrals (Mi and Bonham 1998) amounts to 3.5% of the TCS (Szmytkowski *et al.* 1992) at 35 eV.

Metastables relative yields for collision energies up to 400 eV have been studied in a time-of-flight experiment by van der Burgt and McConkey (1991). Thresholds for several fragmentation processes have been established; the majority of them have been attributed to formation of F atoms in different excited states. No cross-sections have been reported.

Electron attachment. A broad peak for negative-ions formation is centered at about 7.5 eV (Harland and Franklin 1974, Spyrou *et al.* 1983, Curtis and Walker 1989, Weik and Illenberger 1995). Different measurements agree well. The F^-, CF_3^- and F_2^- yields amount, respectively, to 78%, 20% and 2% of the total dissociative attachment CS (Iga *et al.* 1992). Note, however, a different partitioning (50% for CF_3^- and F^-, each) reported by Spyrou *et al.* (1983). The positions of different negative ion peaks move from 6.8 eV for F_2^- to 7.8 eV for CF_3^- (Iga *et al.* 1992). In its maximum the dissociation attachment CS (Iga *et al.* 1992) constitutes only about $8 \cdot 10^{-4}$ of TCS.

Analysis of the angular distributions for each ion species (Le Coat *et al.* 1994) and their kinetic energies (Le Coat *et al.* 1997) indicates that more than one resonance state can be involved in the dissociative attachment between 6 and 12 eV. The parent CF_4^- anion is metastable (see the calculation of Gultsev and Adamowicz 1995) and was observed in electron scattering on CF_4 clusters (Lotter *et al.* 1989).

Resonances. The attribution of the resonant structures observed in vibrational and dissociation CS is not clear as the agreement with theory (Tossel and Davenport 1984, Huo 1988, Winstead *et al.* 1993, Natalense *et al.* 1995, Gianturco *et al.* 1996) is rather poor. The 8 eV broad structure visible in all studied channels has been attributed (Boesten *et al.* 1982) to the T_2 $(l = 1)$ shape resonance. However, Le Coat *et al.* (1994) in their analysis of the angular distribution for negative-ions production indicate two overlapping resonances, a shape one with ${}^2T_2$ symmetry and a Feshbach one, with ${}^2T_1$ symmetry, placed, respectively, at about 6.5 and 7.7 eV. This attribution was confirmed by successive measurements (Le Coat *et al.* 1997) on kinetic energies of F^- fragments.

At about 20–25 eV another, broad maximum is visible in total (Szmytkowski *et al.* 1992), elastic and vibrational (Boesten *et al.* 1982) CS. It has been attributed to the T_2 $(l = 2)$ resonance (Boesten *et al.* 1982).

There is some uncertainty on the existence of a weak resonance at about 0.3 eV. A local maximum was visible in the relative TCS measurements of Field *et al.* (1984). Similarly, the ν_3 vibrational excitations derived from swarm data by Curtis *et al.* (1988) exhibit a peak, above the Born's value (formula (15), part I). This resonance was tentatively attributed to a Rydberg state by Verhaart *et al.* (1978) on the basis of the vibrational structure visible in negative-ions yield.

A sum check performed at selected energies is presented in table V. At very low energies elastic data of Mann and Linder (1992a, b) are summed with ν_3 and ν_4 excitation evaluated from Born approximation (formula (15), part I, with dipole transition moments after Bishop and Cheung 1982). At 1.5 eV and above, the elastic CS of Boesten *et al.* (1992) were used. At 0.16 eV and between 0.4 and 5 eV the summed CS exceed

TABLE V. – *Integral cross-sections for electron scattering on* CF_4.

Energy (eV)	Elastic	Vibrational	Dissociation	Ionization	Sum	Total
0.16	0.62 M	0.44 B			1.06	0.675 F
0.20	0.60 M	5.1 B			5.7	6.1 F
0.40	1.58 M	8.6 B			10.2	8.8 Sz
1.5	7.74 Bo	4.6 B			12.3	10.1 Sz
3.0	10.5 Bo	2.9 B			13.4	12.6 Sz
5.0	12.7 Bo	2.0 B			14.7	13.5 Sz
8.0	13.9 Bo	6.0 M			19.9	20.0 Sz
15	16.9 Bo	0.8**			17.7	17.9 Sz
20	17.63* Bo	0.7**	1.0** W	(0.31 P)	19.3	19.3 Sz
30	17.0 Bo	0.5**	2.5 W	(2.01 P)	20.0	20.4 Sz
50	15.5 S		4.3 W	(4.22 P)	19.8	20.1 Sz
100	12.2 S		5.55 W (1.12 MM)	(5.82 P)	17.8	18.0 Z
150	10.8 S		5.51 W	(5.82 P)	16.3	16.3 Z
200	8.56 S		5.32 W	(5.17 Br)	13.9	14.4 Z
300	6.46 S		4.72 W	(4.66 Br)	11.2	11.6 Z
500	4.68 S		3.78 W	(3.98 Br)	8.46	8.47 Z

* Interpolated data
** Extrapolated data
( ) Not included in summation
B - Born approximation (present work) for ν_3 and ν_4, with dipole transition moments from Bishop and Cheung (1982)
Bo - Bosten *et al.* (1982)
Br - Bruce and Bonham (1993)
F - Field *et al.* (1984), normalized (this work) to Szmytkowski *et al.* (1992) at 0.4 eV
M - Summed vibrational excitations (Mann and Linder 1992b), integrated in this work
MM - Motlagh and Moore (1998), dissociation into neutrals
P - Poll *et al.* (1992)
S - Sakae *et al.* (1989)
Sz - Szmytkowski *et al.* (1992)
W - Winters and Inokuti (1982), total dissociation
Z - Zecca *et al.* (1992)

the total one. This discrepancy can be due to two reasons. The first one is a possible overestimation of the vibrational CS by the Born approximation, as was indicated by measurements of Mann and Linder (1992b) at large angles. The second reason is that, at very low energies, different factors can introduce systematic errors to TCS measurements. At the resonance position (8 eV) the elastic CS of Boesten *et al.* (1992) sums up very well with the vibrational excitation (Mann and Linder 1992b, integrated in the present work) to the TCS value (Szmytkowski *et al.* 1992).

At high energies we summed the dissociation data of Winters and Inokuti (1982) with the elastic CS of Boesten *et al.* (1992) at 20 and 30 eV and Sakae *et al.* (1989) above 50 eV. Agreement of the summed CS with the measured absolute TCS is excellent. Therefore, we suppose that the ionization CS of Poll *et al.* (1992) and Bruce and Bonham (1993) are probably slightly overestimated. According to Motlagh and Moore (1998), the dissociation into neutrals, occurring via the electronic excitation would constitute 5% of TCS (Szmytkowski *et al.* 1992) at 100 eV. This is a similar amount as the electronic excitation CS contribution in CH_4 (see subsect. **2**.1 in part II).

Comparison with CH_4. The CF_4 molecule, due to its symmetry and zero dipole moment, for some aspects resembles the CH_4 molecule. The elastic CS of the two molecules are similar, with a well-pronounced Ramsauer-Townsend minimum. Differently to CH_4, however, the CF_4 total cross-section is highly influenced by vibrational excitations of infrared-active modes both at low energies and in the region of the 8 eV resonance. This difference reflects the molecular structure, *i.e.* high values of transient dipole moments for the CF_4 molecule.

Another difference regards the partitioning between ionization and total CS; it is more marked in CH_4 than in CF_4 (at 500 eV 55% for the CH_4 molecule compared to 45% for CF_4). A similar effect for other hydrocarbons and perfluoro compounds was noticed by Gee and Freeman (1990). The different thresholds for ionization (12.6 eV for CH_4 and 16.9 eV for CF_4) reflect the electronegativity of the outermost atom (0.75 eV for H and 3.4 eV for F). The high energies of dissociated fragments in CF_4 (Bruce *et al.* 1994, van Burgt and McConkey 1991) are probably due to the big difference (ΔE) between the energies of the dissociation and ionization thresholds: $\Delta E = 10.3$ eV for CF_4 (Nakano and Sugai 1992) compared with $\Delta E = 1.2$ eV for CH_4.

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3˙2. *Chlorofluoromethanes (*CF_3Cl, CF_2Cl_2, $CFCl_3$*) and* CCl_4. – Chlorofluoromethanes are widely used in the semiconductor industry for plasma etching and passivation. The CCl_4 and $CFCl_3$ molecules attach electrons at very low energies and are used in electrical switches. All four gases possess strong absorption bands in the infrared and therefore are active as greenhouse gases. Furthermore, they are very stable and this leads to long permanence times in the atmosphere. The role of chlorine-containing gases in the stratospheric ozone destruction is also generally acknowledged (Eckman *et al.* 1987).

The cross-sections and transport coefficients for CF_2Cl_2 and CCl_4 have been reviewed by Novak and Fréchette (1985) and Hayashi (1987). For CF_2Cl_2 an extensive review of total, partial cross-sections and swarm coefficients, containing recommended values, was performed by Christophorou *et al.* (1997).

Total cross-sections for all chlorofluoromethanes and CCl_4 have been measured between 0.5 eV and 50 eV by Jones (1986) using a time-of-flight apparatus and between 80 eV and 4000 eV by Zecca *et al.* (1992) using a Ramsauer-type transmission setup. A linear transmission method with an electrostatic energy selector has been used by Szmytkowski *et al.* (1992) to measure CCl_4 total cross-sections between 0.5 eV and 200 eV. A trochoidal spectrometer has been used between 0.2 and 12 eV by Underwood-Lemons *et al.* (1994) for CF_3Cl and CF_2Cl_2 and by Wan *et al.* (1991) for CCl_4. Cross-sections for scattering into a backward cone for CF_3Cl, CF_2Cl_2, $CFCl_3$ and CCl_4 have been measured by Randell *et al.* (1993). TCS for CF_3Cl, CF_2Cl_2, $CFCl_3$ and CCl_4 are presented in figs. 8–11, respectively. TCS values of Jones (1986) for all four gases and CF_4 up to 20 eV are compared in fig. 12.

As stated by Jones (1986), his measurements at energies above 20 eV suffered from a systematic error due to scattering on the exit apertures; this effect tends to lower the measured cross-sections. For this reason the data reported in figs. 8–12 have been corrected by an energy-dependent factor, according to the error limits given by Jones (1986). The applied correction was +7% at 50 eV descending smoothly to 0% at 4 eV. The corrected data merge well with the results of Zecca *et al.* (1992) at higher energies and almost coincide, in the case of CCl_4, with the measurements of Szmytkowski *et al.* (1992). Note that the recent, remeasured data of Hamada and Sueoka (1995) for CCl_4 are still slightly lower than Jones's and Szmytkowski *et al.*'s sets, although the difference (10% on the average) is smaller than in their previous experiment (Mori *et al.* 1985). The early measurements of Holst and Holtsmark (1931) for CCl_4 agree generally in shape but are lower than the recent results (Jones 1986, Szmytkowski *et al.* 1992). Holst and Holtsmark observed two maxima in TCS, at about 1 and 7 eV; for the second maximum the amplitude reported ($58 \cdot 10^{-20}$ m^2) is close to the recent determination $72.4 \cdot 10^{-20}$ m^2 (Szmytkowski *et al.* 1992). The theoretical work in CCl_4 of Natalense *et al.* (1995) reproduces the general shape of TCS but all calculated structures are shifted to higher energies.

At low energies the data of Wan *et al.* (1991) for CCl_4 agree well with the measurement of Jones (1986) and Szmytkowski *et al.* (1992). In their high-energy limit the data of Wan *et al.* are slightly energy shifted with respect to the other recent measurements. Underwood-Lemons *et al.* (1994) measured TCS for CF_3Cl, CF_2Cl_2 (and CF_3Br, CF_3I, CF_2Br_2). Their data agree very well in shape with the measurements of Jones (1986) and also in absolute values, if corrected by multiplicative factors of 1.25 for CF_3Cl and 1.33 for CF_2Cl_2. This discrepancy in Underwood-Lemons *et al.*'s measurements should be attributed to difficulties in determining the effective, energy-dependent scattering length in their trochoidal spectrometer (Wan *et al.* 1991).

Randell *et al.* (1993) using a magnetically confined beam obtained cross-sections for

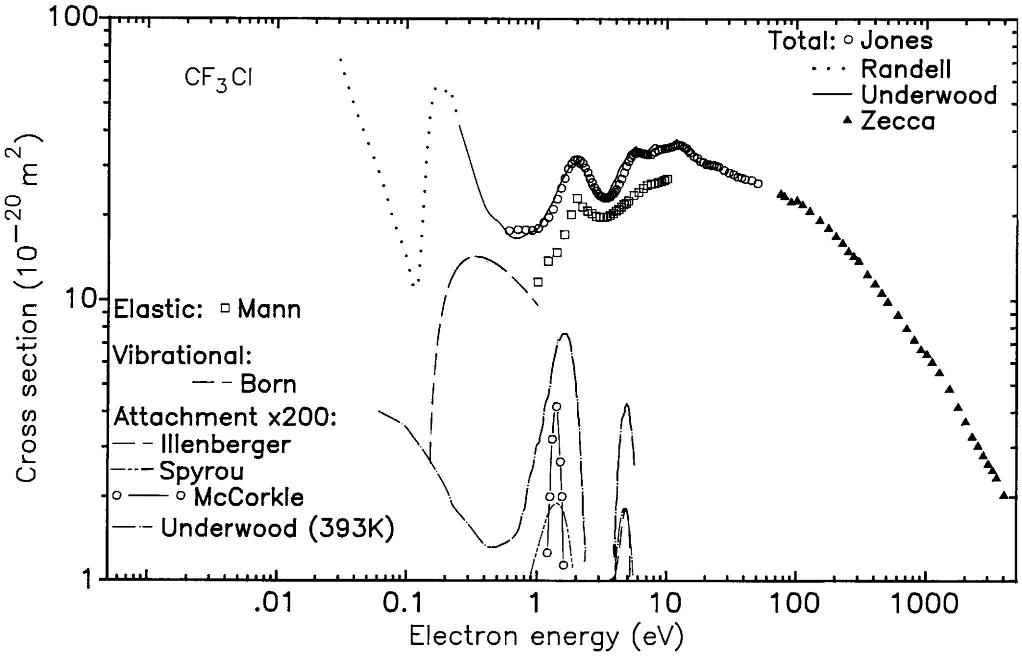

Fig. 8. – Integral cross-sections for electron scattering on CF_3Cl. *Total*: Jones (1986), absolute, corrected (this work: see text) for angular resolution; Underwood-Lemons *et al.* (1994) normalized (this work) by a factor of 1.25; Randell *et al.* (1993), backward scattering, normalized (this work) to Underwood-Lemons *et al.* (1994); Zecca *et al.* (1992), absolute. *Elastic*: Mann and Linder (1992a). *Vibrational*: Born approximation (eq. (15), part I), present work. *Electron attachment:* Spyrou and Christophorou (1985), beam, absolute; Illenberger (1979), beam normalized (this work) to Spyrou and Christophorou (1985) at 4.8 eV; McCorkle *et al.* (1980), swarm; Underwood-Lemons *et al.* (1995), beam, at 393 K.

"backward scattering" in the three chlorofluoromethanes and CCl_4 at very low energies. They normalized the relative data in CF_3Cl and CF_2Cl_2 at 10 meV to the rovibrational excitation CS obtained in the Born approximation (eqs. (14) and (15), part I) and the data in $CFCl_3$ and CCl_4 to the theoretical electron attachment CS obtained assuming an s-wave scattering (Klots 1976). In figs. 8–11 we present the results of Randell normalized to the lowest-energy points of Underwood-Lemons *et al.* (1994) for CF_3Cl and CF_2Cl_2, Jones (1986) for $CFCl_3$ and Wan *et al.* (1991) for CCl_4. Only in the case of CF_3Cl the normalization done by Randell *et al.* has to be corrected by as much as a factor of ten.

Normalized data of Randell *et al.* match pretty well in shape with the measurements by Wan and collaborators (Wan *et al.* 1991, Underwood-Lemons *et al.* 1994) and indicate a sharp rise of TCS below 0.01 eV collision energy. For CF_3Cl and CF_2Cl_2 weak maxima in "backward scattering" CS at about 0.15 eV have been observed, in some correspondence of the maxima in vibrational CS, as evaluated from the Born approximation (see figs. 8, 9).

All four considered gases exhibit several maxima between 1 eV and 15 eV, see fig. 12 in which Jones' data are reported. The amplitude of the first of these peaks rises and shifts to lower energies going from CF_3Cl to $CFCl_3$ and CCl_4. Only for CF_2Cl_2 the first peak is located at an energy lower than that for CCl_4. The three chlorofluoromethanes

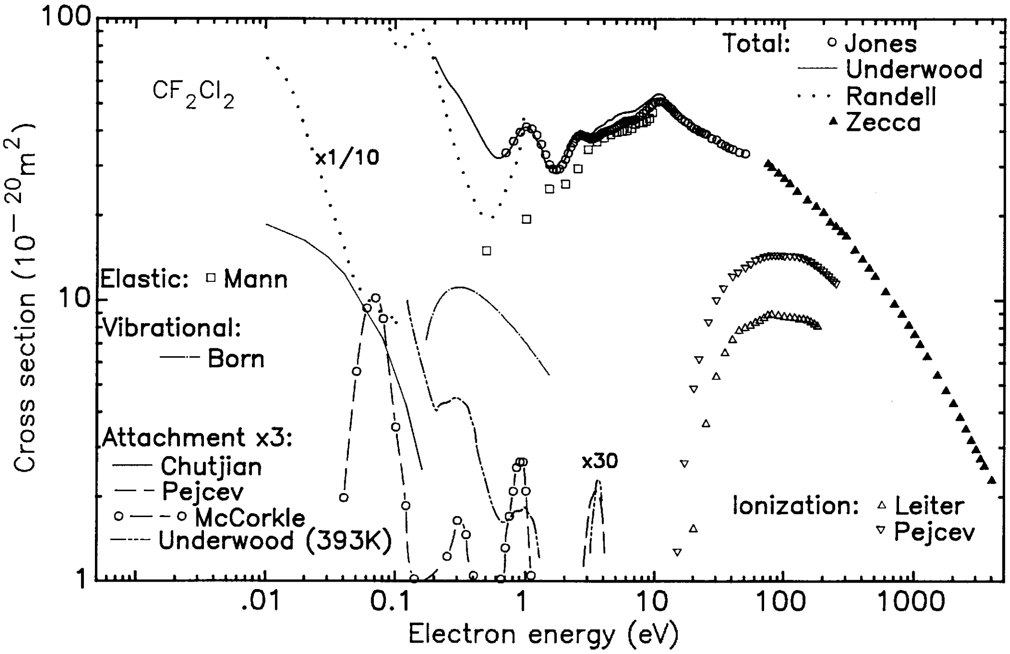

Fig. 9. – Integral cross-sections for electron scattering on CF_2Cl_2. *Total*: Jones (1986), absolute, corrected (this work: see text) for angular resolution; Underwood-Lemons *et al.* (1994), normalized (this work) by a factor of 1.33; Randell *et al.* (1993), backward scattering, normalized (this work) to Underwood-Lemons *et al.* at 0.2 eV; Zecca *et al.* (1992), absolute. *Elastic*: Mann and Linder (1992b). *Vibrational*: Born approximation (eq. (15), part I), present work. *Electron attachment:* Chutjian and Alajajian (1987), analytical formula from photoionization; McCorkle *et al.* (1980), swarm; Pejčev (1979), beam, absolute, low-energy data not shown due to a poor energy resolution; Underwood-Lemons *et al.* (1995), beam, at 393K. *Ionization:* Leiter *et al.* (1989), Pejčev *et al.* (1979).

CF_3Cl, CF_2Cl_2 and $CFCl_3$ exhibit another weak structure between 3.5–5.5 eV and a broad maximum at about 10 eV. Above 15 eV the TCS for CF_3Cl, CF_2Cl_2,$CFCl_3$ and CCl_4 follow, within the experimental error, the same functional dependence on energy (Zecca *et al.* 1992).

Elastic cross-sections for CF_3Cl, CF_2Cl_2 have been measured by Mann and Linder (1992a, b, respectively); the absolute CS scale has been defined by normalization to TCS values of Jones *et al.* (1986) at 4 eV and checked by relative-flow technique. Both for CF_2Cl_2 (Mann and Linder 1992b) and CF_3Cl (Mann and Linder 1992a) the elastic integral CS rises between 1 and 10 eV. For CF_3Cl a maximum has been evidenced at about 2 eV, in correspondence to the first maximum in the TCS. The DCS energy dependencies indicate the presence of a Ramsauer-Townsend minimum below 1 eV for both CF_3Cl and CF_2Cl_2 (Mann and Linder 1992a, b). The DCS for elastic scattering in CF_3Cl and CF_2Cl_2 at 2 eV are forward peaked, differently than in CF_4 (see fig. 13); this has to be attributed to the permanent dipole moments of CF_2Cl_2 and CF_3Cl. At 8 eV the DCS (fig. 13) for all three gases are forward peaked. One also notes a more complex angular dependence of DCS for CF_2Cl_2 than for CF_3Cl and CF_4, both at 2 eV as well as at 8 eV. We recall that CF_2Cl_2 has the lowest symmetry compared to the other

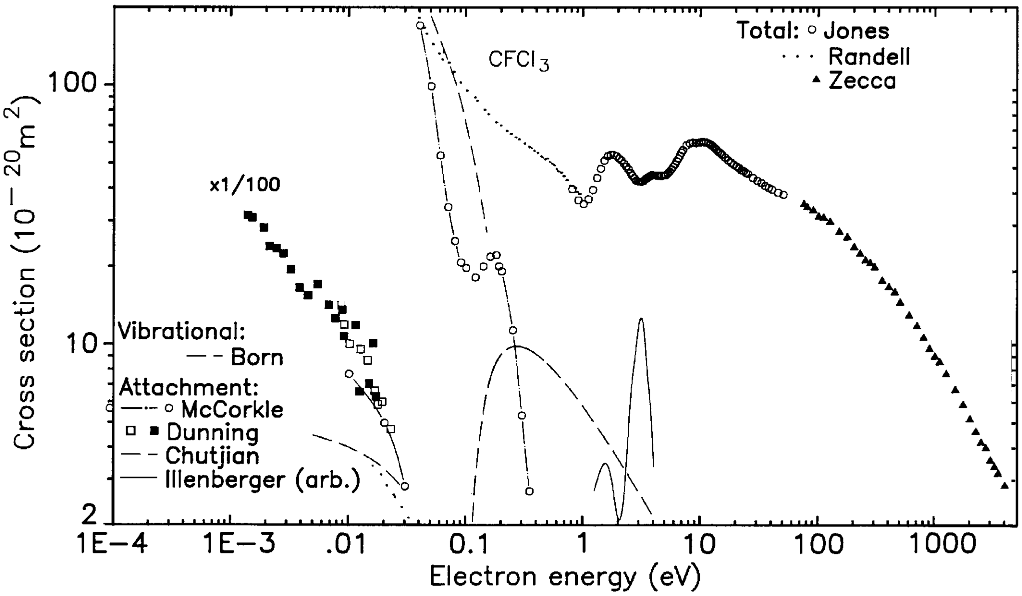

Fig. 10. – Integral cross-sections for electron scattering on $CFCl_3$. *Total*: Jones (1986), absolute, corrected (this work: see text) for angular resolution; Randell *et al.* (1993), backward scattering, normalized (present work) to Jones *et al.* at 0.8 eV; Zecca *et al.* (1992), absolute. *Vibrational*: Born approximation (eq. (15), part I), present work. *Electron attachment*: McCorkle *et al.* (1980, 1982), swarm; Zollars *et al.* (1984), open squares and Dunning (1987), filled squares, Rydberg atoms quenching; Chutjian *et al.* (1984), photoionization technique, analytical formula; Illenberger (1979), beam, arbitrary units.

chlorofluoromethanes. For this reason, CF_2Cl_2 could support more possible resonant states (Mann and Linder 1992b).

Elastic DCS of Daimon *et al.* (1983) for CCl_4 at 70 eV, 200 eV and 400 eV were normalized to the independent-atom-model calculation. In the present work the DCS of Daimon *et al.* have been extrapolated to 0° and then integrated. The comparison of these integral CS with the total (Szmytkowski *et al.* 1992, Zecca *et al.* 1992) and ionization (Leiter *et al.* 1984, 1989) CS suggests that the data of Daimon *et al.* are overestimated by more than a factor of two at 70 eV and by at least a factor of 1.5 at 200 eV. In fig. 11 we have reported these points multiplied by a 0.5 factor. The effects of multiple intermolecular scattering in CF_3Cl elastic DCS at 1 keV were studied by Meier *et al.* (1994).

Vibrational cross-sections have been measured by Mann and Linder (1992a) and (1992b) for CF_3Cl and CF_2Cl_2, respectively.

In CF_3Cl below 1 eV the vibrational excitation functions of the infrared active mode ν_1(CF_3 symmetric stretch) unresolved from the ν_4 mode (CF_3 asymmetric stretch) and of the ν_2 mode (CF_3 symmetric deformation) follow roughly the Born approximation (see Mann and Linder 1992a).

The resonant vibrational excitation evaluated as the difference between Jones' (1986) TCS and the elastic CS (Mann and Linder 1992a) shows three maxima: at about 1.7 eV, 5.5 eV and 8.5 eV. At 1.7 eV the symmetric C-Cl stretching mode ν_3 dominates over the ν_2. At 5.5 eV overtones up to the 6-th level of the $\nu_{1,4}$ unresolved mode are excited. At

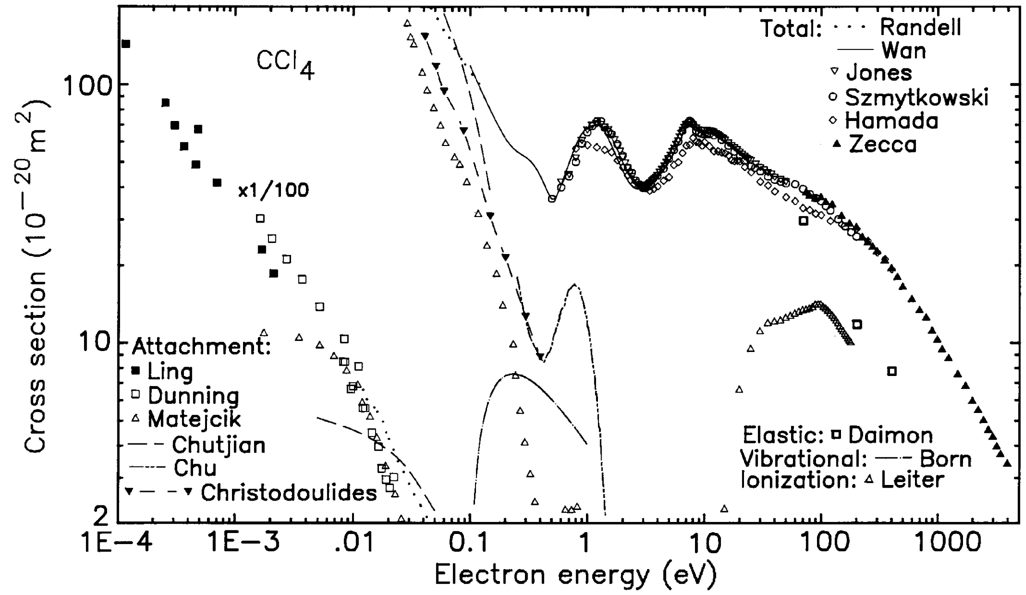

Fig. 11. – Integral cross-sections for electron scattering on CCl_4. *Total*: Randell *et al.* (1993), backward scattering normalized to attachment; Jones (1986), absolute, corrected (this work: see text) for angular resolution error; Wan *et al.* (1991), absolute; Hamada and Sueoka (1995), absolute; Szmytkowski *et al.* (1992), absolute; Zecca *et al.* (1992), absolute. *Elastic*: Daimon *et al.* (1983) rescaled (this work) by a factor of 0.5. *Vibrational*: Born approximation (eq. (15) part I), present work. *Ionization:* Leiter *et al.* (1984), normalized (this work, see text). *Electron attachment*: Ling *et al.* (1992) filled squares, Dunning (1987) and Zolters *et al.* (1984), open squares, Rydberg atoms quenching; Christodoulides and Christophorou (1971), swarm unfold; Chu and Burrow (1990), beam, normalized (present work) to swarm; Chutjian and Alajajian (1985), threshold photoionization, analytical formula; Matejcik *et al.* (1995), beam.

8.5 eV a very weak peak in the ν_2 excitation function is observed.

In CF_2Cl_2 (Mann and Linder 1992b) at energies below 1 eV, the ν_1 (CF_2 symmetric stretch) unresolved from the ν_6 (CF_2 asymmetric stretch) and the ν_8 (CCl_2 asymmetric stretch) infrared active modes are excited with similar intensities. At higher energies the difference between the total (Jones 1986) and the elastic (Mann and Linder 1992b) cross-section exceeds the values of the vibrational excitation evaluated through the Born approximation in the 1–10 eV energy range (Mann and Linder 1992b). In particular, this difference evidences indirect (resonant) vibrational excitation peaks centered at about 1.0 eV and 2.5 eV, and weak large structures around 4 eV and 6 eV. At 1.0 eV the ν_3 (CCl_2 symmetric stretch) and at 4.0 eV the $\nu_{1,6}$ modes prevail. At the 1 eV resonance the vibrational excitation contributes about 40% to the TCS.

For the three chlorofluoromethanes and CCl_4 we have reported in figs. 8–11 the vibrational excitation for infrared active modes as calculated by the Born approximation formula (eq. (15), part I), using transient dipole moments of Bishop and Cheung (1982).

Electronic excitation spectra for chlorofluoromethanes were reported by Verhaart *et al.* (1978) and for CCl_4 by Lee *et al.* (1975). King and McConkey (1978) gave absolute oscillator strength spectra in the region of valence and Rydberg transitions for $CFCl_3$, CF_2Cl_2 and CF_3Cl. Absolute oscillator strengths for excitations in the 7.5–200 eV energy

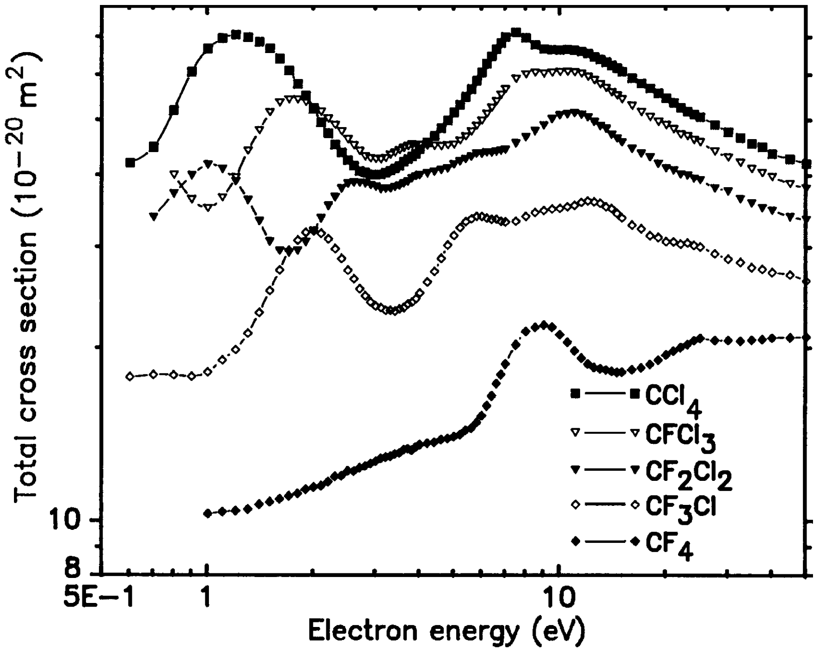

Fig. 12. – Comparison of total cross-sections at low energies for CF_4, CF_3Cl, CF_2Cl_2, $CFCl_3$ and CCl_4 (Jones 1986).

loss range have been given for CF_3Cl , CF_2Cl and $CFCl_3$ by Zhang *et al.* (1991a, 1991b, 1991c, respectively); for inner-shell excitations in all the five gases, CF_4-CCl_4, by Zhang *et al.* (1992); for valence-shell by Au *et al.* (1997). Oscillator strength for inner- and valence-shell excitation in CCl_4 has also been measured by Burton *et al.* (1994).

Optical emission from chlorofluoromethanes is dominated by the de-excitation of several molecular and atomic fragments. Absolute emission cross-sections in the 185–850 nm band for CF_3Cl, CF_2Cl_2, $CFCl_3$ were measured by van Sprang *et al.* (1978) and for CF_2Cl_2 by Jabbour and Becker (1989) and Martínez *et al.* (1992). At 100 eV the summed emission CS in the 670–780 nm region from excited F atoms diminishes with diminishing the number of fluorine atoms in the molecule: 3.3, 2.8, 2.2, $1.7 \cdot 10^{-22}$ m^2, for CF_4, CF_3Cl, CF_2Cl_2 and $CFCl_3$, respectively (van Sprang *et al.* 1978). In a complementary way the summed emission CS from chlorine atoms in various excited states rise: 3.7, 6.2, $9.2 \cdot 10^{-22}$ m^2 for CF_3Cl, CF_2Cl_2 and $CFCl_3$, respectively (van Sprang *et al.* 1978).

Cross-sections for vacuum ultraviolet emission from fluorine atoms transitions $(2p^4 3s)\ ^{2,4}P \rightarrow (2p^5)\ ^2P$ (95.5 and 97.5 nm wavelength) in CF_2Cl_2, SF_6, CF_4 and NF_3 were studied by Roque *et al.* (1991). The emission CS in CF_2Cl_2 compared to other fluorine-containing gases exhibits a more complex energy dependence. This indicates different molecular fragmentation patterns in CF_2Cl_2 than in the other gases.

The emission CS at 100 eV from CCl radicals amounts to $0.29 \cdot 10^{-22}$ m^2 (Jabbour and Becker 1989) for CF_2Cl_2 compared to $0.34 \cdot 10^{-22}$ m^2 for $CFCl_3$ and $0.86 \cdot 10^{-22}$ m^2 for CCl_4 (Kasukabe *et al.* 1993). Relative emission CS at 50–200 eV and lifetimes of excited molecular radicals in CF_2Cl_2 have been given by Martínez *et al.* (1992).

Ionization cross-sections have been measured by Märk and collaborators (Leiter *et*

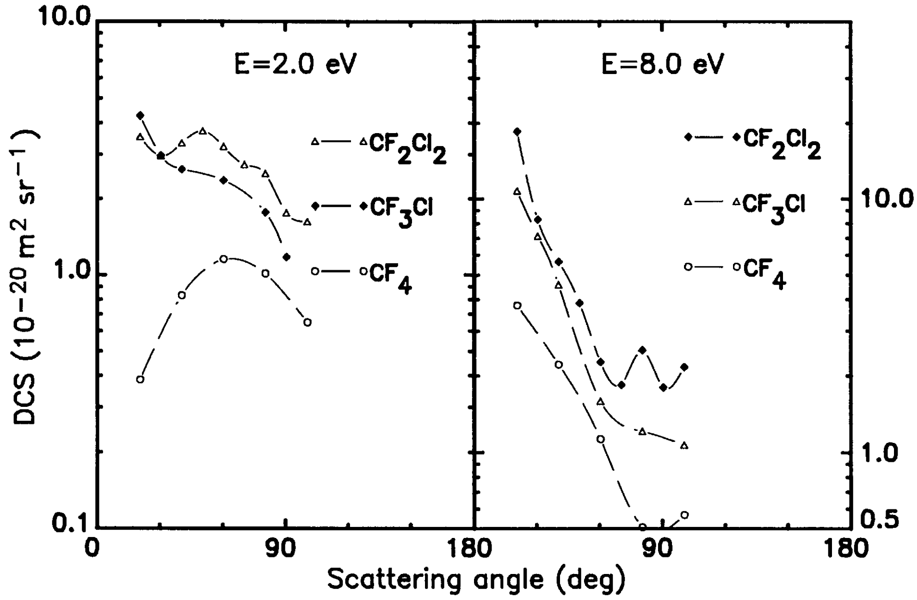

Fig. 13. – Differential cross-sections for elastic scattering on CF_4, CF_3Cl, CF_2Cl_2 at 2.0 and 8.0 eV. Experimental data from the measurements of Mann and Linder (see relevant subsections for references).

al. 1984 and 1989) for CCl_4 and CF_2Cl_2, respectively. As noticed recently (Leiter *et al.* 1989), the early measurements from this group suffered from an underestimation error due to the non-complete collection of ions. Therefore, we have corrected the early measurements for CCl_4 by an energy-dependent factor. The correction has been based on the comparison between old (Stephan *et al.* 1985) and new (Poll *et al.* (1992) measurements for CF_4. The corrected values of the ionization cross-section in CCl_4 are in good agreement with the results of Gryzinski's classical binary encounter approximation (see Leiter *et al.* 1984). The measurements of Pejčev *et al.* (1979) for CF_2Cl_2 are 40% higher than the renormalized results of Leiter *et al.* (1989).

If we adopt the corrected measurements of Leiter *et al.* (1984) different chloro- and fluoromethanes show a similar partitioning scheme: at 175 eV the ionization for CF_4, CF_2Cl_2 and CCl_4 constitutes about 35% of TCS (Zecca *et al.* 1992). This is significantly less than, for example, in methane (about 45%).

A number of different ions were observed for CF_2Cl_2 with CF_2Cl^+ and Cl^+ amounting to 52% and 12%, respectively (Leiter *et al.* 1989) at 100 eV. For CCl_4 the CCl_3^+ (73%) and CCl_2^+ (12%) ions dominate (Leiter *et al.* 1984).

Dissociation processes in CF_2Cl_2 and $CFCl_3$ have been studied by detection of metastables by Allcock and McConkey (1978) but no absolute cross-sections were given.

Dissociative attachment. Chlorofluoromethanes, and in particular CCl_4 and $CFCl_3$, due to their ability to attach electrons at zero collision energy, were subject to numerous investigations. In detail, they were studied by swarm techniques (Christodoulides and Christophorou 1971, Christophorou *et al.* 1971, McCorkle *et al.* 1980, Spyrou and Christophorou 1985, Orient *et al.* 1989, Wang *et al.* 1998), crossed beams (Spence and Schulz 1973, Verhaart *et al.* 1978, Pejčev *et al.* 1979, Illenberger *et al.* 1979, Olthoff *et al.* 1986, Chu and Burrow 1990, Wan *et al.* 1991, Kiendler *et al.* 1996, Hahndorf *et al.* 1994, Underwood-Lemons *et al.* 1995, Matejcik *et al.* 1995, Hahndorf and Illenberger 1997), rare-gas photoionization technique (Chutjian 1981, Chutjian *et al.* 1984, Chutjian and Alajajian 1985, Alajajian and Chutjian 1987, Chutjian and Alajajian 1987), flowing plasma afterglow (Smith *et al.* 1984, Smith and Španěl *et al.* 1994, Španěl *et al.* 1995), microwave radiolysis (Shimamori *et al.* 1992), and Rydberg atoms quenching (Foltz *et al.* 1977, Zollars *et al.* 1986, Harth *et al.* 1989, Ling *et al.* 1992, Popple *et al.* 1996, Finch *et al.* 1997). These techniques cover a wide energy range in a complementary manner: Rydberg atoms quenching the subthermal region (0.01 meV–1 meV, depending on the kind of Rydberg atoms chosen for detection), the photoionization up to 100 meV, swarms up to 1 eV.

Different methods yield, in general, congruent results for attachment coefficients, *i.e.* when the cross-section is averaged over an electron velocity distribution. However, detailed dependencies —both the absolute values and the positions of maxima in the attachment CS measured by different methods— show some discrepancies. A recent comparison for CF_2Cl_2, for example, was done by Wang *et al.* (1998). For this gas the photoionization method (Chutjian and Alajajian 1987) and a recent high-resolution beam experiment (Kiendler *et al.* 1996, Denifl *et al.* 1999) indicate a monotonic rise of the dissociative attachment CS in the zero-energy limit, while some beam and swarm experiments (Illenberger *et al.* 1979, McCorkle *et al.* 1980) show a near-to-zero-energy peak. Reviews of experimental methods have also been performed by Chutjian *et al.* (1996), for the Rydberg atoms quenching method by Dunning (1995), for beam techniques by Illenberger (1992), for flowing plasma afterglow by Smith and Španěl (1994).

Dissociative attachment coefficients (of about $3–4 \cdot 10^{-7}$ cm^3 s^{-1}) in CCl_4 and $CFCl_3$ at room temperature are two orders of magnitude higher than for CF_2Cl_2 (Smith *et al.* 1984, and references therein). These high values reflect the rise of the attachment CS towards zero collision energy. For example, at 40 meV collision energy the attachment CS amounts to 260, 220 and $3.3 \cdot 10^{-20}$ m^2 in CCl_4, $CFCl_3$ and CF_2Cl_2, respectively (Alajajian and Chutjian 1987 and references therein).

A slight decrease of the dissociative attachment coefficients with rising temperature was observed for CCl_4 (Smith *et al.* 1984, Orient *et al.* 1989) and a moderate rise for $CFCl_3$ (Spence and Schulz 1973, Smith *et al.* 1984). A sharp rise (more than 10 times between 300 and 500 K) was observed for CF_2Cl_2 (Smith *et al.* 1984, Wang *et al.* 1998) and a rise by about a factor of two for CF_3Cl (Spyrou and Christophorou 1985, Hahndorf *et al.* 1994).

For CCl_4, the measurements by the high-state Rydberg potassium atoms quenching (Dunning 1987, Ling *et al.* 1992) indicate, within the experimental error, the applicability of Wannier's (Vogt and Wannier 1954) threshold law $\sigma_{\text{att}}(E) \propto E^{-1/2}$ in the 0.01–1 meV energy range and Klots's (1976) simplified formula up to 10 meV. Dissociative attachment CS as high as $5 \cdot 10^{-16}$ m^2 have been reported at 0.01 meV (Ling *et al.* 1992). The lifetime of an intermediate CCl_4^{-*} excited ion has been evaluated to be 7.5 ps (Popple *et al.* 1996)

The data of Dunning and collaborators in CCl_4 (Foltz *et al.* 1977, Zollars *et al.* 1985, Dunning *et al.* 1987) merge well with the dissociative attachment CS at thermal energies obtained from high-resolution beam (Matejcik *et al.* 1995, 1997), threshold ionization (Orient *et al.* 1989, Chutjian and Alajajian 1985) and swarm unfolded data (Christodoulides and Christophorou 1971). A broad peak of about $3 \cdot 10^{-20}$ m^2 (Wan *et al.* 1991) for Cl^- ions was seen at 0.8 eV in beam (Olthoff *et al.* 1986, Chu and Burrow 1990, Oster *et al.* 1989) and swarm (Christodoulides and Christophorou 1971) experiments. A weak peak for the CCl_3^- formation was observed at 1.3 eV, while two peaks, at 1.7 and 6.0 eV were observed for the CCl_2^- ion (Oster *et al.* 1989).

In $CFCl_3$, similarly as in CCl_4, a sharp rise of the negative ion yield in the zero-energy limit was also observed (McCorkle *et al.* 1980, Illenberger *et al.* 1979, Alajajian and Chutjian 1987). The absolute values of dissociative attachment CS are close to those in CCl_4 (Zollars *et al.* 1984, Shimamori *et al.* 1992). At energies of a few meV the attachment CS approaches the theoretical limit for *s*-wave scattering (Chutjian 1981, Orient *et al.* 1989). Measurements of velocity and angular distribution of negative ions produced through electron transfer in collisions with velocity-selected potassium Rydberg atoms were done by Finch *et al.* (1997). The lifetime of the intermediate excited $CFCl_3^{-*}$ was established as about 3.5 ps.

A peak in $CFCl_3$ attachment CS of about $22 \cdot 10^{-20}$ m^2 was observed at 0.18 eV in a swarm experiment (McCorkle *et al.* 1980). Additional peaks, about three orders of magnitude weaker, were observed at 1.6 eV and 3.3 eV with Cl_2^- and F^- ions dominating, respectively (Illenberger *et al.* 1979, Oster *et al.* 1989).

In CF_2Cl_2 Pejčev *et al.* (1979) observed only a large structure at low energies, probably due to a limited energy resolution (200 meV) of their beam. McCorkle *et al.* (1980) in a swarm experiment evidenced three maxima: at 0.07, 0.30 and 0.95 eV. The latter two peaks agree roughly with the swarm-derived dissociative attachment CS of Christophorou *et al.* (1974), Petrović *et al.* (1989) and the beam experiment of Underwood-Lemons (1995) who noticed peaks at 0.2 eV and 1.1 eV. The near-to-zero peak of McCorkle *et al.* was observed in other experiments as a continuous rise of the CS with lowering energies. Kiendler *et al.* (1996) argued that the dissociative attachment CS at near-to-zero energies changes as $1/E$, indicating the *s*-wave character of electron capture. The rise in CF_2Cl_2 is less pronounced than in CCl_4 and CF_3Cl (Chutjian and Alajajian 1987, Christophorou *et al.* 1974). At high temperatures the zero-energy attachment CS rises, at the expense of the 0.2 eV peak (Underwood-Lemons *et al.* 1995, Kiendler *et al.* 1996, Hahndorf and Illenberger 1997). In fig. 9 we present measurements of Underwood-Lemons *et al.* at 393 K only.

At the 1 eV maximum the CF_2Cl_2 attachment CS amounts to about $0.9 \cdot 10^{-20}$ m^2 (see Illenberger *et al.* 1979 and references therein). A maximum, an order of magnitude weaker, was observed also at 3.0–3.5 eV (Pejčev *et al.* 1979, Verhaart *et al.* 1978, Underwood-Lemons *et al.* 1995, Oster *et al.* 1989). Many ions (Cl^-, F^-, $CFCl_2^-$, FCl^-, Cl_2^-) contribute to the dissociative attachment CS at this maximum.

In CF_3Cl two peaks at about 1.4 eV and 4.6 eV, with approximately the same intensity ($1 \cdot 10^{-22}$ m^2, Spyrou and Christophorou 1985) are observed in the total negative ion yield (McCorkle *et al.* 1980, Spyrou and Christophorou 1985, Underwood-Lemons 1995, Hahndorf *et al.* 1994). At 4.8 eV the Cl^- yield dominate (Illenberger *et al.* 1979); FCl^- and F^- ions were observed at about 4.0 eV (Oster *et al.* 1989, Hahndorf and Illenberger 1997). At high gas temperatures (800 K) a near-to-zero-energy peak in the Cl^- yield appears, due to the change in the reactivity mechanism from endothermic to exothermic (Hahndorf *et al.* 1994). The rise of gas temperature enhances and shifts the 1.4 eV peak towards lower energies (compare also with the classical approach of Lehr and Miller 1996).

Relative intensities for negative fragments in chlorofluoromethanes (CCl_4, $CFCl_3$, CF_2Cl_2, $CFCl_3$, CF_4) scale as 1000, 800, 50, 2, (0) for the Cl^- ion and as (0), 4, 6.5, 0.4, 10 for the F^- ion, respectively (Oster *et al.* 1989).

Resonances. Several shape resonances are visible in TCS between 1.0 and 10 eV for the considered molecules. The number of such resonances rises with lowering the symmetry of the target: two resonances for CCl_4, three for $CFCl_3$ and CF_3Cl and four for CF_2Cl_2, see also fig. 12. We note, furthermore, that the corresponding peaks in the TCS rise and move to lower energies when the total atomic mass of the molecule increases. A common feature of these resonances is that the maxima in the dissociative attachment CS are shifted, usually by 0.4–0.5 eV, towards lower energies compared to the maxima in total and/or vibrational excitation CS (see also Mann and Linder 1992a, b).

Some disagreement exists for molecular orbitals involved in the formation of resonant states at higher energies. A general accord exists on the fact that the C-Cl σ^* orbitals are involved in the lowest-energy resonances and that they are stabilized by a fluorine atom (Burrow *et al.* 1982). But higher resonances, located above 2 eV and assigned in vibrational excitation measurements on CF_3Cl and CF_2Cl_2 (Mann and Linder 1992a, b, respectively) to C-F σ^* orbitals, could be either of the π^* type or of a mixed type (Underwood-Lemons *et al.* 1994, 1995).

In CF_3Cl the existence of a low-energy resonance (or even two of them, one of a Rydberg and one of a valence type) in the 0–2eV region was claimed by Verhaart *et al.* (1978) in their electron transmission experiment. A peak at 1.4 eV observed in the electron attachment (Verhaart *et al.* 1978, McCorkle *et al.* 1980) is shifted by -0.5 eV compared to the maximum in TCS (Jones 1986) and in the vibrational CS (Mann and Linder 1992a). The A_1 (C-Cl σ^*) character of this resonance (Underwood-Lemons 1994) leads to the excitation of the C-Cl symmetric stretching vibrations (Mann and Linder 1992a) and to the Cl^- ions production (Illenberger *et al.* 1979).

In CF_3Cl the attribution of the resonance at 5.5 eV, with the E symmetry (Mann and Linder 1992a) to a specific molecular orbital (C-F σ^*, Cl $3p$ or C-Cl π^*) is not clear (see Underwood- Lemons *et al.* 1994 and 1995). We recall that numerous types of ionic fragments appear between 3.9 eV and 4.8 eV (Illenberger *et al.* 1979). Similarly, the 8.5 eV peak in TCS, attributed to the A_1-symmetry resonance, can involve either the C-F σ^*-orbital, as suggested by vibrational excitation studies (Mann and Linder 1992), or the C-F π^*-orbital as suggested by the calculations of Underwood-Lemons *et al.* (1994).

In CF_2Cl_2 the studies of electron attachment (Illenberger 1979, 1982, 1992), electron transmission spectra (Verhaart *et al.* 1978, Burrow *et al.* 1982) and vibrational excitation (Mann and Linder 1986b) allow to evidence four valence-excited resonances of the A_1 (C-Cl σ^*), B_2 (C-Cl σ^*), A_1(C-F σ^*) and B_1(C-F σ^*) type at energies, respectively, 1.0 eV, 2.5 eV, 4 eV and about 6 eV (Mann and Linder 1992). The B_2 resonance, visible in the vibrational excitation channel (Mann and Linder 1992b), apparently does not lead to the production of negative ions. We note that the theoretical assignment (Underwood-Lemons *et al.* 1995) of intermediate B_2 and A_1 resonances to the π^*-type orbitals differs from that of Mann and Linder (1992 a and b).

For $CFCl_3$ three maxima are observed in TCS, at 1.7 eV, 4 eV and 8 eV (Jones 1986). The calculations of Burrow *et al.* (1982) suggest that the peak at 1.7 eV in the TCS (and at 1.5 eV in the electron attachment CS) is associated with the occupation of the e (C-Cl σ^*) orbital while the 4.0 eV peak is associated with the a_1 (C-F σ^*) orbital. In comparison to the lighter molecule CF_3Cl the analogous resonances in $CFCl_3$ are shifted towards lower energies.

In CCl_4 only two maxima are observed in TCS, at 1.2 eV and 7.5 eV (Jones 1996), *i.e.* lower in energy than the corresponding structures in $CFCl_3$. The 1.2 eV maximum has a negative-ion precursor at 0.8 eV (Chu and Burrow 1990).

Sum check. Due to the lack of absolute measurements of partial CS no sum check is possible for chlorofluoromethanes. Several measurements at low energies are not absolute and require the use of normalization procedures.

The measurements of Wan *et al.* (1988) for CCl_4 and of Underwood-Lemon *et al.* (1994)

for CF_3Cl and CF_2Cl_2 indicate the rise of TCS at energies below 0.5 eV. For CF_3Cl and CF_2Cl_2 this rise could point out towards the existence of a Ramsauer-Townsend minimum, as indicated also by energy spectra in the differential DCS measurements (Mann and Linder 1992a, b). Additional peaks below 1 eV were observed for both gases in a magnetically-guided-beam experiment (Randell *et al.* 1993), see figs. 8 and 9. However, we are not able to attribute any partial process to these peaks.

For $CFCl_3$ and CCl_4 the sharp rise in TCS is due to the contribution of the electron attachment. In CCl_4 a good merging between the normalized TCS of Randell *et al.* (1993) and recent electron attachment CS both at 0.01 eV (Ling *et al.* 1992, Dunning 1987, Matejcik *et al.* 1995), as well as at 0.05 eV (Chutjian and Alajajian 1985) has to be noticed. These, as well as swarm experiments (Christodoulides and Christophorou 1971), indicate that the energy dependence of the electron attachment CS changes from $E^{-1/2}$ in the zero-energy limit to E^{-1} at energies above 0.1 eV. However, some differences in absolute magnitudes, probably caused by specific normalization procedures applied in the evaluation of attachment coefficients (see Spanel *et al.* 1995), still exist, see figs. 10 and 11.

For $CFCl_3$ the agreement between normalized TCS (Randell *et al.* 1993) and electron attachment CS (McCorkle *et al.* 1982, Zollars *et al.* 1984, Dunning 1987) is poor. A small (5 meV) energy shift in TCS measurements would explain the difference between the two data sets.

At energies of the order of 100 eV the sum check in CCl_4 indicates an incoherence between the elastic CS of Daimon *et al.* (1984) normalized to the independent-atoms model and the TCS (Szmytkowski *et al.* 1992, Zecca *et al.* 1992). Intermediate-energy absolute partial CS measurements would be of interest for all the gases considered here.

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3˙3. *Methyl halides* ($CH_3F, CH_3Cl, CH_3Br, CH_3I$) *and other halomethanes.* – In this subsection other derivatives of methane will be discussed. In particular, relatively more electron scattering measurements and calculations were performed for the methyl halides CH_3X, fluoromethanes CH_nF_{4-n} and chloromethanes CH_nF_{4-n}, with n=1–3 (CH_4, CF_4 and CCl_4 have been discussed before) than for other halomethanes. We will present these three groups of gases together. Some of the most significant results in other halomethanes will also be mentioned. At the end of this subsection, a few works on other methyl compounds (like CH_3OH) are quoted. For the lack of data no sum check neither separate presentation of partial CS is done for all these gases. Instead, we present in somewhat more detailed way comparative measurements of partial processes. In fig. 14 the total cross-sections for four methyl halides CH_3X (X = F, Cl, Br, I) are compared in the energy range up to 20 eV. In tables VI and VII some information on electron attachment in selected halomethanes is compiled.

The four methyl halide molecules possess high dipole moments of about 1.8 D. In the series (CH_3F, CH_3Cl, CH_3Br, CH_3I) the C-H bond length remains constant (1.1 Å), while the C-halogen atom bond length rises. Chloromethanes play an important role in atmospheric chemistry (Wallington *et al.* 1996). Electron interactions with trifluoromethane CHF_3 have recently been reviewed by Christophorou *et al.* (1997).

Total cross-sections for methyl halides have been measured by the Gdańsk group (Szmytkowski and Krzysztofowicz 1993 for CH_3I, Krzysztofowicz and Szmytkowski 1994 for CH_3Br, Krzysztofowicz and Szmytkowski 1995 for CH_3F, CH_3Cl) in the 0.5–200 eV region using a linear transmission method and by the Maryland group (Benitez *et al.* 1988 —all the four molecules— and Wan *et al.* 1991 for CH_3Cl) in the 0.5–7.5 eV region using a trochoidal spectrometer. The measurements from the two groups agree generally in shape but not in the absolute values: the difference is especially serious for CH_3Cl: at 7.5 eV the data of Benitez *et al.* is 30% lower than that of Krzysztofowicz and Szmytkowski (1995). On the other hand, the measurements of Krzysztofowicz and Szmytkowski in their high-energy limit, 75–200 eV, are 20% lower than the results of Karwasz *et al.* (1999). Also the

Table VI. – *Electron attachment cross-section in chloromethanes. Values of maxima in the dissociative attachment cross-section (in* 10^{-20} m^2*) from beam measurements of Burrow and collaborators. In square parentheses the energies of the peaks (in* eV*).*

Compound	Zero-energy *	Second maximum	Feshbach resonance
CH_3Cl	* *	$2.0 \cdot 10^{-5}$ [0.8] P	$4.9 \cdot 10^{-4}$ [7.4] P
CH_2Cl_2	$8.9 \cdot 10^{-3}$ C	$2.4 \cdot 10^{-2}$ [0.48] C	
$CHCl_3$	4.7 C	3.7 [0.27] C	
CCl_4	$1.3 \cdot 10^{2}$ C	1.9 [0.80] C	

* The zero-energy peak is convoluted with the electron-beam energy-distribution of the experiment

** A signal observed in experiments of Chu and Burrow (1990) was due to impurities (Pearl and Burrow 1993)

C - Chu and Burrow (1990)
P - Pearl and Burrow (1993)

TABLE VII. – *Electron attachment cross-sections (a) and electron attachment rate coefficients (b, c) in some halocarbons and* SF_6*. (a) Near-to-zero-energy dissociative attachment cross-sections (in* 10^{-20} m^2*) from beam experiments. (b) Attachment rate coefficients (in* 10^{-7} cm^3 s^{-1}*) at* 300 K *from pulse radiolysis method. (c) Attachment rate coefficients at a mean electron energy of* 10 meV *(Rydberg* Xe *atoms with principal quantum number* $n = 37$*), in* 10^{-7} cm^3 s^{-1}*.*

Compound	a)	b)	c)
$CHCl_3$	7.2 M	0.02 Sb	
$CFCl_3$		1.8 Sb	5.8 F 6.5 D
CCl_4	$1.8 \cdot 10^3$ M $5.0 \cdot 10^3$ HO	4.0 Sb	4.0 F 7.0 D
CH_2Br_2		1.1 Sb	65 *L
CH_3I	$4.0 \cdot 10^3$ SC	1.2 Sa	4.4 H 20 *L
CF_3I		2.0 Sa	
1,1,1-$C_2Cl_2F_3$		1.1 Sb	6.0 D
SF_6		2.3 Sb	4.0 W 4.0 D

* The attribution of the total quenching rate to the electron attachment is not clear
D - Dunning (1987), several types of Rydberg atoms with $n \sim 100$
F - Foltz *et al.* (1978), $n = 37$
H - Hildebrandt *et al.* (1978), $n = 37$
HO - Hotop *et al.* (1995), CS at 1 meV
M - Matejcik *et al.* (1997), CS at 5 meV
L - Ling *et al.* (1993) potassium Rydberg atoms with $n = 400$ (about 80 μeV collision energy)
Sa - Shimamori *et al.* (1992a)
Sb- Shimamori *et al.* (1992b)
SC - Schramm *et al.* (1999), CS at 0.5 meV
W - West *et al.* (1976), $n = 38$

two sets of data from the Maryland laboratory for CH_3Cl (Benitez *et al.* 1988 and Wan *et al.* 1991) differ by about 15%. Probably, these discrepancies are related to experimental problems in the trochoidal apparatus.

The TCS of all the four methyl halides exhibit a maximum at about 6.5–7 eV, a minimum at about 2–4 eV and a rise in the low-energy limit. The absolute values of the TCS rise passing from CH_3F to CH_3I, see fig. 14.

The fall of TCS in methyl halides between 0.5 and 1 eV (Szmytkowski and Krzysztofowicz 1993, Krzysztofowicz and Szmytkowski 1994, 1995) has an energy dependence closer to $E^{-1/2}$ than to E^{-1} so that it cannot be attributed directly to scattering on a dipole moment (see Itikawa 1978, Norcross and Collins 1982). Also electron attachment does not seem to be the dominant process below 1 eV. For CH_3I, different evaluations (Alajajian *et al.* 1988, Schramm *et al.* 1999) give attachment CS values below $10 \cdot 10^{-20}$ m^2 at 0.1–0.5 eV, while the TCS measurement quoted a value of $96 \cdot 10^{-20}$ m^2 at 0.45 eV (Szmytkowski and Krzysztofowicz 1993).

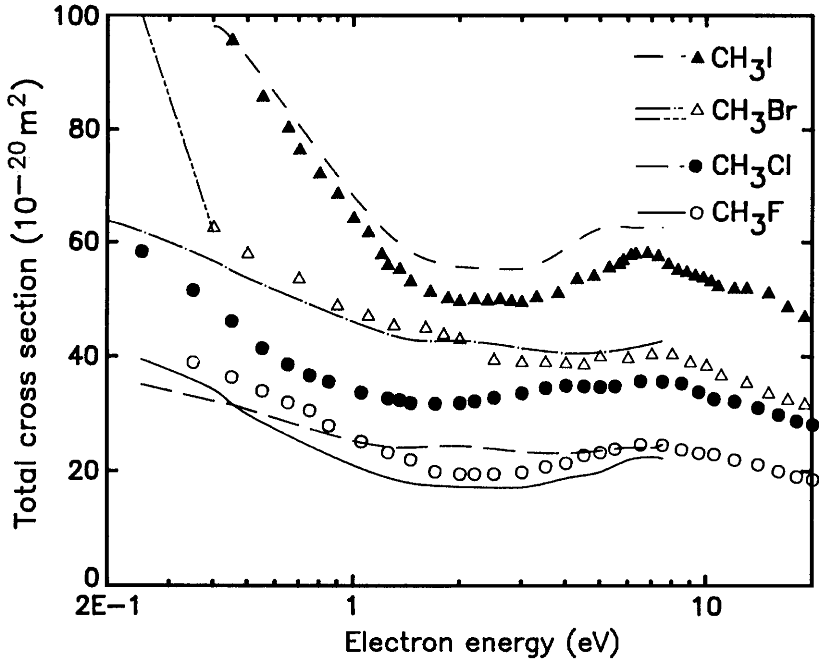

Fig. 14. – Total cross-sections for methyl halides: linear transmission technique (points), Szmytkowski and Krzysztofowicz (1993), CH_3I; Krzysztofowicz and Szmytkowski (1994); CH_3Br Krzysztofowicz and Szmytkowski (1995); CH_3Cl, CH_3F; trochoidal spectrometer (lines), Benitez *et al.* (1988); not shown measurements of Wan *et al.* (1991) for CH_3Cl from the same laboratory. Momentum transfer cross-section (analytical formula) of Petrović and Crompton (1988) for CH_3Br, dash-dot-dot line.

TCS in trifluoromethane (CHF_3) were measured by Sueoka *et al.* (1998) in the 0.7–600 eV range and by Sanabia *et al.* (1998) in a trochoidal spectrometer up to 20 eV. The TCS in CHF_3 exhibits analogies with both CH_4 and CF_4 (Sueoka *et al.* 1998): between 5 and 15 eV it coincides with the CH_4 measurements from the same laboratory and shows another large hump between 20 eV and 30 eV, similar to that in CF_4 (see subsect. **3**˙1 for references). Below 3 eV a sharp rise of the TCS has been observed, attributed to the "*s*-wave scattering" (Sanabia *et al.* 1998). The TCS in the 300–1000 eV energy range was measured in a linear transmission experiment by Iga *et al.* (1999).

TCS in chloromethanes CH_3Cl, CH_2Cl_2, $CHCl_3$ were studied by Holst and Holtsmark (1931) between 0.3 and 25 eV, by Wan *et al.* (1991) between 0.2 and 12 eV and by Karwasz *et al.* (1999) between 75 and 4000 eV. Measurements of Holst and Holtsmark indicated a shape of TCS in chloromethanes similar to that in chlorofluoromethanes, *i.e.* with several maxima between 1 and 10 eV (compare fig. 12). Two of these maxima in the measurements of Holst and Holtsmark are quite distinct for the whole CH_3Cl, CH_2Cl_2, $CHCl_3$, CCl_4 series. The positions of these maxima move to lower energies and their amplitudes rise on going from CH_3Cl to CCl_4. The first maximum moves from $13 \cdot 10^{-20}$ m^2 at about 3 eV to $31 \cdot 10^{-20}$ m^2 at 1.7 eV, and the second one from $26 \cdot 10^{-20}$ m^2 at 7.3 eV to $36.5 \cdot 10^{-20}$ m^2 at 6.2 eV, for CH_3Cl and $CHCl_3$, respectively. The amplitudes of the maxima in the measurements of Wan *et al.* are less pronounced; note that in C_6H_6

the high amplitudes of the structures seen by Holst and Holtsmark are not confirmed by more recent experiments. According to Wan *et al.* the TCS in CH_3Cl, CH_2Cl_2, $CHCl_3$ at 2–12 eV are comprised between $20 \cdot 10^{-20}$ m^2 and $40 \cdot 10^{-20}$ m^2. All these TCS exhibit a rise at low energies. Karwasz *et al.* (1999) in their high-energy measurements observed increasing values of TCS for the CH_4, CH_3Cl, CH_2Cl_2, $CHCl_3$, CCl_4 series. They indicated a scaling of TCS with the molecular polarizability at intermediate (close to 100 eV) energies and the applicability of the additivity rule for TCS in the 4000 eV energy limit.

TCS in other halomethanes (CF_3Br, CF_2Br_2, CF_3I) at 0.2–12 eV were studied by Underwood-Lemons *et al.* (1994).

Swarm experiments. The drift velocity in trifluoromethane CHF_3 at the reduced electrical field up to $3.69 \cdot 10^{-21}$ Vm^2 was measured by Christophorou *et al.* (1981) and up to $80 \cdot 10^{-21}$ Vm^2 by Wang *et al.* (1999). The drift velocity is a monotonically rising function of the reduced field amounting to $7.25 \cdot 10^6$ cm s^{-1} at $80 \cdot 10^{-21}$ Vm^2. The attachment coefficient in methyl chloride CH_3Cl and in methyl bromide CH_3Br up to the reduced fields of $6.2 \cdot 10^{-21}$ Vm^2 were measured in a swarm experiment by Datskos *et al.* (1990 and 1992, respectively). Diffusion and attachment coefficients for thermal electrons in CH_3Br were determined by Petrović and Crompton (1987).

Elastic scattering. Effects of fluorination in the CH_4, CH_3F, CH_2F_2, CHF_3, CF_4 fluoromethane series were studied by Tanaka *et al.* (1997). At 1.5 eV, the CH_4 and CF_4 elastic DCS are similar in shape (compare fig. 3 in part II and fig. 13 in the present subsect. **3**˙2) but scattering on intermediate fluoromethanes CH_3F, CH_2F_2, CHF_3 is forward centered, due to their permanent dipole moment. At 30 eV all the five targets show a minimum of the DCS at 100°–110°, but differently from CH_4 all the fluoromethanes show an additional shoulder at 60°. The amplitude of this latter structure rises with the number of fluorine atoms. Such "interference" effects in DCS, due to the presence of heavier atoms in the molecule, were observed, for instance, in the CO_2, OCS, CS_2 series (see fig. 18 in part II).

DCS for CH_2F_2 at 300, 400, 500 eV were measured by Bromberg (1975). Experimental differential and integral elastic CS for CHF_3 at 300–1000 eV were announced by Iga *et al.* (1999). Theoretical DCS for CHF_3 at 6.5–30 eV were given by Diniz *et al.* (1999); differential and integral CS for CH_2F_2 at 3–30 eV by Nishimura (1998); DCS for CH_3Cl at 0.5–8 eV by Rescigno *et al.* (1997).

Elastic scattering in CH_3Cl was examined between 0.5 and 9.5 eV by Shi *et al.* (1996). At energies up to 1 eV the elastic DCS follows the Born approximation as calculated for rotational excitation; at 3.2, 5.5 and 8 eV it exceeds the Born values, but is still forward centered. The DCS for 100° scattering angle shows a broad maximum at about 3.5 eV, the DCS at 30° shows a minimum at 3 eV and a rise up to the highest (9.5 eV) energy examined. At 8.0 eV and 90° scattering angle the CH_3Cl (Shi *et al.* 1996) and CH_4 (Boesten and Tanaka 1991) DCS are equal.

DCS at 90° in CH_2Cl_2 between 1.0–3.5 eV has been reported by Abouaf and Benoit (1990). The DCS shows a broad maximum at 1.5 eV and a slow fall between 2.5 and 3.5 eV.

DCS in CF_3I at 20°–120° angles, 1.5–60 eV were reported by Okamoto *et al.* (1999). As stated by these authors, the effects of scattering from F and C atoms are rather weak, while contribution from the I atom dominates the DCS. The DCS at all studied energies show a shallow minimum at 30°–50°, a clear hump around 90° and a sharp dip at 120°. The elastic DCS at 100° reaches its maximum value at 4–6 eV. A maximum in the vibrational excitation DCS at 60° for a 0.14 eV energy loss occurs at 5.5 eV and is preceded by a deep minimum at 3 eV.

Intermolecular interference effects in elastic scattering of 1–4 keV electrons on the oriented methyl halides CH_3Cl and CH_3Br were studied at Bielefeld (by Böwering *et al.* 1994, Meier *et al.* 1994 and Volkmer *et al.* 1997 and by Volkmer *et al.* 1992, 1996, respectively). Effects of halogenation on low-energy elastic scattering in CH_nF_{4-n}, CH_nCl_{4-n}, CF_nCl_{4-n}, with $n = 1, 2, 3$, were calculated by Natalense *et al.* (1999).

Vibrational excitation in CH_3Cl was examined by Shi *et al.* (1992, 1996). The excitation function at 100° scattering angle for the ν_3 vibrational mode (C-Cl stretch) shows a maximum at 3.2 eV; the excitation function for the ν_4 mode (CH stretch) shows a maximum at 5.5 eV (Shi *et al.* 1992). At 3.5 eV collision energy, apart from the ν_3 mode and its overtones, the ν_4 and ν_5 (CH_3 *d*-deform) modes with an intensity of about 0.2 times the ν_3 intensity and other modes with smaller intensity are visible (Shi *et al.* 1996). At 5.5 eV the intensity of the ν_4 mode amounts to 1.2 of the ν_3 intensity and the ν_1 (CH *s*-stretch), ν_5, ν_2 (CH_3 *s*-deform) and ν_6 (CH_3 rock) modes are excited with an intensity of about 0.7 of the ν_3 intensity. At 8.5 eV the intensity of the ν_2, ν_6 and ν_4 modes exceed the ν_3 intensity by more than three times and that of ν_1 and ν_5 exceeds it by almost two times. The DCS for the ν_3 mode at 3.2 eV and for the ν_4 mode at 5.5 eV are almost uniform in angle. At 100° the ν_3 DCS is about 6% of the elastic DCS. A theoretical analysis of vibrational excitation and dissociative attachment in CH_3Cl was done by Fabrikant (1991, 1994).

Vibrational excitation in CH_2Cl_2 at 1.0–3.5 eV collision energy was studied by Abouaf and Benoit (1990). Excitation of the ν_3 (CCl_2 *s*-stretch) and its overtones up to $3\nu_3$ was observed both at 1.3 and 3.2 eV, with some excitation of the CH stretch modes as well. The DCS at 1.3 and 2.8 eV for the ν_3 and $2\nu_3$ modes are almost uniform at 40°–90° scattering angles and rise below 40°. Abouaf and Benoit argued that according to selection rules these modes indicate an A_1 symmetry of the resonant states and that the B_2 resonance predicted by the theory at 2.5 eV (Burrow *et al.* 1982) can be responsible for the small rise in DCS observed at low angles. The enhancement of vibrational excitations is visible in the whole energy range studied by Abouaf and Benoit (1990).

Rotational excitation. Due to the high dipole moments of methyl halides, the rotational de-excitation and excitation should contribute a significant part of the TCS at low energies. We are not aware of measurements or calculations for the rotational excitation CS. In CH_3Cl the rise of the DCS at low angles has been attributed (Shi *et al.* 1996) to rotational excitation. Experiments using Rydberg atoms quenching (Hildebrandt *et al.* 1978, Ling *et al.* 1993) indicate that the TCS for CH_3I (and CH_2Br_2) at sub-thermal energies follow the E^{-1} dependence: this could correspond to rotational de-excitation and excitation. However, some discrepancies with the Born approximation were stressed (Ling *et al.* 1993). On the other hand, Schramm *et al.* (1999) explained the very low energy rise of TCS in CH_3I (Ling *et al.*) as due to electron attachment.

Electronic excitation. Forward-scattering electron excitation in CH_3F, CH_3Cl, CH_3Br, CH_3I was studied by Olney *et al.* (1994, 1996, 1997, 1998) in 7–250, 6–350, 6–450, 4.5–488 eV energy loss ranges, respectively. The photoabsorption CS in these gases, as measured with a low (1 eV FWHM) energy resolution, shows a single, wide peak. For example, in CH_3Cl a maximum of $0.80 \cdot 10^{-20}$ m^2 at 16 eV and in CH_3Br of $0.88 \cdot 10^{-20}$ m^2 at 15 eV were observed.

Optical emission. Emission CS in CHF_3 due to atomic and diatomic fragments as well as emission in a continuous band at 200–400 nm were given in the 100–2000 eV collision-energy range by van Sprang *et al.* (1978). The intensity of atomic hydrogen lines and of the CH radical de-excitation lines at 0.4–5 keV impact energy was studied in

CHF_3 by Danilevskii *et al.* (1986). Emission from CHF_3 in the ultraviolet (50–130 nm) range was studied up to 600 eV incident energies by Wang and McConkey (1989); in the 130–520 nm range and at energies up to 1000 eV by Aarts (1985). Emission from CHF_3 in the 200–400 nm spectral range due to electron and UV (11–35 eV) photon excitation was studied by Creasey *et al.* (1990). Electron-collision emission from CH_3F, CH_2F_2 and CHF_3 up to 1000 eV collision energy was measured in the spectral region from 100 to 700 nm by Keller *et al.* (1996, 1998); emission from CH_3F, CH_2F_2, CHF_3 and CF_4 in the 600–900 nm spectral region and up to 500 eV collision energy by Torres *et al.* (1999); emission from CF_3I by Martínez *et al.* (1998).

Emission from CCl fragments formed in electron collisions with $CXCl_3$ (X = H, F, Cl, Br) was studied up to 100 eV by Ito *et al.* (1986) and Kusakabe *et al.* (1993). Emission cross-sections rise by factors of two from $CHCl_3$ to $CFCl_3$ and to $CBrCl_3$.

Ionization CS in CH_3F, CH_3Cl, CH_3Br (and CH_4) were measured between threshold and 200 eV by Vallance *et al.* (1997). The maximum ionization CS increases for heavier targets, amounting to 3.73, 6.91, 8.02, 10.3, $12.25 \cdot 10^{-20}$ m^2 for CH_3F, CH_3Cl, CH_3Br, CH_3I and $CHCl_3$, respectively. Only the CH_4 ionization CS does not follow this rule, being higher ($4.24 \cdot 10^{-20}$ m^2) than that for CH_3F (Vallance *et al.* 1997).

Ionization of CHF_3 was studied in a detailed way by Goto *et al.* (1994). The total ionization CS amounts to $6.74 \cdot 10^{-20}$ m^2 at 120 eV. The CF_3^+ ion is formed with 33% probability at this energy and CF^+ with 43%.

Ionization from space-oriented CH_3Cl molecules was studied by Kasai *et al.* (1993) and from CH_3Cl, $CHCl_3$ and CH_3Br by Aitken *et al.* (1995). Asymmetry effects in the ionization of CH_3Cl are more pronounced for the formation of the CH_3Cl^+ ion than for the CH_3^+ ion (Aitken *et al.*). We are not aware of any theoretical or semiempirical values of ionization CS in halomethanes (except for CF_4).

Dissociation into neutrals in CHF_3 up to 600 eV was measured by Winters and Inokuti (1982). The total dissociation CS maximum in CHF_3 ($5.8 \cdot 10^{-20}$ m^2) is slightly higher than the maximum CS in CF_4 ($5.5 \cdot 10^{-20}$ m^2). Motlagh and Moore (1998) studied dissociation CS in CH_3F, CH_2F_2, CHF_3 (and CH_4, CF_4, C_2F_6, C_3H_8). They observed that the partial CS for dissociation are proportional to statistical weight of pathways leading to the formation of a specific radical. For example, the CS section for formation of the CF_3 radical from the CHF_3 molecule is $1/4$ of the CS for formation of CF_3 from CF_4. These proportions can be considered as a manifestation of a kind of "additivity" rule for partial cross-sections, predicted for total cross-sections (Zecca *et al.* 1999, Karwasz *et. al.* 1999).

In the case of dissociation in fluoromethanes, Motlagh and Moore reported maxima of $1.5 \cdot 10^{-20}$ m^2 for the CF_3 radical formation from CF_4, $0.9 \cdot 10^{-20}$ m^2 from CHF_2 and $0.4 \cdot 10^{-20}$ m^2 from CHF_3; $0.7 \cdot 10^{-20}$ m^2 for CHF_2 formation from CH_2F_2 and $0.5 \cdot 10^{-20}$ m^2 for CH_2F formation from CH_3F. All maxima occur at about 100 eV collision energy. In CHF_3 data of Motlagh and Moore (1998) are in good accord with 20–200 eV measurements of Goto *et al.* (1994). The latter authors reported 0.49, 0.032, 0.092, 0.006 and $0.18 \cdot 10^{-20}$ m^2 for the formation of CF_3, CHF_2, CF_2, CHF and CF, respectively, from CHF_3 at 100 eV. However, successive measurements from this group (Sugai *et al.* 1995), similarly to those for CF_4, give values by a few folds lower.

Electron attachment in methyl halides CH_3X leads to the formation of dissociated X^- negative ions. The total yield of negative ions at low energies exhibits a strong, rising dependence on the gas temperature. This phenomenon was studied by Spence and Schulz (1973) for $CHCl_3$, CH_3Br, CH_3I, (and $CFCl_3$, CF_3Br); by Smith *et al.* (1984) for $CHCl_3$ (and CF_2Cl_2, $CFCl_3$, CCl_4); by Datskos *et al.* (1990), Pearl and Burrow (1993) and Španěl *et al.* (1995) for CH_3Cl; by Petrović and Crompton (1987) and Datskos *et al.* (1992) for CH_3Br. Among different gases electron-attaching at zero-energy, only for CCl_4 and SF_6 no dependence of the CS on the gas temperature was noticed. A review of results on electron attachment at thermal energies was done by Smith and Španěl (1994).

In general, several peaks in negative ions yield are observed in halomethanes: a near-to-zero-energy rise, due to positive electron affinity of these compounds, a second peak below 1 eV and other/others at energies of Feshbach resonances (see, for example, Othoff *et al.* 1986 for CCl_4, CCl_3Br, CCl_2Br_2, CBr_4). However, large discrepancies regarding both the positions and the amplitudes of the peaks can be introduced by gas impurities and/or reactions in the experimental systems (compare Chu and Burrow 1990 and Pearl and Burrow 1993, 1994).

Electron attachment in CHF_3 at thermal electron energies is very weak or absent. A small electron attachment rate constant ($\sim 13 \cdot 10^{-14}$ cm^3 s^{-1}) measured in swarm experiment can be due to impurities (Wang *et al.* 1999).

Dissociative attachment in chloromethanes CH_3Cl, CH_2Cl_2, $CHCl_3$, CCl_4 was measured by Chu and Burrow (1990) and Pearl and Burrow (1993) in a beam experiment. Their results are reported in table VI. For methyl chloride CH_3Cl, Pearl and Burrow (1993) argued that the zero-energy CS seen in their previous experiment (Chu and Burrow 1990) was due to an impurity produced by a chemical reaction on the hot filament. A weak and broad peak of $4.9 \cdot 10^{-24}$ m^2 is centered at 0.8 eV (Pearl and Burrow 1993). Swarm measurements yielded a maximum attachment coefficient of $0.4 \cdot 10^{-12}$ cm^3 s^{-1} in CH_3Cl at thermal energies (Petrović *et al.* 1989).

In $CHCl_3$, Chu and Burrow (1990) reported a value of $4.7 \cdot 10^{-20}$ m^2 for the dissociative attachment CS at zero energy. Another peak was reported at 0.27 eV (Chu and Burrow 1990, Wan *et al.* 1991). Electron attachment in $CHCl_3$ was also measured down to 1 meV in a recent beam experiment (Matejcik *et al.* 1997). Down to 5 meV the CS rises following an E^{-1} dependence; for lower energies it remains constant at about $7.2 \cdot 10^{-20}$ m^2. As stated by Matejcik *et al.* (1997), for electron energies between 20 and 130 meV the electron attachment proceeds via the electron *s*-wave capture, whereas at higher energy (above 0.4 eV) the autodetachment plays a significant role. Note, however, that the measured CS energy dependence (Matejcik *et al.* 1997) is roughly two orders of magnitude below the de Broglie limit for the *s*-wave capture (see Wigner 1948). This conclusion is also confirmed by flowing-afterglow and microwave measurements: at 300 K the attachment rate coefficient is by a factor of 100 lower in $CHCl_3$ than in CCl_4 and $CFCl_3$ (Smith *et al.* 1984, Shimamori *et al.* 1992b).

The early beam experiment on CH_3Br reported a Br^- peak at about 0.35 eV (Stockdale *et al.* 1974). The existence of this peak, increasing in amplitude and moving to lower energies with rising gas temperature, was confirmed also by swarm experiments (Wang and Lee *et al.* 1988, Datskos *et al.* 1992). An electron attachment rate constant of $10.8 \cdot 10^{-12}$ cm^3 s^{-1} has been reported at thermal energies (Datskos *et al.* 1992), in overall agreement with other measurements (Alge *et al.* 1984, Petrović and Crompton 1987). Earlier measurements (Christodoulides and Christophorou (1971) seem to be overestimated. Weak maxima were observed at about 6.9 and 9.4 eV (Stockdale *et al.* 1974).

For CH_3I early measurements (Stockdale *et al.* 1974) reported a single peak for I^- production at 0.15 eV. Other experiments (Shimamori *et al.* 1988, Shimamori *et al.* 1992 a, b, microwave technique; Hildebrandt *et al.* 1978 and Ling *et al.* 1993, Rydberg's atoms quenching; Christophorou 1976, swarm; Alge *et al.* 1984, flowing afterglow; Alajajian *et al.* 1988, threshold photoionization) indicate a rather continuous rise at the zero-energy limit. An electron attachment rate of the order of $300 \cdot 10^{-10}$ cm^3 s^{-1} at about 0.1 eV was reported by Shimamori and Nakatani (1988) and Shimamori *et al.* (1992a) and of $1200 \cdot 10^{-10}$ cm^3 s^{-1} at 300 K by Alge *et al.* (1994), see also table VII.

Alajajian *et al.* (1988) were the first to report a weak maximum in the CH_3I electron attachment CS at 60 meV, superimposed on the low-energy rise. In a recent high-resolution experiment performed down to 0.5 meV collision energy, Schramm *et al.* (1999) noticed than this maximum occurs at the vibrational excitation threshold of the ν_3 mode. They also observed other resonant structures in the dissociative electron attachment CS (I^- ion formation) at the opening of successive vibrational channels ($2\nu_3$ and ν_2 modes). In the 1–4 meV range the measurements of Schramm *et al.* coincide with the dissociative attachment CS as derived (Schramm *et al.* 1999) from Rydberg-atoms experiment (Hildebrandt *et al.* 1978). At 0.5 meV, the electron attachment CS amounts to $4 \cdot 10^{-17}$ m^2, by about a factor of 10 less than the theoretical limit for the *s*-wave capture. Very weak peaks (of the order of 10^{-24} m^2) in CH_3I dissociative electron attachment CS were observed also at about 3.5 eV and 8.5 eV, with H^-, CH^- and I^- ions present (Krishnakumar and Nagesha 1993).

The absolute values of the electron attachment CS in methyl halides increase on going from CH_3Cl to CH_3Br, and to CH_3I. Differently from CCl_4 or SF_6, the attachment CS in methyl halides does not contribute in a significant way to the TCS. Only in CH_3I this contribution is significant, approaching the theoretical limit for the *s*-wave capture (Schramm *et al.* 1999). However, the pulse-radiolysis microwave-cavity method (Shimamori *et al.* 1992a, Sunagawa and Shimamori 1999) indicates, for CH_3I at 0.04 eV, an electron attachment rate coefficient lower by a factor of four than that in CF_3I (Shimamori *et al.* 1992b). The molecules with the highest rate coefficients in the 0.01–0.1 eV range are SF_6, CCl_4, $CFCl_3$, CF_3I and 1,1,1–$C_2F_3Cl_3$ (Shimamori *et al.* 1992b) and CH_2Br_2 (Shimamori *et al.* 1992a).

Dissociative electron attachment CS for other halomethanes (CF_3Br, CF_2Br_2, CF_3I) at 0.2–6 eV were studied in a beam experiment by Underwood-Lemons *et al.* (1995); for CH_2Br_2, $CHBr_3$, CH_2I_2, CHI_3 at 0–4 eV by Modelli *et al.* (1992); for CCl_3Br, CCl_2Br_2, CBr_4 by Olthoff *et al.* (1986). The pulse-radiolysis microwave-cavity method was applied to CF_3Br (Shimamori *et al.* 1992b), CBr_4, $CHBr_3$, $CFBr_3$, CF_2Br_2, CH_2ClBr, $CHClBr_2$, CCl_3Br (Sunagawa and Shimamori 1997), CH_3I, CH_2I_2, CF_3I (Sunagawa and Shimamori 1999). The threshold-photoionization method was used for CH_2Br_2, CF_3Br, CF_2Br_2, CCl_3Br, CH_3I (Alajajian *et al.* 1988) and for flowing plasma afterglow to CF_3Br (Španěl and Smith 1993). In CCl_3Br, the high-resolution beam experiment (Španěl *et al.* 1997) shows a dissociative attachment CS similar in shape to that in $CHCl_3$, but a factor of 10 higher. For low-energy peaks in the dissociative attachment CS, Pearl and Burrow (1994) for a series of normal chloroalkanes $C_nH_{2n+1}Cl$ with $n = 2$–9, and Aflatooni *et al.* (1998) for a series of mono-, di- and trichloroalkanes, showed that the amplitude of the peak σ_A drops exponentially with the attachment energy E_a. Aflatooni *et al.* (1998) give the following approximating formula for σ_A:

$$\sigma_A = 1860 \cdot 10^{-2.55 E_a} \cdot 10^{-20} \mathrm{m}^2 \,, \tag{2}$$

where E_a is given in eV.

Resonances. Spence (1977) discovered a series of Feshbach resonances in CH_3Cl (the first one at 7.5 eV), CH_3Br (6.7 eV), CH_3I (5.9 eV). He indicated a linear correlation between the energies of the resonances (and the corresponding Rydberg states) with the ionization potential of the molecules. The correlation between resonant states visible in low-energy electron transmission spectroscopy and in the inner-shell excitation spectra was studied for the four methyl halides and four chloromethanes by Benitez *et al.* (1988). Electron transmission spectra for fluoro-, bromo- and iodomethanes CH_nX_{4-n} with $n =$ 0–4 (except CH_2F_2) up to 7 eV were reported by Modelli *et al.* (1992), for $CBrCl_3$, CBr_2Cl_2, CBr_4 by Olthoff *et al.* (1986).

For CH_3Cl a shape resonance of $^2A_1$ symmetry at 3.5 eV due to the temporary occupation of the 8 a_1(C-Cl) molecular orbital was observed in electron transmission (Burrow *et al.* 1982) and in vibrational excitation spectra (Shi *et al.* 1992). This resonance is barely visible in the TCS (Krzysztofowicz and Szmytkowski 1995). Another resonant state observed in the vibrational excitation function at 5.5 eV (Shi *et al.* 1992) of ^2E symmetry is principally associated with C-H antibonding orbitals. Theoretical calculations for CH_3Cl were performed of Fabrikant (1991) and Gallup (1993).

A weak shape resonance near 2.4 eV in CH_3Br, similar to that at 3.5 eV in CH_3Cl, was observed by electron transmission spectroscopy (Modelli *et al.* 1992).

Electron transmission spectra for the whole chloromethanes series CH_3Cl-CCl_4 (and $CHFCl_2$, CF_2Cl_2) at 0.2–5 eV were reported by Burrow *et al.* (1982). Both in CH_2Cl_2 and $CHCl_3$ they observed two temporary negative ion states associated with C-Cl σ^*-orbitals: at 1.2 and 3.4 eV for CH_2Cl_2 ($^2A_1$ and $^2B_2$ symmetry, respectively) and at 0.35 eV and 1.8 eV in $CHCl_3$ ($^2A_1$ and ^2E symmetry). The existence of the two resonant states in CH_2Cl_2 was confirmed in studies of vibrational excitation (Abouaf and Benoit 1990), but to both of them the A_1 symmetry was attributed.

Coupling between dissociative attachment and vibrational excitation CS channels has been observed at room temperature in CH_3I (Schramm *et al.* 1992) and at 700 K in CH_3Cl (Pearl and Burrow 1993).

Other methyl compounds. For methanol CH_3OH total (Szmytkowski and Krzysztofowicz 1995, Sueoka *et al.* 1985, 1997) and forward-angle electronic excitation (Burton *et al.* 1992) cross-sections were studied. Total cross-sections for CH_3SH and CH_3NH_2 (Szmytkowski *et al.* 1995, Szmytkowski and Krzysztofowicz 1995, respectively) were reported at 1–250 eV. Electron attachment to CH_3CN via scattering of Rydberg atoms was studied at ultra-low energies by Desfrançois *et al.* (1994) and Popple *et al.* (1995). Dissociation of CH_3CN was observed in fluorescence measurements by Darrach and McConkey (1991).

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3˙4. *Silicon and germanium halides (Si*X_4*, Ge*X_4*).* – Gaseous silicon halides are widely used in semiconductor industries for plasma growth and etching (Sendra *et al.* 1995). In spite of this, their interactions with charged particles are known in a fragmentary way. In this subsection we discuss SiF_4, $SiCl_4$, GeF_4, $GeCl_4$. The total cross-sections for these gases are compared in fig. 15 in a wide energy range. In this subsection we mention also results on some other targets containing silicon atoms, as $SiBr_4$ and SiI_4.

Total, elastic and vibrational excitation. TCS in silicon and germanium halides were studied by the Gdańsk group (SiF_4, Karwasz *et al.* 1998; $SiCl_4$, Możejko *et al.* 1999; GeF_4, Szmytkowski *et al.* 1998; $GeCl_4$, Szmytkowski *et al.* 1997) in the 0.5–250 eV energy range, by Wan *et al.* (1989) for the chlorosilane series (SiH_4, SiH_2Cl_2, $SiHCl_3$) and for tetrahalosilanes (SiF_4, $SiCl_4$, $SiBr_4$, SiI_4) in the 0.2–12 eV range, and by the Trento group (SiF_4, Karwasz *et al.* 1998; $SiCl_4$, Możejko *et al.* 1999) in the 75–4000 eV range. Elastic CS in the 1–40 eV range were calculated by Natalense *et al.* (1995) and Varella *et al.* (1999) but the agreement with experimental TCS is poor.

TCS for SiH_4, SiF_4, $SiCl_4$, $SiBr_4$ and SiI_4 of Wan *et al.* (1989) are shown in fig. 16. Below 0.8 eV the absolute values of the TCS for the SiH_4-SiI_4 series increase with the total atomic number of the molecule. An indication of a similar relation at intermediate energies can be drawn from experimental data at 12 eV (Wan *et al.* 1989), see fig. 16.

TCS data in SiF_4 from the Gdansk and Trento laboratory (Karwasz *et al.* 1998) merge at 80–250 eV within the combined statistical uncertainties, see fig. 15. The low-energy data of Karwasz *et al.* (1998) agree well with the measurements of Wan *et al.* (1989) as far

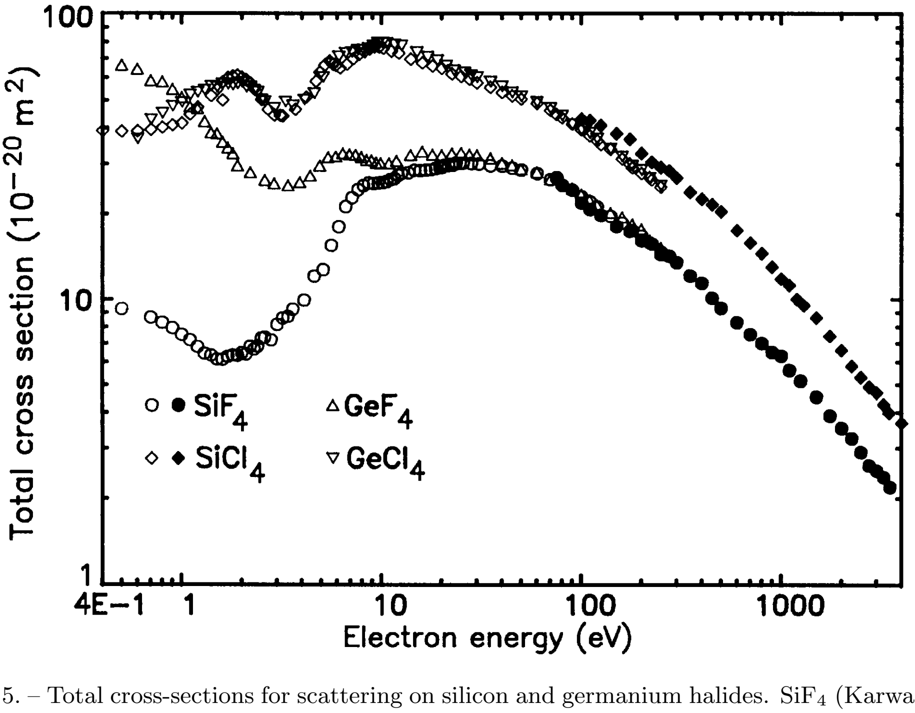

Fig. 15. – Total cross-sections for scattering on silicon and germanium halides. SiF_4 (Karwasz *et al.* 1998): open circles, data from Gdańsk laboratory; full circles, data from Trento laboratory. $SiCl_4$ (Możejko *et al.* 1999): open rhombuses, data from Gdańsk; full rhombuses, data from Trento. GeF_4: Szmytkowski *et al.* (1998). $GeCl_4$: Szmytkowski *et al.* (1997).

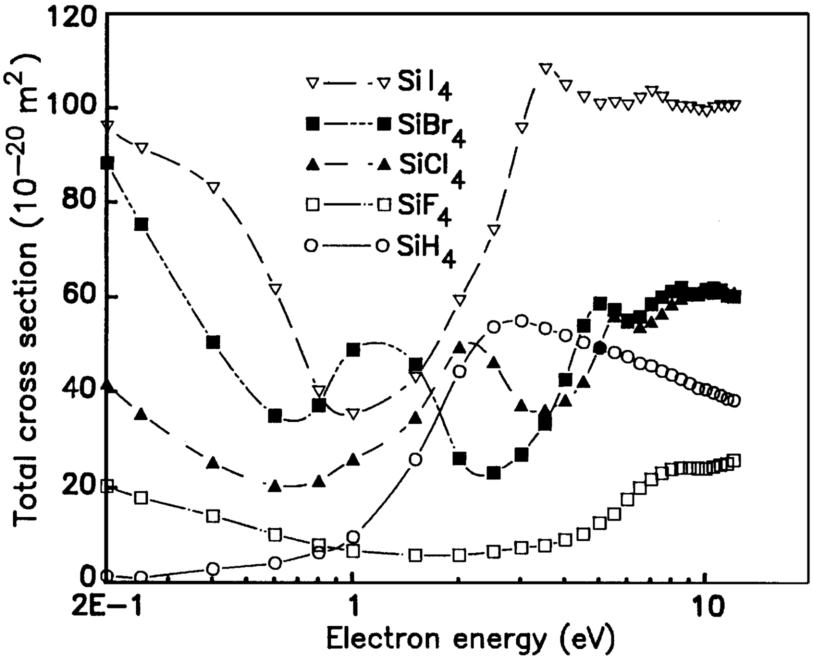

Fig. 16. – Low-energy total cross-sections for scattering on silicon tetrahalides, from Wan *et al.* (1989).

as the shape is concerned, but are slightly (6% on the average) higher. This discrepancy remains well inside the combined experimental error bars: in fact, the uncertainty of the pressure determination in the experiment of Wan *et al.* (1989) alone amounts to 11%. The relative difference is higher at lower energies, amounting to 15% at 1 eV. It is not to be excluded that below 1 eV the TCS measured by the trochoidal spectrometer (Wan *et al.* 1989) are underestimated because of a poor discrimination for the electrons forward-scattered in vibrationally inelastic collisions. TCS in SiF_4 have also been measured by Bonham and collaborators (Ma *et al.* 1989) but we are not aware of tabulated data.

The TCS in SiF_4 exhibits a broad minimum at 1.5 eV and rises quickly (by a factor of three) between 2 and 7 eV. A shoulder structure is visible at 8.5 eV. A maximum value of $30 \cdot 10^{-20}$ m^2 is reached at 24 eV. Above 100 eV the TCS falls monotonically to the value of $2.2 \cdot 10^{-20}$ m^2 at 3500 eV (Karwasz *et al.* 1998). Theoretical calculations (Tossell and Davenport 1984) for the elastic CS in SiF_4 indicate the presence of a very shallow Ramsauer minimum at about 1.5 eV and a rise at low energies. However, the absolute theoretical values exceed the experimental data by a factor of four in the region of the TCS minimum.

The vibrational CS in SiF_4 has been evaluated in the Born approximation by Karwasz *et al.* (1998). They noticed that the low-energy rise of TCS (Wan *et al.* 1989, Karwasz *et al.* 1998) can be explained by direct (non-resonant) vibrational excitation. The difference between the TCS and the vibrational excitation CS estimated with the above procedure (*i.e.* the elastic CS) reaches a minimum of about $1 \cdot 10^{-20}$ m^2 at 0.6–0.8 eV.

The TCS in GeF_4, see fig. 15, shows an unusual, for non-polar molecules, low-energy rise, up to $66 \cdot 10^{-20}$ m^2 at 0.5 eV (Szmytkowski *et al.* 1998). A minimum of about

$25 \cdot 10^{-20}$ m^2 at 2.5 eV and three weak maxima of similar amplitudes, 32–33 $\cdot 10^{-20}$ m^2 at 6.4, 16 and 28 eV were observed. At 250 eV the TCS in GeF_4 amounts to $15.2 \cdot 10^{-20}$ m^2, almost a double value than that for GeH_4 (Karwasz 1995, Szmytkowski *et al.* 1998).

In $SiCl_4$ the measurements from the Gdańsk and Trento laboratory (Możejko *et al.* 1999) differ by about 15%, the difference being constant in the whole 100–250 eV energy range of overlap. We noted a similar discrepancy in GeH_4 — it is probably related to a higher angular-resolutions error in the Gdańsk apparatus (Możejko *et al* 1999). Low-energy data of Możejko *et al.* agree reasonably well in shape with the determination of Wan *et al.* (1989). Similar discrepancies in absolute values as in the case of SiF_4 are observed for $SiCl_4$.

The TCS for $SiCl_4$ (Wan *et al.* 1989, Możejko *et al.* 1999) shows three rather sharp maxima: of $61 \cdot 10^{-20}$ m^2 at 1.9 eV, $69 \cdot 10^{-20}$ m^2 at 5.5 eV, $77 \cdot 10^{-20}$ m^2 at 9.2 eV (Możejko *et al.* 1999). At 3500 eV the TCS amounts to $3.95 \cdot 10^{-20}$ m^2. Agreement with the theory (Tossell and Davenport 1984) is rather poor: the theory predicts a resonant state of T_2 symmetry around 1 eV, while the experimental position is 1.9 eV (Możejko *et al.* 1999).

The TCS in $GeCl_4$ (Szmytkowski *et al.* 1997) shows two rather broad maxima: of $58 \cdot 10^{-20}$ m^2 at 2.0 eV and of $80 \cdot 10^{-20}$ m^2 at about 10 eV. A shoulder structure is visible around 6 eV.

Ionization and electronic excitation. In SiF_4 only a few partial cross-section measurements exist: ionization up to 125 eV (Poll *et al.* 1987), dissociation into neutrals (Nakano and Sugai, 1993) and dissociative attachment (Iga *et al.* 1992). The available data indicate that at 60 eV the most efficient inelastic process is the dissociative ionization, leading to the formation of SiF_3^+ ions; the CS for this process (Poll and Meichsner 1987) amounts to 25% of the TCS. The formation of parent SiF_4^+ ion is one order of magnitude less probable at this energy. Note that in SiH_4 no parent ions were detected in electron-impact ionization (Chatham *et al.* 1984). We also note a relatively low probability of forming ions and radicals in excited states for SiF_4. The overall CS for these processes, as estimated from UV emission, is merely $0.13 \cdot 10^{-20}$ m^2 at 100 eV, four times less than for the CF_4 molecule (Aarts 1986).

The cross-section for dissociation into neutrals in SiF_4 reaches a maximum at 70 eV (Nakano and Sugai 1993), where it amounts to about 3% of the TCS (Karwasz *et al.* 1998). 75% of the neutral radicals yield is due to SiF_3, which exceeds the SiF_2 yield by more than three folds. The SiF and Si signals at 100 eV are about 1/40 and 1/80 of the one for SiF_3, respectively.

Detailed studies for valence and inner-shell electronic excitation in SiF_4 in the limit of forward scattering were performed by Guo *et al.* (1992). The photoabsorption CS measured with a high-resolution (0.048 eV FWHM) apparatus reaches a maximum of $0.97 \cdot 10^{-20}$ m^2 at 13.0 eV; a smaller maximum follows at 23 eV (Guo *et al.*).

Optical emission spectra in SiF_4 due to 200 eV electron impact were studied by Hesser and Dressler (1967). Ultraviolet emission CS were given for ionic fragments by Aarts (1986). Energy-loss spectra at 10–17 eV energy loss in trapped electrons experiment were studied by Curtis and Walker (1989). The optical emission spectrum around 564 (400) nm from SiF_4^+ (GeF_4^+) ions formed in electron impact ionization of SiF_4(GeF_4) was studied by Mason and Tuckett (1987a, b, respectively). Electron momentum distributions of SiF_4 valence-orbitals were measured by Fantoni *et al.* (1986).

In $SiCl_4$ semiempirical values of ionization CS at 30–200 eV have been reported by Deutsch *et al.* (1997). The ionization CS according to this model reaches its maximum at 60 eV where it constitutes 30% of the TCS, while at 200 eV this share rises to 35% of the TCS (Trento data from Możejko *et al.* 1999).

Inner-shell energy loss spectra in chlorosilanes ($SiHCl_3$, SiH_2Cl_2, $SiCl_4$) were reported by Winkler *et al.* (1994). Optical emission in the 350–750 nm range from ionized fragments formed in electron collisions with $SiCl_4$ and $GeCl_4$ was reported by Lambert *et al.* (1988). Vacuum UV fluorescence in GeF_4 excited by 10–25 eV synchrotron radiation was studied by Boyle *et al.* (1998).

Dissociative attachment CS in SiF_4 (Wang *et al.* 1973, Iga *et al.* 1992, Sauers *et al.* 1993), for SiF_3^- (64%), F^- (34%) and some F_2^- production, reaches a maximum of $1.5 \cdot 10^{-22}$ m^2 at 11.4 eV (Iga *et al.* 1992), *i.e.* at a somewhat lower energy than the second peak observed in TCS (Karwasz *et al.* 1998). As noticed by Mann and Linder (1992) for carbon halides CF_3Cl and CF_2Cl_2, the peaks in the electron attachment CS usually precede the maxima in the vibrational excitation. The maximum attachment CS in SiF_4 is slightly lower than the $1.8 \cdot 10^{-20}$ m^2 peak in CF_4 (Iga *et al.* 1992).

Dissociative attachment in chlorosilanes (SiH_3Cl, SiH_2Cl_2, $SiHCl_3$, $SiCl_4$) was measured by Wan *et al.* (1991). Within the sensibility of their apparatus ($2 \cdot 10^{-22}$ m^2), only in the case of $SiHCl_3$ they measured a non-zero dissociative attachment CS: a value of $0.06 \cdot 10^{-20}$ m^2 at "zero energy" and a similar value at the peak position (1.2 eV).

In $SiCl_4$ Dorman (1966) reported a "zero-energy" peak and a maximum at about 7 eV with the Cl^- intensity about ten times higher than that of Cl_2^-. Pabst *et al.* (1977b) fixed the low-energy peak for Cl^- formation from $SiCl_4$ at 1.8 eV and the threshold for this process at 0.5 eV (see also the discussion for $GeCl_4$ below). Another peak for the Cl^- ion formation is centered at 7.5 eV, while peaks for $SiCl_3^-$, $SiCl_2^-$ and Cl_2^- were found at about 7.1, 8.5 and 8.8 eV (Pabst *et al.* 1977b). The determination of Cl^- peak positions is in good agreement with the measurements of Wang *et al.* (1974). Moylan *et al.* (1990) observed some additional signal from the $SiCl_4^-$ ion at 2 eV impact energy.

Pabst *et al.* (1977b) reported dissociative attachment in $SiCl_4$ and $SiBr_4$. A similar pattern of ions (SiX_3^-, SiX_2^-, X_2^-, X^-) was observed in both $SiBr_4$ and $SiCl_4$. The relative intensities of corresponding ions for $SiCl_4$ are shifted by about 1.5 eV compared to $SiBr_4$. No negative ions were reported at near-to-zero energies.

Negative-ion yields and ion energies in $GeCl_4$ were reported by Pabst *et al.* (1977b). Extensive studies, by X-ray absorption, inner-shell electron energy loss spectroscopy, dissociative attachment spectroscopy and *ab inito* calculations, were reported by Guillot *et al.* (1996). Dissociative attachment is dominated by the formation of the $GeCl_3^-$ anion at zero impact energy and the formation of Cl^- and $GeCl_2^-$ anions around 5.6 eV. The existence of a peak for $GeCl_3^-$ at 2 eV (Pabst *et al.* 1977b) was not confirmed by Guillot *et al.* (1996).

Dissociative attachment in tin tetrahalides ($SnCl_4$, $SnBr_4$, SnI_4) was studied by Pabst *et al.* (1977a).

Resonances. Electron transmission spectra at 0.2–12 eV collision energy for silicon tetrahalides and hydrochlorides were obtained by Wan *et al.* (1989). All examined molecules (SiH_4, SiH_2Cl_2, $SiHCl_3$, $SiCl_4$, $SiBr_4$ and SiI_4) but SiF_4 show a resonant state at energies below 3 eV. The energy of these resonances, visible both in the TCS and in the dissociative attachment channels, moves from 2.9 eV in SiH_4 to 2.2 eV in $SiCl_4$, 1.2 eV in $SiBr_4$ and 0.4 eV in SiI_4.

Wan *et al.* (1989) noticed that the sum of the resonance energy and the "term value", *i.e.* the ionization energy of a corresponding (*i.e.* occurring to the same molecular orbital) inner-shell excited state, remains constant (= 6.1 eV) for all the tetrahedral (SiF_4, $SiCl_4$, $SiBr_4$, SiI_4) molecules considered. Based on this observation and the inner-shell excitation data of Fredrich *et al.* (1980), they predicted a resonant energy of 2.9 eV for the

t_2 state of SiF_4. According to the continuum multiple-scattering parametric-exchange molecular-orbitals calculations of Tossell and Davenport (1984) only a broad shoulder in the t_2 resonant channel is visible at 3 eV. However, neither resonant maximum nor a shoulder structure is visible in the experimental TCS (Wan *et al.* 1989, Karwasz *et al.* 1998).

In $SiCl_4$, in analogy to CCl_4, the 2.2 eV peak and the broad feature around 5 eV have been assigned to electron capture into the $\sigma^*(t_2)$ and a higher-lying t_2 orbital, respectively (Wan *et al.* 1989).

In $GeCl_4$, Guillot *et al.* (1996) in electron transmission spectra observed two resonant state, the first one at 1.72 eV of t_2 symmetry. A rather narrow (1.0 eV FWHM) feature was observed at 5.6 eV and tentatively assigned to the electron capture to the 6e orbital. Guillot *et al.* (1996) compared resonant states, as seen in attachment CS in CCl_4, $SiCl_4$ (Pabst *et al.* 1977b), $GeCl_4$, $SnCl_4$ (Pabst *et al.* 1977a), and discussed the "term-values" rule of Wan *et al.* (1989).

Comparison between different molecules. Clear differences in TCS can be observed between hydrides and halides of silicon and germanium, compare fig. 2 for SiH_4 with fig. 15 for SiF_4. TCS in SiH_4 exceeds the SiF_4 one in the whole 1–25 eV energy range, being lower by a factor of two above 100 eV. One notes that the TCS shape in this energy range for tetrahedral molecules CX_4, SiX_4, GeX_4 (X = H, F, Cl) depends rather on external atoms than on the central one. The hydrides exhibit a single maximum of TCS with a value that rises from $24 \cdot 10^{-20}$ m^2 at 8 eV in CH_4 (Zecca *et al.* 1991) to about $55 \cdot 10^{-20}$ m^2 at 3–4 eV in SiH_4 (Szmytkowski *et al.* 1997) and GeH_4 (Możejko *et al.* 1996). The fluorides (CF_4, SiF_4, GeF_4) exhibit a broad maximum at 20–30 eV and another, narrower maximum (a shoulder in the case of SiF_4) at energies slightly below 10 eV. As noticed by Karwasz *et al.* (1998) a maximum of a similar width occurs in the total cross-sections in SF_6. The position of this low-energy maximum moves from 8.5 eV in CF_4 to 7 eV in SF_6 and GeF_4, while the amplitude increases from $21 \cdot 10^{-20}$ m^2 in CF_4 (Szmytkowski *et al.* 1992) to $33 \cdot 10^{-20}$ m^2 in SF_6 (Kasperski *et al.* 1997).

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3˙5. *Trihalides (*NF_3 *and others).* – In this subsection we discuss a few other halides, which do not belong to a particular chemical group. More data, in particular elastic CS measurements, exist for nitrogen trifluoride (NF_3) than for other compounds discussed in this chapter (BF_3, BCl_3, PF_3, PF_5). We are not aware of TCS for any of the gases presented in this chapter.

Nitrogen trifluoride (NF_3)

Elastic and vibrational cross-sections for NF_3 were measured in an absolute experiment by Boesten *et al.* (1996) between 1.5 and 100 eV. In spite of the fact that the molecular geometry, electronic configuration and vibrational modes are in NF_3 the same as in NH_3, the elastic and vibrational CS differ substantially for these two targets. The DCS for elastic scattering in NF_3 are rather uniform in angle between 1.5 and 3 eV, differently than in NH_3, compare fig. 3a in part II. At 8–100 eV the DCS in NF_3 shows only one minimum, with some "interference" structures, like those seen for OCS and CS_2 molecules, compare fig. 18 in part II. The NF_3 integral CS reaches a broad peak with a maximum of $18.4 \cdot 10^{-20}$ m^2 at 4 eV (Boesten *et al.* 1996).

The vibrational excitation functions for the ν_1 and ν_3 stretching modes show a 2 eV wide resonance centered at 3 eV. The excitation functions in NF_3 do not resemble those in NH_3 (Gulley *et al.* 1992) but the ones in PH_3 (Tronc *et al.* 1981). The DCS for the unresolved $\nu_{1,3}$ mode is in NF_3 forward centered at all energies between 0.5 and 9 eV (Boesten *et al.* 1996). At 3 eV the DCS falls by a factor of two between 20° and 60°; then it remains constant up to 130°.

Differential, momentum transfer and integral CS for elastic scattering and excitation to the ^3E and ^1E electronic states in NF_3 were calculated by Rescigno (1995).

Swarms. Early swarm measurements in NF_3 were compiled by Gallagher *et al.* (1983). More recently analysis of swarm parameters (energy distribution, attachment coefficient, drift velocity) in NF_3 and its mixtures with noble gases and N_2 were performed by Ushidora *et al.* (1990).

The optical emission CS from different dissociated fragments of NF_3 was studied by Becker and collaborators (Blanks *et al.* 1987, Blanks and Becker 1987, Roque *et al.* 1991). In particular, emission from fluorine excited atoms was studied: transitions between the lowest excited states and the ground state $(2p^4 3s)\ ^{2,4}P \rightarrow (2p^5)\ ^2P^0$ at 95.5 and 97.5 nm wavelength (Roque *et al.* 1991) and emission in the 620–790 nm range due to transitions between some higher and the lowest excited states $(2p^4 3p) \rightarrow (2p^4 3s)\ ^{2,4}P$ (Blanks *et al.* 1987). In all spectral ranges studied the F emission from NF_3 is higher than the one from the CF_4 and SF_6 series: for the $(2p^4 3s)\ ^2P \rightarrow (2p^5)\ ^2P^0$ transition by a factor of almost 6 and 2, respectively (Roque *et al.* 1991).

Ionization in NF_3 was studied by Reese and Dibeler (1956). Appearance potentials for NF_3^+, NF_2^+, NF^+, N^+, F^+ ions were established as 13.2, 14.2, 17.9, 22.2 and 25 eV, respectively; at 70 eV collision energy the relative abundances are 60, 100, 39, 5.4, 4.8, respectively.

Electron attachment in NF_3 was studied in swarm experiment by Lakdawala and Moruzzi (1980), in a beam experiment by Harland and Franklin (1974) and in a flowing afterglow experiment by Miller *et al.* (1995). The electron attachment CS for the F^- + NF_2 decay channel exhibits a resonant peak of $0.6 \cdot 10^{-20}$ m^2 at 1.7 eV collision energy (Harland and Franklin). The F_2^- and NF_2^- are produced with intensities much lower than F^-, *i.e.* $3 \cdot 10^{-23}$ m^2 and $3 \cdot 10^{-24}$ m^2, respectively. Another, smaller maximum in the F^- cross-section (the F^- + N + 2F decay channel) was reported by Thynne (1969). The electron attachment coefficient was measured by the flowing afterglow method in the 300–550 K temperature range by Miller *et al.* (1995). At room temperature the attachment coefficient is of the order of 10^{-11} cm^3/s. Negative ions in radio-frequency discharge were studied by Hayashi *et al.* (1997).

Phosphorus fluorides (PF_3, PF_5)

Electron excitation for phosphorus halides (PF_3, PF_5, PCl_3) in forward-scattering configuration was studied by Brion and co-workers (Au *et al.* 1997a, c, b, respectively). For the two fluorides, below the ionization threshold (12.3 and 15.5 eV) the photoabsorption CS reaches similar values at its maximum: $0.44 \cdot 10^{-20}$ m^2 at 8.0 eV and $0.42 \cdot 10^{-20}$ m^2 at 14.0 eV, for PF_3 and PF_5, respectively. The photoabsorption CS in PCl_3 rises monotonically from 4.5 eV up to 13.5 eV where it reaches $1.72 \cdot 10^{-20}$ m^2. 53% of this cross-section is due to photoionization (Au *et al.* 1997b).

At 100 eV the photoionization CS in the two fluorides, PF_3 and PF_5 is higher than in PCl_3 ($9 \cdot 10^{-22}$ m^2, $14 \cdot 10^{-22}$ m^2 and $2.8 \cdot 10^{-22}$ m^2, respectively) (Au *et al.* 1997a, c, b). At this energy, PF_2^+ (55%) and PF_4^+ (52%) ions dominate in the ionization pattern of PF_3 and PF_5, respectively.

The electron attachment rate coefficient in PF_5 at 300–550 K is three orders of magnitude lower than in SF_6 (Miller *et al.* 1995). No electron attachment to PF_3 was observed in this experiment.

Boron fluoride (BF_3)

The electron attachment CS in BF_3 shows a large peak between 10 and 12 eV (Harland and Franklin 1974). The maximum ($2 \cdot 10^{-24}$ m^2) of the F_2^- formation CS is reached at 11.2 eV. The F^- cross-section is an overlap of two unresolved peaks, the higher one centered at 10.4 eV ($1 \cdot 10^{-22}$ m^2) and the weaker one at 12.1 eV. The ionization CS reaches a flat maximum of $5.5 \cdot 10^{-20}$ m^2 at 120–170 eV (Kurepa *et al.* 1976).

Boron chloride (BCl_3)

The electron attachment CS was studied in a swarm experiment by Petrović *et al.* (1990). The photoemission CS for the BCl ($A\ ^1\Pi \rightarrow X\ ^1\Sigma^+$) system was studied by Jabbour *et al.* (1988). Vacuum-UV fluorescence in the 9–22 eV energy range in BF_3 and BCl_3 was studied by Boyle *et al.* (1999). Radical and ion compositions in BCl_3 plasmas were studied by Kazami *et al.* (1997).

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3.6. *Linear fluorocarbons (*C_2F_6, C_3F_8*).* – Numerous other halocarbons, in addition to methane-like (subsects. **3**.1–**3**.3) and benzene-like (subsect. **3**.7) were studied by electron scattering, mainly in swarm and electron-attachment experiments. Due to high breakdown voltages (Brand and Kopainsky 1979), fluorinated alkanes and alkenes are used in electrical switches. In this subsection we present total and partial CS for two linear perfluoroalkanes: hexafluoroethane (C_2F_6), see fig. 17, and perfluoropropane (C_3F_8), see fig. 18. Detailed analyses of electron scattering in these gases were performed by Christophorou and Olthoff (1988a and b, respectively). In this subsection we also quote some other works on linear fluorocarbons. These gases are of basic importance both for the semiconductor technology (see, for example, Doh *et al.* 1996) and for the environmental chemistry.

Total cross-sections. The TCS in C_2F_6, C_3F_8, c-C_4F_8 (and CHF_3) have been recently measured by Sanabia *et al.* (1998) in a trochoidal spectrometer up to 20 eV. The TCS for C_2F_6, C_3F_8, C_4F_8 (and CF_4) in the 0.8–600 eV range were presented by Sueoka *et al.* (1997, 1999). Indicative values of the backward-scattering CS in C_2F_6, C_3F_8 (and CF_4) at energies up to 1 eV, 6 eV (and 1 eV), respectively, were obtained using a synchrotron-radiation electron source by Lunt *et al.* (1998); absolute values of the backward-scattering CS were given in the 10–175 meV energy range (Lunt *et al.* 1998).

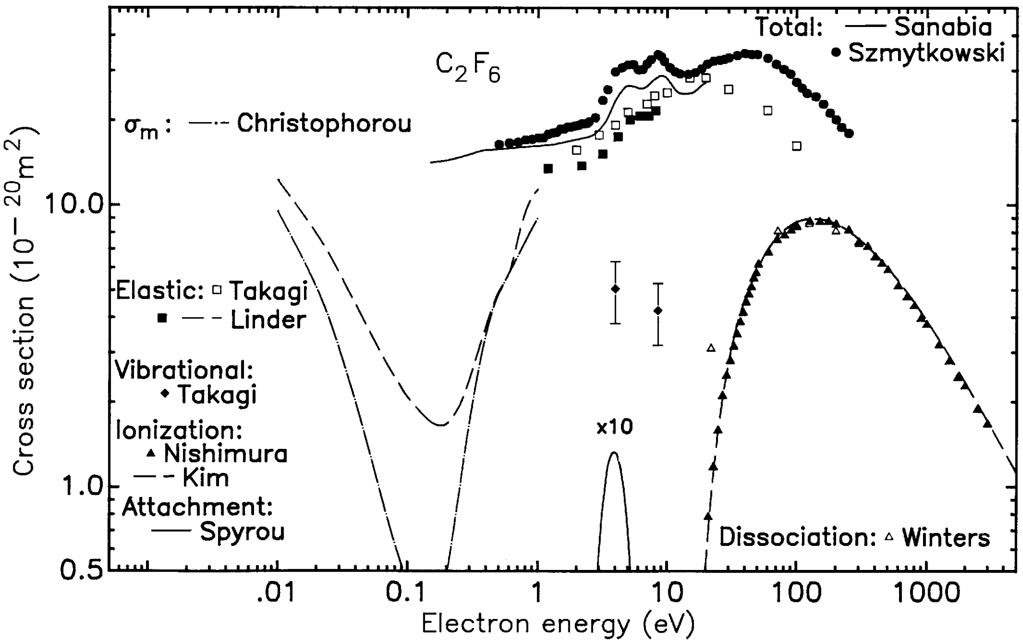

Fig. 17. – Integral cross-sections for electron scattering on C_2F_6. *Total:* Szmytkowski *et al.* (2000); Sanabia *et al.* (1998). *Elastic:* Takagi *et al.* (1994); Linder, experimental and modified effective-range extrapolation, data from Christophorou and Olthoff (1998a). *Momentum transfer:* Christophorou and Olthoff (1998a) recommended values. *Vibrational excitation:* Takagi *et al.* (1994). *Electron attachment:* Spyrou *et al.* (1983), normalized in the maximum to the recommended value by Christophorou and Olthoff (1998b). *Ionization:* Nishimura *et al.* (1999), experimental; Kim stands for the semi empirical model from Nishimura *et al.* (1999). *Dissociation* (ions + neutrals): Winters and Inokuti (1982).

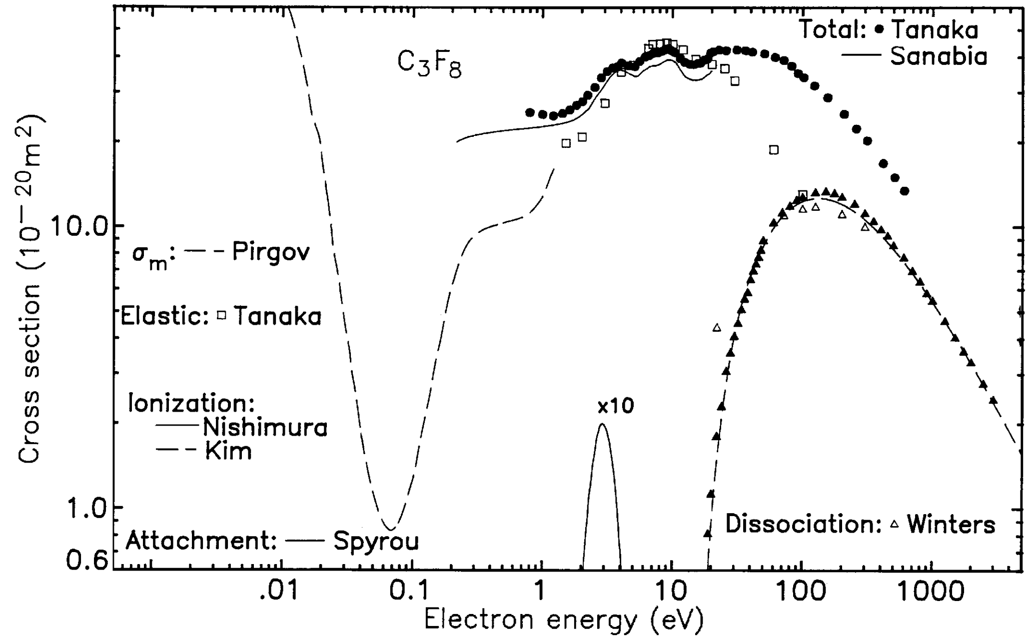

Fig. 18. – Integral cross-sections for electron scattering on C_3F_8. *Total:* Tanaka *et al.* (1999), read from figure; Sanabia *et al.* (1998). *Momentum transfer*: Pirgov and Stefanov (1990). *Elastic:* Tanaka *et al.* (1999). *Electron attachment:* Spyrou *et al.* (1983), normalized in the maximum to the recommended value by Christophorou and Olthoff (1998b). *Ionization:* Nishimura *et al.* (1999), experimental; Kim stands for the semi-empirical model from Nishimura *et al.* (1999). *Dissociation* (ions + neutrals): Winters and Inokuti (1982).

Absolute TCS in C_2F_6 have been measured by Sanabia *et al.* (1998) up to 20 eV and by Szmytkowski *et al.* (2000) in a transmission experiment from 0.5 to 250 eV. Both experiments indicate a decrease of the TCS in low-energy limits reached by their apparatuses (see fig. 17). The backward scattering CS gives a minimum of roughly $3 \cdot 10^{-20}$ m^2 at 0.06–0.08 eV (Lunt *et al.* 1998). The TCS exhibits resonant enhancements at 4.7 and 8.5 eV (Sanabia *et al.* 1998). The TCS values by Szmytkowski *et al.* (2000) are higher than the other two data sets (Sanabia *et al.*, Sueoka *et al.* 1997) and quote CS maxima of $31.3 \cdot 10^{-20}$ m^2 at 5.5 eV, $34.0 \cdot 10^{-20}$ m^2 at 8.5 eV and a broad maximum of $43.3 \cdot 10^{-20}$ m^2 centered around 40 eV.

The TCS in C_3F_8 has been measured by Tanaka *et al.* (1999) in the 0.8–600 eV range. The preliminary measurements of Sueoka *et al.* (1997) are not shown in fig. 17. The TCS energy dependence is to some extent similar to the one in CF_4: the C_3F_8 total cross-section shows a similar maximum at 9 eV, the same large bump at 20–50 eV but, additionally, a weak maximum at 4 eV. The value of TCS in 9 eV maximum, about $42.5 \cdot 10^{-20}$ m^2, is lower in C_3F_8 than in C_3H_8 (Tanaka *et al.* 1999). The low-energy measurements (Sanabia *et al.* 1998) indicate a resonant maximum at 3.6 and a weak structure at 6.1 eV. Both the TCS in C_2F_6 and C_3F_8 fall slowly with lowering energy toward 0.1–0.2 eV (Sanabia *et al.*). Lunt *et al.* (1998) reported a minimum in the backward scattering CS of roughly $6 \cdot 10^{-20}$ m^2 at 0.05–0.1 eV.

Swarm experiments. The early electron swarm data in C_2F_6, C_3F_8, C_4F_{10} were reviewed by Gallagher *et al.* (1983). Recommended momentum transfer CS for C_2F_6 and C_3F_8 were given by Christophorou and Olthoff (1998a and b, respectively). The analysis of swarm data for C_2F_6 and C_3F_8 was also done by Pirgov and Stefanov (1990).

The drift velocity in C_2F_6, C_3F_8, n-C_4F_{10} (and CF_4) were measured at reduced electric fields between $0.03 \cdot 10^{-21}$ Vm^2 and $500 \cdot 10^{-21}$ Vm^2 by Hunter *et al.* (1988). In perfluoroalkanes (CF_4, C_2F_6, C_3F_8), for reduced field values in the 10^{-20} Vm^2 range, the drift velocity is a descending function of this field, indicating the existence of a Ramsauer-Townsend minimum. The effect in C_2F_6 and C_3F_8 is less pronounced than in CF_4; no effect was observed in n-C_4F_{10}. This is consistent with the above-quoted observation in TCS measurements.

Gee and Freeman (1992) measured the electron mobility in C_2F_6 at reduced electric fields values below $2 \cdot 10^{-21}$ Vm^2. The momentum transfer CS falls from $20 \cdot 10^{-20}$ m^2 at 6 meV to about $3.2 \cdot 10^{-20}$ m^2 at 90 meV; then it rises sharply, due to the onset of vibrational excitation channels (Gee and Freeman).

The elastic cross-section in C_2F_6 at 2–100 eV was measured by Takagi *et al.* (1994). The DCS at 2 eV shows a sharp minimum at 20°, which becomes shallower with rising the energy. At 8–20 eV the DCS shows a *d*-wave pattern with two minima at about 40° and 120° and a maximum at 90°. The integral elastic CS shows a single, broad maximum centered at 15–20 eV.

The low-energy measurements in C_2F_6 and the modified effective-range analysis of Merz and Linder (1998) were reported by Christophorou and Olthoff (1998a). According to the analysis of Merz and Linder, the integral elastic CS shows a minimum of $1.6 \cdot 10^{-20}$ m^2 at about 0.2 eV.

The C_3F_8 integral elastic CS (Tanaka *et al.* 1999, note an error in the caption of their table II) shows a maximum in the integral CS coinciding both in position (9 eV) and in value ($45 \cdot 10^{-20}$ m^2) with the one in C_3H_8. However, outside this maximum, the integral CS in C_3F_8 is higher than that in C_3H_8 both at low and high energies.

Elastic CS for fluorinated derivatives of hydrocarbon molecules were announced by Merz and Linder (1998) in their article on C_2H_6.

Vibrational cross-sections in C_2F_6 between 1 eV and 16 eV have been measured by Takagi *et al.* (1994). The excitation functions for the "stretching modes" (0.16 eV energy loss) at 60°, 90° and 120° show an enhancement at 4.5 and at 8.5 eV. At 4.5 eV the ν_1, ν_3, ν_2 stretching modes (all of A_{1g} symmetry) and their higher harmonics are excited; at 8.5 eV both the stretching and bending modes (E_g symmetry) ν_{10}, ν_{11}, ν_{12} are excited. The DCS for stretching modes are forward centered at all studied energies but particularly at the low ones. At 4 eV the vibrational excitation CS amounts to about 26% of the elastic CS and at 8.5 eV to about 17% (Takagi *et al.* 1994).

Vibrational cross-sections in C_3F_8 in the 3–15 eV energy range were reported by Tanaka *et al.* (1999). The energy resolution of this experiment did not allow to resolve individual vibrational modes (including 25 fundamental modes and their overtones). An enhancement of the ν_1 (C-C stretching), ν_2 (C-F_3 stretching) and ν_3 (C-F_2 stretching) mode and their overtones was observed at 3 eV and between 6 and 9 eV. At 6.5 eV and 9 eV, apart from the above modes, also the ν_4 (C-C stretching) and ν_6 (C-F_2 stretching deformation) modes are enhanced. The ν_1 mode becomes more prominent at 4 and 9 eV. DCS at 3 eV are *p*-wave–like for the ν_1 mode and rather *d*-wave–like for the ν_2 and ν_3 modes.

Electronic excitation. We are not aware of electronic excitation integral CS for C_2F_6 and C_3F_8. Electronic excitation in six fluoroethylenes (C_2H_3F; 1,1-$C_2H_2F_2$; cis-1,2-$C_2H_2F_2$; cis-1,1-$C_2H_2F_2$; trans-1,2- $C_2H_2F_2$, C_2HF_3, C_2F_4) and chlorotrifluoroethylene

(C_2F_3Cl) was studied in detail at impact energies of 20 (or 25), 40, 60 eV by Coggiola *et al.* (1976). Relative DCS in the 0°–80° angular range were reported. Two transitions were studied: the "$N \to T$" ($\pi \to \pi^*$) singlet-triplet one at 4.18–4.68 energy loss and the "$N \to V$", optically allowed, at 6–10 eV energy loss (depending on the target). The DCS shows typical angular dependencies: a flat one for the "$N \to T$" excitation and a forward-peaked one for the "$N \to V$" excitation. The relative values of DCS vary by three orders of magnitude from monofluoroethylene (C_2H_3F) to chlorotrifluoroethylene (C_2F_3Cl). Energy loss spectra up to 16 eV energy loss were also reported by Kuppermann *et al.* (1979).

Ionization cross-sections, both theoretical and experimental, on C_2F_6, C_3F_8 (and CF_4) have recently been given up to 3000 eV by Nishimura *et al.* (1999). For both gases the experimental data of Nishimura *et al.* (1999) agree well up to 100 eV with the data of Poll and Meichsner (1985) and with the data of Beran and Kevan (1969) at 20, 35 and 70 eV. The data of Kurepa (1965) are higher and those of Chantry and Chen (1989) for C_3F_8 are lower. In fig. 17 the semiempirical values reported by Nishimura *et al.* (1999) are labeled with "Kim".

Neither in C_2F_6 nor C_3F_8 parent ions were measured (Poll and Meichnser 1987). In both gases the CF_3^+ ion dominates. At 100 eV the branching ratios in C_2F_6 are 33%, 50%, 6% and 11% for $C_2F_5^+$, CF_3^+, CF_2^+ and CF^+ ions, respectively; for C_3F_8 the $C_3F_7^+$, $C_2F_5^+$, $C_2F_4^+$, CF_3^+, CF_2^+ and CF^+ ions scale as 12:5:3:67:3:10 (numerical data from Christophorou and Olthoff 1998a, b).

Dissociation cross-section. The overall CS for ionization and dissociation into neutrals of C_2F_6 and C_3F_8 were measured by Winters and Inokuti (1982) up to 300 eV with a $\pm 20\%$ uncertainty. At 70–300 eV their total (neutrals + ions) CS in C_3F_8 is double than that for CF_4, reaching the maximum value of $11.8 \cdot 10^{-20}$ m^2 at 100–120 eV; in C_2F_6 this maximum amounts to $8.6 \cdot 10^{-20}$ m^2. These values coincide, within the experimental errors, with the total ionization CS of Nishimura *et al.* (1999). In the near-to-threshold region (22 eV) the difference between the ionization CS (Nishimura *et al.* 1999) and Winter and Inokuti's CS amounts to $2.1 \cdot 10^{-20}$ m^2 and $2.6 \cdot 10^{-20}$ m^2 in C_2F_6 and in C_3F_8, respectively, *i.e.* about 6% of the TCS (Szmytkowski *et al.* 2000, Tanaka *et al.* 1999).

The recent measurements of Motlagh and Moore (1998) in C_2F_6 and in C_3F_8 have solely reported the overall CS for dissociation into both the ionized and neutral radicals. For C_2F_6 the overall CS for formation of CF_3 and C_2F_5 radicals was measured. This CS reaches a maximum of about $4.8 \cdot 10^{-20}$ m^2 at 70–100 eV. Subtracting from this value the CF_3^+ partial ionization cross-sections of Poll and Meichsner (1987), a neutral dissociation CS of about $1 \cdot 10^{-20}$ m^2 was deduced (Motlagh and Moore 1998). In C_3F_8 the cross-section for overall dissociation into the neutral and ionized CF_3 and C_2F_5 radicals amounts to $6 \cdot 10^{-20}$ m^2 at 100 eV (Motlagh and Moore 1998).

Electron attachment in fluorocarbons was studied with different methods. In swarm experiments, among others, the following targets were studied: C_2F_6 (Spyrou and Christophorou 1985a); 2-C_4F_8 (Christophorou *et al.* 1974); *c*-C_4F_6 (Datskos *et al.* 1993). Very low-energy experiments using electrons from Kr-threshold photoionization were performed on: 2-C_4F_6 (Chutjian *et al.* 1984); *c*-C_6F_{10}, *c*-C_6F_{12}, C_8F_{16}, 1,1,2-$C_2F_3Cl_3$ (Alajajian and Chutjian 1986); *c*-C_4F_6, *c*-C_4F_8, *c*-C_7F_{14} (Chutjian and Alajajian 1987); 1,1,1-$C_2F_3Cl_3$ (Alajajian *et al.* 1988). Beam experiments were carried out in: C_2F_6, C_3F_8, *c*-C_4F_8 (Harland and Franklin 1974); *c*-C_5F_8, *c*-C_6F_{10}, *c*-C_6F_{12}, C_7F_8, C_8F_{16} (Pai *et al.* 1979); perfluoroalkanes *n*-C_nF_{2n+2} (n = 1–6) and *i*-C_4F_{10} (Spyrou *et al.* 1983); C_3F_8 and C_2H_3Cl (Chantry and Chen 1989); fluoroethylenes C_2F_4, trans-1,2-$C_2H_2F_2$, cis-1,2-$C_2H_2F_2$, 1,1-$C_2H_2F_2$ (Oster *et al.* 1989); C_2H_5Cl (Pearl and Burrow 1993); normal chloroalkanes $C_nH_{2n+1}Cl$ (n = 2–9) by Pearl and Burrow (1994); C_2F_6, C_2F_4 (Weik and Illenberger 1995). Pulse-radiolysis microwave experiments were performed on: 1,1,1-$C_2F_3Cl_3$, 1,1,1-$C_2H_3Cl_3$ (Shimamori *et al.* 1992); in Rydberg atoms quenching: 1,1,1-$C_2F_3Cl_3$, C_5F_8 and *c*-C_7F_{14} (Zollars *et al.* 1984, Dunning 1987); in flowing plasma afterglow: $C_2H_3Cl_3$, $C_2F_3Cl_3$ (Smith *et al.* 1989).

Dissociative attachment only was observed in C_2F_6 (and CF_4), while in C_3F_8 (and *n*-C_4F_{10}) also non-dissociative attachment was measured (Hunter and Christophorou 1984, Spyrou and Christophorou 1985a, b, Datskos and Christophorou 1987, Hunter *et al.* 1987). The thermal attachment rate constant is below 10^{-16} cm^3 s^{-1} in CF_4 and C_2F_6, while it amounts to about $4 \cdot 10^{-11}$ cm^3 s^{-1} in *n*-C_4F_{10} and is not greater than $3 \cdot 10^{-13}$ cm^3 s^{-1} in C_3F_8 (Hunter *et al.* 1987).

In C_2F_6 three fragment negative ions were observed: F^-, CF_3^- and $C_2F_5^-$, with relative peak intensities less than 1000, 316, and 1 (Spyrou *et al.* 1983). The F^- and CF_3^- peaks are centered around 3.9–4.0 eV, while the $C_2H_5^-$ peak is at 4.8 eV. A recommended value of $0.14 \cdot 10^{-20}$ m^2, *i.e.* about 0.5% of the TCS (Szmytkowski *et al.* 2000), has been given for the total electron attachment CS at 4.0 eV (Christophorou *et al.* 1998a).

In C_3F_8 five fragment negative ions were observed: $C_3F_7^-$, $C_2F_5^-$, $C_2F_3^-$, CF_3^- and F^-, with relative peak intensities of 1.7, 66, 1.8, 54 and 1000 (Spyrou *et al.* 1983). The F^- peak is centered at about 2.9 eV while the others at 3.2–3.7 eV. The signal from CF_3^- extends up to 7 eV (Spyrou *et al.* 1983). A recommended value of $0.2 \cdot 10^{-20}$ m^2, *i.e.* about 0.7% of the TCS (Tanaka *et al.* 1999) has been given for the total electron attachment CS at 2.5 eV (Christophorou *et al.* 1998b).

Sum check. The sum of the elastic and vibrational CS (Takagi *et al.* 1994) in C_2F_6 at the maxima of the resonant vibrational excitation (4.0 and 8.5 eV) is somewhat lower than the recent TCS (Szmytkowski *et al.* 2000) and agrees better with the TCS of Sanabia *et al.* (1998), see Table VIII. On the other hand, at 15 eV the elastic CS (Takagi *et al.* 1994) exceeds the TCS of Sanabia *et al.* At 22 eV the sum of the elastic CS (Takagi *et al.* 1994) and the dissociation (neutrals + ions) CS (Winters and Inokuti 1982) agrees within the experimental uncertainty with the TCS of Szmytkowski *et al.* (2000). At 100 eV, the difference between the TCS (Tanaka *et al.* 1999) and the summed ionization (Nishimura *et al.* 1999) and elastic (Tanaka *et al.* 1999) CS amounts to 10% of the TCS and corresponds possibly to the electronic excitation CS.

No absolute values of vibrational CS were given by Tanaka *et al.* (1999) for C_3F_8, so no sum check is possible at low energies, see Table IX. At 6–15 eV the elastic CS (Tanaka *et al.* 1999) exceeds the two (Tanaka *et al.* 1999, Sanabia *et al.* 1998) TCS determinations. Similarly to in C_2F_6, at 22 eV the sum of the elastic CS (Tanaka *et al.* 1999) and the dissociation (neutrals + ions) CS (Winters and Inokuti 1982) agrees very well with the TCS (Tanaka *et al.* 1999). At higher energies the TCS is 10–15% higher than the sum of the ionization (Nishimura *et al.* 1999) and elastic CS; the missing part can correspond to the electronic and/or dissociation-into-neutrals CS.

Other fluorocarbons. The C_2F_4 elastic and vibrational CS have been studied in the 1.5–100 eV energy range by Suzuki *et al.* (1999) and Okamoto *et al.* (1999a, b). The C_2F_4 elastic DCS at 2 eV (Suzuki *et al.* 1999) and 10 eV (Okamoto *et al.* 1999b) are unusually low compared to C_2H_4. The DCS for vibrational excitation in C_2F_4 indicate two broad resonances at 3 eV and 6 eV (Suzuki *et al.* 1999).

The total cross-section in *c*-C_4F_8 was measured at 2–3000 eV by Nishimura (1999) and by Sanabia *et al.* (1998) below 20 eV. The TCS shows a minimum of about $21 \cdot 10^{-20}$ m^2 at 3.5–4.0 eV and an almost a constant value of 38–40 $\cdot\ 10^{-20}$ m^2 at 9–20 eV (Sanabia

TABLE VIII. – *Integral cross-sections for electron scattering on* C_2F_6 *(in* 10^{-20} m^2 *units).*

Energy (eV)	Elastic	Vibrational	Dissociation	Ionization	Sum	Total
2.0	15.5 T					19.0 Sz 17.0 SA
4.0	19.1 T	5.0 T1			24.1	29.5 Sz 23.5 SA
8.5	24.3 T	4.2 T1			28.5	34.0 Sz 28.3 SA
15	28.0 T					29.0*Sz 24.8 SA
20	28.1 T					31.1*Sz
22	27.0*T		3.1 W	(0.98*N)	30.1	31.9*Sz
30	25.3 T			2.65*N	28.0	33.1 Sz
60	21.5 T			6.76*N	28.3	33.0 Sz
72	20.2*T		(8.1) W	7.60*N	27.8	31.2*Sz
100	16.1 T		(8.5) W	8.39 N	24.5	27.1 Sz
125			(8.6) W	8.77 N		24.7*Sz
200			(8.1) W	8.57 N		20.0 Sz

* Interpolated values
( ) Not used for summation
N - Nishimura *et al.* (1999)
T - Takagi *et al.* (1994)
T1- Takagi *et al.* (1994), normalized to elastic, given at 4.0 and 8.5 eV
W - Winters and Inokuti (1982)
Sz - Szmytkowski *et al.* (2000)
SA - Sanabia *et al.* (1998)

et al.). The values of Nishimura agree well in shape with those of Sanabia *et al.* (1998) but are about 10–15% higher; small humps can be seen around 9, 10 and 40 eV; at 3000 eV the TCS amounts to about $4.5 \cdot 10^{-20}$ m^2.

Elastic CS in *c*-C_4F_8 at 3–15 eV were reported by Okamoto *et al.* (1999b). The DCS for this molecule (Okamoto *et al.*) resemble much, both in shape and in absolute values, those for C_2F_6 (Takagi *et al.* 1994). Partial ionization CS and neutral dissociation CS in *c*-C_4F_8 from threshold to 250 eV were measured by Toyoda *et al.* (1997), radical production rates by Sasaki *et al.* (1998) and Sasaki and Kadota (1999), swarm coefficients by Yamaji *et al.* (1999). Itoh *et al.* (1991) gave a set of cross-sections up to 100 eV in *c*-C_4F_8.

Resonances in ethylene C_2H_4 and five fluoroethylenes up to C_4F_4 were studied by Chu *et al.* (1979). The position of resonances observed in transmission current rises from 1.78 eV in C_2H_4 to 3.0 eV in C_2F_4. Fluorination effects on the inner-shell spectra of unsaturated molecules, including five fluoroethylenes, were studied by Robin *et al.* (1988).

TABLE IX. – *Integral cross-sections for electron scattering on* C_3F_8 *(in* 10^{-20} m^2 *units).*

Energy (eV)	Elastic	Dissociation	Ionization	Sum	Total
1.5	19.8 TA				25.3 T
2.0	20.8 TA				27.8 T
5.0	37.5 TA				37.0 T
10	44.3 TA				41.6 T
15	39.15 TA				38.0 T
20	37.6 TA		1.13 N	38.7	41.8 T
22	37.1*TA	4.4 W	(1.81) N	41.5	42.4 T
30	32.9 TA		4.10 N	37.0	42.5 T
60	18.8 TA		10.4 N	29.2	40.0 T
72	17.1*TA	(11.0) W	10.6*N	27.7	39.0 T
100	13.0 TA	(11.6) W	12.8 N	25.8	33.8 T
125		(11.8) W	13.3 N		31.6 T
200		(11.1) W	12.8 N		25.1 T
300		(10.0) W	11.2 N		20.0 T

* Interpolated data
( ) Not used for summation
N - Nishimura *et al.* (1999)
TA - Tanaka *et al.* (1999)
T - Tanaka *et al.* (1999), read from their figure
W - Winters and Inokuti (1982)

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3$\cdot$7. *Hexafluorobenzene (*C_6F_6*).* – Hexafluorobenzene (C_6F_6) is a molecule strongly attaching electrons at low energies. Most of the existing measurements are concerned with this phenomenon. We are not aware of measurements of partial CS. A set of attachment cross-sections is reported in fig. 19 in the 1 meV–2 eV energy range.

Total cross-sections between 0.6 and 250 eV have been measured in a linear transmission experiment by Kasperski *et al.* (1997). The TCS exhibits a very weak maximum of $33 \cdot 10^{-20}$ m^2 at 1.1 eV, a shallow minimum at 3.5 eV and a broad maximum of $60 \cdot 10^{-20}$ m^2 at 25–30 eV. A shoulder structure is visible on the left side of this maximum, at about 15 eV. The TCS dependence from energy is similar to that in C_6H_6, but is shifted to higher energies, compare fig. 2.

The TCS below 1 eV in monohalogenated benzenes, C_6H_5F, C_6H_5Cl, C_6H_5Br, C_6H_5I were studied using a synchrotron-radiation electron source (Lunt *et al.* 1999). Both integral and "backward scattering" CS were determined. In the zero-energy limit the integral CS rise, in good accord with the Born approximation for rotational excitation (Lunt *et al.* 1999), and at 0.1 eV amount to $500\text{-}800 \cdot 10^{-20}$ m^2 for the C_6H_5F-C_6H_5I series. Weak resonant structures in TCS (about $5 \cdot 10^{-20}$ m^2) at 0.7-1.0 eV were observed in C_6H_5F, C_6H_5Cl and C_6H_5Br (Lunt *et al.* 1999).

Electronic excitation. Energy loss spectra in fluorobenzenes for the 3.4–8.5 eV energy

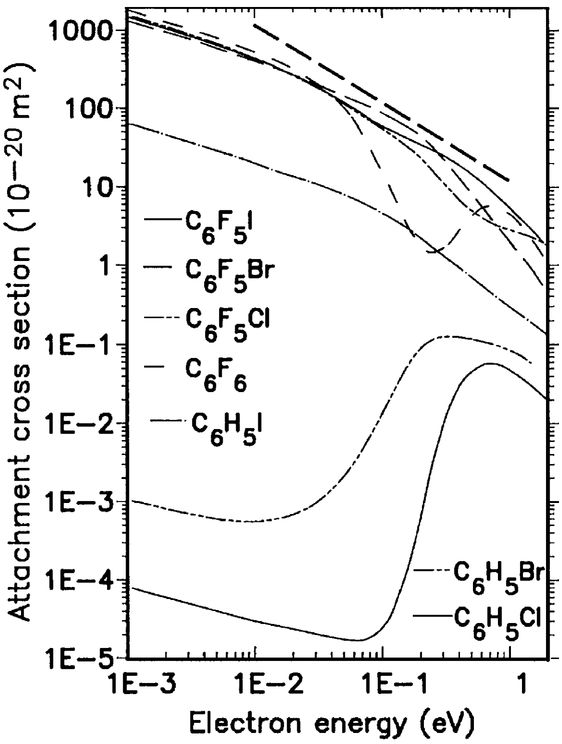

Fig. 19. – Electron attachment cross-sections for monohalomethanes C_6H_5I, C_6H_5Br, C_6H_5Cl (Shimamori *et al.* 1995) and pentafluorobenzenes C_6F_5I, C_6F_5Br, C_6F_5Cl and C_6F_6 (Shimamori *et al.* 1994) from pulse-radiolysis microwave-cavity measurements. The uppermost straight line indicates the theoretical limit for the *s*-wave capture (Wigner 1948).

loss were reported by Frueholz *et al.* (1977, 1979). Transition energies are similar in the whole series C_6H_6-C_6F_6. In C_6F_6 these energies are 3.86 eV for the excitation to the first triplet state ($\tilde{X}^1A_{1g} \rightarrow 1^3B_{1u}$, the symmetry designations correspond to the transitions in benzene), 4.80, 6.36 and 7.10 eV for the excitations to singlet states (1^1B_{2u}, 1^1B_{1u}, 1^1E_{1u}, respectively). The excitation to another triplet, 1^3E_{1u} state, like that in C_6H_6 at 5.59 eV, has not been observed for C_6F_6; instead, the excitation to a singlet state at 5.32 eV was seen (Frueholz *et al.* 1977). The electron excitation in monosubstituted benzene derivatives (including C_6H_5F) was studied by the electron-scavenger method (Christophorou *et al.* 1974).

Ionization. Diebler *et al.* (1957) reported relative ion abundances for C_6H_6 and C_6F_6 at 70 eV collision energy. Fragment ions, in particular $C_5X_3^+$ and CX^+, are generally more abundant in C_6F_6 than in C_6H_6. The $C_5F_5^+$ and $C_5F_4^+$ ions have no analogs in C_6H_6.

Electron attachment. C_6F_6, similarly to SF_6, forms a quasi-stable parent anion, $C_6F_6^-$. The lifetime of the transient vibrationally excited $C_6F_6^{-*}$ ion formed by electron attachment at thermal energies is about 12 μs (Naff *et al.* 1968, Gant and Christophorou 1976, Christophorou *et al.* 1977). The ion can be stabilized in collisions with a buffer gas (N_2, Datskos *et al.* 1993) or in clustering reactions (Hiraoka *et al.* 1990). The electron affinity of C_6F_6 is +0.86 eV (Jordan *et al.* 1976b, Chen *et al.* 1985, Wentworth *et al.* 1987, see also Weik and Illenberger 1995 and Chowdhury *et al.* 1986). The electron attachment has been studied by beam (Fenzlaff and Illenberger 1984, Fenzlaff and Illenberger 1989, Oster *et al.* 1989, Weik and Illenberger 1995), swarm (Gant and Christophorou 1976, Spyrou and Christophorou 1985, Datskos *et al.* 1993), flowing afterglow (Adams *et al.* 1985), threshold photoionization (Chutjian and Alajajian 1985), Rydberg atoms quenching (Hildebrandt *et al.* 1978, Marawar *et al.* 1988) techniques. Woodin *et al.* (1980) used the ion cyclotron resonance spectroscopy to determine the non-dissociative attachment rate coefficients for C_6F_6 (and C_7F_8, c-C_4F_8, C_7F_{14}, CCl_4). They obtained in C_6F_6 attachment rate coefficients a factor of ten lower than in SF_6.

Studies of attachment by the Rydberg atoms technique (Hildebrandt *et al.* 1978, Marawar *et al.* 1988) showed that the rate coefficient is independent of the Rydberg electron velocity distribution. This indicates an *s*-wave capture process. The attachment rate, determined by quenching potassium atoms with principal quantum numbers up to 100, amounts to about $0.45 \cdot 10^{-7}$ cm^3 s^{-1} which corresponds to a cross-section value of about $240 \cdot 10^{-20}$ m^2 at 1.0 meV (Marawar *et al.* 1988). Gant and Christophorou (1976) reported attachment CS of $123 \cdot 10^{-20}$ m^2 at 30 meV and of $8.04 \cdot 10^{-20}$ m^2 at the 0.73 eV peak. Chutjian and Alajajian (1985) studied electron attachment at very low energies for C_6F_6 (and 2-C_4F_8, c-C_5F_8, C_7F_8) using the Kr photoionization technique. They normalized the attachment CS to the rate coefficient $1.5 \cdot 10^{-7}$ cm^3 s^{-1} at 0.05 eV mean electron energy as extracted from swarm experiments (Spyrou and Christophorou 1985). Chutjian and Alajajian gave the following analytical formula for the CS:

$$\sigma_A = N\Big[aE^{-0.5} * \exp[-E^2/\lambda^2] + \exp[-E/\gamma]\Big] \tag{3}$$

with E in eV, $N = 389 \cdot 10^{-20}$ m^2, $a = 8.14 \cdot 10^{-2}$ eV$^{1/2}$, $\lambda = 4.33 \cdot 10^{-3}$ eV, $\gamma = 3.57 \cdot 10^{-2}$ eV. According to these parameters, the attachment CS would amount to $380 \cdot 10^{-20}$ m^2 at 1 meV. Note that a slightly modified formula was given in Chutjian and co-workers' corrigendum of the $C_2H_2Br_4$ data (Alajajian *et al.* 1996):

$$\sigma_A = N\Big[aE^{-0.5} + \exp[-E^2/\lambda^2] + \exp[-E/\gamma]\Big]\,. \tag{4}$$

While the attachment CS in c-C_5F_8 and C_7F_8 approaches the theoretical limit for the s-wave electron capture, the C_6F_6 cross-section is by a few folds lower.

The apparent low-energy attachment coefficient rate in C_6F_6 decreases with increasing gas temperature (Spyrou and Christophorou 1985, Adams *et al.* 1985). This observation has been explained by the rise of the detachment coefficient rate with the increase of temperature (Chen *et al.* 1985, Christophorou 1985, Knigton *et al.* 1992, Datskos *et al.* 1993).

A second peak in electron attachment CS, observed in swarm (Gant and Christophorou 1976, Datskos *et al.* 1993) and pulse radiolysis (Shimamori *et al.* 1994) experiments at about 0.7–0.8 eV, has been associated with the electron capture to the π_6-orbital (Datskos *et al.* 1993). Two more maxima were observed in electron-beam experiments. Around 4.5 eV F^- ions and, in less amount, $C_6F_5^-$ (25%) ions were observed (Fenzlaff and Illenberger 1989, Oster *et al.* 1989). In a broad peak (from 8 to 13 eV) for the F^- ion production, three sub-structures are visible. At 8.5 eV, $C_6F_5^-$ ions are also produced, while at higher energies only F^- is produced (Fenzlaff and Illenberger 1989, Oster *et al.* 1989, Weik and Illenberger 1995). The 8–13 eV structure also shows other fragment anions, like $C_6F_3^-$ (Fenzlaff and Illenberger 1984).

Electron attachment to gases in the pentafluorobenzene series C_6F_5X (X = F, Cl, Br, I) was studied by Herd *et al.* (1989) and Shimamori *et al.* (1993, 1994), and in the monohalobenzene series C_6H_5X (X = F, Cl, Br, I) by Shimamori *et al.* (1995). For all the four pentafluorobenzenes the same rate constant of $2 \cdot 10^{-7}$ cm^3 s^{-1} (independently of the buffer gas used) was measured at thermal energies (Shimamori *et al.* 1993, 1994). The parent anions $C_6F_6^{-*}$, $C_6F_5Cl^{-*}$, $C_6F_5Br^{-*}$, $C_6F_5I^{-*}$ have lifetimes long enough to be stabilized in the collisions with the buffer gas (Shimamori *et al.* 1993, 1994). The electron attachment CS falls monotonically with energy in the 1 meV–1 eV range from about $1.5 \cdot 10^{-17}$ m^2 at 1 meV for all the three C_6F_5Cl, C_6F_5Br, C_6F_5I molecules (Shimamori *et al.* 1994), see fig. 19. The fall, up to 0.01 eV, follows approximately an $E^{-1/2}$ dependence, in agreement with Wigner's (1948) threshold law. At about 0.1 eV the CS in all four gases C_6F_6, C_6F_5Cl, C_6F_5Br, C_6F_5I approaches the s-wave limit for attachment (see fig. 19). In C_6F_6 at 1 meV, according to the measurements of Shimamori *et al.* (1994), the CS is $1.7 \cdot 10^{-17}$ m^2 and shows a maximum at about 0.75 eV, as described before.

In monohalogenated benzenes C_6H_5X, no parent anions were observed but only dissociated X^- ions (Shimamori *et al.* 1995). Only the C_6H_5I dissociative attachment CS shows a monotonic dependence starting from a $6.4 \cdot 10^{-19}$ m^2 value at 1 meV, similar to that in the C_6F_5X group. For C_6H_5Cl and C_6H_5Br a sharp rise of the electron attachment CS by 2–3 orders of magnitude was observed between 0.05 and 0.5 eV (Shimamori 1995 *et al.*), see fig. 19. The maximum CS value in C_6H_5Cl and in C_6H_5Br is $5.5 \cdot 10^{-22}$ m^2 and $1.2 \cdot 10^{-21}$ m^2 at 0.7 and 0.3 eV, respectively (Shimamori *et al.* 1995). Swarm measurements (Gant and Christophorou 1976, Datskos *et al.* 1993) indicated a maximum of attachment CS in these two gases at about 0.8 eV. As estimated by Shimamori *et al.* (1995), the dissociative attachment in C_6H_5I is exothermic by 0.24 eV and in C_6H_5Br, C_6H_5Cl, C_6H_5F endothermic by 0.14, 0.54 and 2.02 eV, respectively.

Several works made a systematic comparison of temporary negative-ion resonance energies for benzene and fluorine substituted benzenes (see, for example, Hahndorf and Illenberger 1997). Naff *et al.* (1968) determined that each fluorine atom added to the benzene ring increases the electron affinity by about 0.4 eV. More recent works (Jordan *et al.* 1976b, Frazier *et al.* 1978) and calculations (Hinde *et al.* 1978, Birch *et al.* 1980) reported a smaller increase of the electron affinity (0.26 to 0.30 eV); for example from −1.15 eV in C_6H_6 to about −0.85 eV in C_6H_5F (Jordan *et al.* 1976b, Frazier *et al.* 1978). A slightly higher increase is observed for other halogen-atom–substituted benzenes, like C_6H_5Cl, C_6H_5Br (Jordan *et al.* 1976b).

Resonances. Frazier *et al.* (1978) used an electron transmission technique to determine the position of resonances in the C_6H_6–C_6F_6 series. They reported two resonant states in C_6F_6: at 0.42 and 4.50 eV. None of these states was seen in the TCS (Kasperski *et al.* 1997). The positions of these resonances are somewhat closer to those in C_6H_6, *i.e.* 1.35 and 4.80 eV (Frazier *et al.* 1978) than the theoretical predictions, 0.13 and 4.02 eV.

Effects in resonant states due to the substitution of hydrogen atoms in C_6H_6 with halogen atoms and different functional groups were also studied by Compton *et al.* (1968), Christophorou *et al.* (1974), Burrow *et al.* (1976), Jordan *et al.* (1976a, b), Giordan and Moore (1983) and those due to the substitution of carbon atoms in C_6H_6 with nitrogen by Pisanias *et al.* (1972) and Nenner and Schulz (1975).

Lunt *et al.* (1999) observed shape resonances in the TCS of C_6H_5F, C_6H_5Cl and C_6H_5Br at about 0.7–1.0 eV. These resonances form a family which, including that in C_6H_6 at 1.17 eV, moves down in energy, illustrating increasing stabilization of the molecular orbital with decreasing electronegativity of the substituent (Olthoff *et al.* 1985). Resonance energies are 0.87, 0.75 and 0.69 eV for C_6H_5F, C_6H_5Cl and C_6H_5Br, respectively (Lunt *et al.* 1999). An additional structure in the C_6H_5F resonance has been attributed (Lunt *et al.* 1999) to a superposition of outgoing and reflected wave functions formed during the resonance lifetime.

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3˙8. *Sulphur hexafluoride (*SF_6*)*. – The very high cross-section for electron attachment at near-to-zero energies promotes the extensive use of SF_6 in electrical switches and high-voltage power lines. For this reason, a number of works have been devoted to modeling SF_6 plasmas and discharges and numerous semiempirical cross-section data sets have been published (see, *e.g.*, Kline *et al.* 1979, Dincer and Govinda Raju 1983, Hayashi and Nimura 1984, Novak and Fréchette 1984, Phelps and Van Brunt 1988, Shimamura 1989, Itoh *et al.* 1988, 1991, 1993, Meyyappan 1997). In particular, numerical sets of electron scattering CS in SF_6 are also available in internet (Morgan 1999, Phelps 1999). Experimental total and partial CS are shown in fig. 20.

Total cross-sections have been measured with use of the time-of-flight absolute method by Ferch *et al.* (1982) in the 0.036–1.0 eV energy range, by Kennerly *et al.* (1979) using the same method at 0.5–100 eV, by Wan *et al.* (1993) at 0.2–12 eV using a trochoidal monochromator, by Romanyuk *et al.* (1984) in the 0.25–25 eV energy range using an electron trap and normalizing their data to those of Kennerly *et al.* (1979) at 7 eV, by Dababneh *et al.* (1988) at 1–500 eV who used a magnetically guided electron (or positron) beam and by Zecca *et al.* (1992) at 75–4000 eV using an absolute transmission method in a modified Ramsauer configuration. The agreement between different results is rather good, as compared in detail by Kasperski *et al.* (1997). The data in the latter paper agree well with the measurements of Dababneh *et al.* (1988) at low energies; at 100 eV the data of Kasperski *et al.* are 10% higher than the measurements of Dababneh *et al.* but coincide with those of Zecca *et al.* (1992). The data of Kennerly *et al.* (1979)

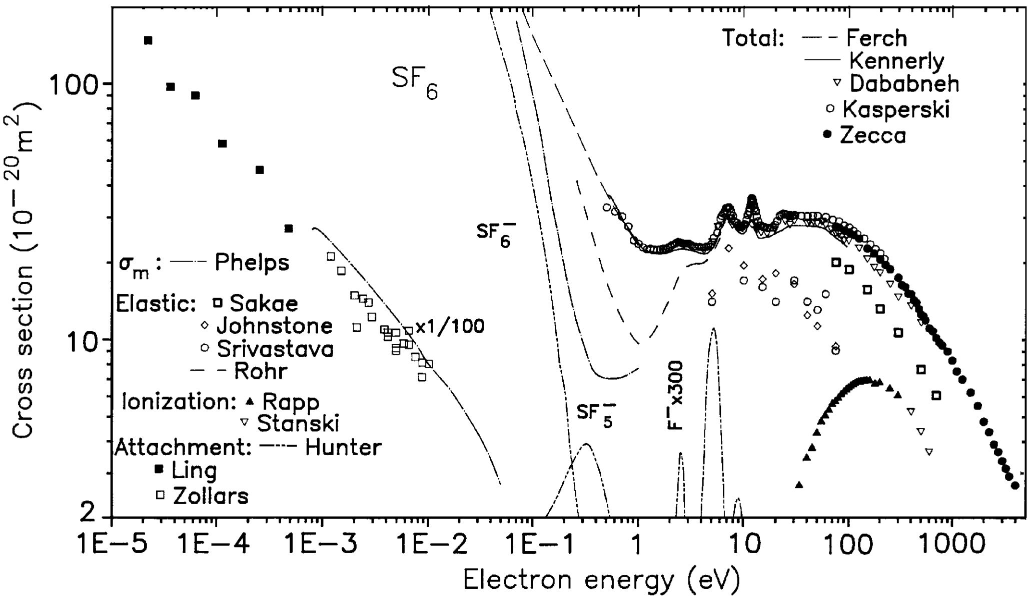

Fig. 20. – Integral cross-sections for electron scattering on SF_6. *Total:* Ferch *et al.* (1982); Kennerly *et al.* (1979); Dababneh *et al.* (1988); Kasperski *et al.* (1997); Zecca *et al.* (1992). *Elastic:* Rohr (1979); Johnstone and Newell (1991); Srivastava *et al.* (1976); Sakae *et al.* (1989). *Momentum transfer:* Phelps (1999), based on Phelps and Van Brunt (1988). *Electron attachment:* Ling *et al.* (1992) and Zollars *et al.* (1985), Rydberg atoms; Hunter *et al.* (1989). *Ionization:* Rapp and Englander-Golden (1965); Stanski and Adamczyk (1983).

above 20 eV are slightly lower than the measurements of Dababneh *et al.* (1988). The difference between the two data sets increases with rising energy. This can be partially attributed to scattering on exit orifices, as stated for measurements from Bonham's group for CH_4 and for chlorofluorocarbons (Jones 1986). At 1–12 eV the data of Kennerly *et al.* (1979) and those of Wan *et al.* (1993) coincide; below 1 eV the TCS of Wan *et al.* is somewhat lower, but the error can also be due to an energy shift. Romanyuk *et al.* (1984) obtained at the cross-section maxima slightly higher values than Dababneh *et al.* (1988) and observed an additional peak at 17 eV. The latter structure does not appear in any other measurements; therefore the data of Romanyuk *et al.* are not shown in fig. 20. At energies above 100 eV the data of Dababneh *et al.* (1988) are somewhat lower than the measurements of Zecca *et al.* (1992). As discussed by Dababneh *et al.*, their data can suffer from a few per cent angular resolutions error in the high-energy limit.

The TCS rises in the limit of zero energy reaching a value of $400 \cdot 10^{-20}$ m^2 at 0.037eV (Ferch *et al.* 1982). In the whole 1–100 eV range the TCS in SF_6 exceeds the value of $20 \cdot 10^{-20}$ m^2. Several maxima observed in the low-energy region have been attributed to resonant states. Their positions have been determined both in TCS measurements and in a transmission experiment using a trochoidal spectrometer (Kennerly *et al.* 1979). The width of the structures in the TCS, a weak one centered at 2.52 eV and two stronger ones, centered at 7.05 and 11.87 eV, is of about 1 eV. No other fluorine-containing molecule (CF_4, SiF_4, GeF_4, C_2F_6, C_3F_8, see figs. 7, 15, 17, 18) shows such narrow maxima in TCS.

Stricklett and Burrow (1991) examined the variation of the TCS for scattering on laser-excited SF_6 molecules. At energies below 1 eV they observed, similarly as it was seen in CO_2 (see subsect. **4**.3 in part II), higher cross-sections for scattering on vibrationally excited states.

Swarms. Early measurements of electron diffusion coefficients in SF_6 were reviewed by Gallagher *et al.* (1983) and analyzed by Phelps and Van Brunt (1988). More recently, the electron drift velocity at intermediate reduced fields ($280–700 \cdot 10^{-21}$ Vm^2) have been measured by Nakamura (1988) and at high reduced fields ($560–3500 \cdot 10^{-21}$ Vm^2) by Lisovskiy and Yegorenkov (1999). This last measurement yielded at $2800 \cdot 10^{-21}$ Vm^2 a lower ($8 \cdot 10^7$ cm/s) drift velocity than the semiempirical model of Itoh *et al.* (1990) but in agreement with the model of Phelps and Van Brunt (1988).

A scattering length of $-9.15a_0$ for SF_6, corresponding to the zero-energy cross-sections of $73.6 \cdot 10^{-20}$ m^2 (not shown in fig. 20), has been obtained by the Fano method (Evans *et al.* 1998).

The elastic cross-section below 6 eV has been obtained by Rohr (1979), between 5 and 75 eV by Srivastava (1976) with 15–55% declared errors, between 5 eV and 75 eV by Johnstone and Newell (1991), between 75 and 500 eV by Sakae *et al.* (1989). The integral elastic CS exhibits a minimum of about $10 \cdot 10^{-20}$ m^2 at 0.5 eV, then rises to about $20 \cdot 10^{-20}$ m^2 at 4 eV (Rohr 1979). The sum of the integral elastic and vibrational CS (Rohr 1979) at 0.5–6 eV, *i.e.* below the threshold for electronic excitation (Sze and Brion 1990) coincides with the TCS of Kennerly *et al.* (1979). On the other hand, the integral CS of Srivastava *et al.* (1976) are systematically lower by 30% than the elastic CS of Rohr (1979). This latter discrepancy could be caused by the normalization procedure (to the He cross-section) in the measurements of Srivastava *et al.* (1976). The elastic CS of Johnstone and Newell (1991) between 5 and 75 eV follows generally the descending trend of Srivastava's *et al.* data and is substantially lower at 75 eV than the result of Sakae *et al.* (1989). The recent integral CS measurements (Cho *et al.* 2000) between 2.7–75 eV agree within the error bar with the results of Rohr (1979) at low energies and with those of Sakae *et al.* (1989) at 75 eV.

The low-energy DCS (Rohr 1979) indicate a direct scattering mechanism at 1 eV, while in the 2–3 eV range and around 7 eV the scattering is dominated by resonances. Enhancement of the elastic DCS (at 20° scattering angle) was also reported at 12 eV (Johnstone and Newell 1991).

The very low-energy DCS at 90° has been studied in the Daresbury synchrotron-light laboratory (Randell *et al.* 1992). The 90° DCS possibly shows a maximum at 0.15 eV. Randell *et al.* pointed out that this could happen because of the channel-coupling effects: the low-energy rise of the CS for the SF_6^- formation depresses the elastic channel by denying it the *s*-wave.

The geometrical structure of the molecule and the interference effects were studied in numerous high-energy scattering experiments (Miller and Fink 1981, Goates and Bartell 1982, Miller and Fink 1992, Meier *et al.* 1993). The elastic scattering at near-to-zero angles was studied by Miller and Fink (1992) at 30 keV. The asymptotic value of the DCS at zero degrees amounts to $257 \cdot 10^{-20}$ m^2/sr.

Vibrational excitation has been studied by Rohr (1977 and 1979) at energies below 10 eV and by Randell *et al.* (1992) at fixed 90° angle between 0.05 and 1 eV. At energies below 1 eV a forward-peaked angular distribution (Rohr 1979) indicates a direct excitation process. The energy loss spectrum at 0.4 eV at 90° (Randell *et al.* 1992) indicates that as much as 50% of the TCS at this energy can be due to the vibrational excitation of the unresolved ν_1 (Raman, strong) and ν_3 (infrared-active, strong) modes and their overtones (see Randell *et al.* for assignment of the states). A sharp peak was observed 60 meV above the vibrational excitation threshold (Rohr 1977). Randell *et al.* stated that the near-to-threshold excitation of the ν_1 mode follows the Born approximation but the ν_3 mode is excited via a resonance mechanism.

At 1 eV the ν_1 mode and its overtones up to $n = 7$ dominate the vibrational excitation (Rohr 1977). An enhancement of the vibrational excitation was observed in the 2–3 eV and 7 eV regions (Rohr 1979) and at 12 eV (Trajmar and Chutjian 1977), in coincidence with resonant peaks in the TCS.

Electronic excitation spectra at 20–30 eV impact energies were studied by Trajmar and Chutjian (1977) and at 400 eV by Simpson *et al.* (1966). DCS at 20 eV for the lowest, 9.8 eV energy loss structure is uniform in angle, while the higher, 11.0, 11.6, 12.8 and 13.3 eV energy loss structures are somewhat forward-centered (Trajmar and Chutjian 1977). A rough evaluation of the integral CS at 20 eV from the data of Trajmar and Chutjian gives a value of about 0.8–$1.0 \cdot 10^{-20}$ m^2.

The inner shell excitations were studied by Hitchcock and Brion (1978), Ying *et al.* (1993), Francis *et al.* (1995), Turci *et al.* (1995). The valence and inner-shell excitations in SF_6, SeF_6 and TeF_6 at high impact energy (2.0–3.7 keV) and zero degree scattering angle were studied by Sze and Brion (1990) but no absolute intensities were given. Electron-ion coincidence measurements at 160–230 eV impact energy were done by Hitchcock *et al.* (1978). Theoretical values of low-angles DCS for some optically allowed transitions were given by Fomonung *et al.* (1996).

The optical emission cross-section for the molecular continuum between 200 and 340 nm amounts to as little as $0.29 \cdot 10^{-22}$ m^2 at 200 eV (Jabbour *et al.* 1988). The overall emission in the 620–790 nm range due to transitions between the highest and the lowest excited states $(2p^43p) \rightarrow (2p^43s)\ ^{2,4}P$ of the fluorine atom equals $1.6 \cdot 10^{-22}$ m^2 at 100 eV, compared to $3.1 \cdot 10^{-22}$ m^2 for CF_4 (Blanks *et al.* 1987, see also Roque *et al.* 1991). The emission spectrum in the 200–600 nm range due to 200 eV electron excitation consists of a broad feature from 200 to 320 nm and several line emissions from excited fluorine fragments (Blanks and Becker 1987).

Dissociation into neutrals was studied by Ito *et al.* (1995) up to 195 eV. The yield of SF_2 radicals reaches a maximum at 145 eV; the relative yields for SF_3 and SF radicals are 0.5 and 0.05 of the one for SF_2. Metastable radicals production was studied by Corr *et al.* (1987). Onsets for F_2 and F production in Rydberg states were observed at 18.7 and 35.0 eV, respectively; no cross-sections were given.

Ionization. The total ionization CS up to 300 eV has been given by Rapp and Englander-Golden (1965) and the normalized partial cross-sections up to 600 eV by Stanski and Adamczyk (1983). The SF_5^+ and SF_3^+ yields amount to about 50% and 15% of the total ionization CS; no stable SF_6^+ ions were observed. Peculiar, with respect to gases like CH_4 or CF_4, is the high-energy (150 eV) at which the ionization CS reaches the maximum; this reflects a high ionization threshold in SF_6 (15.8 eV).

Doubly differential CS for ionization at incident energies of 100 and 200 eV have been measured by Al-Nasir *et al.* (1996).

Electron attachment. SF_6 forms both parent SF_6^- ions and dissociated anions. Different experiments (Rapp and Briglia 1965, Stamatovic and Schulz 1968) proved that electrons are attached to SF_6 at collision energies close to zero. The cross-section for SF_6^- yield derived from Rydberg's atoms quenching (Weast *et al.* 1976, Foltz *et al.* 1977, Hildebrandt *et al.* 1978, Zollars *et al.* 1984, 1985, 1986, Dunning 1987, Ling *et al.* 1992) or laser photoelectron attachment (Chutjian 1981, Chutjian and Alajajian 1985, Klar *et al.* 1992b, 1994) follows, in the zero-energy limit (0.1–10 meV), the threshold $E^{-1/2}$ law for s-wave capture on a polarization potential (Vogt and Wannier 1954, Klots 1976, Gauyacq and Herzenberg 1984). These data merge well at energies above 20 meV with the cross-sections derived from swarm (Hunter *et al.* 1989), threshold photoionization (Chutjian and Alajajian 1985), flowing afterglow (Smith *et al.* 1984, Smith and Španěl 1994), microwave conductivity (Shimamori *et al.* 1992) and beam (Wan *et al.* 1993) experiments. At energies of the order of 0.1 eV (Klar *et al.* 1992b, Wan *et al.* 1993) the slope of the electron attachment CS changes as E^{-1}. Some disagreement regards CS at energies between 0.2–0.3 eV, where a peak for SF_6^- occurs. While Kline *et al.* (1979) and Hunter *et al.* (1989) observed a quick fall of the attachment CS in this region, Wan *et al.* (1993) reported a smoothly changing CS. Wan *et al.* argued that the quick fall observed in previous experiments was an artifact, caused by decay in flight of SF_6^- ions formed in excited vibrational states. Popple *et al.* (1992) in a Rydberg atoms experiment showed that at very low energies the SF_6^{-*} ion can be stabilized in post-collisional interactions between ions.

The attachment rates at sub-thermal energies, about $4 \cdot 10^{-7}$ cm^3 s^{-1}, is lower for SF_6 than for CCl_4 (about $7 \cdot 10^{-7}$ cm^3 s^{-1}, Harth *et al.* 1989, Dunning 1987); the same is found at thermal energies (300 K): $2.3 \cdot 10^{-7}$ cm^3 s^{-1} and $4.0 \cdot 10^{-7}$ cm^3 s^{-1}, respectively (Shimamori 1992). Qualitatively the same result was obtained in flowing afterglow plasma experiments (Smith *et al.* 1984, Smith and Španěl 1994): at 300 K the attachment rate coefficient amounts to $3.1 \cdot 10^{-7}$ cm^3 s^{-1} for SF_6 and $3.9 \cdot 10^{-7}$ cm^3 s^{-1} for CCl_4; at 590 K: $4.0 \cdot 10^{-7}$ cm^3 s^{-1} and $3.5 \cdot 10^{-7}$ cm^3 s^{-1}, respectively (Smith *et al.* 1984). The electron attachment CS in SF_6 reaches lower values at the same energy than that in CCl_4, compare figs. 11 and 20. This, according to the model of Vogt and Wannier (1954), reflects the dependence on molecular polarizability which is $6.54 \cdot 10^{-30}$ m^3 for SF_6 and $10.8 \cdot 10^{-30}$ m^3 for CCl_4.

Klar *et al.* (1992a, 1994), studying dissociative attachment via a high-resolution photoelectron attachment technique, noticed resonant structures in the cross-section at energies coinciding with threshold energies for vibrational excitation of the ν_1 and ν_3 modes.

TABLE X. – *Integral cross-sections for electron scattering on* SF_6 *(in* 10^{-20} m^2 *units).*

Energy	Elastic	Vibrational	Electronic	Ionization	Summed	Total
5.0	21.6 RO 14 S 15.1 J	1.0 RO			22.6 16.1	22.5 K
10	17 S 19.4 J					25.7 K 28.0 KA
20	14 S 18.1 J		1.0 S1		15 19.1	26.0 K 28.2 KA
30	17 S 16.4 J		1.5** S1	1.93 R	20.4 19.8	27.8 K 30.5 KA
50	13 S		1.2** S1	4.35 R	18.6	27.5 K
75	20.0 SA 9.0 S		1.0** S1	5.77 R	26.8	27.7 Z 29.1 KA
100	18.7 SA		0.8** S1	6.53 R	26.0	26.3 Z 27.4 KA
150	15.6 SA		0.6** S1	6.97 R	23.2	22.7 Z
200	13.1 SA		0.7** S1	6.83 R	20.4	20.6 Z 21.7 KA
300	10.6 SA		0.4** S1	6.09 R	17.1	17.4 Z
500	7.59 SA		0.3** S1	4.34 ST	12.2	12.5 Z

** Extrapolated values using Born-Bethe approximation
J - Johnstone and Newell (1991)
K - Kennerly *et al.* (1979)
KA - Kasperski *et al.* (1997)
R - Rapp and Englander-Golden (1965)
RO - Rohr (1979)
S - Srivastava *et al.* (1976), 15–55% declared errors
S1 - A rough evaluation (present work, ±50% possible error) from DCS at 20 eV by Srivastava and Trajmar (1977) and Born-Bethe extrapolation at higher energies
SA - Sakae *et al.* (1989)
ST - Stanski and Adamczyk (1983)
Z - Zecca *et al.* (1992)

We recall a similar observation in the CH_3I molecule, see subsect. **3**˙3.

The SF_5^- yield exhibits a maximum of about $3 \cdot 10^{-20}$ m^2 at 0.3 eV (McCorkle *et al.* 1980, Hunter *et al.* 1989), while the production of other negative ions (F^-, F_2^-, SF_4^-, SF_3^-, SF_2^-) shows peaks at 2.5, 5.0, 9.0, 12 eV (Kline *et al.* 1979, Hunter *et al.* 1989, Fenzlaff *et al.* 1988, Rao and Srivastava 1993).

Little or no dependence on the temperature was observed (Spence and Schulz 1973, Datskos *et al.* 1993, Smith *et al.* 1984, Miller *et al.* 1994) for the SF_6^- yield, and a significant rise with temperature for the SF_5^- yield at low energies (Miller *et al.* 1994, Smith *et al.* 1995, Matejcik *et al.* 1995). This effect has been explained by Matejcik *et* *al.* (1995) as due to the endothermic character of the SF_5^- formation (0.12 eV).

Resonances. Shape resonances have been observed in electron attachment (see Hunter *et al.* 1989), in differential elastic (Rohr 1979), in vibrational excitation (Trajmar and Chutjian 1977), and in total CS (Kennerly *et al.* 1979, Romanyuk *et al.* 1984). Similarly to chlorofluoromethanes, see subsect. **3**˙2, the positions of these resonances seen in the attachment CS are shifted towards lower energies compared to those in the TCS (see fig. 20). The following symmetries, predicted by Dehmer *et al.* (1978), can be assigned to the peaks in transmitted current at the following energies (Kennerly *et al.* 1979): $A_{1\mathrm{g}}$ at 2.52 eV, $T_{1\mathrm{u}}$ at 7.01 eV, $T_{2\mathrm{g}}$ at 11.88 eV, and a broad structure centered at 25 eV of E_g symmetry. The last resonance was also studied in threshold photoelectron spectroscopy (Yencha *et al.* 1997). Stricklett and Burrow (1991) noticed that the $T_{1\mathrm{u}}$ (and $T_{2\mathrm{g}}$) resonance shifts to a lower energy (and enlarges, respectively) for scattering on vibrationally excited molecules.

Sum check. As shown by Rohr (1979), the elastic CS in the 0.5–5.0 eV region sums up with the vibrational CS (Rohr 1979) within the experimental errors to Kennerly's *et al.* (1978) TCS. It is remarkable that at 1 eV the vibrational and elastic cross-sections are of a similar magnitude, $10 \cdot 10^{-20}$ m^2. At 20–50 eV the sum of elastic values by Srivastava *et al.* (1976) with the inelastic processes is significantly lower than the TCS values (Kennerly *et al.* 1979), see Table X. To reach agreement between the summed and experimental TCS, the elastic values of Srivastava *et al.* (1976) should be increased by approximately 40%. The elastic CS of Johnstone and Newell (1991) are higher than those of Srivastava *et al.* at 5–20 eV but lower at 30 and 50 eV.

At energies above 75 eV the sum of the elastic cross-sections of Sakae *et al.* (1989) and the ionization cross-sections of Rapp and Englander-Golden (1965) is almost equal to the absolute TCS values of Zecca *et al.* (1992).

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3˙9. *Other hexafluorides (*UF_6*,* WF_6*). – Uranium hexafluoride* (UF_6). The differential and integral CS, the elastic CS at 10–75 eV and electronic excitation CS at 10, 20, 40 eV in UF_6 have been measured by Cartwright *et al.* (1983) superseding the data of Srivastava *et al.* (1976). The integral elastic CS reaches a maximum of $28.1 \cdot 10^{-20}$ m^2 at 20 eV falling to $7.5 \cdot 10^{-20}$ m^2 at 75 eV; the overall electronic excitation CS at 20 eV amounts merely to $0.4 \cdot 10^{-20}$ m^2 (Cartwright *et al.* 1983).

Ionization of UF_6 was studied experimentally by Compton (1977) up to 1 keV and semiempirically by Margreiter *et al.* (1990). The experimental value at 80 eV is $16 \cdot 10^{-20}$ m^2; this value summed with the partial cross-sections of Cartwright *et al.* (1983) — the elastic value ($7.5 \cdot 10^{-20}$ m^2 at 75 eV) and the electronic excitation one ($0.33 \cdot 10^{-20}$ m^2 at 40 eV) — would give an upper limit on TCS of about $24 \cdot 10^{-20}$ m^2 at 80 eV. This is much lower than the experimental TCS value in WF_6, $34.4 \cdot 10^{-20}$ m^2 at the same energy (Szmytkowski *et al.* 2000).

Tungsten hexafluoride (WF_6). The TCS for this molecule has recently been measured by Szmytkowski *et al.* between 1.2–250 eV and by Karwasz *et al.* (2000) between 75–3500 eV. The total cross-section in WF_6 is similar in shape to that in C_6F_6 (and C_6H_6), see Kasperski *et al.* (1997), but is shifted to higher energies. The TCS in WF_6 rises from $24 \cdot 10^{-20}$ m^2 at 8 eV, reaches a broad maximum of about $38 \cdot 10^{-20}$ m^2 at 40 eV and shows some shoulder structure at about 20 eV. The low-energy maximum in WF_6 at 3 eV is much higher ($31 \cdot 10^{-20}$ m^2) than that in C_6F_6 at 1 eV.

The two TCS measurements in WF_6 disagree somewhat in the energy overlap, the data of Szmytkowski *et al.* being 25% higher at 100 eV and 10% at 200 eV than the data of Karwasz *et al.* The data of Karwasz *et al.* can be somewhat overestimated in their low-energy limit, due to beam instabilities; on the other hand, the data of Szmytkowski at 300 eV can suffer from a higher angular resolutions error than those of Karwasz *et al.* (2000). However, all these possibilities do not explain the discrepancy. In the high-energy range the TCS falls from $28 \cdot 10^{-20}$ m^2 at 200 eV to $5.0 \cdot 10^{-20}$ m^2 at 3000 eV.

Formation of negative ions in WF_6 was studied by Thynne and Harland (1973), de Wall and Neuert (1977), Hildebrand (1977), Dispert and Lackmann (1977). Electronic excitation energy loss spectra were studied by Rianda *et al.* (1979).

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