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Cross Sections for Electron Collisions with Molecular and Atomic Oxygen **FREE**

Mi-Young Song ; Hyuck Cho; Grzegorz P. Karwasz ; Viatcheslav Kokoouline ; Jonathan Tennyson ; Klaus Bartschat 



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ABSTRACT

Electron collision cross section data are compiled from the literature for electron collisions with the oxygen molecule O₂ and the atom O. Cross sections are collected and reviewed for total scattering, elastic scattering, momentum transfer, rotational excitation, vibrational excitation, electronic excitation, dissociative processes, and ionization. The literature has been surveyed up to the end of 2024. For each of these processes, the recommended values of the cross sections are presented with an estimated uncertainty.

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1. Introduction

Earth, the blue planet as seen by Apollo astronauts, would not appear blue without oxygen in the atmosphere. In fact, James Lovelock, when asked by NASA in the 1970s if there were life on Mars, answered “No,” on the basis of the color of the atmosphere of the Red Planet. Oxygen in the Earth’s atmosphere is a “by-product,” which results from the first billion years of life.

Both atomic oxygen, O, and molecular oxygen, O₂, are open-shell species with triplet ground states: ³P and ³Σ_g⁻, respectively. This distinguishes molecular oxygen from other diatomic atmospheric molecules.

Peculiar features of the O₂ molecule include low thresholds for excitation to the singlet electronic states a¹Δ_g and b¹Σ_g⁺ at 0.98 and 1.63 eV, respectively, and also for the spin-allowed but symmetry-forbidden ³Σ_u⁺ state (the Herzberg system at 6.47 eV). Furthermore, a low threshold for the dissociation into neutrals (5.12 eV) makes both the O₂ molecule and the O atom the species that determine the radiation budget and the Earth’s atmospheric chemistry. The Sun’s spectrum predominantly contains wavelengths from 160 to 3000 nm (0.41–7.75 eV) with 97.9% irradiance falling in this range:¹ oxygen species, including ozone (O₃), contribute significantly to the harvesting of solar power flux. The human eye is sensitive to wavelengths longer than 380 nm, where there is an abrupt fall in absorption by O₃, see Ref. 2, and shorter than 760 nm, i.e., where the A-band of the O₂ molecule starts. Hence, oxygen defines the visible range of sunlight due to absorption in the Earth’s troposphere.³

One interesting application of the particular features of molecular oxygen is its use in the optical treatment of melanoma.⁴ Here, a pharmaceutical containing a photosensitizer, designed to accumulate in the tumor tissue, is supplied to the patient. Then, the tumor is illuminated with infrared (IR) light, causing electronic excitation of the O₂ molecule to a metastable singlet state. Singlet O₂ is

highly reactive and its creation leads to the internal burning of the tumor.^{5,6}

The cross section for oxygen molecules due to electron impact is an important parameter in plasma science and engineering, affecting the fundamental processes that govern plasma conditions. Ionization, dissociation, and excitation reactions contribute to the production of reactive oxygen species (ROS), particularly electrons, atoms, and ions, which directly affect the applications of plasma in various fields. Given the critical role that oxygen plasma plays in key technologies, including semiconductor etching, spacecraft propulsion, plasma medicine,⁷ and environmental applications,⁸ there is a need to improve our understanding of electron impact cross sections.

There have been a number of compilations of electron collision cross sections for oxygen. Itikawa and co-workers^{9,10} dedicated their review papers to total and partial cross sections of the O₂ molecule; Zecca, Karwasz, and Brusa,¹¹ Brunger and Buckman,¹² and Anzai *et al.*¹³ compared O₂ cross sections with some other molecules; the Landolt-Börnstein compilation gives recommended total,¹⁴ elastic,¹⁵ momentum transfer,¹⁶ and ionization¹⁷ cross sections. Itikawa and Ichimura¹⁸ reviewed total and partial cross sections for atomic oxygen, while Laher and Gilmore¹⁹ reviewed its ionization and electronic excitation cross sections.

The review by Itikawa¹⁰ remains a standard reference for modeling electron diffusion processes in oxygen.²⁰ However, since that review new, accurate measurements of O₂ total cross sections (TCS) at very low energies, where sharp resonant structures appear, have been made, and substantial progress has also been achieved in theoretical methods. The latter now enable calculations of not only elastic scattering, but also vibrational and electronic excitation cross sections, both for the molecule and the oxygen atom, including their metastable species.

The present review covers the bibliography up to the end of 2024.

2. O₂ Molecule

2.1. Total scattering cross section

TCS are usually measured by employing de Beer's attenuation method. This approach requires only the target gas pressure and the electron currents to be monitored. Hence, the potential accuracy of the measured TCS is high, about 5%–10%. Details of experimental techniques have been outlined in our previous review on electron collisions with methane.²¹ However, in the case of O₂ we find somewhat larger discrepancies between data from different laboratories (cf. Fig. 1) than was the case, for example, for CH₄; see Ref. 21.

At low energies, Salop and Nakano²² applied Ramsauer's method (i.e., a perpendicular magnetic field as the energy selector); Subramanian and Kumar²³ used a photoelectron source (UV photons produced from a microwave discharge in noble gases) and an electrostatic mirror energy analyzer. Measurements referred to as Zecca *et al.*²⁴ were obtained in two laboratories: in Trento with an "aperture" energy monochromator and retarding field analyzer and in Gdańsk with a cylindrical electrostatic monochromator. The energy resolution in both experiments was similar, about 70 meV. The "Gdańsk" apparatus was also used by Szmytkowski, Maciag, and Karwasz.²⁵ Kanik, Nickel, and Trajmar²⁶ measured the TCS in the energy range 5–300 eV using a linear transmission method. A rather long (144 mm) scattering cell assured good angular resolution; the declared systematic errors were within 2%.

The agreement with older experiments, like that by Salop and Nakano,²² is particularly poor in the few eV region. The main reason is, probably, the lack of adequate analyzers for the inelastically scattered electrons: this effect tends to underestimate the TCS. Also, Subramanian and Kumar's²³ cross sections are lower than the majority of other results in the region 2–5 eV. A similar discrepancy with results from that laboratory was observed for noble gases.²⁷ A probable reason is the complexity of the normalization

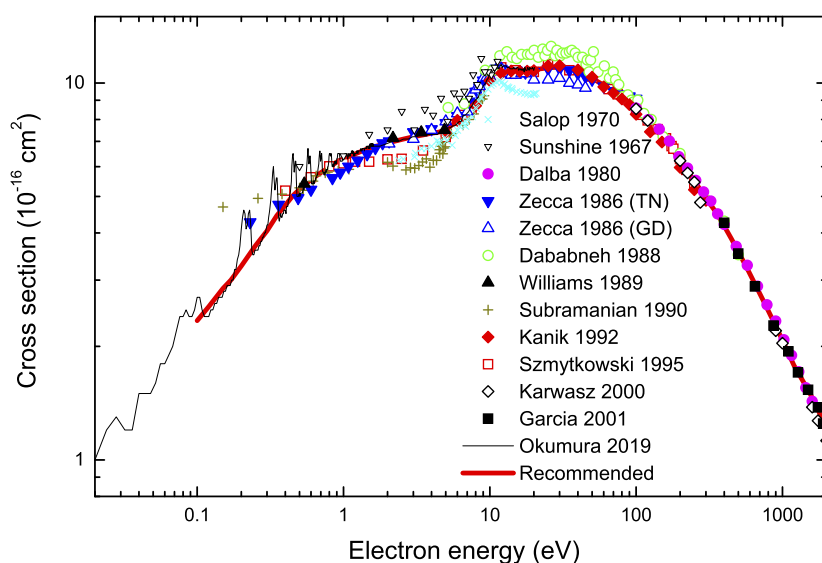


FIG. 1. Comparison of experimental TCS for electron scattering on O₂: black inverted triangles;²⁸ cyan x;²² pink circles: high-energy data from the Trento lab;²⁹ blue inverted triangles: low-energy data from the Trento lab;²⁴ blue open triangles: Gdańsk lab;²⁴ green open circles;³⁰ red diamonds;²⁶ red open squares;²⁵ black open diamonds: improved high-energy data from the Trento lab;¹⁴ black squares;³¹ thin black line.³² The thick red line represents our recommended values. For the TCS in the very-low energy range, see Fig. 2.

procedures required for the photoelectron source. Early data by Sunshine, Aubrey, and Bederson²⁸ were obtained using the molecular-beam recoil method and differ by about +10% from other experiments. Note that the recoil method was used predominantly for “exotic” (and highly polar) targets, like metal halides.¹⁴

The TCS by Dababneh *et al.*³⁰ were obtained using an apparatus designed for both positron and electron scattering, with a long scattering cell (109 cm) and a weak guiding magnetic field. Corrections were estimated for forward scattering. These data are somewhat higher than other sets in the energy range 10–100 eV. In the high-energy range, there are measurements from two laboratories, Trento University - earlier by Dalba *et al.*²⁹ and newer, with an improved angular resolution by Karwasz, Brusa, and Zecca,¹⁴ and from Madrid University by García, Blanco, and Williard;³¹ only the latter measurements³¹ were obtained using a retarding field analyzer and hence are more reliable.

The very-low-energy electron scattering on the O₂ molecule is characterized by the ²Π_g resonance, which is clearly visible as a vibrational-like structure in the TCS. We compare measurements in the 0–1.5 eV energy range in Fig. 2. Field and collaborators^{33,34} used synchrotron radiation as the source of photoelectrons and a longitudinal focusing magnetic field. The energy resolution of their apparatus was 3 meV. They reported, respectively, the signal of scattered electrons into the 60°–120° angular range³³ and the cross sections for the backward hemisphere (90°–180°) in the 10–175 meV range.³⁴ Extrapolating the scattering length from the backward scattering result, they obtained $0.34 \times 10^{-16} \text{ cm}^2$ for the TCS. The absolute TCS from the Canberra time-of-flight apparatus³⁵ and the Tokyo synchrotron-based measurements³² agree reasonably well, both in the magnitude and the positions of the resonant peaks.

The recommended TCS values are given in Table 1. In the very-low energy range (0.1–1 eV), they are based on the nonresonant

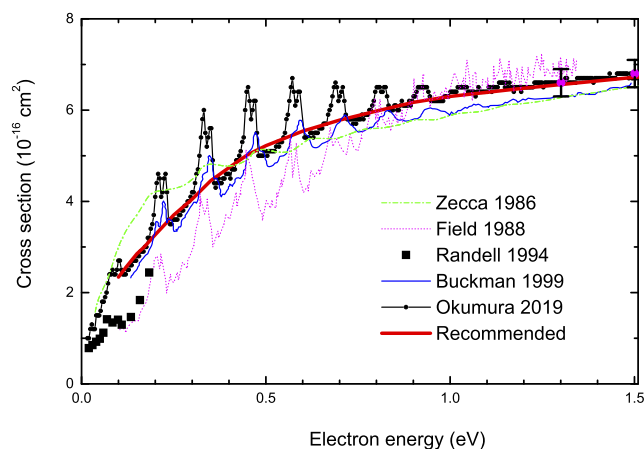


FIG. 2. Experimental TCS for electron scattering from O₂ in the very-low-energy range: green dash-dotted line: absolute TCS from the Trento lab;²⁴ magenta dotted-line: signal of scattered electrons into the 60°–120° angular range,³³ normalized to the present recommended TCS at 1 eV; black squares: backward scattering cross section;³⁴ blue line: absolute TCS from the Canberra lab;³⁵ black points and line: Tokyo absolute TCS.³² At 1.3 and 1.5 eV, we show the total error bars. The thick red line is our recommended TCS. Apart from the TCS of Okumura *et al.*,³² all other data are digitized from the figures in the papers.

TABLE 1. Recommended TCS for O₂. The uncertainty below 1.0 eV is about 10%, between 1 and 500 eV about 5%, and 7% above 500 eV

Electron energy (eV)	Total cross section (10 ⁻¹⁶ cm ²)	Electron energy (eV)	Total cross section (10 ⁻¹⁶ cm ²)
0.1	2.34	11	10.7
0.2	3.27	12	10.8
0.3	4.05	15	10.7
0.4	4.74	20	10.8
0.5	5.22	25	10.97
0.6	5.54	30	11.0
0.7	5.78	40	10.8
0.8	5.97	50	10.3
0.9	6.17	60	9.87
1.0	6.30	70	9.52
1.2	6.48	80	9.23
1.5	6.72	90	8.98
2.0	6.93	100	8.68
2.5	7.08	120	7.97
3.0	7.20	150	7.21
3.5	7.28	200	6.24
4.0	7.36	250	5.51
4.5	7.41	300	4.94
5.0	7.52	400	4.17
6.0	7.93	500	3.58
7.0	8.39	600	3.11
8.0	9.16	700	2.76
9.0	9.90	800	2.49
10.0	10.4	1000	2.08

background values from Okumura *et al.*,³² between 1 and 100 eV on the absolute TCSs of Refs. 24–26, above 100 eV on Refs. 26, 29, and 31. The uncertainty in the recommended TCS is 5%–10%. The detailed TCS in the very-low-energy range, from the experiment by Okumura *et al.*,³² is given in Table 2.

Somewhat surprisingly (as the two experimental methodologies are quite distinct), the presently recommended TCS (based on the most recent measurements) agree within 5% with the recommended integral elastic cross sections; see Table 4. The agreement is almost perfect up to 4 eV, i.e., at energies below where electronic excitations are significant.

2.2. Elastic scattering cross section

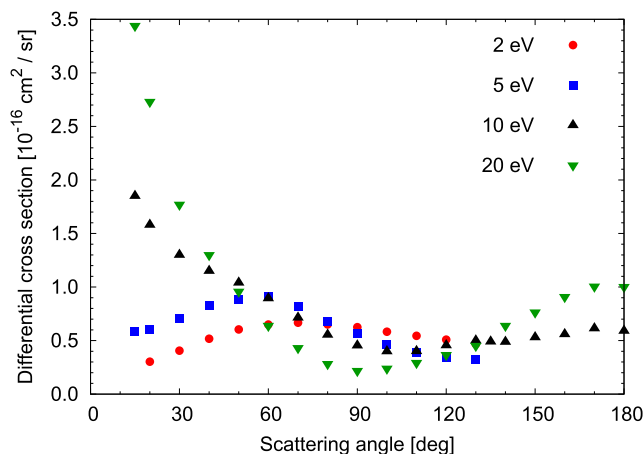
Experimental studies of the elastic angle-differential cross section (DCS) and the integral cross section (ICS) for electron scattering with molecular oxygen are much more abundant than for atomic oxygen. There have been many reports on measurements of the elastic DCSs and ICSs. Here we focus on those results that are important for our recommendations. Shyn and Sharp³⁶ performed experiments in the 2–200 eV energy range extending them to larger scattering angles than other researchers normally did. However, their cross sections generally proved to be a little larger than other measured cross section at energies around 10 eV and below for most molecules they studied, including molecular oxygen. Iga *et al.*³⁷

TABLE 2. Recommended TCS for O₂ in the very-low-energy range from the experiment by Okumura *et al.*³² The uncertainties are within $\pm 0.2 \times 10^{-16} \text{ cm}^2$

Electron energy (eV)	Total cross section (10^{-16} cm^2)	Electron energy (eV)	Total cross section (10^{-16} cm^2)
0.016	1.0	0.801	6.5
0.020	1.0	0.861	6.0
0.024	1.2	0.921	6.5
0.032	1.2	1.001	6.4
0.040	1.5	1.101	6.4
0.060	1.8	1.301	6.6
0.080	2.4	1.501	6.8
0.100	2.7	1.771	6.8
0.120	2.4	2.171	7.0
0.140	2.7	2.571	7.1
0.160	2.9	2.971	7.2
0.180	3.2	3.971	7.3
0.200	4.2	4.971	7.5
0.220	4.2	5.971	7.8
0.240	3.5	6.971	8.3
0.260	3.6	7.971	9.0
0.300	4.2	8.971	9.8
0.340	5.2	9.971	10.6
0.380	4.4	10.971	10.9
0.420	4.9	11.971	11.2
0.460	5.8	12.971	11.1
0.500	5.1	13.971	10.9
0.540	5.3	14.971	10.9
0.580	6.1	15.971	10.9
0.621	5.5	16.971	10.9
0.661	5.7	17.971	10.8
0.701	6.3	18.971	10.9
0.741	5.8	19.971	10.8

reported cross sections for 300–1000 eV, while Sullivan *et al.*³⁸ conducted their experiment at the lower energy range of 1–30 eV. Green *et al.*³⁹ repeated the same measurement at 5, 7, and 10 eV to confirm the results of Sullivan *et al.* Later, Linert, King, and Zubek⁴⁰ measured the cross sections near backward scattering angles using an angle-changing device for the energy region of 7–20 eV. For our recommended DCSs, we mostly rely on Sullivan *et al.*³⁸ combined with, if available, Linert, King, and Zubek⁴⁰ at backward angles. The DCS uncertainties vary between 7% and 10% depending on the electron energies and the angular ranges. The recommended DCSs are presented in Fig. 3 for four representative electron energies. The entire set of recommended DCSs is given in Table 3.

The elastic ICS are derived from the DCSs by integrating them over all scattering angles. For the forward and backward scattering angles, where experimental DCSs are generally not available, extrapolation techniques are used that will not be described here. There are several previous reviews on the elastic ICSs of electron scattering with molecular oxygen: Buckman, Brunger, and Elford¹⁵ recommended ICSs for the energy region of 1–100 eV using the DCSs from several groups, while Itikawa¹⁰ followed the recommendation of

**FIG. 3.** Recommended DCSs for O₂ for representative incident electron energies. The uncertainties vary between 7% and 10% depending on the electron energies and the angles.

Buckman, Brunger, and Elford¹⁵ with an extension to 100–1000 eV using the data of Kanik, Trajmar, and Nickel.⁴¹

For our recommendation, we compiled the previously reported elastic ICSs from the literature cited in the discussion of the elastic DCSs above. Since we recommend Sullivan *et al.*³⁸ and Linert,

TABLE 3. Recommended DCS of O₂ (in $10^{-16} \text{ cm}^2 \text{ sr}^{-1}$). The uncertainties vary between 7% and 10% depending on the electron energies and the angles

Angle (deg)	2.0 eV DCS	3.0 eV DCS	5.0 eV DCS	7 eV DCS	10 eV DCS	15 eV DCS	20 eV DCS	30 eV DCS
12						3.03		
15			0.585	0.877	1.85	2.76	3.44	5.08
20	0.303	0.418	0.603	0.836	1.58	2.29	2.73	3.84
30	0.406	0.552	0.706	0.853	1.30	1.71	1.77	2.02
40	0.517	0.644	0.824	0.910	1.15	1.38	1.30	1.11
50	0.604	0.728	0.886	0.931	1.04	1.11	0.958	0.654
60	0.650	0.770	0.914	0.881	0.894	0.844	0.639	0.420
70	0.667	0.743	0.815	0.780	0.714	0.599	0.431	0.270
80	0.651	0.685	0.677	0.620	0.554	0.423	0.282	0.184
90	0.625	0.605	0.565	0.500	0.453	0.333	0.218	0.137
100	0.583	0.536	0.464	0.421	0.399	0.298	0.239	0.130
110	0.544	0.470	0.391	0.371	0.401	0.304	0.293	0.166
120	0.509	0.424	0.343	0.369	0.455	0.409	0.367	0.257
130	0.468	0.386	0.323	0.401	0.500	0.468	0.452	
132								0.390
135				0.408	0.490			
140				0.433	0.487	0.588	0.639	
144								0.666
150				0.464	0.53	0.647	0.764	
160				0.473	0.559	0.727	0.908	
170				0.478	0.613	0.812	1.005	
180				0.474	0.590	0.819	1.002	

King, and Zubek⁴⁰ for the DCSs, we use them again for our recommended ICSs in the low energy (1–20 eV) range. The ICSs of Shyn and Sharp³⁶ are too high in the 2–10 eV energy range; however, from 40–200 eV, there are no ICSs reported except for those of Shyn and Sharp.³⁶ Their measurements are generally accepted as reliable in the energy region above 10 eV. Furthermore, at 20 and 30 eV, the measurements of Sullivan *et al.*³⁸ and Shyn and Sharp³⁶ match reasonably well. Therefore, we recommend Shyn and Sharp's ICS in the 40–200 eV energy region.

In the higher energy range, Shyn and Sharp's ICSs do not match smoothly with those of Iga *et al.*³⁷ who reported ICSs for 300–1000 eV. Daimon *et al.*⁴² also derived ICSs for 200–500 eV; these three ICS sets for the 200–1000 eV region come from different laboratories and show some disagreement with each other. Kanik and Trajmar⁴¹ combined the ICS/DCSs of Shyn and Sharp,³⁶ Iga *et al.*,³⁷ and Daimon *et al.*⁴² to derive the ICS in the high energy (200–1000 eV) region, and the result matches the ICSs of Shyn and Sharp at 200 eV.

In summary, we use Sullivan *et al.*³⁸ from 1 to 20 eV, Shyn and Sharp³⁶ for 20–200 eV, and Kanik and Trajmar⁴¹ with Iga *et al.*³⁷ for 200–1000 eV to form our recommendation of the elastic ICSs. The uncertainty of the ICSs below 10 eV is about 20%, and from around 10–1000 eV about 10%–15%. The recommended results are presented in Fig. 4 and Table 4.

2.3. Momentum transfer cross section

There have been several previous reviews on the elastic momentum transfer cross sections (MTCSS) of electron scattering with oxygen molecules. Elford, Buckman, and Brunger¹⁶ recommended MTCS in the low-energy range (<0.3 eV) based on the analysis of electron transport coefficient data provided by Yousfi (1987) through “personal communication.” See “87You1” in references for Sec. 6.3.5.6 of Ref. 16. At energies above 0.6 eV, Elford, Buckman, and Brunger¹⁶ preferred the cross section derived by Itikawa *et al.*⁹ from beam data. Later, Itikawa¹⁰ updated the recommended MTCS by modifying them with the DCSs of Linert, King, and Zubek,⁴⁰ but the contribution of the “personal communication” component, which originated from Elford, Buckman, and Brunger,¹⁶ was still retained in the low-energy range.

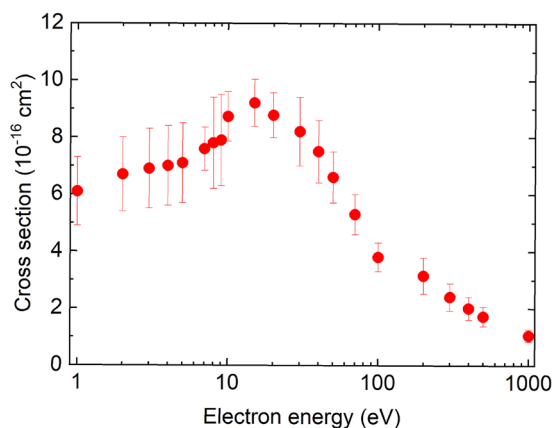


FIG. 4. Recommended elastic ICS for O₂.

TABLE 4. Recommended elastic ICS for O₂. The uncertainty below 10 eV is about 20%, and above 10 eV about 10%–15%

Electron energy (eV)	ICS (10 ⁻¹⁶ cm ²)
1	6.10
2	6.70
3	6.90
4	7.00
5	7.10
7	7.59
8	7.89
9	7.99
10	8.73
15	9.21
20	8.73
30	8.20
40	7.50
50	6.60
70	5.30
100	3.80
200	3.15
300	2.40
400	2.00
500	1.72
1000	1.05

Our policy in recommendation is that we compile and use only data published in peer-reviewed journals. Following this policy, the recommendation of Elford, Buckman, and Brunger¹⁶ based on a private communication is not acceptable. The MTCS values are derived in two ways: for energies above 1 eV, they are derived from integrated DCSs similar to the derivation of ICSs, while in the very-low-energy region (<1 eV), they are derived from swarm experiments. In the energy region from 1 to 200 eV, for the same reason as for the ICS case, we recommend the MTCS derived from Sullivan *et al.*,³⁸ Linert, King, and Zubek,⁴⁰ Shyn and Sharp.³⁶ For 300–1000 eV Iga *et al.*³⁷ reported MTCS values. Here Iga *et al.* and Shyn and Sharp match quite smoothly. Therefore, in the high-energy region, we recommend these DCS-derived MTCS. At low energies, a few swarm measurements have been reported. Itikawa showed some of them, for example by Hake and Phelps,⁴³ in his old review.⁴⁴ But the swarm data are quite scattered and not consistent. In 2003, Jeon⁴⁵ published extensive electron collision cross sections including the MTCSs for the oxygen molecule obtained from an electron swarm study, but they did not provide uncertainty estimates. We take these MTCSs for 0.001 eV up to 0.8 eV and, together with the beam data and recommend values for the MTCS from 0.001 to 1000 eV. The uncertainties of the MTCSs are about 20% from 1 to 10 eV and about 10%–15% from 10 to 1000 eV. The recommended results are presented in Fig. 5 and Table 5.

2.4. Rotational excitation cross section

In its ground electronic state X ³Σ_g⁻, the main isotopologue ¹⁶O₂ (as well as the ¹⁸O₂ isotopologue) can have only odd values of the nuclear rotation angular-momentum quantum number, *N*.

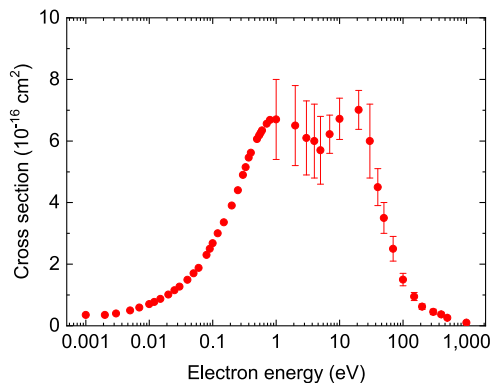


FIG. 5. Recommended elastic MTCS for O₂. The uncertainties from 1 to 10 eV are about 20%, and from 10 to 1000 eV about 10%–15%.

There are no experimental or accurate theoretical data available on rotational excitation of O₂. The previous reviews Itikawa,¹⁰ Tanaka *et al.*,⁴⁶ and Alves *et al.*⁴⁷ recommended using cross sections obtained with the Born approximation for electron impact rotational excitation from N to $N \pm 2$. Specifically,⁴⁸

TABLE 5. Recommended elastic MTCS for O₂. The uncertainties from 1 to 10 eV are about 20%, and from 10 to 1000 eV about 10%–15%. Below 1 eV, Jeon⁴⁵ did not provide uncertainties for their MTCS

Electron energy (eV)	MTCS (10 ⁻¹⁶ cm ²)	Electron energy (eV)	MTCS (10 ⁻¹⁶ cm ²)
0.001	0.35	0.50	6.06
0.002	0.35	0.54	6.18
0.003	0.40	0.57	6.26
0.005	0.50	0.60	6.34
0.007	0.59	0.71	6.56
0.010	0.70	0.80	6.68
0.012	0.77	1.0	6.70
0.015	0.87	2.0	6.50
0.020	1.01	3.0	6.10
0.025	1.15	4.0	6.00
0.030	1.27	5.0	5.70
0.040	1.49	7.0	6.22
0.050	1.70	10	6.72
0.060	1.88	20	7.01
0.008	2.30	30	6.00
0.090	2.50	40	4.50
0.10	2.68	50	3.50
0.12	3.00	70	2.50
0.15	3.36	100	1.50
0.20	3.90	150	0.95
0.25	4.40	200	0.62
0.30	4.90	300	0.45
0.33	5.15	400	0.37
0.37	5.46	500	0.26
0.40	5.62	1000	0.10

$$\sigma_{N' \leftarrow N}(E_{el}) = \frac{8\pi Q_v^2}{15a_0^2} c_{N',N}, \quad (1)$$

where a_0 is the Bohr radius. The coefficients $c_{N',N}$ are nonzero only for $N' = N \pm 2$, i.e.,

$$c_{N+2,N} = \frac{(N+1)(N+2)}{(2N+1)(2N+3)} \sqrt{1 - \frac{B_v(4N+6)}{E_{in}}},$$

$$c_{N-2,N} = \frac{N(N-1)}{(2N-1)(2N+1)} \sqrt{1 + \frac{B_v(4N-2)}{E_{in}}},$$

where B_v and Q_v are the rotational constant and the quadrupole moment of the vibrational level, respectively, and E_{el} is the energy of the incident electron. For the lowest vibrational levels of O₂ in its ground electronic state, one can use the experimental values $B_0 = 1.792 \times 10^{-4}$ eV and $Q_0 = -0.230 a_0^2$ obtained^{49,50} for the ground vibrational level $v = 0$ of O₂ ($X^3\Sigma_g^-$).

This approximation shows that the rotational excitation cross section is small compared to that of molecules with permanent dipole moments. However, detailed results should be used with caution because the approximation neglects the important fine-structure effects arising from the coupling of the electron spin with the rotational motion.⁵¹ Previous studies on electron impact rotational excitation suggested that short-range interactions dominate over long-range quadrupole effects for molecules without a permanent dipole moment.⁵²

2.5. Vibrational excitation cross section

Vibrational excitation of O₂ in its ground electronic state $X^3\Sigma_g^-$ is strongly influenced by the O₂ $^2\Pi_g$ resonant state,^{53,54} situated ~ 0.4 eV above the $X^3\Sigma_g^-$ state. The resonance appears also in the total and elastic cross sections at energies below 1 eV (see Figs. 1 and 2) with a clearly seen vibrational structure. The vibrational levels in that resonant state produce resonances in the e-O₂ spectra, spaced by ~ 0.1 eV. In low-resolution experiments (such as those by Shyn and Sweeney⁵⁵), one observes a single feature, the electronic resonance. Another resonance is situated around 10 eV above the ground state of O₂. It corresponds to several purely dissociative electronic resonances⁵⁶ of O₂⁻ and, therefore, does not have a fine vibrational structure at high resolution.

Cross sections for vibrational excitation have been measured since 1971 by Allan,⁵³ Linder and Schmidt,⁵⁷ Wong, Boness, and Schulz,⁵⁸ Noble *et al.*,⁵⁹ Brunger, Middleton, and Teubner,⁶⁰ and Linert and Zubek.⁶¹ There have been several theoretical studies for determining the cross sections, in particular by Laporta, Celiberto, and Tennyson,⁵⁴ Noble *et al.*,⁵⁹ Higgins *et al.*,⁶² and Alt and Houfek.⁶³

In the previous review by Itikawa¹⁰ (the same data were recommended in a later review⁴⁶), for energies below 1 eV, i.e., in the region where the $^2\Pi_g$ resonance influences the vibrational excitation process, cross sections derived from the measurements by Allan⁵³ were recommended, while the recommended cross sections at higher energies were based on the results by Shyn and Sweeney,⁵⁵ except for the $v = 0 \rightarrow v' = 1$ transition at 10 eV, for which the cross section by Linert and Zubek⁶¹ was recommended.

Since the two last reviews,^{10,46} two theoretical studies were published. Laporta, Celiberto, and Tennyson⁵⁴ used an R-matrix

approach to find energies and widths of electronic resonances as a function of internuclear separation, and the vibrational motion was accounted for in the excitation process using the boomerang model. Cross sections for vibrational excitation transitions between all 42 vibrational levels of O₂ were computed. Later, Alt and Houfek⁶³ used the UK molecular R-matrix code⁶⁴ and a nonlocal resonance model for vibrational motion in the theory of electron-molecule scattering, accounting for the spin-orbit coupling. They presented computed cross sections for seven transitions $v = 0 \rightarrow v' = 1 - 7$.

The results of the two recent theoretical studies agree well for the energies of vibrational resonances, but the cross sections for certain transitions differ by as much as a factor of 4. The nonlocal resonance model, employed by Alt and Houfek,⁶³ is known to be very sensitive—more than the boomerang model of Ref. 54—to accurate energies of the electronic resonances. The results by Laporta, Celiberto, and Tennyson⁵⁴ agree better with the measurements.^{53,59} Therefore, we recommend the theoretical data of Ref. 54, apart from the non-resonance part (1–8 eV and above 12 eV) of the 0–1 transition where the experiment data by Noble *et al.*⁵⁹ are more appropriate. The uncertainty of the calculations⁵⁴ was not discussed by the authors, so it is reasonable to use the experimental uncertainty⁵⁹ (20% or less).

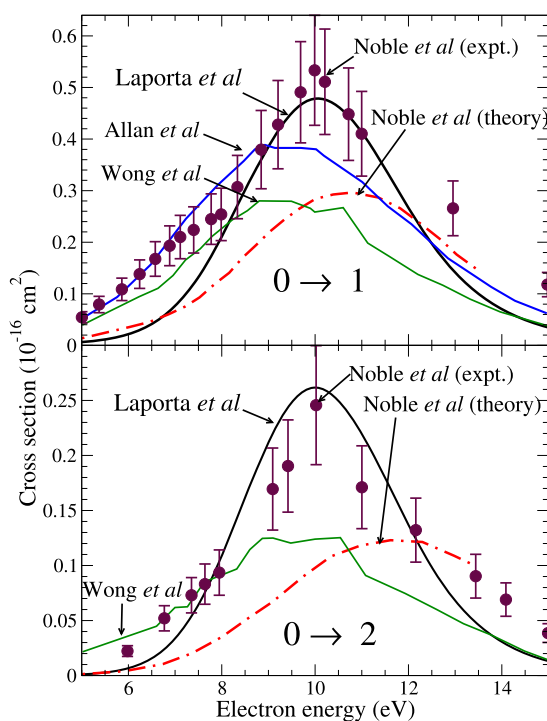


FIG. 6. Comparison of available data on vibrational excitation of O₂ starting from the ground vibrational level to $v = 1$ and 2. The figure shows data from three experimental studies by Noble *et al.*,⁵⁹ Wong, Boness, and Schulz,⁵⁸ and Allan,⁵³ and from calculations by Noble *et al.*⁵⁹ and Laporta, Celiberto, and Tennyson.⁵⁴ The data from Ref. 54 are recommended, except the non-resonance part (1–8 eV and above 12 eV) of the 0–1 transition, where the experiment data by Noble *et al.*⁵⁹ are recommended.

Figure 6 compares the $v = 0 \rightarrow v' = 1$ and 2 cross sections⁵³ recommended in the previous review¹⁰ with the cross section by Laporta, Celiberto, and Tennyson⁵⁴ (recommended in this review) and those of a few other studies. Figure 7 gives a few examples of the recommended cross sections in the lower-energy region of the ²Π_g resonance. The complete data for the recommended cross sections are available in numerical form as supplementary material of the original study.⁵⁴

2.6. Electronic excitation cross section

A particularity of molecular oxygen, compared to other atmospheric gases like N₂, NO, CO₂ or H₂O, is the presence of two low-lying metastable electronic states, a¹Δ_g and b¹Σ_g⁺, with low excitation thresholds of 0.98 and 1.63 eV, respectively. Two O₂ bands lie on the red edge of the visible spectrum; these bands are used for remote sensing of Earth's atmosphere: the A-band centered at 762 nm, arising from the b¹Σ_g⁺ ($v = 0$) → X³Σ_g⁻ ($v = 0$) transition,⁶⁵ and the B-band, 15 times weaker, centered around 690 nm and arising from the b¹Σ_g⁺ ($v = 1$) → X³Σ_g⁻ ($v = 0$) transition.⁶⁶ As already mentioned, the IR part of the absorption spectrum, related to the excitation of the a¹Δ_g state, is used in the photodynamic treatment of melanoma.^{5,6}

Higher in energy, as seen in forward-angle electron scattering spectra^{67–69} (that are directly related to the photoabsorption), the so-called Herzberg's pseudo-continuum, resulting from excitation to the overlapping c¹Σ_u⁻, A'³Δ_u and A³Σ_u⁺ states, extends between

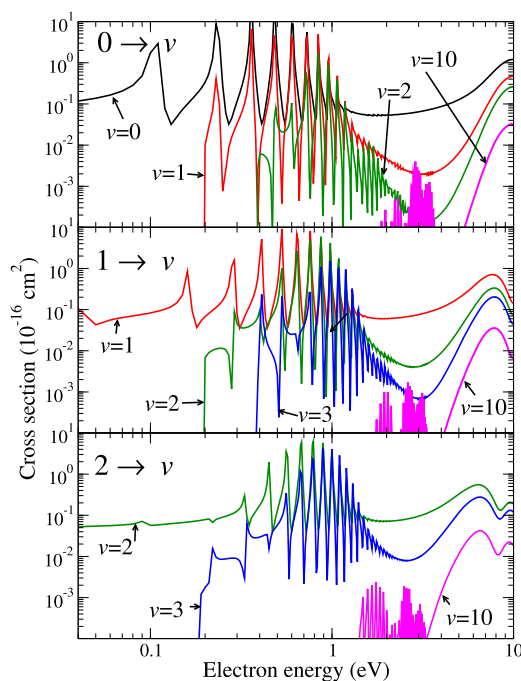


FIG. 7. Examples of recommended cross sections for vibrational excitation for several transitions obtained by Laporta, Celiberto, and Tennyson.⁵⁴ The upper panel shows transitions from $v = 0$ to 0, 1, 2, and 10. The middle panel gives the transitions from $v = 1$ to 1, 2, 3, and 10, and the lower panel from $v = 2$ to 2, 3, and 10.

about 5 and 7 eV. Excitations to these states influence production of the O^- ion via dissociative electron attachment (DEA)⁷⁰ and the production of stratospheric ozone;⁷¹ the de-excitation processes produce the equatorial night-glow.⁷² Next, a much stronger structureless band in the forward-scattering electron spectra^{68,73} extends from 7 to 9.5 eV and corresponds to the excitation to the $b^3\Sigma_u^-$ state (the Schumann–Runge continuum in optical spectra). Finally, still below the ionization threshold, two sharp peaks due to excitation to $E^3\Sigma_u^-$ in $v' = 0$ and $v' = 1$ vibrational states are visible in energy-loss electron spectra^{68,73} at 10.0 and 10.3 eV, respectively. Detectable⁷⁴ in night-glows are also transitions between excited states, like $c^1\Sigma_u^- \rightarrow b^1\Sigma_g^+$.

In the reviews by Itikawa¹⁰ and Brunger and Buckman,¹² as well as in a later review by Tanaka *et al.*,⁴⁶ recommended cross sections for electronic excitations were derived from experimental data. For excitation of the $a^1\Delta_g$ and $b^1\Sigma_g^+$ states from the ground state $X^3\Sigma_g^-$, the experimental data by Shyn and Sweeney⁷⁵ were recommended. The excitation energies of the $c^1\Sigma_u^-$, $A'^3\Delta_u$ and $A^3\Sigma_u^+$ states are close to each other (6.12, 6.27, and 6.47 eV, respectively⁷⁶), so that it is difficult to separate contributions of individual states into measured results in energy-loss experiments. Thus, in the previous review, Itikawa¹⁰ recommended only their sum. For excitation of the $^3\Sigma_u^-$ state and some higher electronic states, even though some experimental data are available,^{75,77} Itikawa¹⁰ did not recommend the data due to the large uncertainty. Therefore, the data recommended in the previous reviews^{9,10,46} based on the experimental results are very limited, except for the $a^1\Delta_g$ and $b^1\Sigma_g^+$ states.

At present, first-principle calculations are an alternative to experiment in similar situations. There have been several theoretical studies on electronic excitation of O_2 by electron impact. Teillet-Billy, Malegat, and Gauyacq⁷⁶ used a multichannel effective range theory to model e- O_2 excitation. Machado *et al.*⁷⁸ employed the Schwinger variational iterative method and the distorted-wave approximation in their calculations. Furthermore, Noble and Burke,⁵⁶ Middleton *et al.*,⁷⁹ Tashiro, Morokuma, and Tennyson,⁸⁰ Singh and Baluja,⁸¹ Huang, Zhang, and Cheng⁸² used versions of the UK molecular R-matrix code^{64,83,84} to compute cross sections for excitation and de-excitation of O_2 electronic states for a large number of transitions.

All the cited theoretical calculations were performed for a fixed internuclear distance, close to the equilibrium of O_2 , situated near $2.287 a_0$. A more accurate theoretical approach would have to account for the vibrational motion of the molecule. This will generally flatten the peaks seen in the fixed nuclei calculations. However, given that experimental results are scarce and, for higher excited states, have very large or unspecified uncertainties, the theoretical data can be recommended for electronic excitation of O_2 .

In this review, we recommend theoretical cross sections obtained in the latest R-matrix study.⁸² In the earlier study by Tashiro, Morokuma, and Tennyson,⁸⁰ very similar parameters as in the R-matrix approach were used. Hence the results of Refs. 80 and 82 are close to each other. In particular, optimized orbitals were employed in both studies, in contrast, for example, to another relatively recent study by Singh and Baluja,⁸¹ in which Hartree–Fock orbitals were employed. The use of optimized orbitals produced more accurate excitation energies in Refs. 80 and 82. Consequently, we expect the excitation cross sections to also be more accurate.

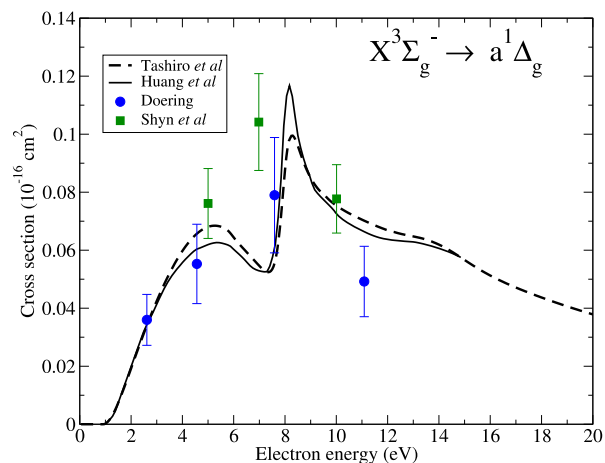


FIG. 8. Electronic excitation cross section for the $X^3\Sigma_g^- \rightarrow a^1\Delta_g$ transition. Solid line: Huang, Zhang, and Cheng⁸² (recommended); dashed line: Tashiro, Morokuma, and Tennyson;⁸⁰ circles: experiment by Doering;⁸⁵ squares: experiment by Shyn and Sweeney.⁷⁵

Figure 8 compares the recent theoretical results^{80,82} and the available experimental data for the $X^3\Sigma_g^- \rightarrow a^1\Delta_g$ transition. The solid line represents the calculations by Huang, Zhang, and Cheng⁸² (recommended), the dashed line the calculations by Tashiro, Morokuma, and Tennyson,⁸⁰ the circles the experiment by Doering,⁸⁵ and the squares the experiment by Shyn and Sweeney.⁷⁵ The previous review¹⁰ recommended the latter experimental cross section.⁷⁵

Figure 9 depicts the recent theoretical predictions^{80,82} and the experimental⁷⁵ data for the $X^3\Sigma_g^- \rightarrow b^1\Sigma_g^+$ transition. For this transition, the previous review¹⁰ also recommended the experimental cross sections.⁷⁵

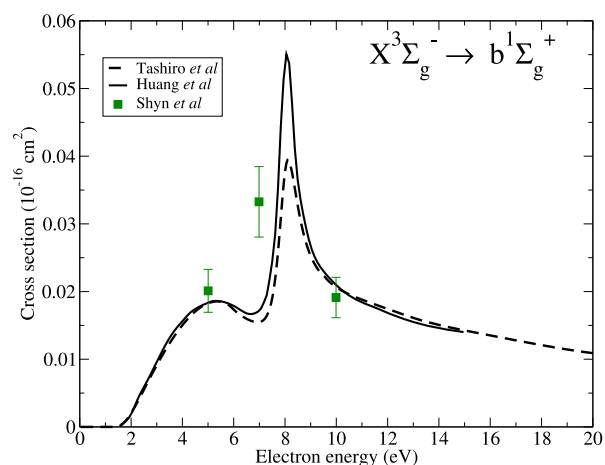


FIG. 9. Similar to Fig. 8 for the $X^3\Sigma_g^- \rightarrow b^1\Sigma_g^+$ transition. Solid line: Huang, Zhang, and Cheng⁸² (recommended); dashed line: Tashiro, Morokuma, and Tennyson;⁸⁰ squares: Shyn and Sweeney.⁷⁵

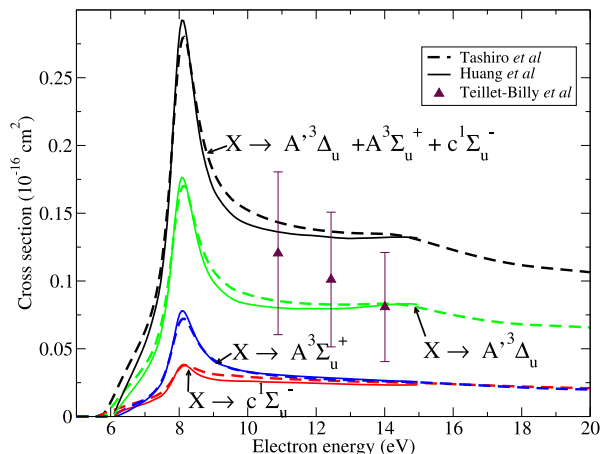


FIG. 10. Electronic excitation cross section for the $X^3\Sigma_g^- \rightarrow c^1\Sigma_u^-$ (red lines), $X^3\Sigma_g^- \rightarrow A^3\Sigma_u^+$ (blue lines), and $X^3\Sigma_g^- \rightarrow A'^3\Delta_u$ (green lines) transitions. Solid lines: Huang, Zhang, and Cheng⁸² (recommended); dashed lines: Tashiro, Morokuma, and Tennyson.⁸⁰ Upper black curves are the sum of the three excitation cross sections while the triangles with uncertainties are measurements of this sum by Teillet-Billy *et al.*⁸⁶

In Fig. 10, theoretical cross sections^{80,82} for excitation of the $c^1\Sigma_u^-$, $A^3\Sigma_u^+$, and $A'^3\Delta_u$ states are shown. The black lines represent sums of the cross sections for the three transitions. The symbols in the figure are the experimental data,⁸⁶ which also represent the sum of the three contributions.

Figure 11 shows cross sections for transitions starting from the $a^1\Delta_g$ state, including the elastic process. In addition to the theoretical predictions, experimental data points⁸⁷ are shown for the $a^1\Delta_g \rightarrow b^1\Sigma_g^+$ and $a^1\Delta_g \rightarrow X^3\Sigma_g^-$ transitions. Figure 12 presents the

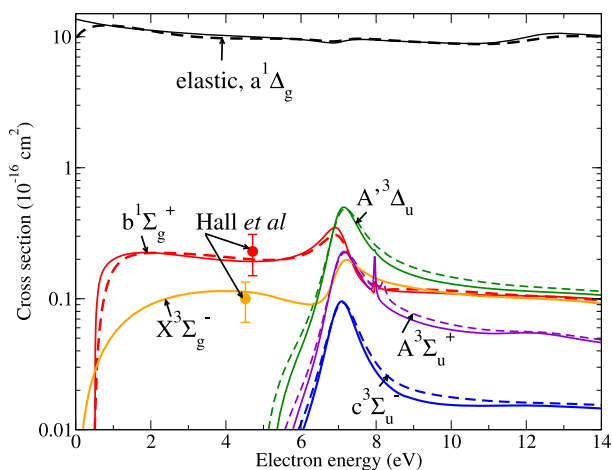


FIG. 11. Cross sections for elastic and inelastic transitions starting from the metastable $a^1\Delta_g$ state. Solid lines: Huang, Zhang, and Cheng⁸² (recommended); dashed lines: Tashiro, Morokuma, and Tennyson.⁸⁰ Red and orange circles are the experimental data⁸⁷ for the $a^1\Delta_g \rightarrow b^1\Sigma_g^+$ and $a^1\Delta_g \rightarrow X^3\Sigma_g^-$ transitions, respectively.

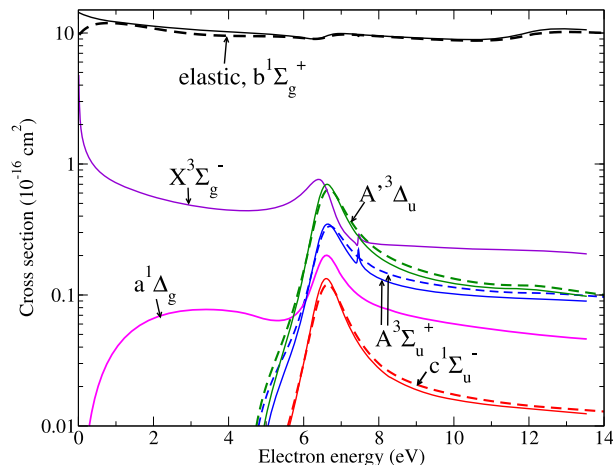


FIG. 12. Similar to Fig. 11 for the elastic and inelastic transitions starting from the metastable $b^1\Sigma_g^+$ state. The cross sections are taken from Ref. 80.

cross sections⁸⁰ for the elastic and inelastic transitions starting from the $b^1\Sigma_g^+$ state.

2.7. Neutral dissociation cross section

Photodissociation of the O_2 molecule in Earth's stratosphere is the key process for the formation of ozone. The oxygen molecule is characterized by a low dissociation energy (5.12 eV, see recent photodissociation studies⁸⁸), as compared, for example, to N_2 (9.79 eV). O_2 is also an example of an interdependence of the electronic excitation and the dissociation of the molecule: all electric dipole allowed transitions lie above the first dissociation limit and appear to dissociate.⁸⁹

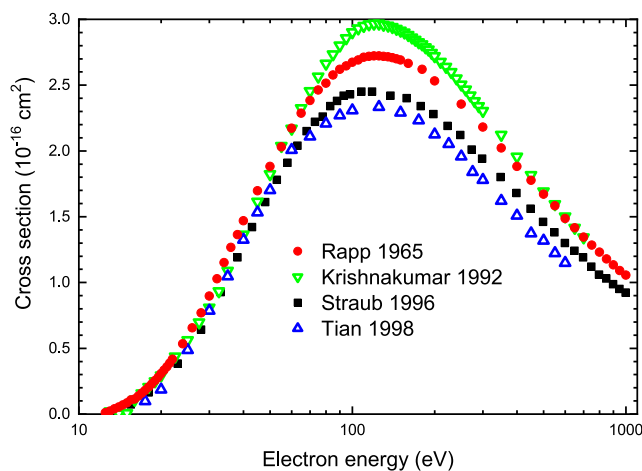


FIG. 14. TCS for electron impact ionization of the O_2 molecule. Solid (red) circles are the gross total (i.e., the overall current of ions) ionization cross section from Ref. 94; (green) open triangles are the counting (i.e., the sum of partial) ionization cross sections from Krishnakumar and Srivastava.⁹⁶ The (blue) open triangles are from Ref. 97. The (black) solid squares are the counting cross sections from Straub *et al.*⁹⁸ renormalized by Lindsay and Mangan.¹⁷

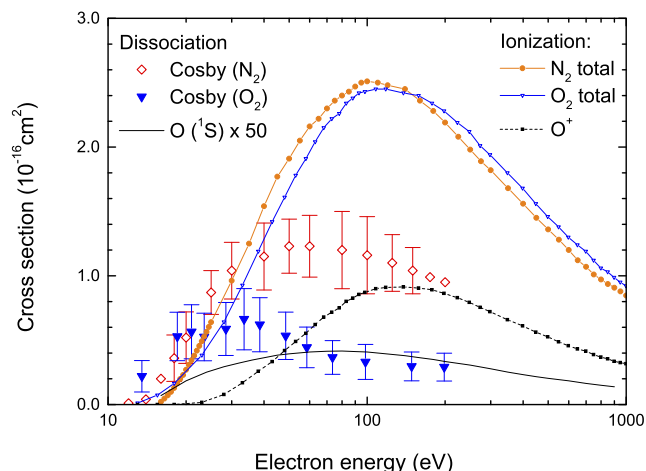


FIG. 13. Experimental TCS for dissociation of O_2 into neutral atoms. Absolute cross sections for the total dissociation for O_2 and N_2 are by Cosby,^{89,90} while data for the production of the metastable $O(^1S)$ atom are by LeClair and McConkey.⁹² In comparison, the total ionization cross section in O_2 and N_2 is taken from the review by Lindsay and Mangan.¹⁷

Absolute cross sections for electron-impact dissociation into two neutral O atoms have been determined by Cosby.⁸⁹ He used a position-sensitive detector, allowing him to observe correlation between the dissociated fragments (but not allowing him to discriminate between their particular electronic state). Cosby⁸⁹ deduced that there are two (overall) dissociation channels: production of $O(^1D) + O(^3P)$ fragments from electronically excited $b^3\Sigma_u^-$, $B'^3\Sigma_u^-$ and $2^3\Pi_u$ states of O_2 , and production of $O(^3P) + O(^3P)$ fragments from electronically excited $c^1\Sigma_u^-$, $A'^3\Delta_u$ and $A^3\Sigma_u^+$ states. The maximum cross section for total dissociation into neutrals amounts to $0.66 \times 10^{-16} \text{ cm}^2$ at about 35 eV; the cross section for the production of the neutral fragment with a kinetic energy $> 2.7 \text{ eV}$ is ten times smaller at that energy.

Figure 13 compares the TCS for the dissociation into neutrals in O_2 by Cosby⁸⁹ with those in N_2 by the same author.⁹⁰ The total dissociation cross section for O_2 has a maximum of less than half of that for N_2 , even though the ionization cross sections are almost identical for the two molecules. See our previous recommendations for N_2 .⁹¹

Production of the metastable $O(^1S)$ atom was measured by LeClair and McConkey.⁹² As seen from Fig. 13, this cross section is a factor 50 smaller than the TCS for dissociation into neutrals determined by Cosby.⁸⁹ Recommended cross sections for the electron-impact dissociation of O_2 into neutral atoms are given in Table 6. The overall uncertainty of these values is $\pm 35\%$.

2.8. Ionization cross section

Ionization of the oxygen molecule has been extensively studied, starting from early experiments by Tate and Smith.⁹³ The agreement between different datasets is generally quite good. Early measurements by Tate and Smith,⁹³ and by Rapp and Englander-Golden⁹⁴ yielded only a gross total (i.e., the total ion current produced).

TABLE 6. Recommended cross sections for the dissociation into neutrals of O_2 . Data are from Cosby.⁸⁹ The uncertainty is about $\pm 35\%$

Electron energy (eV)	Dissociation cross section (10^{-16} cm^2)	Electron energy (eV)	Dissociation cross section (10^{-16} cm^2)
13.5	0.220	48.5	0.534
18.5	0.529	58.5	0.444
21.0	0.565	73.5	0.366
23.5	0.525	98.5	0.331
28.5	0.587	148.5	0.296
33.5	0.663	198.5	0.291
38.5	0.610		

Later, mass selectors, like the sector magnetic field⁹⁵ or time-of-flight spectrometers,⁹⁶ also allowed partial cross sections, i.e., for single ions produced, to be determined. The disadvantage of the latter experiments was that they required normalization procedures, usually to helium⁹⁶ or argon.⁹⁵ The most recent generation of experiments^{97–101} uses position-sensitive detectors, which allow the simultaneous tracking of all the ions produced.

Figure 14 compares total ionization cross sections from different laboratories. Note that measurements by Rapp and Englander-Golden⁹⁴ are gross total ionization cross sections (i.e., the total current of ions), while those by Krishnakumar and Srivastava,⁹⁶ Tian and Vidal,⁹⁷ and Straub *et al.*⁹⁸ are the sum of all partial cross sections. Correcting the gross total of Rapp and Englander-Golden⁹⁴ for double ionization⁹⁷ makes their results almost coincide with the counting cross sections of Straub *et al.*⁹⁸ However, an uncertainty of about 5% in the total (counting) ionization cross section⁹⁸ still remains.

Ionization into the parent ion, i.e., O_2^+ , dominates the total ionization cross section; see Fig. 15. The two recent measurements^{97,98} almost coincide; the discrepancy with other earlier sets^{95,96} can be

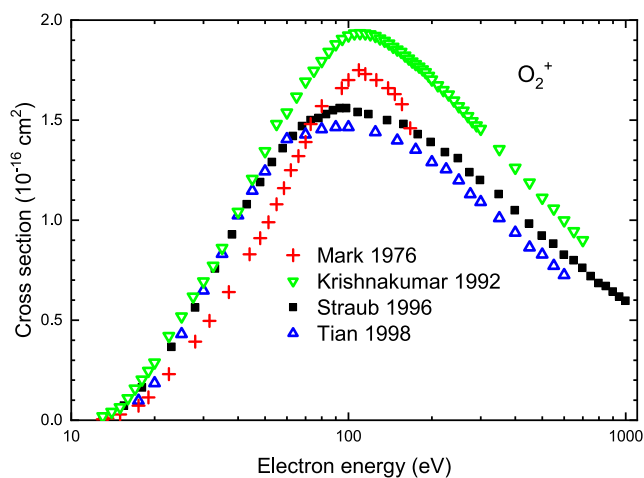


FIG. 15. Partial cross section for the formation of the O_2^+ ion. Red crosses represent Ref. 95, for the other symbols see Fig. 14.

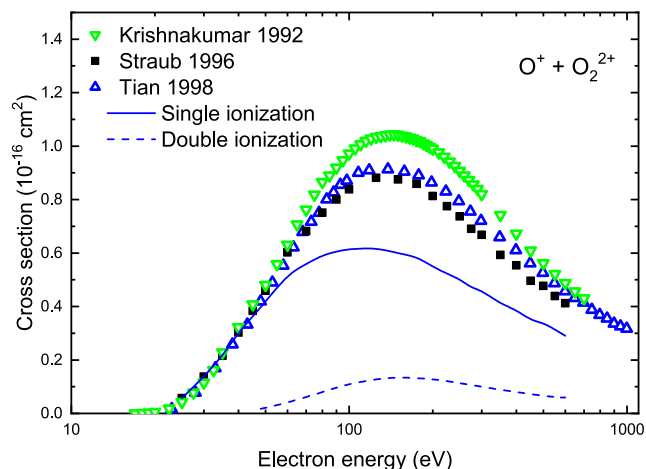


FIG. 16. Partial cross section for the formation of the O^+ ion. The signal from O^+ ions is experimentally indistinguishable from the O_2^{2+} signal. For the symbols, see Fig. 14. The lines represent the production of O^+ ions via single, i.e., $O^+ + O$, or double ($O^+ + O^+$) ionization, by Tian and Vidal.⁹⁷

attributed to the normalization procedures mentioned above and/or differences in the detection efficiency of the mass spectrometers used.

Doering and Yang¹⁰² measured the energy of secondary electrons and thereby determined the electronic state of the O_2^+ ion. At 100 eV, the branching ratios between the ground ionic $X^2\Pi_u$ and excited $a^4\Pi_u$ and $b^4\Sigma_g^-$ states (with respective ionization thresholds^{103,104} 12.2, 16.3, and 18.4 eV) are 9:5:2.

The production of O^+ ions (in the majority of experiments indistinguishable from the O_2^{2+} ion) is roughly half of the O_2^+ yield, see Fig. 16. The same figure shows the contribution to the production of the O^+ ion via single, i.e., $O^+ + O$, or double ($O^+ + O^+$) ionization.⁹⁷

The early measurement on $^{17}O^{16}O$ by Märk⁹⁵ and the recent experiments with position-sensitive detectors^{99–101} allowed the separate yield of O_2^{2+} ions to be measured: at 100 eV it amounts to roughly 10% of the O^+ signal.⁹⁹ However, the spread between different data obtained with different methodologies is large; see Fig. 17. Hence, we are unable to recommend data for this case.

The O_2^{2+} ion has a bond energy¹⁰⁵ of -2.65 eV. Therefore, it is metastable with a lifetime⁹⁹ of about 1–2 μ s. Techniques using angular coincidence^{106,107} and measurements of the kinetic energy release⁹⁹ allows the identification of the decay pathways of molecular ions. According to Bull, Lee, and Vallance,⁹⁹ O^+ ions are (at 100 eV) predominantly produced via dissociation of the $B^2\Sigma_g^-$ excited state of the O_2^+ ion, with dissociation asymptotes $O^+(^4S) + O(^3P)$ and $O^+(^4S) + O(^1D)$. The precursors of the most intense asymptotic channel $O^+(^2D) + O(^3P)$ is unclear. In total, at 100 eV, 68% of atomic ions are produced in the ground 4S state, 25% in the 2D state, and 8% in the 2P electronically excited states.

Figure 18 shows the partial cross section for the formation of the doubly charged atomic ion O^{2+} . Its maximum yield is roughly 1% of the O_2^+ signal. Recent measurements (not shown in the figures) by Lomsadze *et al.*¹⁰⁸ coincide with those by Straub *et al.*⁹⁸ Studies of

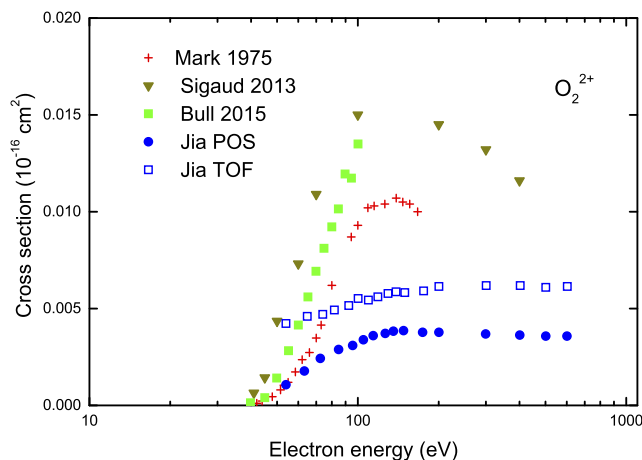


FIG. 17. Partial cross section for the formation of the O_2^{2+} ion. Red crosses;⁹⁵ inverted dark yellow triangles;¹⁰⁰ green squares;⁹⁹ open and closed blue circles¹⁰¹ by time-of-flight and position-sensitive methods, respectively. The data were read from the figures in the papers.

O_2 molecules heated in a shock wave,¹⁰⁹ up to 5000 K, did not reveal, within the experimental uncertainty, any difference in ionization, as compared to 300 K.

Our recommended ionization cross sections are based on the review by Lindsay and Mangan¹⁷ and shown in Fig. 19. The values are given in Table 7. The uncertainty is 5% on the total ionization and the O_2^+ yield, and 7% on the O^+ and 10% on the O_2^{2+} yield.

2.9. Dissociative electron attachment cross section

In 1965, Rapp and Briglia¹¹⁰ derived the DEA cross sections of O_2 using the method of total ionization measurement. The cross sections show a single peak centered at the electron energy of 6.5 eV with a cross section of 1.41×10^{-18} cm². Rapp and Briglia did not

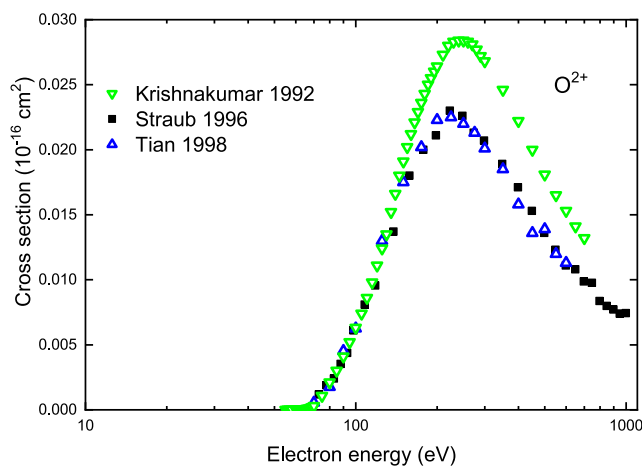


FIG. 18. Partial cross section for the formation of the O_2^+ ion. For symbols, see Fig. 14.

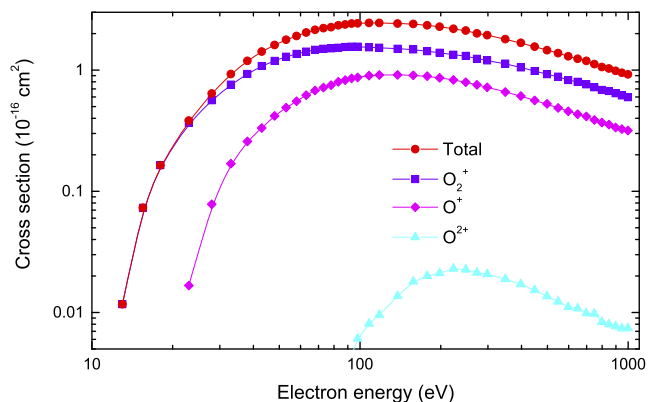


FIG. 19. Recommended total and partial cross sections for ionization of the O_2 molecule. Data from the review by Lindsay and Mangan.¹⁷ Recommended values are given in Table 7.

provide an uncertainty for this measurement. We conservatively suggest that it would be no more than 20%, inferred from their experiments using the positive-ion measurement device that was also used in deriving the DEA cross section. In the same year, Christophorou *et al.*¹¹¹ measured the DEA cross sections of O_2 using a swarm setup; these cross sections are in agreement with the results of Rapp and Briglia. The DEA of ground state O_2 occurs via the following process: $e^- + O_2(X^3\Sigma_g^-) \rightarrow O_2^-(X^3\Sigma_g^-) \rightarrow O^-(^2P) + O(^3P)$.

Laporta, Celiberto, and Tennyson¹¹² calculated vibrational excitation and DEA cross sections as function of the initial O_2 vibrational state using resonance curves computed by the R-matrix method. For low vibrational states, they found that DEA largely goes via the $^4\Sigma_u^-$ resonance state but for vibrationally excited states DEA can occur with a much lower threshold via the low-lying $^2\Pi_u$ resonance state of O_2^- .

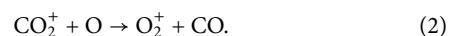
To determine the angular distribution of O^- from DEA to O_2 , Van Brunt and Kieffer¹¹³ assumed the $^2\Pi_u$ symmetry to provide the dominant contribution. Later, Prabhudesai, Nandi, and Krishnakumar¹¹⁴ obtained evidence for the involvement of the $^4\Sigma_u^-$ resonance in DEA of O_2 for the first time from angular distribution measurements of O^- ions over the entire 2π angular range by employing the velocity map imaging technique. Some DEA experiments with hot O_2 or with metastable oxygen molecules^{115,116} were reported, but they are not included in the present evaluation. Since Rapp and Briglia¹¹⁰ with Christophorou *et al.*¹¹¹ provide the only absolute DEA cross sections, the previous reviews^{10,117} recommended the DEA cross sections of O_2 by Rapp and Briglia.¹¹⁰ We recommend the same cross sections, which are given in Fig. 20 and Table 8.

3. Atomic Oxygen

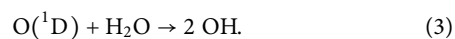
Miller and Banks¹¹⁸ note that “atomic oxygen is the predominant species in low-Earth orbit and is contained in the upper atmosphere of many other planetary bodies.” Together with its ion, it is also the dominant species in Earth’s ionosphere. In the ionosphere of Venus, a small proportion of oxygen atoms ($\approx 1\%$) assures production of O_2^+ ions via the reaction with CO_2^+ ions¹¹⁹ as

TABLE 7. Recommended cross sections in (10^{-16} cm^2) for ionization of O_2 . The data are from Ref. 17. The uncertainty is 5% on the total ionization and the O_2^+ partial cross section, 7% on the O^+ , and 10% on the O^{2+} cross section. We are unable to recommend values for O_2^{2+} ions due to a large spread in recent data; see Fig. 17

Energy (eV)	O_2^+	$O^+ (+O_2^{2+})$	O^{2+}	Total
13.0	0.0117			0.0117
15.5	0.0730			0.0730
18.0	0.164			0.164
23	0.366	0.0167		0.383
28	0.563	0.0781		0.641
33	0.758	0.169		0.927
38	0.929	0.258		1.19
43	1.08	0.333		1.42
48	1.19	0.419		1.61
53	1.29	0.490		1.78
58	1.36	0.553		1.91
63	1.42	0.621		2.04
68	1.47	0.679		2.15
73	1.50	0.717	0.001 18	2.22
78	1.51	0.751	0.001 89	2.26
83	1.53	0.801	0.002 41	2.34
88	1.55	0.827	0.003 52	2.38
93	1.56	0.855	0.004 38	2.42
98	1.56	0.871	0.006 10	2.43
108	1.54	0.900	0.008 08	2.45
118	1.53	0.910	0.009 56	2.45
138	1.50	0.913	0.013 7	2.42
158	1.48	0.905	0.018 0	2.40
178	1.43	0.891	0.020 0	2.34
198	1.39	0.864	0.021 1	2.28
223	1.34	0.830	0.0230	2.19
248	1.31	0.794	0.022 6	2.12
273	1.24	0.755	0.021 3	2.01
298	1.20	0.721	0.020 7	1.94
348	1.13	0.659	0.018 9	1.80
398	1.05	0.611	0.017 1	1.68
448	0.983	0.562	0.015 3	1.56
498	0.923	0.526	0.013 6	1.46
548	0.882	0.487	0.012 3	1.38
598	0.827	0.457	0.011 1	1.30
648	0.800	0.432	0.010 8	1.24
698	0.761	0.415	0.009 87	1.19
748	0.720	0.388	0.009 77	1.12
798	0.686	0.369	0.008 37	1.06
848	0.671	0.355	0.007 99	1.03
898	0.643	0.336	0.007 70	0.987
948	0.617	0.326	0.007 40	0.950
998	0.597	0.317	0.007 43	0.922



In the Earth’s troposphere, the metastable 1D state triggers production of OH radicals, which are the main oxygenating agent via the reaction¹²⁰



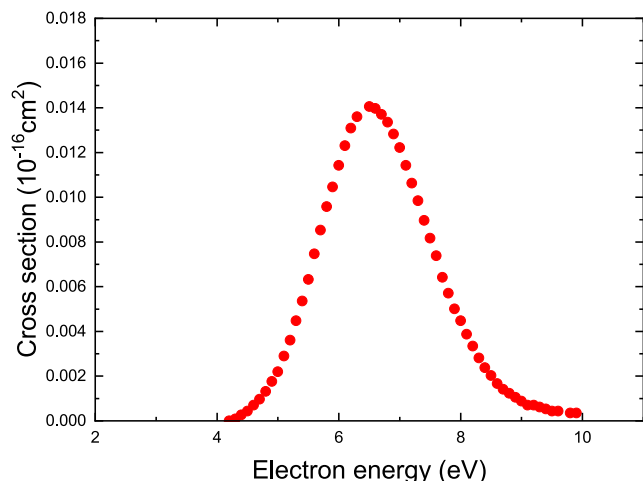


FIG. 20. Recommended DEA cross sections for O_2 .

An interplay of the 557.7 nm (green) and 630.0 nm (red) emission lines of atomic oxygen may explain the variation of colors in the boreal aurora, while quiet-time airglow continuum may be due to the chemiluminescence from the reaction¹²¹



Measurements of total, state-specific angle-integrated, and angle-resolved DCS for atomic oxygen are subject to much higher uncertainty than those for molecular oxygen. Therefore, few experimental results are available. Sunshine, Aubrey, and Bederson²⁸ used a recoil-beam method to measure TCS, with a stated uncertainty of $\pm 20\%$. Williams and Allen¹²² employed an electrostatic monochromator and an orientable detector to determine both elastic and TCS. Even if the uncertainty of such a method is usually 20%, their¹²² TCS at low energies for molecular oxygen agree pretty well with our recommended values, see Fig. 1. However, as the atmospheric processes depend primarily on the specific electronic state of the oxygen atom, and such data are unavailable experimentally, we base our discussion in this chapter on comparison of theoretical results.

3.1. Total cross section

Figure 21 shows the TCS, as well as the contributing parts originating from elastic, elastic plus excitation, and ionization processes. The situation depicted here is quite typical. Only a few experimental data, often with substantial error bars, are generally available, and they may be insufficient to be used in a comprehensive collisional-radiative model (CRM). Not surprisingly, the situation deteriorates even more when it comes to state- and angle-resolved data, as will be shown further below.

Many theoretical approaches, on the other hand, are limited to particular energy ranges. The standard close-coupling method, with only a few discrete physical target states in the expansion, is generally suitable at low energies below the ionization threshold, while perturbative Born-based approaches are more appropriate for higher energies, particularly for optically allowed transitions.

TABLE 8. Recommended DEA cross sections for O_2 . The uncertainty is no more than 20%

Electron energy (eV)	DEA (10^{-16} cm^2)	Electron energy (eV)	DEA (10^{-16} cm^2)
4.2	0.00×10^{-00}	7.1	1.14×10^{-2}
4.3	8.79×10^{-5}	7.2	1.06×10^{-2}
4.4	2.64×10^{-4}	7.3	9.84×10^{-3}
4.5	4.39×10^{-4}	7.4	8.96×10^{-3}
4.6	7.03×10^{-4}	7.5	8.17×10^{-3}
4.7	9.67×10^{-4}	7.6	7.38×10^{-3}
4.8	1.32×10^{-3}	7.7	6.41×10^{-3}
4.9	1.76×10^{-3}	7.8	5.71×10^{-3}
5.0	2.20×10^{-3}	7.9	5.01×10^{-3}
5.1	2.90×10^{-3}	8.0	4.48×10^{-3}
5.2	3.60×10^{-3}	8.1	3.87×10^{-3}
5.3	4.48×10^{-3}	8.2	3.34×10^{-3}
5.4	5.36×10^{-3}	8.3	2.81×10^{-3}
5.5	6.33×10^{-3}	8.4	2.37×10^{-3}
5.6	7.47×10^{-3}	8.5	2.02×10^{-3}
5.7	8.52×10^{-3}	8.6	1.67×10^{-3}
5.8	9.58×10^{-3}	8.7	1.41×10^{-3}
5.9	1.05×10^{-2}	8.8	1.23×10^{-3}
6.0	1.14×10^{-2}	8.9	1.05×10^{-3}
6.1	1.23×10^{-2}	9.0	8.79×10^{-4}
6.2	1.31×10^{-2}	9.1	7.03×10^{-4}
6.3	1.36×10^{-2}	9.2	7.03×10^{-4}
6.5	1.41×10^{-2}	9.3	6.15×10^{-4}
6.6	1.40×10^{-2}	9.4	5.27×10^{-4}
6.7	1.37×10^{-2}	9.5	4.39×10^{-4}
6.8	1.34×10^{-2}	9.6	4.39×10^{-4}
6.9	1.28×10^{-2}	9.8	3.51×10^{-4}
7.0	1.22×10^{-2}	9.9	3.51×10^{-4}

As will be discussed and illustrated further in the subsections below, we believe that the B-spline R-matrix with pseudo-states model of Tayal and Zatsarinny¹²³ produced by far the most comprehensive and reliable dataset. In this model, 19 spectroscopic bound states were coupled with 1097 pseudo-states representing the target continuum and core-excited autoionizing states up to about 50 eV above the ionization threshold. This model will be referred to as BSR-1116 below.

3.2. Elastic scattering and momentum transfer cross sections

We start this section with angle-differential elastic cross sections (DCSs), since those were measured for five energies in the experiment carried out by Williams and Allen.¹²²

Figure 22 shows a comparison of their data with predictions from the very elaborate B-spline R-matrix (BSR) calculation performed by Tayal and Zatsarinny¹²³ mentioned above. That calculation is an update on previous work by the same authors¹²⁵ and another one by Plummer *et al.*¹²⁶ Based on the structure description (energy levels and oscillator strengths) given in the tables

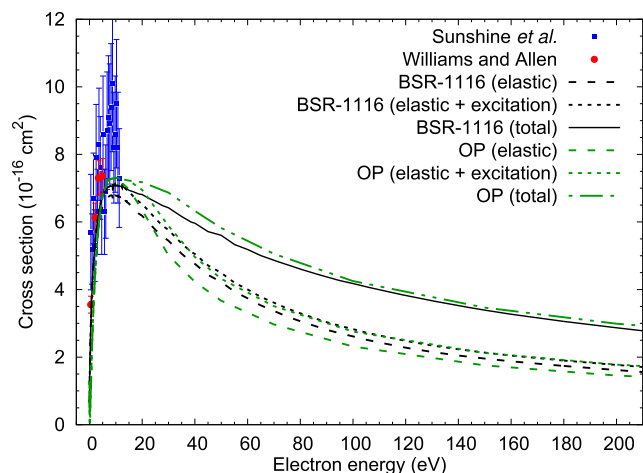


FIG. 21. Angle-integrated total (elastic + excitation + ionization) cross sections for electron collisions with oxygen atoms in the $(2p^4)^3P$ ground state. The experimental data are from Sunshine *et al.*²⁸ and Williams and Allen.¹²² The theoretical predictions are from Tayal and Zatsarinny¹²³ (BSR-1116) and Blanco and García¹²⁴ using a complex optical model potential (OP).

by Tayal and Zatsarinny,¹²³ we put a high level of confidence in their work. Since relativistic effects are almost certainly negligible at the level of accuracy desired for the collisions of interest in the present assessment, it seems unlikely that any further improvement of the theoretical model would lead to significant changes in the predictions.

Looking at Fig. 22, which we generated from the transition-matrix elements available to us, we see overall good agreement between experiment and theory for scattering angles larger than about 60° , while there are significant discrepancies at smaller angles. In particular, theory predicts that the DCS decreases toward small scattering angles, while the experimental data keep increasing, with a likely maximum at or near the forward direction. We checked that this is not an issue of an insufficient number of partial waves included in the calculation.

We note that Plummer *et al.*¹²⁶ made similar predictions in their presumably best calculation [Fig. 3(e) of their paper]. Consequently, we favor theory over experiment in this case. In fact, Fig. 23 shows a contour plot of the DCS on a narrow energy-angle grid. Only at the high end of this energy scale does the DCS approach its maximum near the forward direction. The numerical data used to generate this figure for 31 energies up to 20 eV are available in the [supplementary material](#).

The angle-integrated elastic (ICS) and MTCS are presented in Fig. 24. The larger experimental DCS for angles below 60° are consistent with the generally larger values reported by Williams and Allen¹²² compared to theory. This is particular visible in the ICS, while the factor $1 - \cos \theta$ in the angle-differential form of the MTCS reduces the effect in the MTCS. The BSR predictions are available on a narrow energy grid up to 200 eV.

3.3. Selected excitation cross sections

We now select a few excitation cross sections to illustrate the general situation. The figures are based on those of Tayal

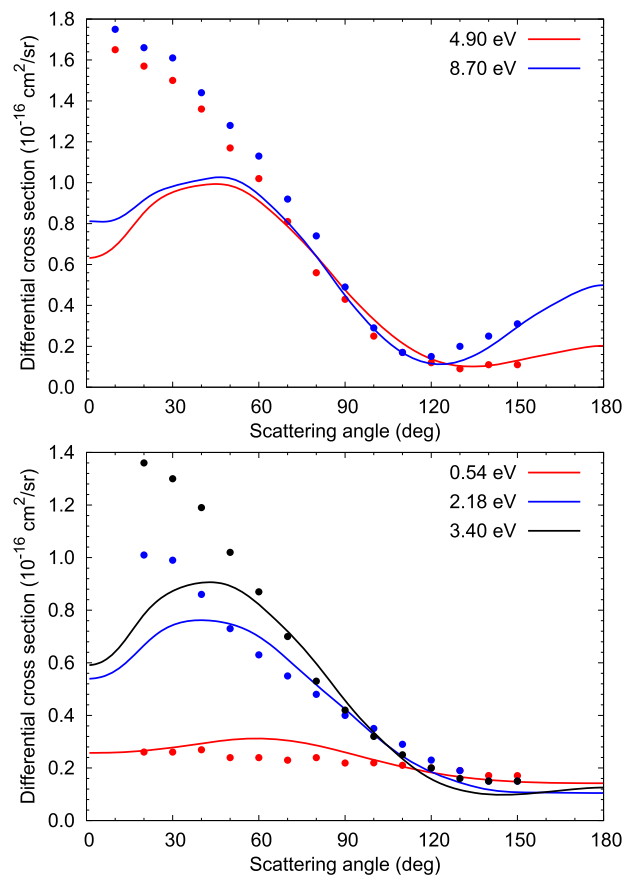


FIG. 22. Angle-differential elastic cross sections for electron collisions with atomic oxygen in the $(2p^4)^3P$ ground state for the five energies measured by Williams and Allen¹²² (dots). The experimental data are compared with the theoretical predictions from Tayal and Zatsarinny¹²³ (solid lines).

and Zatsarinny,¹²³ where more can be found. The datafile in the [supplementary material](#) contains results for many more state-to-state transitions that would likely be needed to set up a complete CRM. In fact, for such a model, emission cross sections, i.e., accounting for the population of excited states via cascading, may be more suitable than the direct excitation cross sections the present manuscript is devoted to. Some emission cross sections were shown by Tayal and Zatsarinny,¹²³ more can be found in the [supplementary material](#), and many more can be generated from the energy levels and oscillator strengths given therein.

Figure 25 shows two examples of excitation cross sections for optically allowed transitions from the $(2p^4)^3P$ ground state. While the few available experimental data agree well with each other, we note the large error bars (up to $\approx 30\%$). Noteworthy, increasing the number of coupled states drastically reduces the theoretical predictions, in particular for the $(2p^4)^3P \rightarrow (2p^33s)^3D^0$ transition. Even though the results from the most extensive BSR calculation with 1116 coupled states lie significantly below the four points (two from each experiment, with the measured value for 30 eV barely agreeing

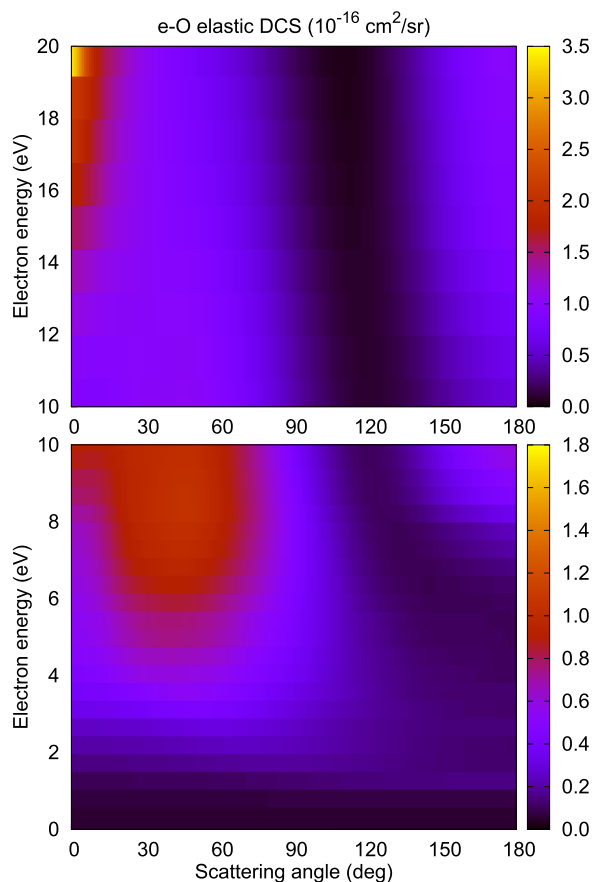


FIG. 23. Contour maps of the angle-differential elastic cross section for electron collisions with atomic oxygen in the $(2p^4)^3P$ ground state. The data were generated from the transition-matrix elements of Tayal and Zatsarinny.¹²³ Note the different color scales in the energy ranges 10–20 eV (top) and 0–10 eV (bottom) that were used to clearly illustrate the behavior of the DCS at small angles.

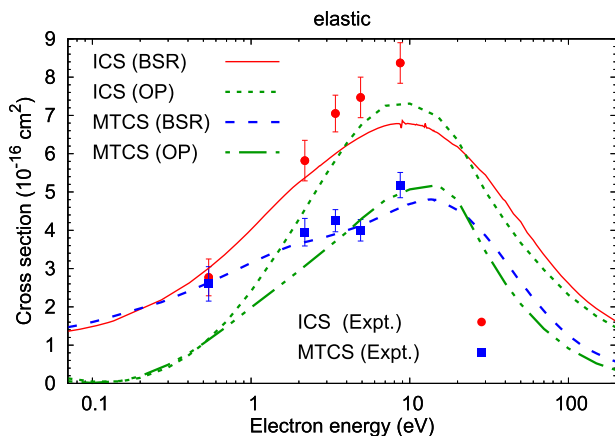


FIG. 24. Angle-integrated elastic and MTCS for electron collisions with atomic oxygen in the $(2p^4)^3P$ ground state. The experimental data of Williams and Allan¹²² are compared with the recommended theoretical BSR predictions from Tayal and Zatsarinny¹²³ and the optical-potential (OP) calculation of Blanco and Garcia.¹²⁴ See text for details.

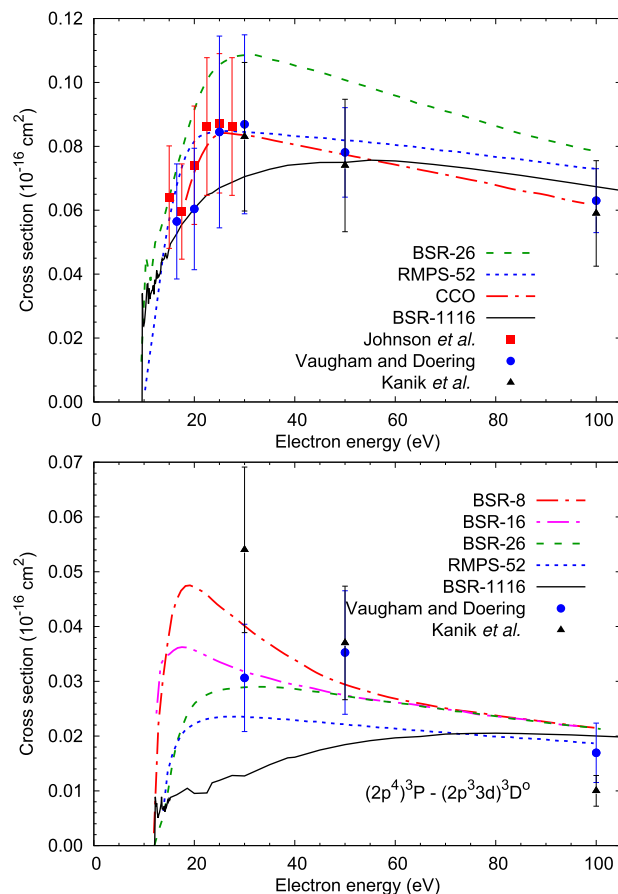


FIG. 25. Angle-integrated excitation cross sections for the optically allowed $(2p^4)^3P \rightarrow (2p^3 3s)^3S^o$ (top) and $(2p^4)^3P \rightarrow (2p^3 3s)^3D^o$ (bottom) transitions. The numbers behind the models indicate the number of states in the close-coupling expansion. The experimental data are from Johnson *et al.*,¹²⁷ Vaughan and Doering,¹²⁸ and Kanik *et al.*¹²⁹ while the theoretical predictions are: BSR-8, BSR-16, and BSR-26;¹²⁵ RMPS-52;¹³⁰ CCO;¹³¹ BSR-1116.¹²³

with each other within the error bars given), we recommend those theoretical predictions.

Figure 26 shows three examples of excitation cross sections for optically forbidden transitions from the $(2p^4)^3P$ ground state. The situation regarding the experimental data is similar to the previous examples. There are only a few data points that often, though not always, agree with each other within the large error bars given. Except for the $(2p^4)^3P \rightarrow (2p^3 3s)^5S^o$ transition, the convergence of the theoretical predictions with the number of coupled states is quite good, with the largest calculation generally predicting the smallest cross section for individual discrete state-to-state transitions, in particular from the ground state. This is a well-known result, which makes sense in light of the fact that the TCS (see above) tends to be rather stable with regard to variations in theoretical models. Consequently, the flux that can go into additional channels needs to be made up for. Once again, we recommend the BSR-1116 results, which are available for many energies in the [supplementary material](#), for modeling applications.

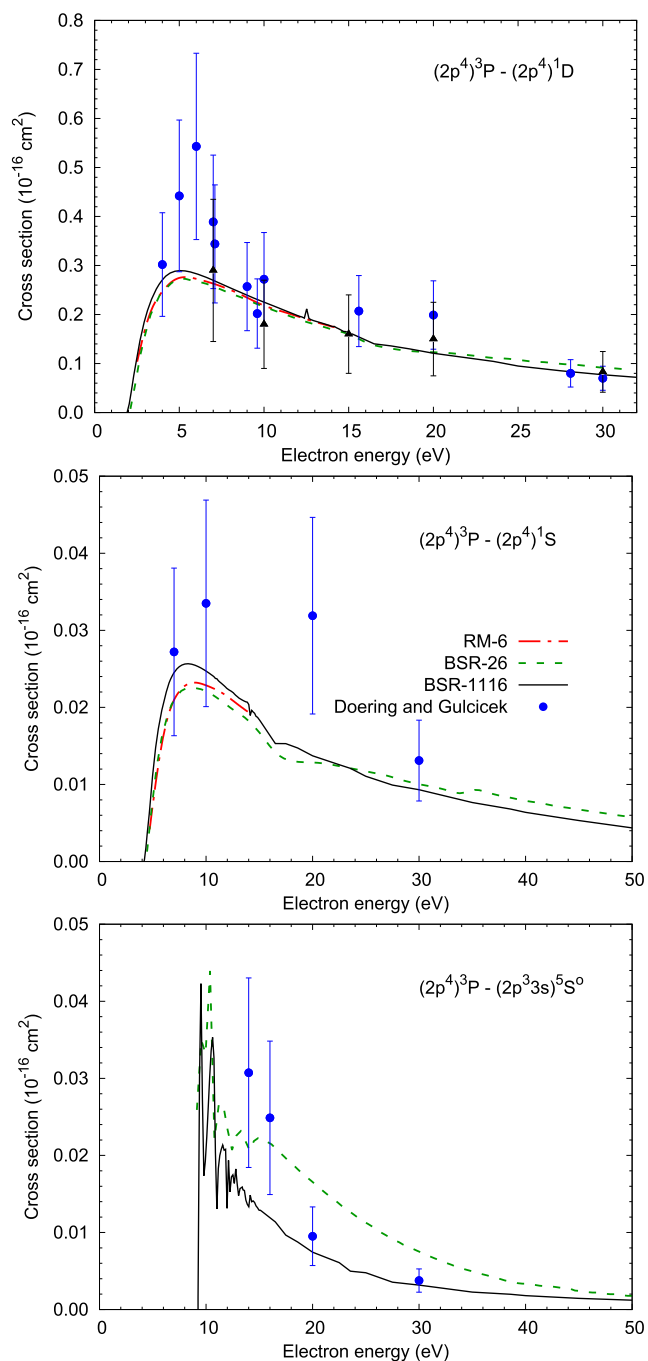


FIG. 26. Angle-integrated excitation cross sections for the optically forbidden $(2p^4)^3P \rightarrow (2p^4)^1D$ (top), $(2p^4)^3P \rightarrow (2p^4)^1S$ (center), and $(2p^4)^3P \rightarrow (2p^3 3s)^5S^0$ (bottom) transitions. The experimental data are from Doering,¹³² Shyn and Sharp,¹³³ and Doering and Gulcicek^{134,135} for the 1S and $^5S^0$ final states, respectively. The theoretical predictions are: RM-6,¹²⁶ BSR-26,¹²⁵ and BSR-1116.¹²³

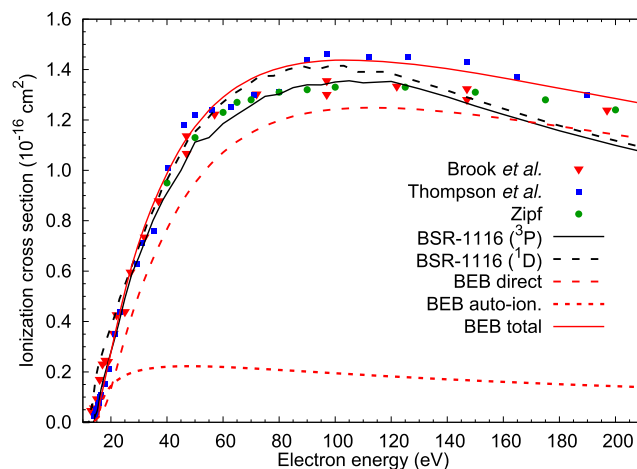


FIG. 27. Angle-integrated ionization cross section for electron collisions with oxygen atoms in the $(2p^4)^3P$ ground state. The experimental data are from Refs. 136, 138, and 139 and the BEB results from Kim and Desclaux.¹³⁷ Also shown are the BSR-1116 predictions from Tayal and Zatsarinny¹²³ for both the $(2p^4)^3P$ and $(2p^4)^1D$ initial states.

3.4. Ionization cross sections

We finish this section with the ionization cross section for electron collisions with oxygen atoms in the $(2p^4)^3P$ ground state. As is often the case (see Fig. 21 above), the ionization cross section is generally larger than even the sum of all individual excitation cross sections, and experimental data from different studies tend to agree reasonably well with each other. Here, too, the BSR-1116 predictions appear to be preferable, with the additional benefit of

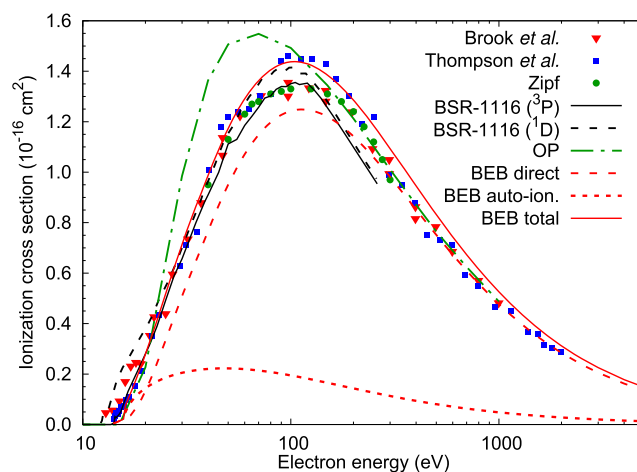


FIG. 28. Same as Fig. 27 on an extended logarithmic energy scale. Also shown are the optical-potential (OP) calculations from Blanco and García.¹²⁴

them being available on a dense and extensive energy grid. While we do not show such results here, we note that the TCS includes de-excitation processes as well. For details, see the paper by Tayal and Zatsarinny.¹²³

Experimental and theoretical ionization cross sections for atomic oxygen are compared in Figs. 27 and 28 on linear and logarithmic energy scales, respectively. The overall agreement is good. Brook *et al.*¹³⁶ observed an ion signal already at 12.9 eV, i.e., below the ionization threshold (13.62 eV) of the $(3p^4)^3P$ ground state. They also mention the possibility of ionization from the metastable $(3p^4)^1D$ state. For this reason, we also include the BSR-1116¹²³ cross section for ionization of this state. The Bethe–Born binary encounter model (BEB) of Kim and Desclaux¹³⁷ agrees well with the experimental total cross ionization cross section, provided the contribution of ionization plus electronic excitation is added. The formation of the O^{2+} ions in the energy range 200–2000 eV amounts to about 3% of that of the O^+ ions.^{136,138}

4. Summary and Future Work

As shown in this review, electron interactions with oxygen (both molecular and atomic) show several unusual features compared to other species.

For the molecule, the most prominent features in the energy range below 1 eV (i.e., in the “infra-red” range) are sharp resonant structures that are visible in the total and vibrational cross sections, due to a temporary capture of the interacting electron by the O_2 target. Sharp resonant enhancements (at energies above 6 eV) are also present in electronic excitation cross sections, both for optically allowed and forbidden transitions. Low values of the energy thresholds for the two long-lived singlet excited states and the small value for the dissociation into neutral atoms require, for any modeling of oxygen plasma or Earth’s atmosphere, also the inclusion of cross sections for excited states, oxygen atoms and ions. We note that cross sections for the transition from the electronically excited states are particularly high (and show the transitions have low excitation thresholds). However, for successful modeling, more precise lifetime values of these species should be derived from spectroscopic data.⁶⁶ Due to the importance of the oxygen molecule, there has been a significant amount of work performed on nearly all cross sections. Therefore, we are able to make recommendations as summarized in Fig. 29. The one exception concerns the weak electron impact rotational excitation process, for which only estimates based on a very simplified theoretical treatment are available.

Figure 30 shows a selection of the most important recommended cross sections for the oxygen atom. For the elastic, momentum-transfer, and all excitation cross sections, we recommend the BSR-1116 predictions. They are from a highly sophisticated theoretical model, with an accurate target structure description, and have been checked for convergence regarding the number of states in the close-coupling expansion. The results are available on a narrow energy grid between the respective thresholds and 200 eV, beyond which they can be extended, if necessary, using the known dependence of such cross sections at high energies. Alternatively, the high-energy (200 eV and above) predictions of the optical-potential (OP) model by Blanco and García¹²⁴ could be used. There is a small discontinuity to be seen in the graph, which is due to the BSR-1116 and OP results not matching up perfectly at 200 eV. For ionization,

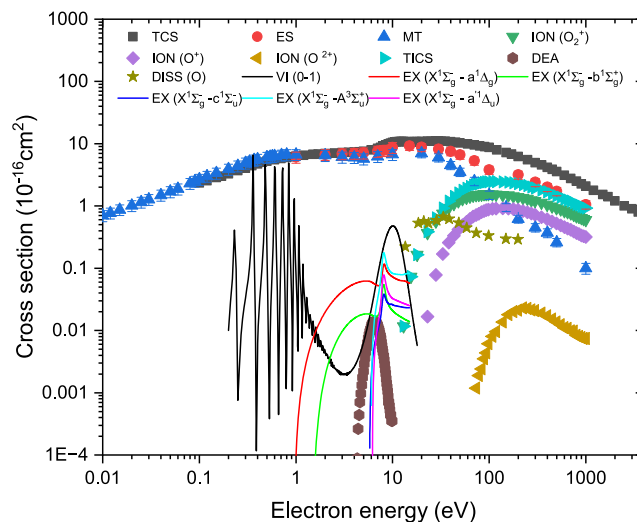


FIG. 29. Recommended angle-integrated cross sections for the oxygen molecule.

we recommend the most recent experimental data of Thompson *et al.*,¹³⁸ which agree very well with the BEB predictions of Kim and Desclaux.¹³⁷ Overall, we expect the recommended cross sections to be accurate to at least 20% for those that are sufficiently large to seriously matter in CRM models.

We specifically mention again the surprisingly high electron-impact ionization cross section for the oxygen atom, which is about twice as large as that for the O_2 molecule. This may explain why the O^+ ion accounts for almost all ionic species in Earth’s atmosphere at an altitude of 500 km altitude. However, possible reactions with other atmospheric components certainly depend on the specific electronic state of the oxygen atoms. More research is needed before definite conclusions can be drawn.

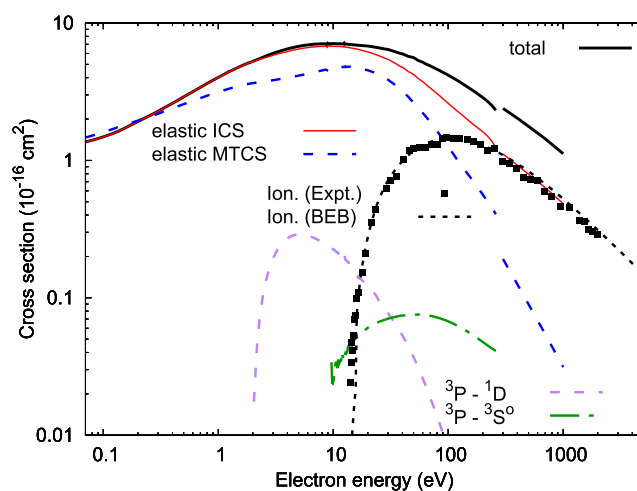


FIG. 30. Selected examples of recommended angle-integrated cross sections for the oxygen atom. See text for details.

Recent flybys¹⁴⁰ near Ganymede showed that interactions of energetic electrons with oxygen species may dominate atmospheric processes also on Jupiter's moons. Hence, data on electron scattering from oxygen may prove to be needed even more in astrophysics than in geophysics.

5. Supplementary Material

See [supplementary material](#) for recommended electron-impact collision cross section datasets for O and O₂ across various collisional processes.

Acknowledgments

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Finally, the complete validation of the present cross sections, both for the molecule and the atom, may be done via their implementations in modeling laboratory plasma⁴⁷ and atmospheric²⁰ processes.

6. Author Declarations

6.1. Conflict of Interest

The authors have no conflicts to disclose.

7. Data Availability

The data that support the findings of this study are available from the corresponding author upon reasonable request and its [supplementary material](#).

8. References

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