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Total and elastic electron scattering cross sections from ozone at intermediate and high energies

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Abstract

Total cross sections for electron scattering from O_3 molecules in the energy range 350–5000 eV have been measured for the first time. The experimental method used was based on the measurement of the attenuation of a collimated electron beam through an O_3–O_2 mixture in combination with use of an electron energy loss technique to determine the purity of the ozone sample. Differential and integral elastic cross sections have also been calculated using a scattering potential in the framework of the independent-atom model. The present theoretical and experimental results are compared with earlier calculations available in the literature.

1. Introduction

Energy deposition models for atmospheric and biological applications require cross-section data for secondary electron interactions over a wide energy range. In principle, data for all of the possible processes are needed for collision energies ranging from the high energy of the primary electrons to the low energies reached by those electrons slowed in successive collisions. In such processes total scattering cross sections play an important role since they determine the mean free path of the electrons through the scattering medium. Due to the importance of electron collisions in planetary atmospheres, total scattering cross sections have been measured to a high degree of accuracy for most *stable* atmospheric atoms and molecules. However few cross sections have been reported for unstable chemically reactive species (e.g. atomic oxygen and ozone) [1].

Ozone is a minor constituent of the Earth's atmosphere, but its presence in the stratosphere is crucial in controlling the UV intensity reaching the Earth's surface and hence any reduction

in global ozone levels can have dramatic consequences for the terrestrial ecosystem. The discovery of a significant loss in ozone concentrations over Antarctica (and more recently in Arctic regions), a phenomena popularly called the *ozone hole*, has led to an international scientific research programme to understand both the dynamics and chemical reactivity of the ozone in the atmosphere. Thus several research groups have recently studied the interaction of ozone with both electrons [2, 3] and photons [4]. However, due to difficulties producing and handling ozone in the laboratory, experimental data for electron scattering from ozone remain scarce especially for intermediate and high energies and therefore at present the importance of the interaction of primary (auroral) electrons with ozone in the upper atmosphere remains unquantified. In this work we have measured, for the first time, the total electron scattering cross section from ozone in the energy range 350–5000 eV. These results are compared with calculated differential and integral inelastic cross sections to ascertain the role of ionization and excitation of the ozone molecule in the auroral region.

2. Experimental method and procedure

2.1. Ozone production

Ozone is an inherently unstable and explosive gas and must be handled with care. Preparation of ozone samples used in the experiments was accomplished using the mobile ozone production apparatus designed and constructed at University College London. Ozone was prepared by passing oxygen through an electric discharge in a commercial ozonizer (Fischer Ozon 502). The product ozone (typically with concentrations of only a few per cent) was adsorbed onto silica gel cooled to 195 K. The excess oxygen was subsequently pumped away leaving pure ozone impregnated onto the cooled silica gel which could then be slowly warmed to room temperature and the desorbed ozone stored in a passivated glass bulb for subsequent transfer into the electron scattering apparatus. The ratio of O_3/O_2 could be monitored using the energy loss technique described below. Samples with an ozone purity of between 70 and 80% were routinely obtained.

2.2. Cross-section measurements

The experimental apparatus used in these transmission measurements has been described previously [5, 6] and will be only briefly reviewed in this paper. The primary electron beam, produced by an emitting filament, was collimated into a 1 mm diameter beam and deflected by a combination of electrostatic plates and a transverse magnetic field. Typical operating currents were between 10^{-9} to 10^{-10} A when recording energy loss spectra and between 10^{-13} to 10^{-14} A when performing attenuation measurements. Typical electron energy resolutions under these conditions were 500 meV. The collision chamber was defined by two apertures each of 1 mm diameter separated by a length of 100 mm. The transmitted electrons were energy analysed by an electrostatic hemispherical spectrometer combined with a retarding field. Under these conditions a constant energy resolution of about 0.8 eV was obtained over the whole energy range reported here. The acceptance angle of the analyser was of the order of 10^{-5} sr. Electrons were detected at the exit of the energy analyser by a two-stage microchannel plate operating in pulse counting mode. The collision chamber and the inlet gas line were constructed from stainless steel, PTFE and glass to avoid reactive processes with ozone. The gas pressure in the chamber was measured with an absolute capacitance manometer (MKS Baratron 127 A). The ultimate pressure in the region of the energy analyser and electron detector was of the order of 10^{-7} Torr.

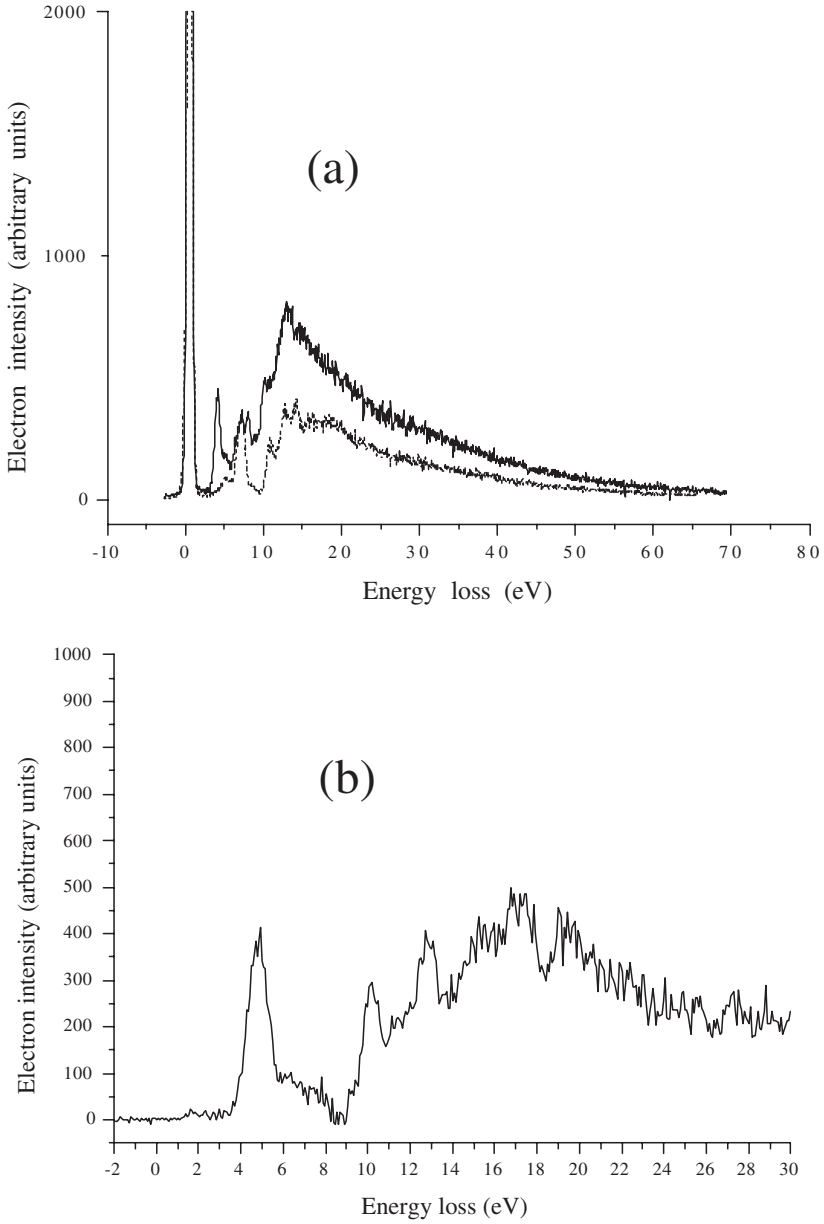

Figure 1. (*a*) Energy spectra of electrons scattered at 0° for 2500 eV incident energy: ——, with 20 mTorr of a O_3–O_2 mixture in the gas cell; – – –, for 20 mTorr of pure O_2. (*b*) Energy loss spectrum of O_3 obtained by subtracting the above spectra.

3. Results

3.1. Electron energy loss spectra

Typical energy loss spectra for electrons transmitted through the gas cell containing an O_3–O_2 admixture and pure O_2 are shown in figure 1(*a*). It can be seen that the Hartley band, centred at 4.9 eV (characteristic of ozone) and the Schumann–Runge band centred at 8.8 eV (characteristic of molecular oxygen) are able to be resolved by the electron analyser. By normalizing the

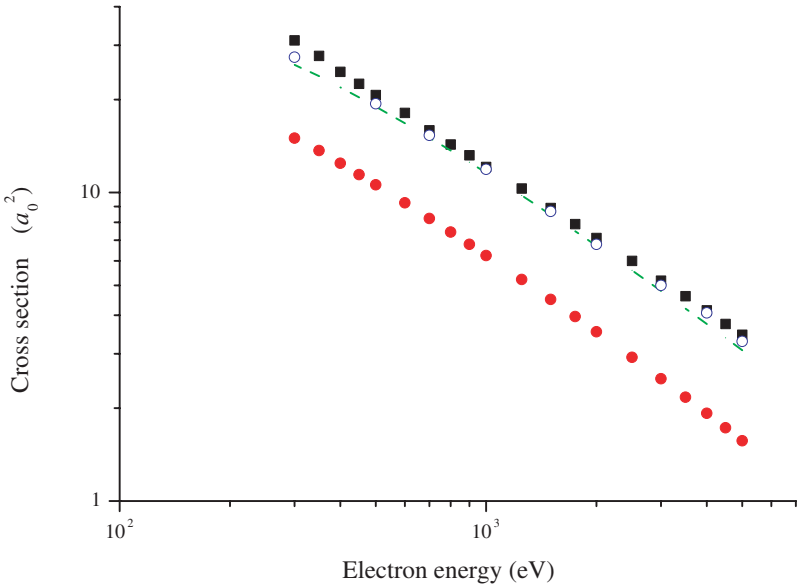

Figure 2. Integral cross sections for electron scattering by O_3. ■, present total cross section measurements; ○, total cross section calculated by Joshipura [14]; ●, elastic cross sections calculated in this study; – – –, results obtained by adding the ionization cross sections calculated by Kim *et al* [12] to the present elastic cross sections.

(This figure is in colour only in the electronic version)

magnitude of both spectra to the Schumann–Runge band intensity, the energy loss spectrum for ozone can be obtained by simple point-by-point subtraction (figure 1(*b*)). An energy loss spectrum recorded at high energies and zero degrees is essentially the same as a photoabsorption spectra, hence, using the known oscillator strength values for both the Hartley band and the Schumann–Runge [4,7] and measuring the corresponding line intensities in the energy loss spectra allows the proportion of ozone in the mixture to be determined. This methodology was used to monitor the O_3/O_2 ratio throughout the course of these measurements, the ratio was found to be constant during any data collection period and the ratio is believed to be accurate to within 6%.

3.2. Total scattering cross section measurements

The total cross section measurements were carried out by measuring the attenuation of the electron beam as the pressure in the gas cell was varied between 0 to 40 mTorr. Decay curves obtained in this way give the total cross section of the mixture ($\sigma_T(O_3\text{–}O_2)$) from the slope of a semilogarithmic plot of the transmitted intensity versus pressure. The total cross sections for electron scattering from ozone ($\sigma_T(O_3)$) were derived from the following equation:

$$\sigma_T(O_3) = \frac{1}{X(O_3)}[100\sigma_T(O_3\text{–}O_2) - X(O_2)\sigma_T(O_2)] \tag{1}$$

where $X(O_3)$ and $X(O_2)$ represent the concentrations, in per cent, of ozone and oxygen respectively, and $\sigma_T(O_2)$ are the corresponding total cross sections for electron scattering from oxygen which were measured in the same apparatus and reported in an earlier paper [6]. The experimental total scattering cross sections from ozone obtained by this procedure are shown in figure 2 and listed in table 1.

Table 1. Total cross sections for electron scattering by ozone in the energy range 350–5000 eV.

	Total cross section (a_0^2)	
Energy (eV)	This experiment	Theory (Joshipura [14])
300		27.4
350	27.7	
400	24.6	
450	22.5	
500	20.7	19.4
600	18.1	
700	15.9	15.3
800	14.3	
900	13.2	
1000	12.1	
1250	10.3	
1500	8.91	8.68
1750	7.90	
2000	7.12	6.79
2500	6.00	
3000	5.18	5.00
3500	4.61	
4000	4.15	4.07
4500	3.75	
5000	3.46	3.29

3.3. Error analysis

A detailed analysis of the systematic errors present in the experiment can be found in previous papers [5, 6]. These include pressure gradients in the gas cell, derivation of the actual path (absorption) length and the effect of the electrons being scattered in the forward direction. A Monte Carlo simulation of the electron transport through the gas cell has shown that the contribution of the electrons elastically scattered into the detection angle is lower than 1% and that multiscattering processes are negligible in this experiment [8]. The uncertainty in the pressure measurement was assumed to be lower than 1% (manufacturer data). It is then possible to derive an apparent cross section for the admixture of O_3–O_2. Each measurement was repeated at least five times to ensure that any statistical uncertainties were lower than 2%. Taking into account these partial errors we can estimate a total error of 3–4% in the total cross sections measured for the admixture of O_3–O_2. It is now necessary to derive the cross section for pure ozone. As described in section 2.1, the O_3/O_2 concentrations were continuously checked using measured energy loss spectra. By assuming that the oscillator strength uncertainties were about 2% for the Schumann–Runge band of oxygen [7] and less than 5% for that of the Hartley band of ozone [4], a total error of about 6% can be derived for the O_3/O_2 concentrations. By quadratic combination of the mentioned error sources the total error for the total cross sections from ozone presented in this work will be of the order of 7%. However, for comparison with theoretical results discussed later in this paper, a rounded error of 10% may be appropriate.

4. Discussion

Since there are no other experimental data with which to compare the present results and hence validate our cross section derivations, we have performed some simple scattering calculations.

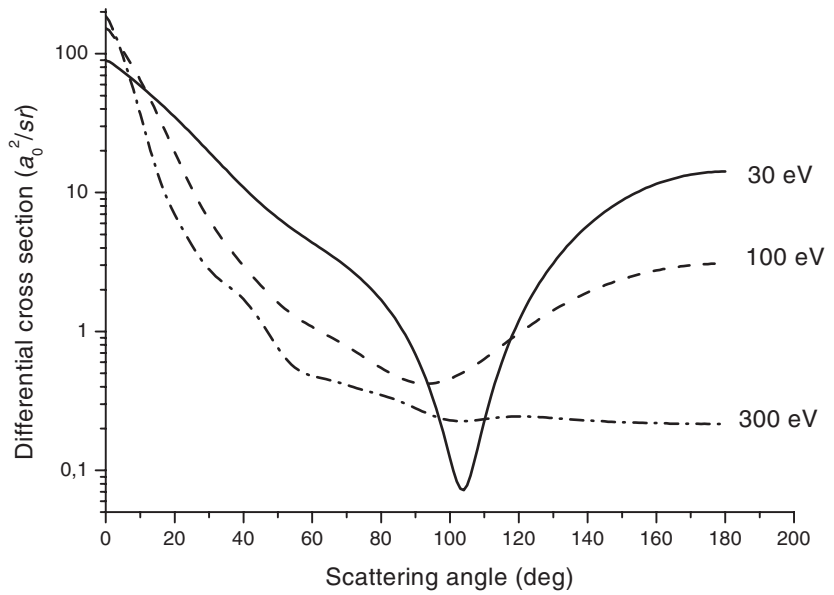

Figure 3. Differential cross sections for electron scattering by O_3 at 30, 100 and 300 eV.

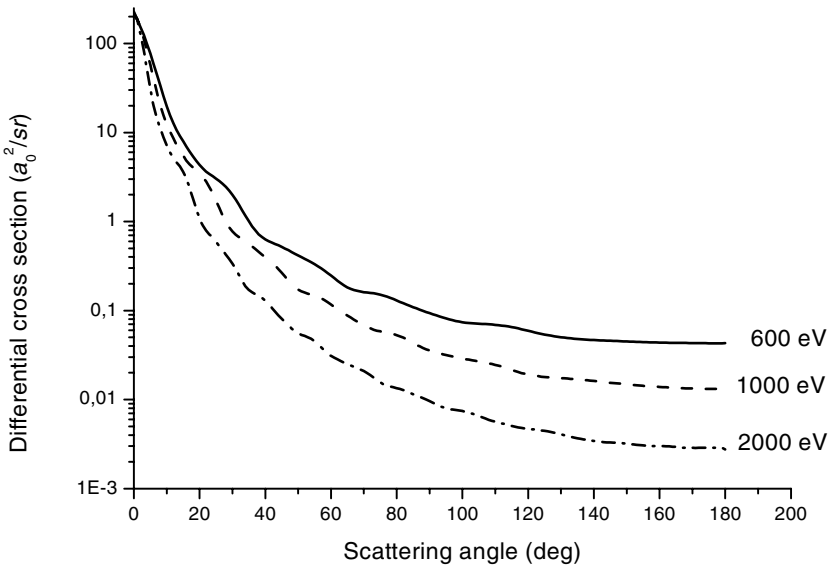

Figure 4. Differential cross sections for electron scattering by O_3 at 600, 1000 and 2000 eV.

The scattering potential method used in this work to calculate both differential and integral elastic cross sections has been described in previous papers [9, 10]. In this calculation we assume that the electron energy is high enough to validate the independent-atom model [11] and that constituent atoms can therefore be replaced by a scattering potential including static, exchange and polarization terms. Such an approximation has been shown to provide results at these energies in agreement with the experiments for other atomic (Ne, Ar, Kr) and molecular (N_2, CO, O_2) targets (see [6,9,10]). The differential cross sections obtained by this procedure

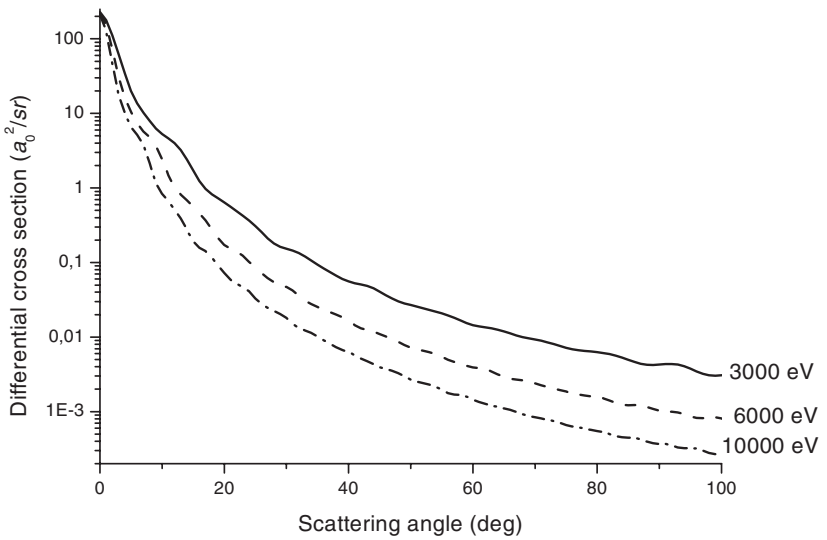

Figure 5. Differential cross sections for electron scattering by O_3 at 2000, 6000 and 10 000 eV.

for the electron scattering by O_3 in the energy range 30–10 000 eV are shown in table 2 and representative values are plotted in figures 3–5. The integral elastic cross sections deduced from these calculations are shown in figure 2. As this figure shows, these values are about half of the measured total cross section. This is to be expected since, at these high energies, inelastic scattering processes (dominated by ionization) provide a significant part of the total cross section.

Accurate ionization cross sections for O_3 have been calculated by Kim *et al* [12] using the binary-encounter Bethe model [13]. Cross section values obtained by adding the ionization cross section of Kim *et al* [12] with the integral elastic we have calculated should therefore be very close to the measured total cross sections. Results derived from this procedure are also shown in figure 2, excellent agreement is found suggesting that the present total scattering cross sections are indeed accurate.

Total electron scattering cross section calculations have also been carried out by Joshipura [14] using an optical potential method. Results of these calculations are shown in table 1 and figure 2. As can be seen, there is an excellent agreement between the present experimental data and the theoretical data of Joshipura [14].

Finally, in order to evaluate the importance of the relative cross sections in oxygen–ozone mixtures, it would be interesting to compare data for both molecules. In figure 6(*a*) the total cross sections for both oxygen and ozone are shown and in figure 6(*b*) the elastic differential cross section at 1 keV for both oxygen and ozone are presented. Due to the relative size of the molecules we might expect that the cross sections for ozone will be 50% higher than for oxygen. In fact the total cross sections for ozone are about 60% higher than those of oxygen for the considered energy range. This difference can be attributed to the higher molecular polarizability of ozone (21.7 a_0^3), compared to oxygen (10.7 a_0^3). In the differential elastic cross section, figure 6(*b*), for scattering angles above 60° the cross sections for ozone at 1 keV are about 50% higher than for oxygen, but at small angles, where interference terms are appreciable, this ratio oscillates between a minimum of 29% at 9° and a maximum of 125% at zero angle.

Table 2. Elastic cross sections for electron scattering by ozone in the energy range 30–10 000 eV.

Angle (deg)	Electron energy (eV)										
	30	60	100	200	300	600	1000	2000	3000	6000	10 000
0	89	132	152	173	186	207	218	227	228	220	212
1	87.8	129	147	164	172	185	190	186	178	153	128
2	84.8	122	136	146	150	153	149	129	111	72.7	45.3
3	81	114	125	130	131	125	112	83.4	62.4	31.2	17.7
4	77.4	107	115	115	112	99.1	81.9	51	34	16.2	10.1
5	74.1	100	105	101	95	77.2	57.9	30.9	20	10.5	6.56
6	71	93.6	96	88.3	79.9	59.1	40.5	20	13.7	7.39	5.15
7	67.8	87.1	87.5	76.5	66.5	44.8	28.4	14.3	10.2	5.7	3.75
8	64.7	81.1	79.4	65.9	55	33.8	20.5	11.1	7.89	4.79	2.13
9	61.6	75.4	71.7	56.5	45.1	25.6	15.6	8.83	6.26	3.69	1.16
10	58.8	69.8	64.6	48.1	36.8	19.7	12.4	7.15	5.29	2.44	0.838
11	56	64.6	58.1	40.9	30	15.6	10.3	5.94	4.64	1.48	0.667
12	53.4	59.6	51.9	34.5	24.5	12.7	8.64	5.15	4	1.01	0.512
13	50.7	54.9	46.4	29.1	20	10.7	7.35	4.62	3.23	0.816	0.389
14	48.2	50.5	41.3	24.5	16.6	9.16	6.29	4.15	2.41	0.684	0.274
15	45.8	46.3	36.6	20.7	13.9	7.95	5.47	3.62	1.72	0.561	0.192
16	43.5	42.4	32.4	17.5	11.8	6.96	4.83	3.01	1.24	0.455	0.157
17	41.3	38.7	28.6	14.9	10.1	6.11	4.38	2.38	0.969	0.367	0.142
18	39.1	35.3	25.3	12.8	8.84	5.4	4.04	1.81	0.823	0.282	0.116
19	37	32.1	22.3	11.1	7.81	4.81	3.75	1.37	0.728	0.212	0.091
20	35.1	29.2	19.6	9.69	6.97	4.33	3.47	1.07	0.642	0.172	0.0727
21	33.2	26.5	17.3	8.55	6.25	3.95	3.16	0.894	0.558	0.154	0.059
22	31.4	24.1	15.3	7.62	5.64	3.65	2.82	0.79	0.485	0.142	0.0516
23	29.6	21.8	13.5	6.83	5.09	3.42	2.44	0.718	0.423	0.123	0.0473
24	28	19.7	12	6.18	4.62	3.22	2.07	0.655	0.366	0.102	0.0411
25	26.4	17.9	10.7	5.61	4.19	3.04	1.72	0.592	0.31	0.0853	0.0329
26	24.9	16.2	9.55	5.11	3.82	2.85	1.42	0.53	0.256	0.0725	0.0277
27	23.5	14.7	8.58	4.67	3.5	2.66	1.18	0.475	0.211	0.0619	0.0247
28	22.1	13.3	7.75	4.28	3.22	2.45	0.993	0.425	0.18	0.0545	0.0224
29	20.8	12.1	7.02	3.92	2.99	2.22	0.862	0.38	0.163	0.0504	0.0204
30	19.6	11	6.39	3.6	2.8	1.99	0.772	0.336	0.153	0.0471	0.018
31	18.5	10	5.85	3.32	2.63	1.76	0.712	0.293	0.145	0.0422	0.0152
32	17.4	9.13	5.37	3.06	2.49	1.54	0.668	0.251	0.134	0.036	0.0131
35	14.6	7.07	4.24	2.46	2.18	1.01	0.561	0.17	0.0938	0.0254	0.0102
40	10.9	4.89	2.98	1.89	1.71	0.632	0.398	0.129	0.0557	0.0164	0.0063
45	8.34	3.6	2.15	1.57	1.18	0.519	0.266	0.0809	0.0409	0.011	0.0039
50	6.56	2.76	1.61	1.28	0.763	0.417	0.172	0.0555	0.0269	0.0071	0.0026
55	5.3	2.14	1.28	0.978	0.549	0.332	0.148	0.0453	0.0208	0.0053	0.0019
60	4.36	1.67	1.08	0.712	0.479	0.247	0.117	0.0309	0.0145	0.0039	0.0014
65	3.6	1.3	0.92	0.534	0.447	0.182	0.088	0.025	0.0119	0.0029	0.0011
70	2.92	0.995	0.782	0.451	0.412	0.161	0.0682	0.0209	0.0093	0.0019	0.0008
75	2.28	0.744	0.655	0.429	0.378	0.151	0.0585	0.0156	0.0072	0.0018	0.0006
80	1.69	0.526	0.547	0.429	0.349	0.13	0.0531	0.0135	0.0062	0.0015	0.0005
85	1.14	0.344	0.469	0.433	0.317	0.109	0.0433	0.0115	0.0049	0.0012	0.0004
90	0.683	0.218	0.427	0.435	0.28	0.0936	0.0354	0.0096	0.0042	0.0010	0.0003
95	0.333	0.174	0.423	0.44	0.248	0.0815	0.0317	0.0080	0.0037	0.0008	0.0003
100	0.122	0.235	0.456	0.45	0.229	0.0739	0.0289	0.0074	0.0030	0.0008	0.0002
110	0.227	0.704	0.636	0.468	0.234	0.0691	0.0245	0.0056	0.0024	0.0006	0.0002
120	1.19	1.55	0.969	0.467	0.244	0.0593	0.0191	0.0046	0.0019	0.0004	0.0001
130	3.1	2.58	1.42	0.463	0.238	0.0502	0.0174	0.0040	0.0016	0.0004	0.0001
150	8.79	4.64	2.38	0.513	0.222	0.0449	0.0148	0.0032	0.0011	0.0003	<0.0001
180	14.2	6.24	3.08	0.583	0.216	0.043	0.0132	0.0027	0.0002	<0.0001	
Integral	60.0	41.6	30.4	19.5	15.0	9.35	6.37	3.59	2.50	1.31	0.801

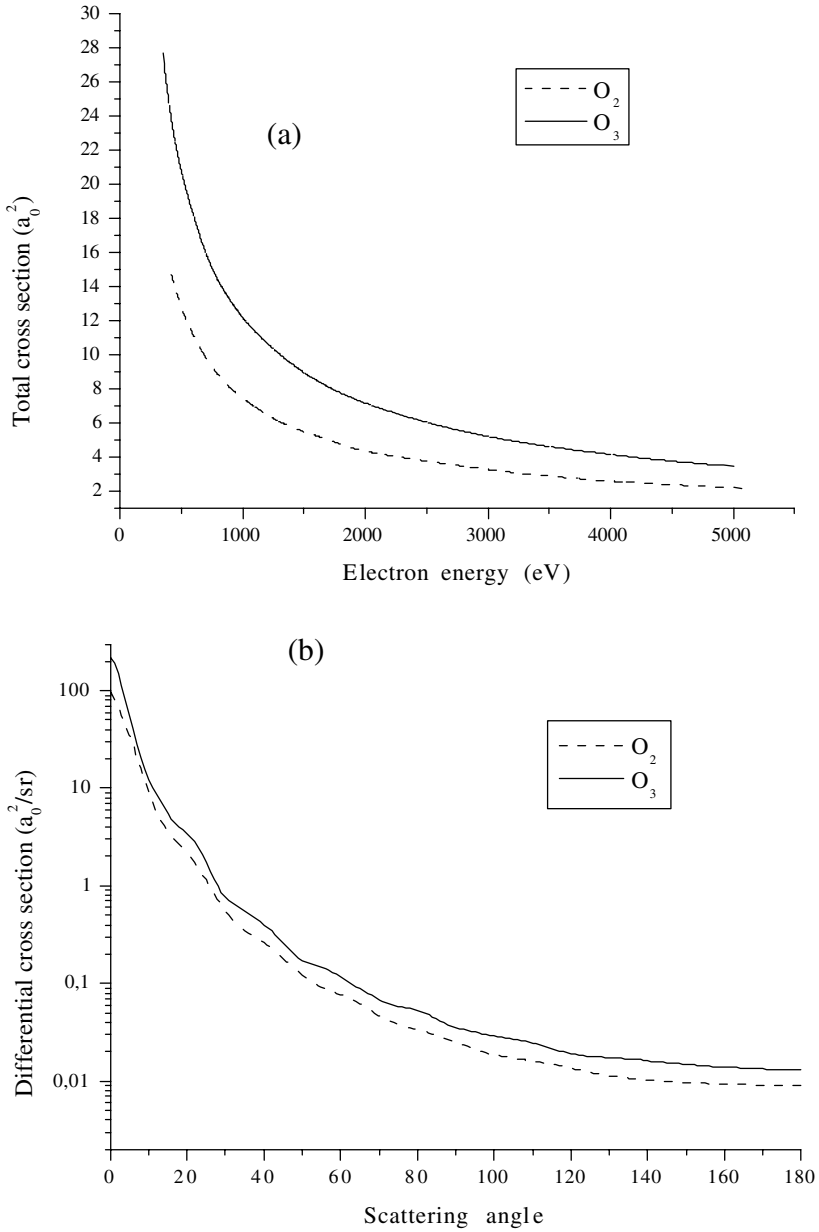

Figure 6. Comparison between the cross sections for ozone and oxygen. (*a*) Total cross sections for electron scattering from 300 to 5000 eV. (*b*) Differential elastic cross sections for 1000 eV electron energy.

5. Concluding remarks

The first measurements of the total cross sections for electron scattering by ozone in the energy range 350–5000 eV have been presented. These results are important in modelling the energy deposition in the upper atmosphere when the auroral electrons penetrate into the lower

ionosphere and mesosphere, for example during the impact of solar flares. The perturbation of the upper ozone column by solar induced electron precipitation may be analysed and net ozone loss derived. Such calculations may then allow the stability of ozone levels on other planetary systems to be evaluated.

Acknowledgments

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