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Electron–molecule absolute total cross sections: O_2 from 0.2 to 100 eV

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Abstract. Absolute total cross sections for e-O_2 scattering, measured with two different apparatuses in two laboratories, are presented. The overall energy range of the measurements covers from less than 0.2 to 100 eV. The absolute error of these measurements is less than ±7%, including the angular-resolution error. The degree of consistency of the two measurements is discussed and a comparison with previous results is given. The results presented here are believed to be more accurate than previous ones reported in this energy range.

1. Introduction

The total cross section for e^--O_2 scattering was measured in the 1920s (Brüche 1927, Ramsauer and Kollath 1930) and more recently by Sunshine *et al* (1967), Salop and Nakano (1970) and Dalba *et al* (1980a). A limited energy range was covered in each experiment and the agreement in magnitude between the different results is not satisfactory. On the other hand, oxygen being one of the components of the atmosphere, these cross sections can be of importance for several fields of fundamental and applied research.

At the University of Trento and at the Technical University of Gdańsk two independent programmes were underway, concerned with total cross section measurements, firstly in the so called low-energy range (0–100 eV) at both laboratories and secondly in the intermediate energy range (100-3000 eV) at the laboratory at Trento. This paper presents the joint effort of the two laboratories for e^--O_2 cross section measurements at low energies. As will be seen the two apparatuses used for these measurements were quite different, and comparison of the two sets of measurements can be of mutual reinforcement.

2. Description of the apparatuses

The apparatuses employed for the present measurements have already been used (Dalba *et al* 1980b, Szmytkowski *et al* 1984) and described elsewhere (Calicchio *et al* 1982) in the past. Here only a short description will be given with the purpose of reporting some changes and of discussing differences which could be relevant for the final measured results.

The Gdańsk apparatus (Szmytkowski *et al* 1984) was equipped with a cylindrical 127° electrostatic electron monochromator. The energy spread of the beam was kept around 70 meV during this experiment. The electron beam was passed through a 30.5 mm long scattering chamber and detected with a Faraday-cup collector. The target gas pressure in the scattering chamber was measured with a MKS Baratron meter. The measuring head was kept at a constant temperature of 322 K whilst the gas chamber temperature was around 312 K. The head temperature coefficient and the thermal transpiration effect were allowed for in the data reduction. The background pressure in the spectrometer chamber was around 2×10^{-6} Torr, with a gas chamber pressure of 2×10^{-3} Torr. The measurements were carried out for a given energy in a series of runs using a range of target pressures and different sets of voltages on the electron optics. The presented results are the average values over a number of runs. The laboratory facility (vacuum system, electronics, magnetic-field compensation) were the same as described in Szmytkowski *et al* (1984).

The Trento apparatus was equipped with an 'aperture' monochromator (Calicchio *et al* 1982). The energy FWHM of the beam during these measurements was between 65 and 90 meV. The gas chamber was 30 mm long with 1 mm diameter entrance and exit apertures. The transmitted beam was analysed by a rough retarding lens, with an energy resolution of about 0.2 eV. The detector was a Faraday cup. A MKS Baratron meter was used to measure the gas pressure in the collision chamber. Head and gas chamber temperatures were 323 and about 338 K respectively. Again the head temperature coefficient and the thermal transpiration correction were taken into account. The background pressure in the spectrometer chamber was around 1×10^{-5} Torr at gas chamber pressures in the high (10^{-3}) range. A diverter valve (Basta *et al* 1976) was used to keep the background pressure constant whilst changing the gas chamber pressure. The data collection was made by an on-line computer. A typical measurement run spanned less than a decade in energy. To cover the entire range from about 0.1 to 100 eV, several different voltage sets were therefore used. Different ranges were measured between three and seven times. Each measurement run consisted of a number of measurements at intervals of 10 meV in the low-energy range up to 0.2 eV in the highest range. Each channel was measured over seven pressures. The procedure has already been described (Dalba *et al* 1980b). The splicing and joining of the cross section data for the different energy ranges were made as described by Dalba *et al* (1980b). The laboratory facility was the same as described in this paper.

It has been noted that the two apparatuses are quite different. One major difference will now be discussed. In the Trento apparatus the retarding analyser and the entrance of the Faraday cup are very close to the exit aperture of the scattering chamber. The pressure inside those electrodes can therefore be substantially higher than the background pressure in the apparatus. It was checked by the Gdánsk group that such a geometry can influence the effective length to be used in the data reduction formula, thus increasing the measured values of the total cross section. The systematic error introduced by this effect could be as high as 5%. Unfortunately the Trento measurements were completed before the beginning of the collaboration and the apparatus has since been modified. It is therefore impossible to check experimentally this concern by changing the geometry of the region between the gas chamber and collector in the Trento apparatus. Further comments on this problem will be given in the section reporting the results.

3. Experimental procedure and error discussion

A complete discussion of the possible systematic errors in the Gdańsk apparatus can be found in Szmytkowski *et al* (1984). The only difference is in the gas purity which was 99.99% for O_2, the main contaminant being N_2. The error associated with the gas contamination was therefore smaller than in Szmytkowski *et al* (1984). The electron energy scale was determined within ± 50 meV against the well known resonant structure around 2.3 eV in N_2. The associated uncertainty in the cross section is less than 1% over the entire energy range.

A similar discussion of the systematic errors in the Trento apparatus was given by Dalba *et al* (1980b). The error in the pressure measurements for O_2 was higher than for the previous experiment. This difference was due to the fact that the capacitance manometer temperature was not tracking the gas chamber temperature. It is believed that, after correction for the thermal transpiration effect, a residual error of $\pm 1\%$ can be safely assumed. The energy scale was calibrated by referring to the known position of the low-energy O_2 resonances. The value given by Land and Raith (1974) was used for the position of the third peak in the O_2 cross section (360 ± 5 meV). Due to the relatively poor energy resolution of the Trento apparatus, the uncertainty in the energy scale can be assumed to be ± 20 meV. The associated uncertainty in the total cross section is less than 1% for energies below 1 eV, decreasing at higher energies.

The incomplete discrimination against electrons scattered at small angles in the forward direction due to finite angular resolution systematically lowers the measured total cross sections. Both apparatuses had nearly equal detector angular acceptances (approximately 3×10^{-3} sr). However, the Trento gas chamber had circular apertures 1 mm in diameter and the Gdańsk gas chamber had a rectangular exit slit of 0.35 mm $\times$ 3 mm. The effective angular acceptances (as defined by Lazzizera and Zecca (1983)) were 3.8×10^{-4} and 1.1×10^{-3} for the Gdańsk and Trento apparatuses respectively. A larger angular resolution error is therefore to be expected in the Trento measurements. The effect of the angular-resolution error on the measured total cross section was evaluated from the differential elastic cross section of Trajmar *et al* (1972) and Wakiya (1978a, b). The estimated error is less than 3% at 100 eV decreasing at lower energies.

The linear sum of all possible systematic errors (including the angular-resolution error) for the Gdańsk experiment was less than 6% at all energies. The random error (evaluated as the maximum deviation from the average) was always less than 2%.

The linear sum of all possible systematic errors for the Trento apparatus was 6.5% below 1 eV, decreasing to 5.5% above this limit, and increasing again to 7.5% at 100 eV. The random error was less than 4% for energies above 1 eV rising to 10% at 0.2 eV. Points below 0.2 eV reported in figures 1(*a*) and 2 are to be regarded as qualitative only because the apparatus transmission function severely distorts the measured cross section in this energy region.

4. Results and discussion

The O_2 cross sections measured in present experiments are shown in figures 1(*a*) and (*b*) for the energy ranges from 0.1 to 20 and from 1 to 200 eV respectively. The existing absolute experimental data of Ramsauer and Kollath (1930), Sunshine *et al* (1967) and those of Salop and Nakano (1970) are plotted on the same figure. A few lowest points of a previous measurement performed by Dalba *et al* (1980a) for intermediate

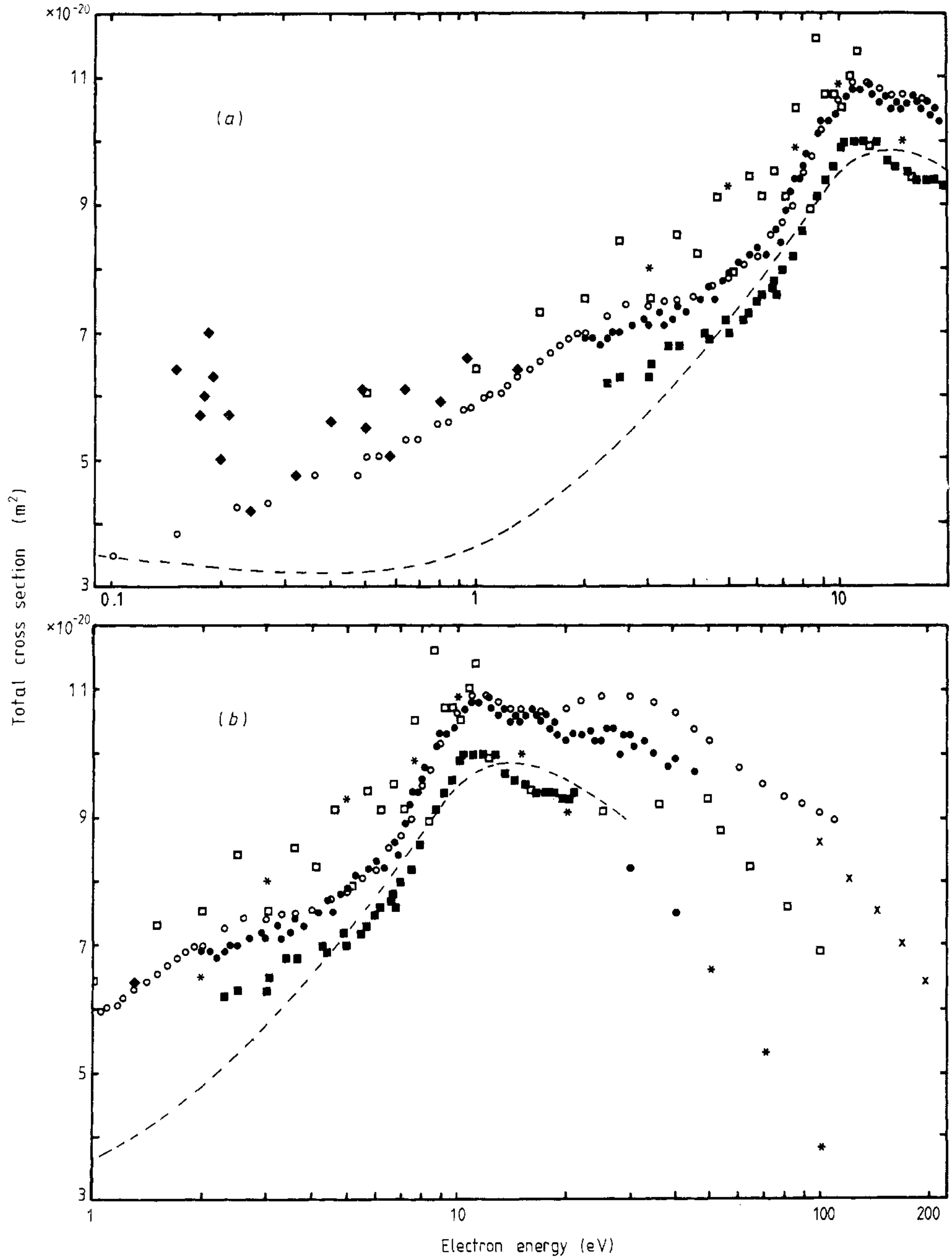

Figure 1. e^-–O_2 total cross sections from (*a*) 0.1 to 20 eV and (*b*) 1 to 200 eV. ●, present Gdańsk results; ○, present Trento results; □, Sunshine *et al* (1967); ■, Salop and Nakano (1970); ◆, Ramsauer and Kollath (1930); *, Shyn and Sharp (1982), elastic; - - -, Fisk (1936), elastic theory; ×, Dalba *et al* (1980a).

energies are also included. For comparison the theoretical elastic cross section calculations of Fisk (1936) and the recent elastic cross section measurements of Shyn and Sharp (1982) are presented as well. Table 1 gives the numerical data for the same authors in the energy range from 0.1 to 100 eV at selected energies. The data of Brüche (1927) given in table 1 were omitted in figure 1 for clarity. We now want to compare the results obtained in Gdańsk (full circles) and in Trento (open circles). The two sets of measurements are in excellent agreement from 4 to 17 eV, the Trento measurements being slightly higher from 2 to 4 eV and increasingly higher from 17 to 45 eV. The discrepancy is about 6% at 30–45 eV.

In § 2 it was stressed how the high pressure at the exit aperture of the scattering chamber can increase the effective interaction length. A constant error up to +5% over the whole energy range of the Trento data could be accounted for by this effect. No such regularity can be observed in the data and the increasing discrepancy at energies higher than 17 eV has to be explained by a different effect. The angular-resolution error does not play a role in this case: as a matter of fact from an angular-resolution error we could expect that the Trento measurements fall lower at higher energies. It is worth mentioning that 17 eV is one of the junction energies for the splicing of the Trento data. The 100 eV cross section of Dalba *et al* (1980b) seems to be more reliable than the present one because of the better accuracy of the Ramsauer-type apparatus at intermediate energies. There is a suspicion that most of the discrepancy can arise from instrumental effects in the Trento measurements. The O_2 cross section, as evidenced in this work, rises gradually from a value of 4×10^{-20} m^2 at 0.2 eV to a broad maximum which peaks at a value of about 11×10^{-20} m^2 close to 11 eV and then decreases very slowly with energy. The initial increase is mainly due to the rise in the elastic cross section which dominates in this energy interval with a broad maximum near 11 eV (Fisk 1936, Shyn and Sharp 1982). Measurements of Trajmar *et al* (1971, 1972) and Wakiya (1978a, b) indicate that the total contribution of inelastic processes (vibrational and electronic excitation) is about 1% of the total at 4 eV increasing to 7% at 10 eV. The partial cross sections for these processes have their maxima between 7 and 12 eV. Some contribution to the broad hump centred at 11 eV can be attributed to resonant scattering via the compound negative-ion state ($^4\Sigma_u^-\ O_2^-$). Evidences for such a process were observed in vibrational-excitation spectra by Wong *et al* (1973) and Tronc and Azria (1979) as a bell-shaped energy dependence with a broad peak near 10 eV. The relatively slow decrease in the total cross section above 12 eV is related to the ionisation process whose contribution (Rapp and Englander-Golden 1965) increases up to about 30% of the total at an electron energy of 100 eV. Contributions from elastic as well as other inelastic processes above 20 eV substantially decrease (Trajmar *et al* 1971, 1972, Wakiya 1978a, b, Shyn and Sharp 1982). A second broader hump seems to be visible from about 20 to 50 eV, but this could be instrumental as already discussed.

The comparison of our results with previous existing cross section measurements (figure 1) shows that the shapes are in reasonable agreement, except for the minimum found by Ramsauer and Kollath (1930) close to 0.25 eV. The existence of such a shallow minimum in the vicinity of 0.3 eV follows also from the calculations of Fisk (1936). As shown in figure 2, no such minimum was observed for energies down to 0.1 eV or below in the present measurement. A non-reproducible rise of the cross section was present in some of the Trento low-energy runs at energies below 0.05 eV. Such a rise can be an artefact introduced by the apparatus and therefore no assessment can be made on the existence of a minimum below 0.1 eV. We note here that the

Table 1. e^-–O_2 total cross sections. The data of Shyn and Sharp (1982) (SS) are elastic cross section measurements. The data of Fisk (1936) (F) are theoretical calculations for the elastic cross section. B, Brüche (1927); R, Ramsauer and Kollath (1930); SAB, Sunshine *et al* (1967); SN, Salop and Nakano (1970); TN, present Trento results; GD, present Gdańsk results.

	Total cross section (10^{-20} m^2)						Elastic cross section (10^{-20} m^2)	
eV	B	R	SAB	SN	TN	GD	SS	F
0.23		4.0, 4.4			4.27			3.2
0.36					4.75			3.2
0.49		6.1	6.0		4.95			
0.60		5.9, 6.2			5.21			3.2
0.84		5.9			5.59			3.4
0.95	4.3, 5.1	6.6	6.4		5.78			3.6
1.08	5.3, 5.5				6.00			
1.25	5.8	6.4			6.22			
1.45	5.8		7.3		6.47			4.1
1.65	5.2, 5.8				6.72			
1.85	6.3				6.92			
2.05	6.6		7.5		7.00	6.9	6.5	
3.00			7.5	6.3, 6.5	7.40	7.1	8.0	5.8
4.00	7.1		8.2		7.54	7.5		6.5
5.00			7.9	7.0	7.83	7.9	9.3	7.3
6.00				7.4, 7.6	8.17	8.3		7.8
7.00			9.1	8.0	8.70	8.4		
7.50	8.3			8.2	8.95	9.3		8.4
8.00	9.1		9.9	8.6	9.48	9.6		
8.50	8.8				9.73	9.8		
9.00	9.7				10.15	10.3		9.1
9.50	9.5				10.40	10.35		
10.00	9.2		10.7, 10.5		10.63	10.4	10.9	
11.00	9.6			10.0	10.91	10.8		9.7
12.00	9.8		9.9	10.0	10.90	10.9		9.8
13.00				9.8	10.80	10.6		9.8
14.00	9.3			9.6	10.70	10.5		9.8
15.00					10.70	10.5	10.0	9.8
16.50				9.4		10.6		9.7
17.50	9.1				10.65	10.6		9.7
20.00	9.1			9.3	10.70	10.2	9.1	9.6
25.00	8.9		9.1		10.90	10.2		9.3
30.00	9.1				10.90	10.3	8.2	
35.00			9.2		10.80	10.0		
40.00	8.5				10.60	9.9	7.5	
45.00	8.4				10.40	9.7		
50.00			9.3		10.20		6.6	
60.00					9.79			
70.00					9.52		5.3	
80.00			7.6		9.32			
90.00					9.21			
100.00			6.9		9.08		3.8	

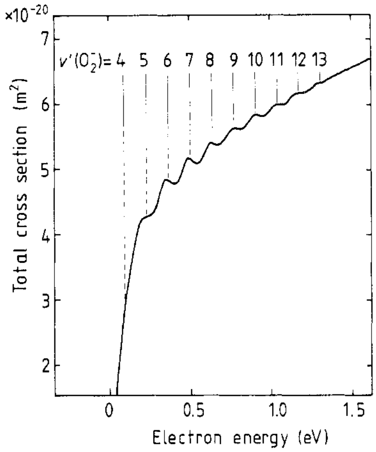

Figure 2. e^--O_2 total cross sections from 0 to 1 eV; the structure is associated with a $^2\Pi_g$ resonant state of O_2^-. The absolute values are not directly comparable with those of figure 1(*a*) (see text).

momentum transfer cross section measurements by Hake and Phelps (1967) do not support the existence of such a minimum down to 0.01 eV. We also note that a sharp rise or a sharp fall in the cross section is produced in most apparatuses if gas admission causes a change in the contact potential of the scattering chamber to the cathode. This change causes a shift of the entire transmission curve: a 10 meV shift could explain the rising shape of the Ramsauer and Kollath (1930) measurements at the lowest energies. Further work in this region ($E < 0.5$ eV) is required to clarify the behaviour of electron-molecule cross sections. Other hypotheses (air leak, water contamination, impurities) cannot account for this discrepancy. Some disagreement between the present and the previous data exists in the absolute values. Below 10 eV our results are 10-20% lower than those of Ramsauer and Kollath (1930) and Sunshine *et al* (1967) but are about 10-20% higher than those of Brüche (1927) and those of Salop and Nakano (1970). Above 11 eV our results are in general larger than those of other groups. In spite of these discrepancies, due to the fairly large errors in all the existing measurements, we can assess that all results fall within the range of combined errors from the results presented here.

We now want to discuss figure 2 which shows a typical run obtained with the Trento apparatus for the 0-1 eV range. This run was chosen because it was obtained with the best energy resolution ($E \simeq 65$ meV) and therefore the resonances are more clearly visible. The absolute values of the cross section in figure 2 do not correspond strictly to those of figure 1(*a*) because the values given in this last figure are average values of five independent runs of the type shown in figure 2.

The oscillatory structure in this energy region was first observed by Boness and Hasted (1966) in transmitted-current experiments and later studied in more detail by Spence and Schulz (1970) and Boness and Schulz (1970). The structure was explained in terms of vibrational excitation of the ground electronic state of O_2 via the $^2\Pi_g$ O_2^- resonant state. According to the investigation of Land and Raith (1974), the $v' = 4$, 5 and 6 peaks are split by spin-orbit coupling into $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ components, separated by 20 meV. Such fine structure was obscured in this experiment by the 65 meV FWHM of the electron beam. Figure 2 is the first presentation of the detailed absolute total cross section in this resonant region: previous evidence has been obtained for the vibrational excitation cross section. Peaks from $v' = 9$–13 have not been observed before.

The resonant structure observed by Sanche and Schulz (1972) from 8 to 13 eV was not observable in the total cross section: the resonances are very small compared with the non-resonant part of the cross section itself.

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Note added in proof. After this paper was submitted for publication, two new measurements of the O_2 total cross section in this energy range were reported. The values obtained by Kwan *et al* (1985) are generally higher than the present by about 10% from 5.2 to 60 eV. The agreement from 80 to 500 eV with the present data and with the previous measurements of the Trento group (Dalba *et al* 1980a) is much better (a few per cent). The measured cross sections of Katayama *et al* (1985) are consistently lower than the present measurements by about 10% over the entire energy range from 2 to 100 eV.

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