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Measurements of absolute total cross sections for electron scattering from triatomic polar molecules: SO₂ and H₂S

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Abstract

Absolute total electron-scattering cross sections (TCSs) have been measured in the energy range from 0.5 to 370 eV for SO₂ and from 6 to 370 eV for H₂S molecules. Measurements have been carried out using modified electron spectrometer working in a linear transmission mode. The present results are compared to published experimental TCS data. Some aspects important for achieving accurate absolute total cross sections in an electron transmission experiment are discussed.

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1. Introduction

Electron scattering on atoms and molecules is an important tool in investigation of electron-induced processes in matter. Among variety of measurable quantities describing the scattering process, the *grand* total cross section (TCS) which contains global information on the scattering probability is considered to be one of the most reliable; the physical quantities which are necessary to determine the TCS can be measured directly and therefore TCS values can be obtained without any normalization procedure. Declared overall experimental systematic errors of published TCS data are usually relatively low (3–20%).

In spite of the conceptual simplicity of methods used to determine total electron-scattering cross section and the effort by many researchers, remarkable differences still exist in the magnitude and/or shape of electron-energy dependencies of the TCSs measured in different laboratories, even for very common targets (cf. [Brunger and Buckman, 2002](#)). Observed differences, which in

some cases distinctly exceed declared combined experimental uncertainties, are mainly related to systematic factors, which are often difficult to recognize and their importance is not easy to estimate.

An experimental technique used commonly in the total cross section determination is the transmission method (see [Bederson and Kieffer, 1971](#); [Ce Ma et al., 1989](#)) in its numerous modifications. The method is based on measurements of the attenuation of a monoenergetic projectile-particle beam transmitted through the volume filled with target particles maintained at constant pressure and temperature. In the ideal transmission experiment, the total cross section, $Q(E)$, at each impact energy E is related to the attenuation of projectile beam and can be derived from the Bouguer-de Beer-Lambert (BBL) formula

$$Q(E) = \left(\int_a^b n(x) dx \right)^{-1} \ln \frac{I_0(E)}{I_n(E)}, \quad (1)$$

where $I_n(E)$ and $I_0(E)$ are intensities of transmitted projectile-beam of energy E detected in the presence or absence of the target in the scattering volume, respectively; $n(x)$ is a spatial distribution of the target number density along the whole projectile trajectory, while

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integration is performed over the entire path of the projectile beam where $n(x) \neq 0$.

There are two serious inherent problems arising in the transmission technique associated with:

(i) the incomplete discrimination by the detector system against the projectiles that are scattered through small angles in the forward direction and which contribute to the “unscattered” signal; this effects in lessening the measured TCS from its true value. The inaccuracy of the measured electron-scattering TCSs, related to this effect, increases with increasing impact energy and/or with increasing value of electric dipole moment of the target. Commonly employed method to deal with inelastic forward scattering is to put an energy-analyzer in front of the projectile detector. This method, however, is unable to resolve the electrons scattered elastically in the forward direction, back into the primary beam, from those unscattered (Bederson and Kieffer, 1971); the uncertainty related to the elastic scattering-in contribution can be quite significant. Another solution of the problem is to correct the measured data with respect to the forward scattering effect. However, to estimate the amount by which the measured TCS may be lowered due to imperfect discrimination against small-angle electron scattering, the detector discrimination angle and the absolute angular distributions of scattered electrons are necessary;

(ii) inevitable effusion of the target particles through the orifices of the scattering chamber. Therefore, the $n(x)$ distribution and the limits of the path length over which scattering events are possible cannot be precisely defined and the actual value of the integral in Eq. (1) is not easy to estimate. The problem even increases in the case of condensable targets and when the scattering region is not free of electric and magnetic fields (Bederson and Kieffer, 1971; Golden, 1978).

In actual experiment, fulfilment of all the conditions, at which the BBL attenuation law is justified, is rather difficult task. Due to this reason, discrepancies amongst the total cross section data from different laboratories for the same targets exceed even 50%, especially at extremes of applied energies and around TCS maxima and minima (see Trajmar and McConkey, 1994; Christophorou and Olthoff, 2000). Therefore, to improve the quality of recommended TCS data sets it is accustomed to perform a number of independent measurements maintaining experimental conditions as perfect as possible.

The SO_2 molecule, for which a considerable number of the electron-scattering TCS measurements have been already performed (Sokolov and Sokolova, 1981; Zubek et al., 1981; Dababneh et al., 1985; Szmytkowski and Maciąg, 1986a; Olthoff et al., 1991; Zecca et al., 1995), is a good example of problems arising at TCS measurements. At low electron-impact energies, below 10 eV, the

deviations between the earliest TCS results and those recently obtained are exceptional—the results differ nearly by order of magnitude. For higher energies, where only newly published results are available, the accord is more satisfactory and results lie, in general, within limits of combined experimental errors. The measurements mentioned above, but that of Sokolovs', were performed with the transmission method in different modes; Sokolov and Sokolova (1981) employed an electron cyclotron resonance technique. Similar behaviour with respect to deviation between the earliest and the recent low-energy measurements is also noticeable for published e^- - H_2S scattering data. To date, however, measurements of the TCS for e^- - H_2S scattering include only few experiments carried out by Sokolov and Sokolova (1981), Zubek et al. (1981), Szmytkowski and Maciąg (1986b) and by Zecca et al. (1992).

The observed disaccordance between electron-scattering total cross sections obtained in different laboratories prompted us first to renew and then to extend our measurements of TCS for H_2S and SO_2 molecules using modified transmission experimental setup.

2. Experimental

The reported TCS experiments were performed with an electrostatic electron spectrometer working in a linear configuration at single collision conditions. The apparatus and procedure have been described in detail elsewhere (e.g. Szmytkowski and Mozejko, 2001). Briefly, the target particles are irradiated by a quasi-monoenergetic ($\Delta E = 80$ meV, fwhm) electron beam and the attenuation of the electron current passing through the target volume is measured. Other quantities taken in the course of the experiment are: an electron beam energy, E , target vapour pressure, p , the temperature, T_c , and the length, L , of the scattering cell.

The integral in Eq. (1) is replaced, within an accuracy of 1% (Nelson and Colgate, 1973), with the product, nL , of the geometrical distance between orifices of the scattering cell, and the target density number, $n = p/k\sqrt{T_c T_m}$, derived from the target gas pressure measured in the center of the scattering cell; T_m ($= 322$ K) is the temperature of the manometer head, k is the Boltzmann constant. A thermal transpiration effect is accounted for (Knudsen, 1910).

In general, the present apparatus setup is similar to that employed in experiments carried out in the same laboratory at eighties (Szmytkowski and Maciąg, 1986a,b). However, in order to reduce possible systematic errors some significant modifications have been made. At either orifice of the scattering cell more efficient removal of the target gas flowing from the target cell was ensured—this change should lower

uncertainty of estimated value of the integral in Eq. (1), as well as to reduce disturbances of the primary electron beam related to the presence of the target particles in the electron optics region. In front of the electron-detector entrance, a retarding field element is applied to discriminate against electrons which are scattered inelastically in the forward direction and which might be accepted by the electron collector; the retarding element is effective in discriminating against electrons which have suffered an energy loss of slightly more than 0.1 eV. The solid angle subtended at the Faraday cup detector is distinctly reduced, from 3 to nearly 0.6 msr.

The statistical uncertainty (one standard deviation of the weighted mean value) of the measured TCSs is less than 1.5% over the entire energy range investigated. The overall systematic uncertainty—estimated as a combination of potential systematic errors of measured individual quantities used for the derivation of TCS—amounts to 9% below 2 eV, gradually decreases to about 5% around 20 eV and increases again to 7% at the highest applied energies.

The sulfur dioxide (99.98%) and the hydrogen sulfide (99.5%), both from Merck, are used directly from supplied cylinders without any further purification.

3. Results and discussion

The absolute total electron-scattering cross sections presented in this work are the average of results obtained in two experiments carried out recently, some years apart.

3.1. Sulphur dioxide, SO₂

The total cross section for electron impact energy from 0.5 to 370 eV for SO₂ is shown in Fig. 1 together with the other available data for the comparison. In general, the present e⁻–SO₂ results are in fair agreement with respect to the shape and magnitude with those of Dababneh et al. (1985) and Olthoff et al. (1991) over the whole overlapping energy range. Nevertheless, below 1 eV our results are distinctly lower than the measurements of Dababneh et al. (1985) and higher than those of Olthoff et al. (1991). Above 1 eV the results of both groups are consistently lower than the present TCS values, though the agreement of present data with those of Olthoff et al. (1991) is better. A striking dissaccordance of the Sokolov and Sokolova (1981) low-energy findings with the present and other recent measurements is noted both with respect to the TCS magnitude and to the shape of the TCS energy dependence. Above 100 eV the present data are in good accord with intermediate-energy measurements of Zecca et al. (1995).

As it is seen in Fig. 1, both sets of our results, the old (Szmytkowski and Maciąg, 1986a) and new one, are

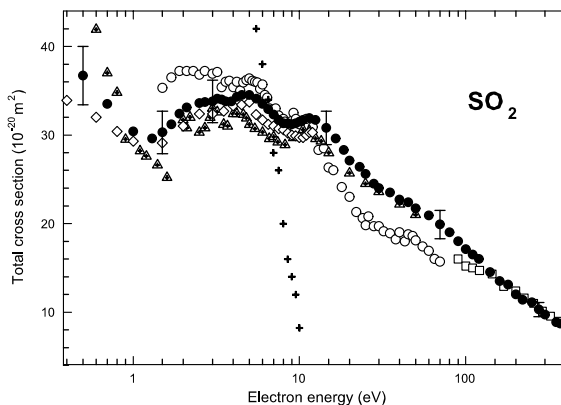


Fig. 1. Experimental total cross sections for e⁻–SO₂ scattering: crosses, Sokolov and Sokolova (1981); crossed triangles, Dababneh et al. (1985); open circles, Szmytkowski and Maciąg (1986a); diamonds, Olthoff et al. (1991); open squares, Zecca et al. (1995); filled circles, present; error bars represent overall experimental uncertainties.

within the combined experimental errors. However, at impact energies between 1.5 and 6 eV the present data are consistently lower, while being distinctly higher at energies above 20 eV. The observed difference may be in part explained in terms of improvements made in the present experimental setup: (i) better gas pumping in the vicinity of the orifices of the scattering chamber and, in consequence, more adequate estimation of the integral in Eq. (1) should result in lowering of the measured TCSs, approximately to the same degree over all energy range investigated; (ii) on the other hand, the use of discrimination against electrons being scattered inelastically back into the primary beam increases the present results in relation to previous ones—however, this effect becomes more appreciable with increasing impact energy.

3.2. Hydrogen sulfide, H₂S

Present absolute electron-scattering total cross sections measured for H₂S between 6 and 370 eV are shown in Fig. 2 along with experimental results of Sokolov and Sokolova (1981), and recent measurements of Zecca et al. (1992). For H₂S, just as for SO₂, the substantial disagreement with early low-energy measurements of Sokolov and Sokolova (1981) is clearly visible. The systematic discordance of Sokolovs' results with those obtained in other laboratories, in a later period, suggests serious systematic error in the experimental procedure of Sokolov and Sokolova (1981). At intermediate energies our results are in very good agreement with results of Zecca et al. (1992) obtained with the Ramsauer technique. It is worth noting that, in contrast to SO₂

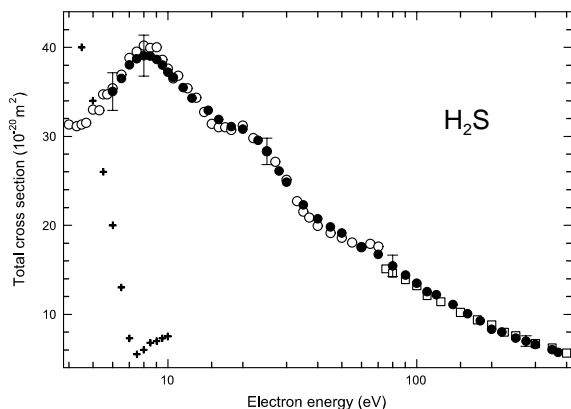


Fig. 2. Electron-scattering total cross sections measured for H₂S molecule: crosses, Sokolov and Sokolova (1981); open circles, Szmytkowski and Maciąg (1986b); open squares, Zecca et al. (1992); filled circles, present; error bars represent overall experimental uncertainties.

data, the present H₂S results are in good accord with previous data of Szmytkowski and Maciąg (1986b). The reason for such noticeable difference between our old and new results for H₂S in comparison to that for SO₂ may be partly related to the fact that the evacuation of the H₂S gas from the exterior of the scattering cell is more effective than of the SO₂. On the other hand, because the electric dipole moment of H₂S (= 0.97 D) is nearly twice lower than that for SO₂ molecule (= 1.63 D) (Lide, 1995-96), and consequently electron scattering in forward direction is considerably less intensive for H₂S (Jain et al., 1990; Varella et al., 1999) than for SO₂ (Raj and Tomar, 1997; Natalense et al., 1999), therefore the old TCS results for H₂S were less altered on account of the lack of discrimination against forwardly scattered electrons.

Closer inspection of e⁻-SO₂ and e⁻-H₂S total cross section curves (Figs. 1 and 2) reveals that for electron impact energies above 60 eV, the energy dependence of both measured TCSs can be reasonably approximated with the $Q \sim E^{-a}$ function (a is close to 0.5) indicating that the electron-scattering TCS for the investigated molecules is proportional to the time needed by the electron to cover the distance in the vicinity of the target molecule.

4. Summary

The absolute total electron-scattering cross sections were measured for H₂S and SO₂ molecules over wide energy range from low energies up to 370 eV. Above 60 eV, the intermediate-energy dependence of both TCS curves can be approximated with the regression formula

$Q = AE^{-0.5}$. Present results show good agreement with recently published experimental TCSs, establishing together a consistent set of total cross section data for H₂S and SO₂ molecules spanned between low and high impact energies.

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