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Electron scattering on C_6F_6 and SF_6 molecules

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Abstract. Total absolute cross sections for electron scattering on hexafluorobenzene, C_6F_6, and sulfur hexafluoride, SF_6, molecules, have been measured as a function of impact energy from 0.6 to 250 eV. The total cross section for C_6F_6 exhibits a very broad peak stretching from 10 to 100 eV with some weak features near 9.5 and 15 eV superimposed on the peak. Apart from the well-known low-energy resonant structures in the SF_6 total cross section function, a new weak resonant feature close to 25 eV has been noticed in the present experiment, in accordance with earlier theoretical calculations.

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1 Introduction

Perfluorinated compounds are widely used as etching agents in manufacturing of submicron-scale electronic devices (e.g. CF_4 [1, 2]) or as gaseous insulating materials in the electrical industry (e.g. SF_6, for references see [3, 4]). For optimal design of gaseous insulators, there must be full identification and understanding of basic processes preventing transition of a gas medium from an insulating to conducting state under an imposed electric field, and this requires access to comprehensive and reliable sets of quantitative electron-impact cross section data.

Among the cross sections which can be experimentally determined for a particular target the total scattering cross section is the most reliable. It may thus be useful for normalization or estimation of the upper limit of cross sections for specific electron-induced processes obtained in relative units. It may also serve as a quantitative test of the validity of scattering theoretical models and computational procedures.

The first absolute total cross sections for SF_6 molecule were reported by Kennerly et al. [5] for impact energies from 0.5 to 100 eV. Their results revealed the presence of a few distinct resonant structures. Total cross sections below 1 eV were determined by Ferch et al. [6], and for energies between 0.25 and 25 eV by Romanyuk et al. [7]. Intermediate energy total cross section (1–500 eV) was obtained by Dababneh et al. [8], while high energy data (75–4000 eV) by Zecca et al. [9]. Most of these transmission experiments invoked the use of magnetic fields, either to discriminate between electrons of various energies [7, 9] and/or to guide the projectile beam [6, 7, 8, 9]. Resonant behaviour of experimental cross section was quite well reproduced by elastic integral cross section calculations of Dehmer et al. [11], Gyemant et al. [12] and Gianturco et al. [13]. Their calculations shed some light on the nature of the observed features. Total (elastic + absorption) $e^- - SF_6$ cross section calculations have been carried out recently by Jiang et al. [10].

We are not aware of any experimental or theoretical electron scattering total cross sections for C_6F_6 molecule.

The aim of the present study was to measure accurately absolute total cross sections for electron scattering on C_6F_6 and SF_6 molecules over a wide energy range, from 0.6 to 250 eV.

2 Experimental procedure

To determine total cross section (TCS) for electron scattering on C_6F_6 and SF_6 molecules, we have employed the transmission method. The method relates the cross section to the transparency of the target at a given pressure for a beam of projectiles (cf [14]).

In the reported experiment, the apparatus setup was based on the electrostatic electron spectrometer described in detail elsewhere [15]. The spectrometer consisted of an electron gun with tungsten thoriated filament, a 127° electrostatic cylindrical deflector, a system of electron lenses, a scattering chamber of length L = 30.5 mm, followed by a retarding field analyzer and a Faraday cup collector.

Electrons of a quasimonoenergetic beam with an energy spread of 70 meV which passed the interaction volume without being scattered were detected by the Faraday cup. To discriminate electrons scattered inelastically in the forward direction at near-zero angles a retarding field analyzer was used.

The total cross section $Q(E)$ at a given energy, E, was evaluated from absolutely measured quantities: the intensities of electron currents, I_0 and I_g, with and without gas in the scattering chamber, respectively, the pressure, p, of the

gas target in the scattering cell, and its temperature, T, as follows:

$$Q(E) = \frac{kT}{pL} \ln \frac{I_0(E)}{I_g(E)} . \quad (1)$$

Due to a divergence between the temperature of target gas, T_g, and of the MKS capacitance manometer gauge, T_m, pressure readings were corrected for thermal transpiration effect, according to the Knudsen formula [16]. The absolute measurements of all those quantities were performed with high accuracy. Experimental procedure was controlled by a computer.

Typical experimental conditions were as follows: (i) pressure of the sample in the scattering volume was kept below 100 mPa at low impact energies and did not exceed 200 mPa at the highest energies applied, where cross sections are distinctly lower, (ii) background pressure in the vacuum chamber was less than 2 μPa, (iii) electron current intensities were between 1 and 100 pA. The energy scale of the electron beam was established with an accuracy of $\pm$50 meV by reference to the resonant oscillatory structure of N_2 around 2.3 eV.

Statistical uncertainties (one standard deviation of weighted mean values) are about 1% below 1 eV and do not exceed 0.6% at higher energies.

The direct sum of potential individual systematic errors has been estimated to be up to 7% below 5 eV, decreasing below 4% between 10 and 100 eV, and increasing to 5% at the highest applied energies. The main contribution to the resulting systematical error comes from: (i) the inability to eliminate electrons elastically scattered in the forward direction, (ii) the imperfect discrimination of electrons inelastically scattered with small energy losses into small forward angles, (iii) the uncertainty of electron impact energy (subject to accuracy of scaling); especially important in the region of strong changes of total cross section function, (iv) the uncertainties in the measurements of the electron beam intensity, (v) the inability to correctly determine the length of the interaction region in a target of inhomogeneous density.

The C_6F_6 (Aldrich, 99.9% pure) vapour was purified before use by subjecting it to numerous freeze-pump-thaw cycles at the liquid N_2 temperature to remove air and other impurities not frozen at this temperature. The SF_6 sample (of Matheson purity) was used directly from the cylinder without any further purification.

3 Results and discussion

3.1 Hexafluorobenzene, C_6F_6

The energy dependence of the present experimental total cross section for electron scattering on hexafluorobenzene molecule is shown in Fig. 1. No data are available for comparison. Numerical absolute values are presented in Table 1.

The most prominent feature of the measured $e^- - C_6F_6$ total cross section is its relatively high magnitude throughout the examined energy range, it always exceeds the value of 28×10^{-20} m^2. With respect to the shape of total cross section function a few clearly distinct energy ranges can be distinguished.

Table 1. Absolute total cross section (TCS) for electron scattering on C_6F_6 molecules in units of 10^{-20} m^2

Energy (eV)	TCS	Energy (eV)	TCS	Energy (eV)	TCS
0.6	31.6	3.6	29.4	23.1	59.2
0.7	33.0	4.1	29.9	25.6	60.1
0.8	32.7	4.6	31.3	28	60.1
0.9	33.1	5.1	32.3	30	60.4
1.0	33.4	5.6	35.2	35	60.2
1.1	33.3	6.1	36.3	40	59.7
1.2	32.5	6.6	38.0	45	58.4
1.3	32.6	7.1	40.7	50	56.6
1.4	31.6	7.6	42.0	60	53.8
1.5	31.8	8.1	44.6	70	51.0
1.6	31.7	8.6	46.7	80	49.3
1.7	31.3	9.1	48.5	90	47.0
1.8	31.2	9.6	48.6	100	46.0
1.9	31.1	10.1	47.6	110	43.3
2.0	31.0	10.6	50.7	120	42.0
2.1	30.5	11.6	52.7	140	39.3
2.2	29.9	12.6	54.3	160	36.8
2.3	30.4	13.6	55.2	180	34.6
2.4	30.4	14.6	56.2	200	33.6
2.5	30.0	15.6	55.9	220	31.9
2.6	30.0	16.6	56.0	250	29.9
2.9	29.2	18.6	56.9		
3.3	28.8	20.6	58.0		

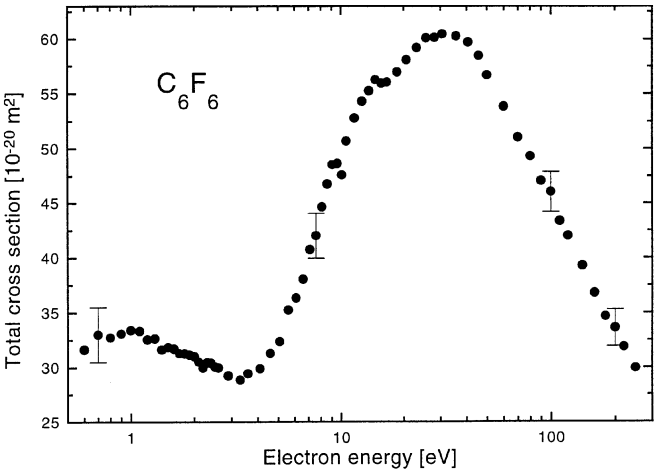

Fig. 1. Absolute total cross section for electron scattering on C_6F_6 molecule: (•), present experiment

At the lowest energies applied, ranging from 0.6 to 4 eV, the cross section for electron scattering on C_6F_6 is a slow-changing function of impact energy with a plane hump of 32×10^{-20} m^2 around 1 eV. Certain features in this energy range, located around 0.45 and slightly below 0.8 eV, have also been observed in electron attachment [17, 18, 19, 20] as well as in electron transmission [21] experiments, respectively, and have been attributed to the resonant capture of the extra electron into the π^* orbital, with formation of a transient $C_6F_6^-$ anion. It should be noted that results of electron attachment experiments on the C_6F_6 molecule [17, 19, 22, 23] suggest that, at near-zero impact energies, below those applied in the present experiment, cross section increases by a few orders of magnitude, due to very efficient production of a metastable ($\tau \simeq 12\mu$s, [24]), undissociating

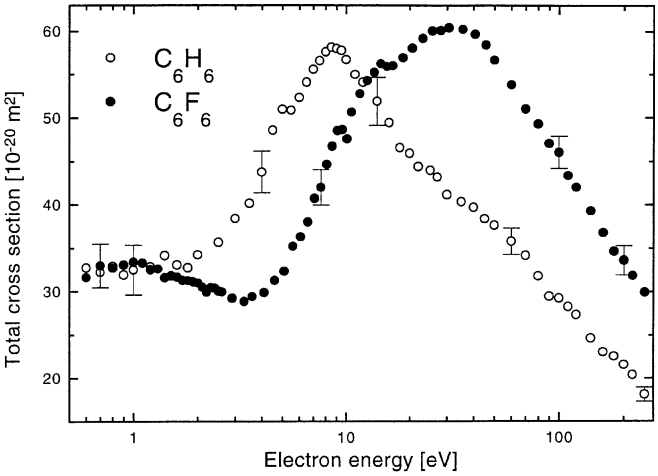

Fig. 2. Comparison of absolute total cross sections for electron scattering on C_6H_6 and C_6F_6 molecules: (○) - C_6H_6, [30]; (●) - C_6F_6 present experiment

negative parent ion, $C_6F_6^{-(*)}$, in its electronic ground, but vibrationally excited, state.

Starting from 3.5 eV, total cross section increases sharply with energy, from $28 \times 10^{-20}\,m^2$ up to values over $55 \times 10^{-20}\,m^2$ occurring between 15 and 60 eV and reaches its maximum value of $60 \times 10^{-20}\,m^2$ in the vicinity of 30 eV. Above 40 eV our results show a continuous decrease in cross section with increasing energy, down to $30 \times 10^{-20}\,m^2$ at 250 eV. On the low-energy side of the very broad peak at least two weak structures can be discerned: one situated around 9.5 eV, the other – close to 14 eV. Both features are attributable to resonant capture of an impinging electron in the field of an excited electronic state with formation of a temporary negative core-excited resonance. The resonance may decompose either through re-emission of the additional electron, or via dissociative channel with the creation of negative and neutral fragments. Proof of resonant origin of the structures between 8 and 15 eV has been obtained in the studies of dissociative electron attachment processes [25, 26, 27, 28, 29] leading to the formation of F^-, $C_5F_3^-$ and $C_6F_5^-$ anions. Unlike the long-lived zero-energy resonance, the states beyond 8 eV seem to have very short autodetachment lifetime [28].

In the present experiment, we cannot with all certainty isolate the resonant structure observed near 4.5 eV in the transmission spectra [21] and in the negative ion yield curves [25, 26, 27, 28, 29]. This may be due to low intensity of the resonance process at 4.5 eV, making it difficult to separate from the sharp increase of cross section in this energy range.

In spite of general similarity (with respect to the shape) of total cross section function for C_6F_6 molecule to that for other ring molecule – C_6H_6, some distinct differences can be seen: the curve for C_6F_6 is clearly shifted towards the higher energies and the main maximum is much broader (Fig. 2).

3.2 Sulfur hexafluoride, SF_6

The total absolute electron scattering cross section function for the SF_6 molecule obtained in the present experiment is shown in Fig. 3, together with earlier absolute measurements [5, 6, 7, 8, 9]. Numerical total cross section data are listed in Table 2.

Table 2. Absolute total cross section (TCS) for electron scattering on SF_6 molecules in units of $10^{-20}\,m^2$

Energy (eV)	TCS	Energy (eV)	TCS	Energy (eV)	TCS
0.5	32.8	5.6	26.1	14.6	27.8
0.6	31.6	5.8	27.7	15.1	27.5
0.7	30.2	6.0	29.6	15.6	27.5
0.8	27.6	6.2	30.4	16.6	27.2
0.9	24.2	6.4	31.0	17.6	27.3
1.0	23.6	6.6	31.6	18.6	27.4
1.1	22.9	6.8	32.6	19.6	28.0
1.2	22.5	7.0	32.7	20.6	29.0
1.3	22.6	7.2	32.9	21.6	30.3
1.4	22.5	7.4	32.4	22.6	30.7
1.5	22.3	7.6	31.6	23.6	31.0
1.6	22.5	7.9	30.4	24.6	30.9
1.7	22.6	8.2	28.9	25.6	30.7
1.8	22.6	8.6	28.5	26.6	30.3
1.9	22.9	8.9	27.9	27.6	30.6
2.0	23.1	9.2	27.5	28.6	30.3
2.1	23.4	9.6	27.5	29.6	30.5
2.2	23.6	9.9	27.9	30.6	30.6
2.3	23.9	10.2	28.2	35	30.4
2.4	23.9	10.6	29.3	40	30.3
2.5	24.0	10.9	30.6	45	30.4
2.6	23.9	11.2	31.6	50	30.4
2.7	23.8	11.4	32.6	60	30.1
2.8	23.6	11.5	33.4	70	29.3
2.9	23.7	11.6	33.5	80	28.9
3.0	23.7	11.7	34.2	90	27.8
3.1	23.7	11.8	35.3	100	27.4
3.2	23.5	11.9	35.7	110	26.5
3.4	23.3	12.0	35.3	120	25.7
3.6	23.1	12.1	34.9	140	24.8
3.8	23.0	12.2	34.4	160	23.5
4.0	22.9	12.4	33.6	180	22.5
4.2	22.9	12.6	32.5	200	21.7
4.4	23.0	12.9	31.6	220	20.6
4.6	23.1	13.2	30.2	250	18.7
4.9	23.5	13.6	28.9		
5.2	24.9	14.1	27.9		

Agreement of the present and earlier results, as far as magnitude is concerned, is satisfactory throughout the overlapping energy range, although the present results are consistently higher (Fig. 4), by about 5–10%, from those of Kennerly et al. [5] and by 5% from those of Dababneh et al. [8]. The present results are also on average 8% above those obtained in the experiment of Romanyuk et al. [7]. However, the discrepancies observed remain within the limits of combined experimental uncertainties. Very good agreement of the present total cross section above 100 eV is seen with intermediate energy part of the measurements of Zecca et al. [9].

A distinctive feature of the $e^- - SF_6$ total cross section is a number of resonant structures visible from thermal energies up to near 30 eV. Resonant increase of cross section below 1 eV is connected with creation of a long lived ($\tau > 1\mu s$) negative ion state, $SF_6^{-(*)}$, at near-zero energies [31], though direct scattering processes are also significant [32, 33]. Three more resonant features have already been observed in earlier TCS absolute [5, 6, 7, 8] measurements. The first of them, a weak hump connected with the formation

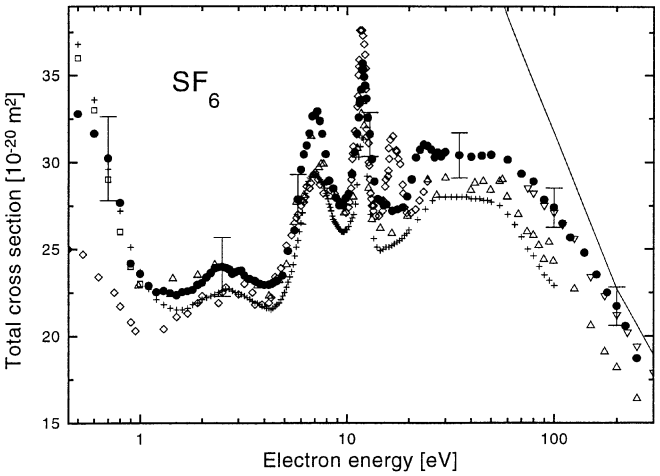

Fig. 3. Absolute total cross section for electron scattering on SF_6 molecule: experimental: (●), present; (+), [5]; (□), [6]; (◊), [7]; (△), [8]; (▽), [9]. Theoretical: (–), [10]

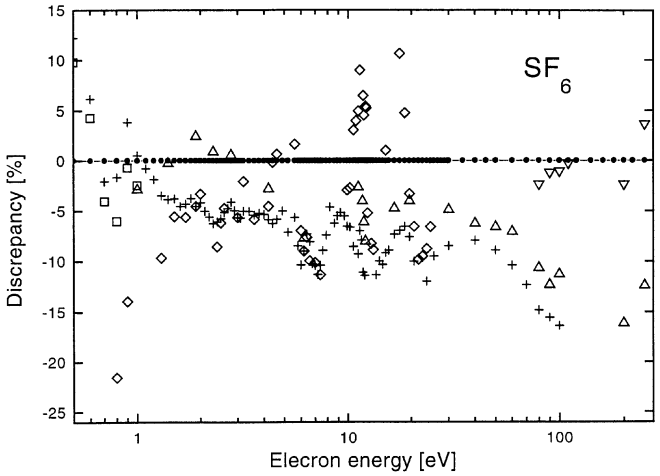

Fig. 4. Discrepancies between experimental total cross sections for electron scattering on SF_6 molecule. Symbols the same as in Fig. 3

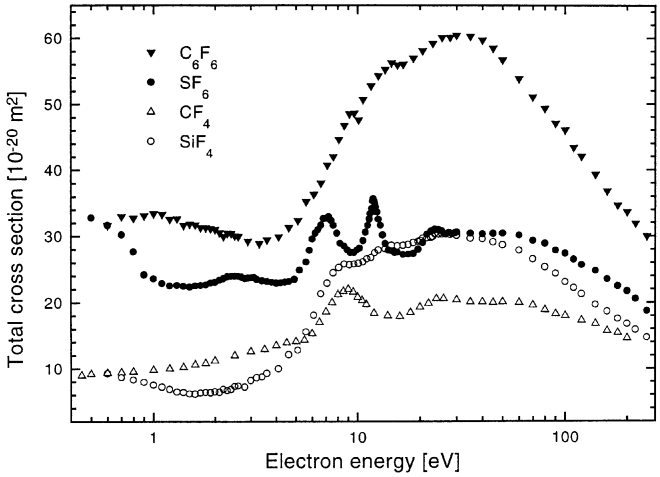

Fig. 5. Total cross sections for electron scattering on perfluorinated molecules: C_6F_6, present results; SF_6, present results; CF_4 [34]; SiF_4, [35]

of a shape resonance of A_{1g} symmetry, is centered at 2.5 eV. The other two, clearly visible resonant t_{1u} and t_{2g} states are situated at 7 and 12 eV, respectively. A further, weaker peak has been observed in the present experiment near 25 eV at the left-side edge of a very broad maximum. This feature may be related to the shape resonance (e_g) found near 27–28 eV in multiple scattering calculations [11, 12, 13] and associated with the sulphur atom. A shift in the calculated structures towards higher energies may be an effect of ignoring the vibrational effects in the calculations. A very weak hump in this energy region was also visible in the experiment of Dababneh et al. [8]. The absence of this structure in the measurements of Kennerly et al. [5] is probably due to poorer energy resolution of the TOF experiment at higher energies. A similar but much weaker structure around 25 eV has also been observed on the low-energy periphery of the very broad maximum in the total electron – CF_4 cross section function [34]. A barely visible change in the course of the curve, within the limits of statistical experimental uncertainties, can be seen near 25 eV also for C_6F_6 (cf Figs. 1 and 5) and SiF_4 [35] molecular targets. It should be noted that we have not observed the peak, centered near 17 eV, clearly visible in the total cross section measured by Romanyuk et al. [7] even though the energetical resolutions of both experiments were comparable; neither was the 17 eV peak visible in other earlier total cross section measurements.

Though TCS calculations of Jiang et al. [10] quite well reproduce the energy dependence of cross section above 70 eV, they give overvaluated total cross sections. Computations merge into experimental data at high energies only. The disaccord rapidly increases when impact energy decreases; at 100 eV computed results exceed experimental values more than 15% while at 10 eV more than 100%. Calculations do not reveal any resonant effects.

An exceptionally broad maximum of the electron-sulfur fluoride scattering cross section function, spanning from 20 to 60 eV, seems to be characteristic for perfluorinated compounds (cf: CF_4 [34]; SiF_4 [35]; C_6F_6, (Fig. 5)). Calculations [11, 12, 13] and experiment [36, 37] suggest that the main contribution to this maximum comes from direct elastic and numerous weak resonant scattering processes, although above 40–50 eV the contribution of ionization effects may also be significant [38, 39, 40].

4 Conclusions

In the present experiment total absolute cross sections were measured by the transmission method for electron scattering on SF_6 and C_6F_6 target molecules for energies from 0.6 to 250 eV. In the total cross section for SF_6 we have observed additional resonant peak centered near 25 eV, slightly below that predicted by theoretical calculations. Results obtained for C_6F_6 molecule are characterized by a very broad hump between 15 and 60 eV of cross section magnitude in excess of 55×10^{-20} m^2. At energies about 9.5 and 15 eV two weak resonant structures have been observed.

To determine the actual configurations of these resonances further more detailed experiments and calculations are needed. The present measurements along with earlier findings indicate that at energies from about 20 eV up to 60–70 eV perfluorinated compounds behave in a similar fashion – their TCS functions show very broad flat maximum.

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