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Electron scattering by sulfur tetrafluoride (SF₄) molecules

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Abstract

Absolute total cross section (TCS) for electron scattering from sulfur tetrafluoride (SF₄) molecules was measured in a linear transmission experiment at energies ranging from low (0.1 eV) to intermediate (370 eV). Below 1.6 eV the TCS function increases steeply towards lower energies and shows small resonant-like maximum near 0.4 eV. Two other distinct enhancements are located at higher energies: a narrow one is peaked at 12 eV, and a very broad hump is centred near 40 eV. Our experimental TCS results are compared with the previous TCS measurements at low impact energies and at intermediate energies—with our total cross section estimations based on calculations of elastic and ionization cross sections. The TCS for SF₄ is also compared with SF_{*n*} (*n* = 1, 2, 6) total cross sections.

1. Introduction

Interest in electron-assisted processes for series of sulfur fluorides has considerably increased recently (e.g. Ziegler and Gutsev 1992, Sauers *et al* 1993, Tarnovsky *et al* 1998, Ali *et al* 2000, Baluja and Tossell 2003, 2004). This is partly due to recognition of these compounds as by-products of sulfur hexafluoride (SF₆) decomposition in plasma mixtures. SF₆ plays a key role in many applied areas such as the plasma-based processing of submicro-scale electronic devices and/or as a gaseous dielectric in high-voltage electrical equipment. The presence of very reactive radicals, even as trace impurities, in gaseous mixtures may significantly influence the efficiency of plasma-enhanced processing or drastically change gas insulating properties. For understanding, modelling and controlling the gas phase reactions in plasma, knowledge of basic physico-chemical events—among them those involving electrons—occurring in a medium containing SF₆ is of crucial importance. For this purpose accurate quantities

describing the electron-induced processes—cross sections, rate and transport coefficients—for all components of plasma are needed.

Sulfur tetrafluoride (SF_4) has been found as one of the by-products of SF_6 decomposition in plasma discharges (Herron and Tsang 1987, Sauers 1987, Tuszewski *et al* 2004); as a reagent it is used in the chemical industry for synthesis of fluorine containing compounds and becomes useful for carbonic surface treatment. However, while for SF_6 the works on electron scattering are quite numerous (cf Christophorou and Olthoff 2004), electron scattering data available in the literature for SF_4 are rather scarce. Experiments with SF_4 molecules involving electrons were pioneered by Kimura and Bauer (1963) and Ewing and Sutton (1963) and concerned electron diffraction study of the SF_4 molecular structure. Further electron- SF_4 scattering experimental works covered thermal and low impact energies, and were largely confined to negative-ion formation by dissociative electron attachment (Harland and Thynne 1971, Chen and Chantry 1972, Babcock and Streit 1982, Wan *et al* 1993, Sauers *et al* 1993, Miller *et al* 1994), appearance of positive ions (Hildenbrand 1973), and the total low-energy cross section measurement (Wan *et al* 1993). At high electron energies Bodeur and Hitchcock (1987) investigated valence electron excitation. Till now, absolute cross section measurements have not been available for energies above 7 eV. On the theoretical side, energetics of dissociative electron attachment was studied by Tossell (1991), electronic and geometrical structure of single charged anion was investigated by Ziegler and Gutsev (1992), while electron-induced single ionization cross sections were calculated by Tarnovsky *et al* (1998) and Ali *et al* (2000).

The purpose of the present work is to provide the accurate absolute electron-scattering total cross section for a SF_4 molecule over a wide impact energy range. We do hope that the present results give impulse for further more detailed experimental and theoretical investigations for sulfur fluorides. Studies for that family of compounds may give some insight into the role of the molecular exterior, in that case fluorine atoms, in the scattering dynamics.

2. Experimental details

Total cross sections have been measured employing a linear electron-beam transmission technique (Bederson and Kieffer 1971) under single-collision conditions across energies from low (0.1 eV) to intermediate (370 eV). The experimental set-up and procedure applied in the present study have been intensively used in a long series of absolute TCS measurements and were described in detail earlier (e.g. Szmytkowski *et al* 1997, Szmytkowski and Możejko 2001); therefore, only a brief outline is given here.

The electrostatic electron spectrometer consists of a thermionic electron source, a 127° cylindrical energy-dispersing element, a system of electron-optical lenses controlling the trajectory and energy of the electron beam, a scattering cell followed by a retarding field analyser and a Faraday cup collector. The magnetic field in the electron optics volume of the spectrometer is reduced to a value below $0.1 \mu\text{T}$. The electrons of desired energy E are fired into the reaction cell filled with the target gas of interest. Those electrons which cross the reaction volume and emerge from the cell through the exit orifice are energy discriminated on their route to the detector with the retarding field element which prevents inelastically scattered electrons being collected with a Faraday cup.

The total cross section, $Q(E)$, at each electron impact energy E is derived by measuring intensities of the transmitted electron current in the presence, $I(E, p)$, and absence, $I(E, p = 0)$, of the target molecules in the reaction cell, and applying the Bouguer-de

Beer–Lambert relationship

$$Q(E) = \frac{k\sqrt{T_m T_c}}{pL} \ln \frac{I(E, 0)}{I(E, p)},$$

in which the thermal transpiration effect (Knudsen 1910) is accounted for. Electron intensities $I(E)$, the target gas pressure p , the electron path length in the scattering chamber L , the temperature of the mks absolute manometer head T_m and the temperature of the scattering cell T_c were measured directly and therefore the obtained total cross sections are in absolute scale. As a reference for the energy scale, the resonant structure visible at around 2.3 eV in N₂ was used. The uncertainty of the energy scale was estimated to be nearly 0.1 eV mostly due to high reactivity of SF₄ with electron optics elements.

Before starting the essential TCS measurements the whole electron optics was passivated with SF₄ during long-lasting pilot runs. It was noticed that the current of electrons leaving the electron gun was sensitive to changes of the partial pressure of SF₄ in the electron optics volume and in consequence might affect the measured cross section values. To keep the conditions in the electron optics region nearly invariable, the target gas was supplied alternately into the collision cell or its surrounding. As a result, the pressure in the electron optics volume was constant (~ 1 mPa) while the pressure in the scattering cell changed over three orders of magnitude, depending on whether the target gas was supplied into the cell or not. It was found that the TCS values obtained at the same energy were, within the random experimental uncertainties, independent of the applied target pressures (0.5–1.1 Pa) and the electron-beam intensity (less than 0.1 nA).

The final TCS value at each energy is a weighted mean of results from series (4–10) of individual runs (7–10 in series). The statistical variations of the measured TCS are below 1% over the entire energy range investigated. The estimated systematic uncertainty in our measured absolute cross sections amounts to 7–9% below 1–2 eV, decreases gradually to 5–6% in the energy range 10–100 eV, and reaches again about 6–7% at higher applied energies. A commercially supplied sample of SF₄ (of 94% purity) was used directly from the container without further purification.

3. Computational methods

Theoretical approaches and computational procedures employed in the present work are the same as we have used in previous calculations (Możejko *et al* 2002, Możejko and Sanche 2003, Szmytkowski *et al* 2004). Thus only a brief description of the theoretical and numerical issues is provided here.

To investigate elastic electron collisions with studied molecules the independent atom method (IAM) (Mott 1965) has been used. In that approximation the electron-molecule scattering problem is reduced to electron scattering by atoms constituting the molecule. This reduction is based on the following assumptions: (i) each atom of the molecule scatters independently, (ii) redistribution of atomic electrons due to molecular binding is unimportant and (iii) multiple scattering within the molecule is negligible. Thus, this approach is valid and can provide reasonable results for intermediate- and high-collision energies only (e.g. Joshipura and Vinodkumar 1997, Możejko *et al* 2002, and references therein). The elastic integral cross section (ICS) within the IAM method is given by

$$\sigma(E) = \frac{4\pi}{k} \sum_{i=1}^N \text{Im} f_i(\theta = 0, k) = \sum_{i=1}^N \sigma_i^A(E),$$

where E is the energy and $k = \sqrt{2E}$ is the wave number of the incident electron, $f_i(\theta, k)$ is the scattering amplitude due to the i th atom of the molecule and θ is the scattering angle. The atomic elastic ICS for the i th atom of the target molecule, $\sigma_i^A(E)$, has been computed according to

$$\sigma^A = \frac{4\pi}{k^2} \left(\sum_{l=0}^{l_{\max}} (2l+1) \sin^2 \delta_l + \sum_{l=l_{\max}}^{\infty} (2l+1) \sin^2 \delta_l^{(B)} \right).$$

To obtain phase shifts, δ_l , and the elastic electron–atom cross section, σ^A , partial wave analysis has been employed and the radial Schrödinger equation,

$$\left[\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} - 2(V_{\text{stat}}(r) + V_{\text{polar}}(r)) + k^2 \right] u_l(r) = 0,$$

has been solved numerically under the boundary conditions

$$u_l(0) = 0, \quad u_l(r) \xrightarrow{r \rightarrow \infty} A_l \hat{j}_l(kr) - B_l \hat{n}_l(kr),$$

where $\hat{j}_l(kr)$ and $\hat{n}_l(kr)$ are the Riccati–Bessel and Riccati–Neumann functions, respectively. The electron–atom interaction has been represented by the sum of static, $V_{\text{stat}}(r)$, (Salvat *et al* 1987) and polarization, $V_{\text{polar}}(r)$, (Padial and Norcross 1984) model potentials. The exact phase shifts have been calculated for l up to $l_{\max} = 50$ while those remaining, $\delta_l^{(B)}$, have been included through the Born approximation.

Electron-impact ionization cross sections have been obtained using the binary-encounter-Bethe (BEB) approach (Hwang *et al* 1996). Within this formalism the electron-impact ionization cross section per molecular orbital is given by

$$\sigma_{\text{BEB}} = \frac{S}{t+u+1} \left[\frac{\ln t}{2} \left(1 - \frac{1}{t^2} \right) + 1 - \frac{1}{t} - \frac{\ln t}{t+1} \right],$$

where $S = 4\pi a_0^2 N R^2 / B^2$ ($a_0 = 0.5292 \text{ \AA}$, $R = 13.61 \text{ eV}$), $u = U/B$, $t = T/B$, and T is the energy of the impinging electron. The electron binding energy B , kinetic energy of the orbital, U , and orbital occupation number, N , were obtained for the ground states of the molecules with the Hartree–Fock method using the GAMESS code (Schmidt *et al* 1993), and the Gaussian 6-311G+(d) basis set. Because the valence orbital energies obtained in this way usually differ from experimental ones, we also performed outer valence Green function calculations of correlated electron affinities and ionization potentials (Zakrzewski and Niessen 1994) with the GAUSSIAN code (Frisch *et al* 2001). Finally, the total cross section for electron-impact ionization was obtained as the sum of σ_{BEB} for all molecular orbitals.

4. Results and discussion

4.1. Sulfur tetrafluoride, SF_4

Figure 1 shows the variation of absolute electron-scattering TCS for SF_4 measured in this work at energies ranging from 0.1 to 370 eV (the numerical TCS values are listed in table 1). Experimental low-energy TCS data obtained earlier by Wan *et al* (1993) are also included for comparison. According to the shape, in the overlapping energy range both experimental cross section curves resemble well each other, while the magnitude of the present results is systematically higher by about 16–22%. Though the difference is still within the limits of combined experimental uncertainties, it deserves some comment: the TCS for SOF_2 , the main impurity of our sample ($\sim 5\%$), has in the low-energy range similar shape and magnitude to that of SF_4 (cf Wan *et al* 1993; in fact the magnitude of the TCS for SOF_2 is even

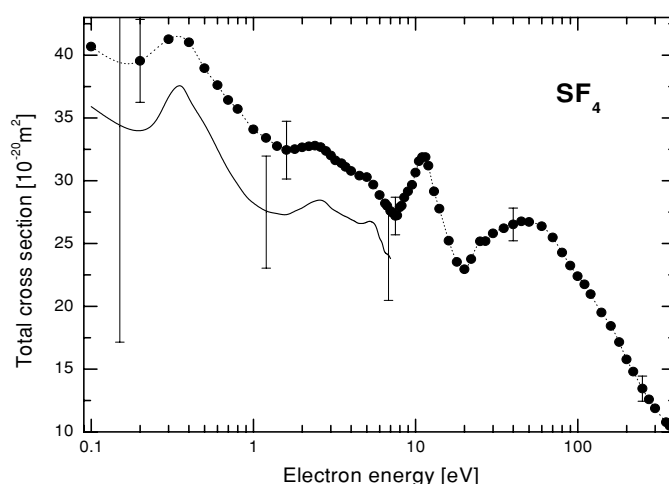


Figure 1. Energy dependence of experimental cross sections for the electron-SF₄ scattering: ●, present paper; dotted line is drawn to guide eye; —, Wan *et al* (1993) (error bars at selected points represent overall experimental uncertainties).

Table 1. Absolute total cross section (TCS) for electron scattering from sulfur tetrafluoride (SF₄) molecules in units of 10⁻²⁰ m².

Energy (eV)	TCS	Energy (eV)	TCS	Energy (eV)	TCS	Energy (eV)	TCS
0.1	40.7	3.2	31.6	10	30.7	70	25.5
0.2	39.5	3.5	31.4	10.5	31.6	80	24.3
0.3	41.3	3.7	31.1	11	31.9	90	23.2
0.4	41.0	4.0	30.8	11.5	31.9	100	22.4
0.5	39.0	4.5	30.4	12	31.2	110	21.8
0.6	37.6	5.0	30.3	13	29.1	120	21.0
0.7	36.4	5.5	29.7	14	27.8	140	19.5
0.8	35.7	6.0	28.9	16	25.2	160	18.4
1.0	34.1	6.5	28.2	18	23.5	180	17.2
1.2	33.4	6.7	28.0	20	23.0	200	15.8
1.4	32.7	7.0	27.6	22	23.8	220	14.8
1.6	32.4	7.2	27.4	25	25.2	250	13.4
1.8	32.5	7.5	27.2	27	25.2	275	12.6
2.0	32.7	7.7	27.2	30	25.8	300	11.9
2.2	32.7	8.0	27.9	35	26.2	350	10.8
2.4	32.8	8.2	28.0	40	26.5	370	10.5
2.6	32.7	8.5	28.7	45	26.8		
2.8	32.4	9.0	29.1	50	26.7		
3.0	32.0	9.5	29.7	60	26.4		

slightly lower), also the TCS for SF₆ (<1% in the sample) is between 0.5 and 6 eV, distinctly lower than that for a SF₄ (see figure 4); taking that into account, one could expect the present TCS values to be rather slightly lower than those for a pure SF₄ sample. That is why we believe that the larger low-energy TCS values in the present experiment cannot be related to lower purity of our SF₄ sample compared to those obtained by Wan *et al* (1993) with pure (99+%) SF₄.

Regarding variability of the present TCS energy function, four distinct energy regions can be discerned. The low-energy TCS function rapidly decreases from nearly 42×10^{-20} m² at

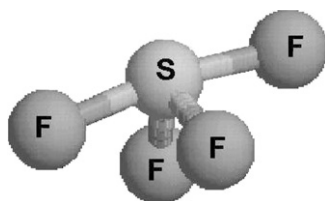


Figure 2. Schematic diagram of the SF₄ molecular geometry.

0.4 eV down to $33 \times 10^{-20} \text{ m}^2$ near 1.6 eV. At 0.4 eV the TCS exhibits a small maximum preceded by a shallow minimum near 0.2 eV. Towards lower energies the TCS still tends to increase. Such behaviour of the low-energy e^- -SF₄ TCS dependence is predominantly related to direct scattering with some contribution of indirect (resonant) processes.

In its ground state a SF₄ molecule, of C_{2v} symmetry, has a seesaw geometry (see figure 2). The molecule has a moderate permanent electric dipole moment ($\mu = 0.63 \text{ D}$, Tolles and Gwinn 1962) and high electric static polarizability ($\alpha \sim 6 \times 10^{-30} \text{ m}^3$, Babcock and Streit 1981; $8 \times 10^{-30} \text{ m}^3$, Miller *et al* 1995). The slowly moving electron projectile spends a relatively long time in the long-range dipole field of the SF₄ molecule and this results in a distinct increase of the cross section function towards zero energy. A pattern reflecting an indirect scattering process, where the impinging electron is attached temporarily to form negative-ion resonant states, SF₄^{-*}, is superimposed on the smooth background. The resonances decay via autodetachment of the extra electron to the parent molecule in its rovibrational excited levels or decompose into a variety of neutral and negative fragments. Evidence for the resonant contribution in the region below 1.5 eV comes from experiments on electron attachment to a SF₄ molecule (Harland and Thynne 1971, Chen and Chantry 1972, Babcock and Streit 1982, Sauers *et al* 1993, Wan *et al* 1993, Miller *et al* 1994). At near-zero energy, Chen and Chantry (1972) and Sauers *et al* (1993) observed the formation of a temporary parent negative ion SF₄^{-*}. This anion decays into electron and the parent molecule with a lifetime of about 10 μs or may decompose with the formation of F⁻, F₂⁻ or SF₃⁻ fragment ions (Chen and Chantry 1972). Above thermal energies, Harland and Thynne (1971) observed the F⁻ fragment anion with the maximum efficiency located at 0.9 eV and the SF₃⁻ ion peaked at 1.35 eV. Sauers *et al* (1993) reported the formation of the F⁻ ion with a peak near 0.6 eV. Wan *et al* (1993) measured total electron attachment cross section and close to 0.7 eV, in the local maximum, obtained the value of $1.1 \times 10^{-20} \text{ m}^2$. These low-energy resonant effects are reflected mostly in the TCS structure located around 0.4 eV and amount to only a few per cent of the TCS value.

Beyond 1.6 eV, up to 7.5 eV, the TCS decreases rather slowly with increasing energy. Two weak features in that part of the TCS energy function can be distinguished: a small hump is located around 2.5 eV and a weak shoulder can be barely discerned near 5 eV. At 7.5 eV the TCS energy function has its next minimum of the value $27 \times 10^{-20} \text{ m}^2$.

A more prominent resonant-like feature is located between 7.5 and 20 eV with the maximum ($32 \times 10^{-20} \text{ m}^2$) near 12 eV. The 12 eV enhancement is similar in shape and location to the SF₆ resonant structure (see figure 4) and most probably has the same origin related to the central sulfur atom.

Beyond the deep minimum ($23 \times 10^{-20} \text{ m}^2$) located at 20 eV, the TCS rises gradually to its very broad maximum ($27 \times 10^{-20} \text{ m}^2$) around 35–50 eV and falls off slowly towards higher energies. That broad enhancement is a characteristic, common feature of the electron-scattering TCS for all perfluorides studied so far and must be related to fluorine atoms. On the low energy side of the enhancement, near 25 eV, another weak structure is visible which may

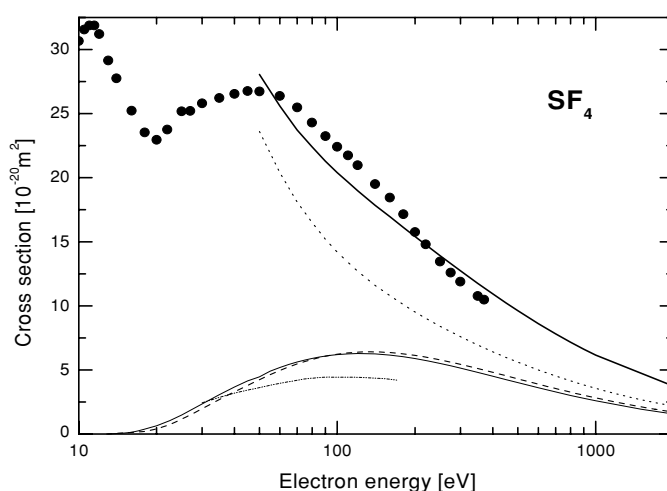


Figure 3. Comparison of present (●) experimental e^- -SF₄ TCS and theoretical cross sections: —, total (elastic + ionization), present; ·····, elastic (IAM), present; —, ionization (BEB), present; - - -, ionization (MAR), Tarnovsky *et al* (1998); - · - ·, ionization (BEB), Ali *et al* (2000).

be resonant in origin, such as that between 25 and 30 eV for a SF₆ molecule (figure 4). Between 100 and 200 eV, on the monotonically decreasing TCS energy function, some weak bulge is discernible which may reflect the ionization cross section enhancement with the maximum observed in this energy range. In the intermediate energy region, experimental points are well described with the regression formula: $Q(E) \sim E^{-0.5}$, which means the intermediate-energy TCS is proportional to the time the impinging electron spends in the vicinity of the molecule. At the highest applied energy, at 370 eV, the TCS amounts to slightly above $10 \times 10^{-20} \text{ m}^2$.

In figure 3 we have compared our computed total (elastic plus ionization) cross section with the present experimental TCS. Both elastic and ionization components are also shown for completeness together with ionization cross sections calculated by Tarnovsky *et al* (1998) using the modified additivity rule (MAR) approximation and by Ali *et al* (2000) with the BEB approach.

The agreement of experimental TCS with that calculated is reasonable; differences do not exceed 10%. That indicates the intermediate energy TCS comprises mostly elastic scattering and ionization. As the independent atom model works properly only at rather high impact energies, the calculated integral elastic cross section becomes more and more uncertain below 100 eV, and the calculated total cross section exceeds drastically the experiment below 60 eV. There is also a good agreement in the shape of the present ionization cross section with that calculated previously (Tarnovsky *et al* 1998, Ali *et al* 2000). Discrepancies visible in the magnitude between the present and Ali *et al* (2000) ionization cross sections are rather small (usually less than a few per cent); however, as both cross sections were obtained within the same BEB formalism, they deserve some comment. Our calculations are higher in the energy range from 15 eV to 90 eV while above 90 eV are lower than results reported by Ali *et al* (2000). The present ionization cross section peaks at 120 eV with a magnitude of $6.28 \times 10^{-20} \text{ m}^2$ while the maximum in Ali *et al* calculations peaks around 135 eV with a value of $6.41 \times 10^{-20} \text{ m}^2$. The observed discrepancies are related to the slightly different computational approaches. We have used in computations the geometry of a SF₄ molecule which is very similar to the experimental one of Tolles and Gwinn (1962) while that used

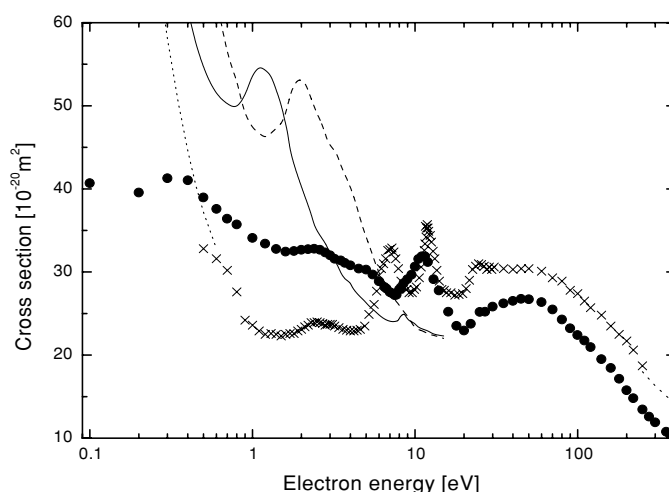


Figure 4. Comparison of electron-scattering total cross sections for some sulfur perfluorides; experimental TCS: SF₄ (●, present), SF₆ (×, Szmytkowski *et al* 1997; ·····, Christophorou and Olthoff 2004); theoretical total (elastic + inelastic): SF (—, Baluja and Tossell 2003); SF₂ (---, Baluja and Tossell 2004).

Table 2. Comparison of binding energies, *B*, for selected HOMOs of a SF₄ molecule used in the present study and in the work of Ali *et al* (2000); experimental ionization energies (IE) are from Costa *et al* (1981).

MO	Binding energies (eV)		IE (eV)
	Present	Ali <i>et al</i>	Costa <i>et al</i>
6b ₂	16.23	18.29	15.90
11a ₁	16.07	18.29	15.90
6b ₁	15.75	18.03	15.05
2a ₂	15.51	17.84	15.05
12a ₁	12.95	12.82	12.85

by Ali *et al* (2000) is closer to theoretical ones (Irikura 1995, Bauschlicher and Ricca 1998). The differences between the experimental and theoretical geometry amount to about 0.05 Å in bond length and less than 3° in bond angles. Moreover, in *ab initio* calculations of the binding energies, *B*, of the highest occupied molecular orbitals (HOMO) we have used outer valence Green function calculations of correlated electron affinities and ionization potentials in which configuration interactions are incorporated (Zakrzewski and Niessen 1994) with the GAUSSIAN code. In the calculations of Ali *et al* (2000) only the ionization potential has been corrected. Binding energies, *B*, for selected HOMOs of SF₄, obtained in the present work and those of Ali *et al* (2000) differ substantially (see table 2); for the ‘core’ orbitals both sets of *B* values (not included in the table) are in excellent agreement. Our binding energies are in good agreement with the experimental ionization energies obtained by Costa *et al* (1981) from the photoelectron spectra (table 2).

4.2. Comparison with SF_{*n*} (*n* = 1, 2, 6)

In this section we compare available total cross sections for sulfur perfluorides pointing out the similarities and differences. Figure 4 shows our experimental electron-scattering TCSs for

SF₄ together with those for SF₆ (Szmytkowski *et al* 1997, Christophorou and Olthoff 2004) and with theoretical low-energy total (elastic + excitation + ionization) cross sections for the two simplest sulfur perfluorinated radicals, SF (Baluja and Tossell 2003) and SF₂ (Baluja and Tossell 2004). At low energies cross sections for all compared targets distinctly increase towards thermal energies. For SF₄, SF₂ and SF that increase is dominated by direct electron scattering in the permanent electric-dipole field of the target. Besides, some contribution from the resonant scattering is also discernible: the lowest energy resonant maximum in the experimental TCS for SF₄ is located near 0.4 eV, the peak in calculated cross section for SF occurred at higher energy, 1.1 eV, while that for SF₂ is shifted to 2 eV. In contrast, the low-energy behaviour of the TCS for a nonpolar SF₆ molecule is partly related to exceptionally high efficiency of the electron attachment which for SF₆ appeared to be almost two orders of magnitude higher than that for SF₄ (Wan *et al* 1993). It is interesting that around 0.5 eV the ratio of total cross sections for SF, SF₂ and SF₄ is the same as the ratio of respective dipole moments.

Between 0.5 and 6 eV the TCS for a SF₄ molecule exceeds by 30–40% that for SF₆—the molecule of larger geometrical size. Near 2.5 eV, TCS functions for SF₄ and SF₆ show weak humps which in the case of SF₆ was associated with the formation of shape-resonance (Dehmer *et al* 1978).

Around 7 eV the most distinct differences between cross sections are visible: the TCS curve for SF₄ has its minimum near 7.5 eV while the TCS for SF₆ has its marked resonant maximum close to 7.2 eV; the cross section for SF exhibits a weak minimum at 7.5 eV followed by a small resonance structure at 8.4 eV; in contrast, the cross section for SF₂ between 5 and 15 eV monotonically decreases.

Beyond 10 eV up to 370 eV, SF₄ and SF₆ TCS curves behave in a very similar manner. Both TCSs exhibit distinct maxima near 12 eV and above minimum near 20 eV they have very broad enhancement centred around 40 eV with some weak structure discernible near 25 eV. The maximum at 12 eV and the structure near 25 eV were found to be, for SF₆, mainly atomic in character and were associated with the central sulfur atom (Dehmer *et al* 1978, Gyemant *et al* 1980, Gianturco *et al* 1995, Winstead and McKoy 2004). Such close similarity in the shape of TCS for SF₄ and SF₆ may indicate the same origin of the structures visible in the compared TCS energy dependences. In the intermediate energy range the ratio of both TCSs is nearly constant: values for SF₄ are systematically lower, nearly 0.8–0.9 of these for SF₆, which is in good agreement with the observation that at intermediate and high energies the intensity of the electron scattering is correlated with the size of target.

In addition, we estimated the gas-kinetic radius r of a SF₄ molecule and van der Waals coefficient b . The relationship between the b coefficient, the gas-kinetic cross section and the radius r is used (Hirschfelder *et al* 1964). The estimation is based on our observation that between 320 and 360 eV the TCS for the majority of perfluorinated molecules studied so far is very close to their gas-kinetic cross section (e.g. Szmytkowski *et al* 2004a, 2004b, and references therein). The obtained values are $r = 1.8 \times 10^{-10}$ m and $b = 0.06$ L mol⁻¹; no other evaluations are available for comparison. We have found, however, that our estimated values of r and b for SF₄ are nearly equal to findings for PF₃ molecules (Lide 1995–1996), which were obtained with quite different methods; above 7 eV, the present TCS for SF₄ closely resembles the shape and magnitude of the TCS for a PF₃ molecule (Szmytkowski *et al* 2004b).

5. Conclusion

We reported the absolute total cross sections for 0.1–370 eV electrons scattered by SF₄ molecules measured using a linear transmission method. The present experimental TCSs are

nearly 20% higher in the overlapping energy range (0.1–7 eV) than the data of Wan *et al* (1993). Our calculated intermediate-energy total cross section (elastic + ionization) reproduces quite satisfactorily the experimental TCS data. The most pronounced TCS features are (i) the sharp increase below 1.5 eV with the weak resonant peak near 0.4 eV, (ii) the narrow resonant-like structure centred near 12 eV and (iii) the very broad enhancement peaked around 40 eV, also observed earlier for other perfluorinated molecules. The gas-kinetic radius of a SF₄ molecule is estimated on the basis of the present TCS results. Some similarities and differences between the TCS for SF₄ and total electron-scattering cross section data for other sulfur perfluorides are pointed out and discussed. Further experiments, especially those in vibrational channels, as well as low-energy calculations are encouraged for better understanding the electron–SF₄ scattering processes.

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