

Total absolute cross section measurements for electron scattering on CS₂ molecules

Czesław Szmytkowski

Department of Physics, Technical University of Gdańsk, 80-952 Gdańsk, Poland

Received 7 July 1987

Abstract. The absolute total electron scattering cross section for CS₂ was measured from 0.4 to 80 eV using a linear transmission method. A minimum cross section ($17 \times 10^{-20} \text{ m}^2$) occurs near 0.8 eV followed by a very broad maximum ($53 \times 10^{-20} \text{ m}^2$) around 9 eV, with a monotonic decrease at higher energies. Comparison is made with existing experimental and theoretical integrated cross sections.

The scattering of electrons on carbon disulphide molecules has been a subject of relatively few works. First experiments dealt mainly with the dissociative attachment processes (Kraus 1961, Dorman 1966, Ziesel *et al* 1975, Dressler *et al* 1987). More extensive studies were made on electron impact excitation of CS₂ (Foo *et al* 1971, Hubin-Franskin and Collin 1971, 1975, Hubin-Franskin *et al* 1980, 1983, Dance *et al* 1978, Flicker *et al* 1978, Wilden and Comer 1980, Ajello and Srivastava 1981). More recently Sohn *et al* (1987) have measured differential cross sections for elastic scattering and vibrational excitation of the fundamental vibrations of CS₂. A new light has been thrown on resonant processes in electron scattering on CS₂ after detailed studies performed by Dressler *et al* (1987). Electron impact ionisation processes in CS₂ were studied by Fiquet-Fayard *et al* (1968), Hubin-Franskin *et al* (1980), Zmbov *et al* (1980) and Miletic *et al* (1980). However, one must stress that the spectra obtained in the majority of experiments gave intensities not marked on the absolute scale. The only theoretical studies on electron-CS₂ scattering have been performed by Lynch *et al* (1979) who employed the continuum multiple-scattering method.

The results of absolute measurements of the total electron scattering cross sections for CS₂ are presented in this paper. The measurements were made with a linear transmission spectrometer (see, e.g., Szmytkowski *et al* 1984) and cover an energy range 0.4–80 eV. Preliminary results between 1 and 20 eV were reported by Szmytkowski (1983).

The experimental procedure is based on the relation between the attenuation of electron current and total cross section $\sigma(E)$. If the electron beam of primary intensity I_0 travels a distance L in the homogeneous target of density n particles per unit volume, then the output current I_g is given by the Beer–Lambert relation

$$I_g(E) = I_0(E) \exp[-nL\sigma(E)]$$

where E is the electron energy.

In the present experiment the electron beam, before entering a 30.5 mm long scattering chamber was energy selected by a 127° electrostatic cylindrical deflector.

The electrons which left the scattering region through the exit orifice of the chamber were detected by a Faraday cup. The absolute electron energy scale was determined with an accuracy of ± 80 meV in relation to the resonance structure in the transmitted electron current around 2.3 eV in molecular nitrogen. The number density n of the target vapour was determined from the ideal gas law ($p = nkT$). The absolute pressure p in the scattering volume was measured with a capacitance manometer and was in the range of 0.04–0.2 Pa, while the pressure outside the scattering cell was typically three orders of magnitude lower. The manometer head was kept at a temperature of 322 ± 1 K whilst the scattering cell temperature was sustained between 316 and 322 K. The gas pressure readings have been corrected for the thermal transpiration effect (Knudsen 1910). The target vapour was let alternately into the scattering cell and outer vacuum volume in such a way that the electron optics was exposed to the same partial pressure of the vapour in both modes of operation (with and without the target in the scattering cell).

The measurements were carried out at a given energy for a series of runs using a range of target pressures and different sets of electron-beam-controlling parameters. The final results are the weighted means of the mean cross sections obtained in different series of individual runs.

The statistical uncertainties (one standard deviation of weighted mean values) over the entire energy range were lower than 2%. The overall systematic error was calculated as the direct sum of all single contributions. This error is equal to 9% below 4 eV decreasing to 6% at higher energies.

Vapour of CS₂ was obtained from the liquid of Analar purity (a stated boiling point range of 319–319.5 K). It was used without further purification other than repeated freeze-pump-thaw cycles to remove dissolved gases.

The measured total cross section values (at selected energies) are presented in table 1 and compared with integrated elastic cross sections calculated by Lynch *et al* (1979) and experimental integrated normalised total (elastic+vibrational) cross sections of Sohn *et al* (1987) in figure 1. The agreement of the reported cross sections with the data of Sohn *et al* (1987) with respect to the shape is good but the results of Sohn *et al* are, on average, about 25% lower in magnitude. The disagreement is slightly outside the combined uncertainties of both experiments. The total cross sections of Sohn *et al* (1987) include integral normalised elastic and vibrational cross sections for excitation of fundamental modes only. At the same time their measurements show that the cross

Table 1. Total absolute cross sections for electron-CS₂ scattering in units of 10^{-20} m² (for selected energies).

| Energy (eV) | Cross section | Energy (eV) | Cross section | Energy (eV) | Cross section |
|----------------|------------------|----------------|------------------|----------------|------------------|
| 0.4 | 22.4 | 3.5 | 47.3 | 20 | 45.9 |
| 0.6 | 18.5 | 4.0 | 50.6 | 25 | 39.0 |
| 0.8 | 17.2 | 5.0 | 52.0 | 30 | 35.2 |
| 1.0 | 19.4 | 6.0 | 51.6 | 35 | 32.7 |
| 1.4 | 25.2 | 7.0 | 53.1 | 40 | 31.0 |
| 1.8 | 31.8 | 8.0 | 52.2 | 45 | 30.0 |
| 2.0 | 33.1 | 9.0 | 53.0 | 50 | 27.8 |
| 2.2 | 35.7 | 10.0 | 51.6 | 60 | 25.3 |
| 2.5 | 37.8 | 12.0 | 51.6 | 70 | 23.4 |
| 3.0 | 41.6 | 16.0 | 49.7 | 80 | 22.0 |

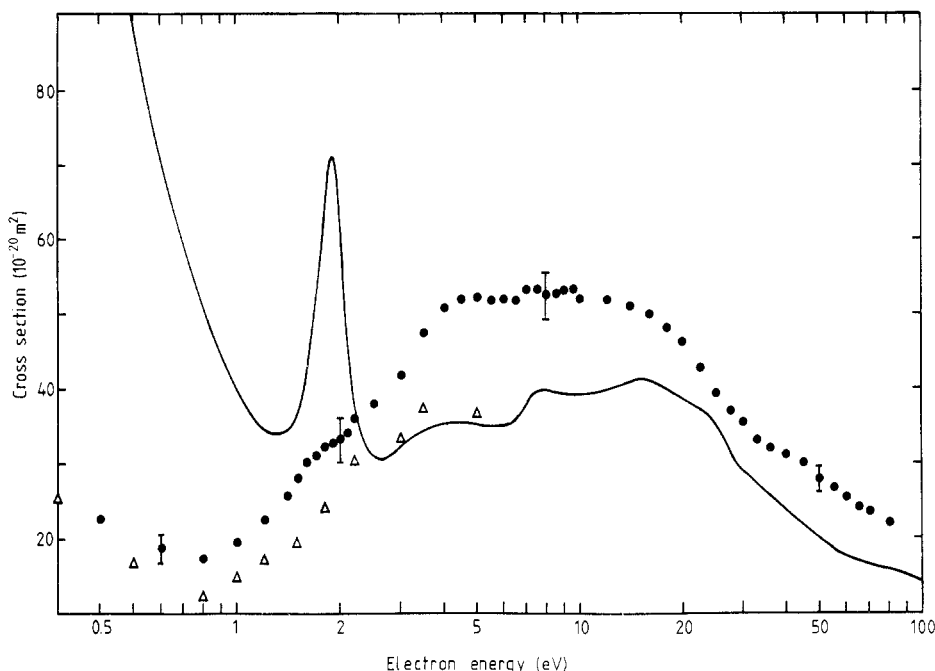


Figure 1. Total e⁻-CS₂ scattering cross sections. Experimental: Δ , Sohn *et al* (1987), normalised integrated (elastic + vibrational); \bullet , this work, absolute. Theoretical: full curve, Lynch *et al* (1979), integrated elastic. The error bars correspond to the overall experimental uncertainties at some selected points.

sections for vibrational excitation of overtones contribute a small fraction to the total scattering cross section. Also the dissociative attachment cross section in this energy range (Ziesel *et al* 1975) is at least two orders of magnitude lower than the total cross section. Taking the above facts into account the disagreement seems to be somewhat disturbing, especially because the results obtained in both laboratories for the OCS molecule (Sohn *et al* 1987, Szymkowski *et al* 1984) are in much better agreement.

The calculations performed by Lynch *et al* (1979) show that, in general, the energy dependence of elastic cross sections for valence isoelectronic molecules CO₂, OCS and CS₂ is similar. In the case of the first two molecules calculations agree quite satisfactorily with the experiment (see, e.g., Szymkowski *et al* 1984, 1987). For CS₂, however, certain significant differences are seen (figure 1) between the experimental results and the theoretical curve. The most visible difference is the presence of a sharp resonance maximum around 1.8 eV in the calculated cross section attributed to the formation of the $^2\pi_u$ CS₂⁻ shape resonant state. The presence of a weak resonance band in this energy range has already been noted in transmission experiments of Burrow (unpublished, see Ziesel *et al* 1975) and Dressler *et al* (1987) as well as in threshold electron spectra by Dance *et al* (1978). A slight change of slope of the present cross section, seen around 1.8 eV, might be a demonstration of this resonance. However, the very recent experiment of Sohn *et al* (1987) did not confirm the presence of a resonant state of $^2\pi_u$ symmetry near the considered energy either in the elastic or vibrational channels. It should be noted that the calculations of Lynch *et al* (1979) do not include the motion of nuclei. Calculations performed for CO₂ (Lynch *et al* 1979) show that taking into consideration the vibrations leads to essential broadening

and lowering of the resonance peaks or even to a complete smearing out of weak resonances in the integrated cross section. A similar effect may, however, result in experiment from finite energy resolution. Another difference between experiment and the calculations of Lynch *et al* (1979), common for CO₂, OCS and CS₂ molecules, is an overestimation of the calculated cross sections in the lowest-energy region.

The sharp increase of the total cross section above 0.8 eV may be partly due to the existence of a number of weak overlapping resonances. Their existence has been recently reported by Dressler *et al* (1987). Further resonances, in addition to the 1.8 eV resonance, were also predicted in calculations of Lynch *et al* (1979).

Above the first ionisation threshold (10.06 eV), an increasing role in the scattering process is played by ionisation phenomena. At 30 eV the cross section for ionisation (Ziesel *et al* 1975) amounts to 22% of the total cross section and, by analogy with SO₂ and H₂S (triatomic molecules containing a sulphur atom), it probably increases up to about 40% at 80 eV.

Results of calculations of e⁻-CS₂ scattering cross sections, performed using the variable-phase approach, will be published in a future article.

Acknowledgments

The author is grateful to K Maciąg for his assistance in the preliminary stages of this work, to Dr M Zubek for valuable comments and to Professor H Ehrhardt for making his results available prior to publication. This work has been supported in part by the Polish Ministry of Science and Higher Education within Programme CPBP 01.06 under Project 3.01.

References

- Ajello J M and Srivastava S K 1981 *J. Chem. Phys.* **75** 4454-63
Dance D F, Keenan G A and Walker I C 1978 *J. Chem. Soc. Faraday Trans. II* **74** 440-4
Dorman F H 1966 *J. Chem. Phys.* **44** 3856-63
Dressler R, Allan M and Tronc M 1987 *J. Phys. B: At. Mol. Phys.* **20** 393-402
Fiquet-Fayard F, Chiari J, Muller F and Ziesel J P 1968 *J. Chem. Phys.* **48** 478-82
Flicker W M, Mosher O A and Kuppermann A 1978 *J. Chem. Phys.* **69** 3910-16
Foo V Y, Brion C E and Hasted J B 1971 *Proc. R. Soc. A* **322** 535-54
Hubin-Franskin M-J and Collin J E 1971 *Bull. Soc. R. Sci. Liège* **40** 361-84
— 1975 *J. Electron Spectrosc. Relat. Phenom.* **7** 139-49
Hubin-Franskin M-J, Delwiche J, Poulin A, Leclerc B, Roy P and Roy D 1983 *J. Chem. Phys.* **78** 1200-12
Hubin-Franskin M-J, Marmet P and Huard D 1980 *Int. J. Mass Spectrom. Ion Phys.* **33** 311-24
Knudsen M 1910 *Ann. Phys., Lpz.* **31** 205-29
Kraus K 1961 *Z. Naturf. a* **16** 1378-85
Lynch M G, Dill D, Siegel J and Dehmer J L 1979 *J. Chem. Phys.* **71** 4249-54
Miletić M, Ereš D, Veljković M and Zmbov K F 1980 *Int. J. Mass Spectrom. Ion. Phys.* **35** 231-42
Sohn W, Kochem K-H, Sheuerlein K-M, Jung K and Ehrhardt H 1987 *J. Phys. B: At. Mol. Phys.* **20** 3217-36
Szmytkowski Cz 1983 *Proc. 13th Int. Conf. on Physics of Electronic and Atomic Collisions* ed J Eichel, W Fritsch, I V Hertel, N Stolterfoht and U Wille (Berlin: Springer) Abstracts of contributed papers p 242
Szmytkowski Cz, Karwasz G and Maciąg K 1984 *Chem. Phys. Lett.* **107** 481-4
Szmytkowski Cz, Zecca A, Karwasz G, Oss S, Maciąg K, Marinković B, Brusa R S and Grisenti R 1987 *J. Phys. B: At. Mol. Phys.* **20** submitted
Wilden D G and Comer J 1980 *Chem. Phys.* **53** 77-84
Ziesel J P, Schulz G J and Milhaud J 1975 *J. Chem. Phys.* **62** 1936-40
Zmbov K F, Miletić M and Veljković M 1980 *Bull. Soc. Chim. Beograd* **45** 23-8