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Absolute total cross section for electron scattering on water in the energy range 25–300 eV

Z Sağlam and N Aktekin

Department of Physics, University of Gazi, Ankara, Turkey

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Abstract. Absolute total electron scattering cross sections for water molecules measured in the 25-300 eV incident energy range using a linear electron transmission device are presented. The results are compared with previous data.

1. Introduction

Collisions of electrons with water molecules play an important role in atmospheric and interstellar space processes, radiation biology and chemistry. Reliable absolute total electron scattering cross sections are needed in these areas as well as for the normalisation of non-absolute cross sections. However, the experimental data, which have been taken using various techniques for this quantity, are fragmentary. The first measurements of the total cross section for water molecules were carried out by Brüche (1929) (Ramsauer type, 4.8-46 eV), Sokolov and Sokolova (1981) (electron cyclotron resonance, 0.25-7 eV), Sueoka *et al* (1986) (time-of-flight, 1-400 eV), Zecca *et al* (1987) (Ramsauer type, 80-3000 eV), Szymtkowski (1987) (linear transmission, 0.5-80 eV), Nishimura and Yano (1987) (linear transmission, 7-500 eV). Recently Jain (1988) calculated for the first time the total (elastic and inelastic) cross section for electron-H_2O scattering in the energy range 10-3000 eV by employing semi-empirical spherical complex optical potentials. However there are discrepancies between the various experimental results (Szymtkowksi 1987) and Zecca *et al* (1987) suggested further measurements of the total cross section for e-H_2O scattering that would serve as a check on the theoretical works and as an evaluation of the accuracy of electron scattering experiments.

The present measurements have been performed on a linear transmission device designed for 4-300 eV electron scattering by Nickel *et al* (1985). The present article describes the apparatus and experimental procedure and presents the total electron scattering cross section result for H_2O in the 25-300 eV incident energy range.

Section 2 will describe the apparatus used to obtain the result and section 3 will outline the experimental procedure. In section 4 the present result and associated errors are summarised and compared with previously measured and theoretically calculated results.

2. Apparatus

The apparatus used in this study is that of Nickel *et al* (1985) with a sample purification (handling) unit added. This unit consists of a rotary pump with a liquid nitrogen trap

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and kovar seal glass sample bottle. A block diagram of the linear transmission device is shown in figure 1. The construction can be considered in four sections as shown in the figure. The outer vacuum jackets of each section are constructed from non-magnetic type 321 stainless steel. All apertures and deflectors are constructed from molybdenum. The entire device is enclosed in a mu-metal shield to reduce the effects of Earth's magnetic field.

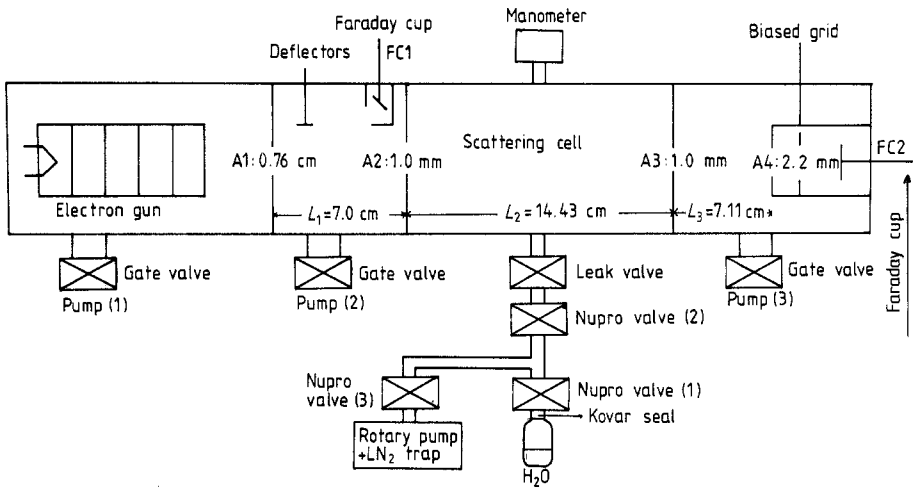

Figure 1. Attenuation apparatus for measuring total cross sections.

The first section contains a six-element cylindrical-tube electron gun capable of generating a 5 μA beam in the selectable energy range of 4–300 eV with an energy resolution of 0.35 eV FWHM. The gun enclosure is differentially pumped to minimise such deleterious effects as filament cooling and poisoning due to gases entering the region through the 0.762 cm diameter aperture A1.

The second section serves three purposes. First, it acts as a differential pumping chamber to remove gas effusing from the scattering chamber. (It is important to keep the target gas density outside the scattering chamber well below 1% of the density inside the chamber so that a well defined scattering length exists.) Second, it contains a Faraday cup, FC1, which serves to monitor the stability of the incident electron beam. Finally, it contains an orthogonal set of electrostatic beam deflectors which aid in-beam steering.

The third section, the scattering chamber, is a stainless-steel tube 14.43 cm long bounded by apertures A2 and A3. Both aperture openings are 1 mm in diameter. Gas is fed to the chamber through a leak valve and the pressure in the scattering chamber is monitored by an MKS Barotron capacitance manometer. The MKS unit consists of a model 310 BHS 1 Torr full scale sensor head and a model 170M-6C electronics unit. The temperature of the scattering chamber is monitored with a calibrated thermistor.

The fourth section again serves as a differential pumping chamber but also contains the detector, a gridded Faraday cup. The opening of the detector aperature, A4, is 2.2 mm in diameter and is located 7.1 cm from A3. The grid, when properly biased, serves to discriminate against electrons inelastically scattered in the forward direction.

The output of the detector, FC2, is monitored on an electrometer. FC2 is shielded and +45 V is applied to prevent secondary electron emission effects.

3. Experimental procedure

In the linear transmission experiment, electrons of known energy are transmitted through the scattering chamber and are detected by the Faraday cup. To a good approximation the detected current, $I_d(n)$ is given by

$$I_d(n) = I_d(0) \exp(-Q_m nL) \tag{1}$$

where n is the target gas density in the scattering cell, L is the scattering length, and Q_m is the 'measured' total cross section. The measured cross section differs from the true cross section Q because the transmitted current detector cannot totally discriminate against electrons elastically scattered in the forward direction at angles which are smaller than the access source angle of the detector. The fractional deviation between Q and Q_m is given by

$$\frac{Q - Q_m}{Q} = \frac{2\pi}{Q} \int_0^{\theta_{max}} \frac{dQ}{d\Omega} \sin\theta \, d\theta \simeq \frac{1}{Q} \left|\frac{dQ}{d\Omega}\right|_{\theta=0} \langle \Delta\Omega \rangle \tag{2}$$

where $|dQ/d\Omega|_{\theta=0}$ is the differential total scattering cross section in the forward direction (if discrimination against inelastic forward scattering is not made), $\langle \Delta\Omega \rangle$ is the solid angle subtended by the detector averaged over the length of the scattering chamber, and θ_{max} is the maximum scattering angle which can contribute to the transmitted signal. We will not distinguish between Q_m and Q (Nickel *et al* 1985). A plot of $\ln I_d(n)$ as a function of n yields a straight line whose slope is $-QL$. As an example of the absorption measurement a logarithmic plot is shown in figure 2.

In this experiment the detected current is measured as a function of pressure in the scattering cell for a particular incident electron energy. The density in the scattering cell is derived from the pressure P, using the ideal gas law $P = nKT$, where T is the measured temperature of the scattering cell. Using a least-squares fitting program, we

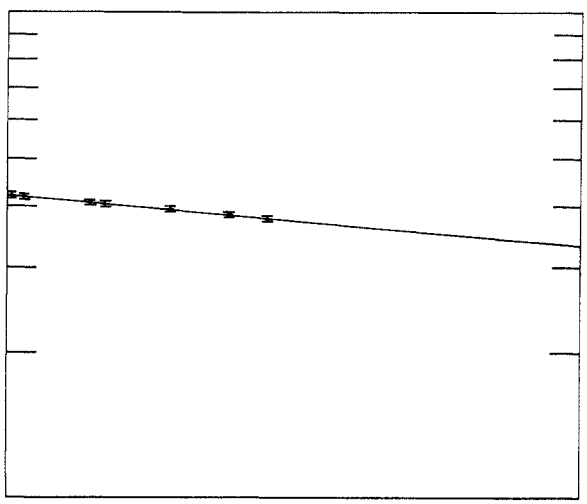

Figure 2. A logarithmic plot of the absorption measurement.

obtained the best fit slope of the $\ln I_d(n)$ line and finally obtained Q. For all the incident electron energies the maximum pressure is chosen as about 5×10^{-4} Torr. At this maximum pressure the detected current drops to about 0.7-0.9 times its value at zero pressure. This ensures that multiple scattering can be ignored.

To minimise the drifts in the manometer and in the incident electron beam we took all measurements between the starting pressure and the maximum pressure. After each run, the pressure is returned to the same starting value and $I_d(n)$ is recorded to monitor any drifts in the incident electron beam flux. Typically drifts of a few per cent are obtained and are corrected for by assuming that the drifts occurred linearly over the period of the measurement. All of the measurements reported here were made with the incident electron current in the 10^{-10}-10^{-11} A range where the results are independent of the current. The temperature of the capacitance manometer sensor head is maintained at 45 °C while the temperature of the scattering cell is typically 29-32 °C. Thus we might expect the pressure in the scattering chamber to be slightly less than the pressure indicated by the MKS unit due to thermal transpiration effects. The effects of thermal transpiration can be taken in to account by the relation (Edmonds and Hobson 1965):

$$P_s = a(T_s/T_m)^{1/2}P_m \tag{3}$$

where P_s and T_s are the pressure and temperature in the scattering chamber, P_m is indicated by the MKS Baratron, T_m is the temperature of the MKS sensor, and a is a constant which depends on the geometry over which the temperature gradients occur. If the gradients occur over an ideal aperture, Nickel *et al* (1985) expect $a=1$ and

$$P_s = 0.976P_m. \tag{4}$$

Thus if they first calculated their cross section using the thermostatted MKS readings, they would need to revise them upwards by 2.4% to take thermal transpiration effects in to account, assuming the temperature gradients take place over an ideal aperture. If the temperature gradients do not take place over an ideal aperture, $a>1$, and its value depends on the particular geometry involved, Nickel *et al* (1985). They have determined the effects of thermal transpiration on their measurements by comparing cross sections obtained with MKS thermostatted with those obtained with the MKS unit in thermal equilibrium with the scattering cell. They find thermal transpiration effects to be important only for He and Ne. The cross sections for He calculated using the thermostatted MKS readings need to be revised upwards by 2% to account for thermal transpiration while those for Ne need to be revised upwards by 1%. No thermal transpiration correction was needed for Ar and Xe. So the thermal transpiration effect varies with atomic/molecular species (such as molecular diameter) or this may be due to the particular experimental arrangement.

We also determined the effect of thermal transpiration on our measurements by comparing cross sections obtained with the MKS thermostatted with those obtained with the MKS unit in thermal equilibrium with the scattering cell at high incident energies (100-300 eV). We find the thermal transpiration effect to be about 1%.

All water samples used in the measurements were doubly distilled, deionised and degased. Before the sample was fed to the scattering chamber through a leak valve, the gas line, from the chamber to the sample bottle, was pumped to 2×10^{-7} Torr (typically). We were not able to do the energy calibration, so we have assumed an unknown shift of 0.7 eV.

4. Results and discussion

The results of the present experiment are given in table 1 together with statistical errors. An estimated ±2% systematic error has to be added to the statistical errors. The present data are compared with the experimental results of Brüche (1929), Sueoka *et al* (1986), Zecca *et al* (1987), Szymtkowski (1987), Nishimura and Yano (1987) and the first theoretically calculated total cross section values of Jain (1988) in figure 3.

The results of Brüche (1929) are lower by about 2-9% than the present results in the energy range 25-40 eV. The data of Brüche taken by using the Ramusauer type

Table 1. Total electron scattering cross sections (Å^2). The numbers in parentheses refer to statistical errors (%).

Impact energy (eV)	Cross section
25	13.50 (2.3)
30	12.36 (2.8)
35	11.39 (1.5)
40	10.76 (1.3)
50	10.37 (1.3)
60	9.90 (2.9)
70	9.01 (0.9)
80	8.44 (1.0)
90	7.90 (0.3)
100	7.49 (1.1)
120	6.79 (0.7)
150	5.99 (2.6)
200	5.17 (2.6)
250	4.46 (1.1)
300	4.01 (2.0)

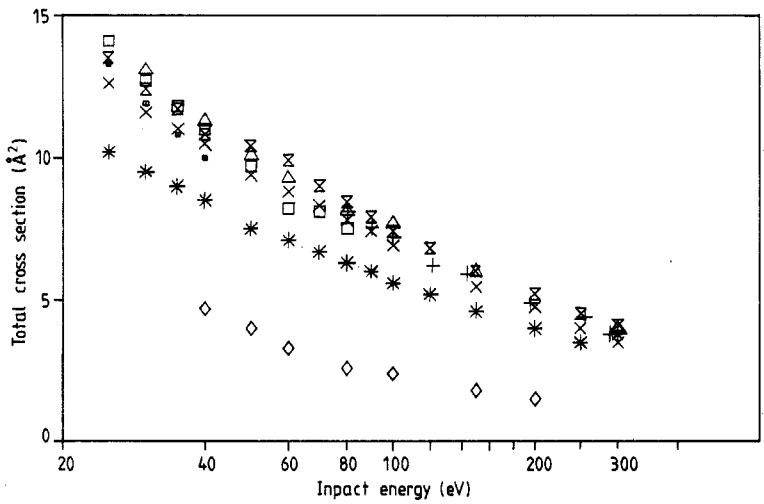

Figure 3. Total scattering cross sections for H_2O: ⊡, Brüche (1929); *, Sueoka *et al* (1986); +, Zecca *et al* (1987); □, Szymtkowski (1987); ×, Nishimura and Yano (1987); Δ, Jain (1988) ⧗, present.

apparatus with the technique of the 1920s, are also lower than those obtained by Szymtkowski (1987), by on average 20% in the energy range 1-12 eV.

The results of Zecca *et al* (1987) are lower by about 3 to 10% than the present results over the whole energy range of overlap (80-300 eV). We note that the higher the energy is the larger the discrepancies. The reason for this increase might be that the effective path length is larger than the physical length of the gas cell. In addition, the angular acceptance of their apparatus is relatively larger than the present apparatus.

The results of Szymtkowski (1987) are higher by about 1 to 4% than the present results between 25-40 eV, but are lower than our values by about 7 to 21% between 50-80 eV. At high energies there is serious disagreement. We note the same type of disagreement between the data of Szymtkowski and Nishimura and Yano (1987). The values obtained by Symztkowski are higher by as much as 12% in the range 25-50 eV, but are lower than the values of Nishimura and Yano by about 5%, in the range 50-80 eV, although in both experiments cell lengths and pressure ranges were close to each other. If we compare Szymtkowski's results with that of Zecca *et al* at 80 eV (comparison can be made only for 80 eV) the data of Szymtkowski are 8% lower than those of Zecca *et al* (1987). In the result of Szymtkowski, the thermal transpiration is not taken into account and discrimination was not made against forward scattering during the detection of electrons, so the measured total cross section should be systematically lower especially at high impact energies.

The results of Nishimura and Yano (1987) taken by using a linear transmission device, are lower by about 3 to 14% than the present results over the whole range of overlap (25-300 eV). The overall systematic uncertainty, assumed to be due to the measurement of currents, the target gas pressure including the temperature correction and the estimate of scattering length, was estimated to be 18%. The statistical error varies from 9 to 25%. So their results have as much as 43% total error.

The measurements of Sueoka *et al* (1986) are lower than all the other cross sections including the present result. The discrepancies are as much as 40% in the energy range 25-300 eV. This shows that a time-of-flight experiment with strong longitudinal magnetic field is not well suited for accurate absolute measurement. In addition inelastic forward scattering cannot be discriminated against energetically in this experiment. The calculated values of Jain (1988) and the present results are in excellent agreement (±1%) above 100 eV. The present results are in agreement within 5% over the range of overlap (25-100 eV). The discrepancies increase at low energies. As he stated in his paper it might be worthwhile to employ a better energy-dependent polarisation potential below 100 eV.

5. Discussion of errors

The statistical errors for each point are given in table 1. Each data point is the average of measurements for four samples. For each sample at a given electron beam energy at least three runs (in some cases 30) were made: for each run at least five measurements were taken.

The statistical error quoted is given by

$$\% \text{ error} = \frac{1}{\bar{Q}} \left(\sum_{i=1}^{N} \frac{(Q_i - \bar{Q})^2}{N} \right)^{1/2} \tag{5}$$

Where $\bar{Q}$ is the average cross section over four samples, Q_i is the average cross section for each sample, N is 4.

Four sources of systematic errors were mainly considered.

(i) Pressure measurement. The MKS manometer is specified by the manufacturer to be accurate to better than 1% over the ranges used in this experiment. An error of ±1% is assigned in the pressure measurements.

(ii) Effective path length L. The physical length of the scattering cell (L_2) is 14.43 cm. Any gas in the differential pumping chambers of lengths L_1(7.0 cm) and L_3 (7.1 cm) respectively (see figure 1) will make the effective attenuation differ from the physical length L_2 and will tend to yield high values for the measured cross section. The error associated with effective path length considerations is given by

$$(Q_m - Q)/Q = \alpha(L_1 + L_3)/L_2 \simeq \alpha \tag{6}$$

where α is the ratio of the density in the differential pumping chambers to the density in the scattering chamber. For our case $\alpha < 0.01$ and an error of −1% is assigned to this effect.

(iii) Scattering in the forward direction. The true cross section may differ from the measured cross section because of the contribution to the transmitted current from forward scattering. A biased grid in the Faraday cup is used to discriminate against electrons inelastically scattered in the forward direction. In this apparatus $\theta_{max} = 0.89°$ and $\langle \Delta\Omega \rangle = 2.2 \times 10^{-4}$ sr. Under these conditions the error introduced by forward scattering is negligible compared with other errors (Nickel *et al* 1985).

(iv) Thermal transpiration. In order to estimate the error caused by thermal transpiration, the measurements were repeated at 100, 200 and 300 eV keeping the MKS unit in thermal equilibrium with the scattering chamber at laboratory temperature. The cross sections obtained by this procedure differ from those obtained with the MKS unit kept at 45 °C (thermostatted) by about 1%.

The shift in the energy scale was assumed to be about 0.7 eV. So the error in the energy range 25-300 eV should be small because the results seem to be pretty energy independent in this region.

Combining all systematic errors, we assign a total systematic error of ±2% to the present data.

Taking the linear combination of all systematic errors and the statistical uncertainty the total experimental error is about 5%.

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