Differential cross sections for electron impact vibrational excitation of molecular oxygen in the angular range 15°–180°

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Abstract

Absolute differential cross sections have been measured for excitation of the $v = 1$–4 vibrational levels of the $X^3\Sigma_g^-$ ground state of molecular oxygen at an electron impact energy of 10 eV in a wide scattering angle range, from $15°$ to $180°$. In the measurements, a recently constructed double hemispherical electron spectrometer has been used which employs the magnetic angle-changing technique to observe the backward scattering of electrons. The integral excitation cross sections for the above vibrational levels have been also determined through integration of the measured differential cross sections. A detailed comparison of the obtained cross sections has been made with the results of previous measurements.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Absolute electron impact cross section data for molecules relevant to atmospheric physics and chemistry and to modelling of gaseous discharges and laboratory plasmas are measured for elastic and inelastic processes [1, 2]. These molecules include oxygen, which is the second most abundant molecule in the Earth's atmosphere. In the case of oxygen, the experimental cross sections are used in the analysis of auroral and airglow emissions of the atmosphere [3] and to model electron energy transfer in the cooling process of electrons in the ionosphere [4]. The oxygen molecule is also an interesting object of fundamental research because of the open-shell electronic configuration in its ground state with two unpaired electrons.

In the present work, we have measured absolute differential cross sections for excitation of the $v = 1$–4 vibrational levels of the $X^3\Sigma_g^-$ ground state of molecular oxygen at an incident electron energy of 10 eV. The measurements have been carried out with a recently constructed double hemispherical electron spectrometer, over a wide scattering angle range, from $15°$ to $180°$. The backward electron scattering was reached by using the magnetic angle-changing

technique [5–7]. The incident electron energy of the present measurements (10 eV) lies close to the centre of the $^4\Sigma_u^-$ negative ion resonance (9.5 eV) which decays into the vibrational levels of the $X\,^3\Sigma_g^-$ ground state with high autodetachment probability [8].

Previously, absolute differential cross sections for excitation of the $v = 1$–4 vibrational levels of the $X\,^3\Sigma_g^-$ state for selected values of energy in the 5–15 eV range have been measured in the scattering angle range of 10°–90° by Brunger *et al* [9] and earlier in a wider angular range of 12°–156° by Shyn and Sweeney [10]. Wong *et al* [11] presented cross sections for the above vibrational levels at 25° while Allan [8] gave differential cross sections for vibrational levels up to $v = 8$ at 90°. Both these measurements [8, 11] have been done at fixed scattering angles as functions of electron energy in the range of 4–15 eV. The cross sections of Shyn and Sweeney and Brunger *et al*, in the angular range of their overlap, show noticeable differences with respect to absolute values and shapes of their angular dependences. For example, at the energy of the present measurements (10 eV), the absolute values of both measurements for the $v = 1$ level differ by a factor of approximately 2. Further, the cross sections of Brunger *et al* show minima at 30° in the angular dependences which are not borne out in the results of Shyn and Sweeney. This disagreement with respect to the shapes of the results proceeds up the $v = 4$ vibrational level. The discrepancies between the above two measurements may be partly due to normalization of the vibrational cross sections to different elastic cross sections which are not in agreement (see [12] for a comparison of these elastic cross sections).

The aim of the present work is to provide new measurements of the above vibrational differential cross sections to resolve some of the inconsistencies between previously published results. The present differential cross sections measured over a wide scattering angle range have also allowed accurate integral cross sections to be determined without extensive extrapolation over a region of higher scattering angles up to 180°.

2. Experimental details and procedures

The electron spectrometer used in the present measurements consists of a source of incident electrons, an analyser of scattered electrons and a magnetic angle changer which encompasses the collision centre. A schematic diagram of the spectrometer is shown in figure 1. In the electron source, an electron gun produces a beam of electrons which are focused on the entrance of a double hemispherical deflector. Electrons leaving the hemispherical deflector with a narrow energy spread are accelerated and focused on a molecular beam by a triple-electrode cylindrical lens. The molecular beam is formed by effusion of the target gas from a single tube with 0.6 mm inner diameter. Electrons scattered at a given angle are decelerated by a cylindrical lens to an energy transmitted by the analyser and focused on the entrance aperture of the double hemispherical deflector identical to that used in the electron beam source. A two-electrode lens is placed behind the exit aperture of the analyser and focuses transmitted electrons on a channel electron multiplier. The scattered electron analyser can be rotated around the molecular beam axis over an angular range from −90° to 90° with respect to the direction of the incident electron beam. This allows studies of electron scattering in the angular range from 0 to 90° without the use of the magnetic angle changer.

The electron gun (figure 1) incorporates a Pierce diode system R and a triple-electrode cylindrical lens which has an inner diameter of 10 mm. The filament is a tungsten A50 cathode (manufactured by Agar). Two sets (*x* and *y*) of deflecting electrodes D1 which serve to change the position of the focused electron beam across the entrance aperture of the hemispherical deflector are placed within the third electrode of the cylindrical lens (identical sets of deflecting electrodes D2 and D3 are placed in two other cylindrical lenses). This
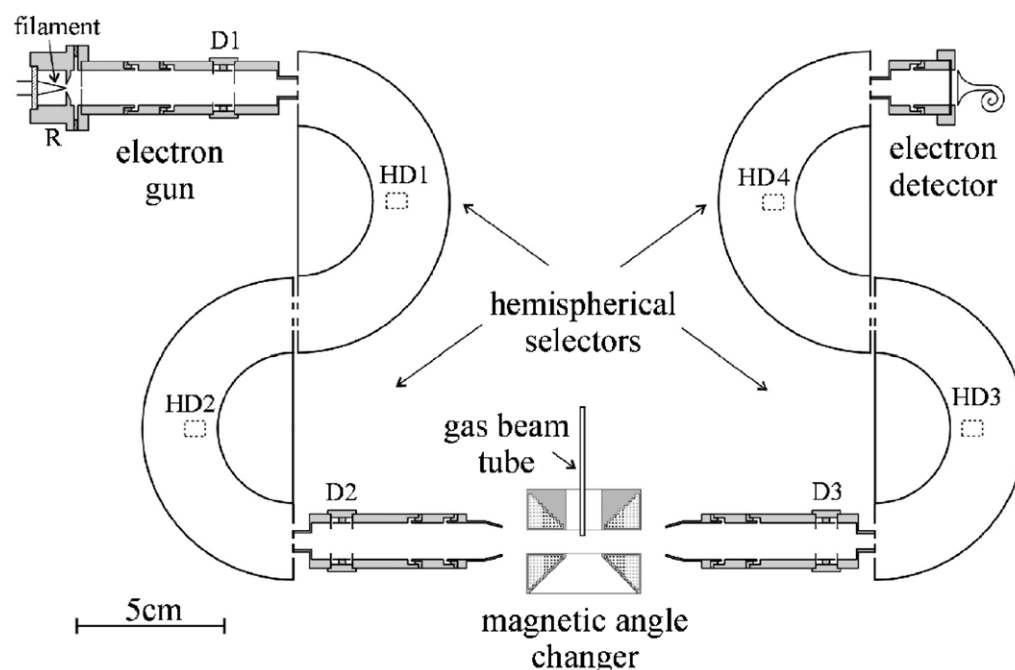
Figure 1. Diagram of the double hemispherical electron spectrometer which incorporates the magnetic angle changer. D1–D3 and HD1–HD4 are electron beam deflectors inserted in the cylindrical lenses and hemispherical deflectors respectively.

electrode also contains an aperture which limits the angular divergence of the focused electron beam to $\alpha = \pm 4°$.

The double hemispherical deflector consists of two single $180°$ selectors arranged in series (figure 1). Each selector has two hemispherical electrodes, the outer electrode of 50 mm radius and inner electrode of 25 mm radius. The entrance and exit apertures of the deflectors of 1 mm diameter are placed at a radius of 37.5 mm. Each selector is equipped with a pair of deflecting electrodes, HD1–HD4, to correct in the selector the position of the transmitted electrons which could be diverted by stray electric fields and residual magnetic fields. The fringing fields at the hemispherical deflectors' entrance and exit planes are corrected by using a set of ring electrodes as introduced by Jost [13].

The magnetic angle changer which surrounds the electron scattering centre produces a localized, static magnetic field that is perpendicular to the scattering plane. The incident electrons and the scattered electrons are deflected in the magnetic field [5]. The electrons scattered at the angles from $90°$ to $180°$ are observed on the opposite side of the molecular beam with respect to the deflected unscattered beam and can thus be detected by the electron analyser. The deflection angle depends on the magnetic field and that dependence when measured at given electron energies can be used to select the required values of scattering angles by adjusting the strength of the magnetic field.

The magnetic angle changer consists osf two pairs of coils, the inner pair and the outer pair, as shown in figure 1. The coils have conical shapes and each inner coil has 21 turns of a PTFE-covered copper wire while the outer coils have 34 turns each [7]. The currents in the inner and outer coils flow in opposite directions and are adjusted to cancel the magnetic dipole

moment of the coil arrangement. This is achieved for the ratio $1:-0.327$ of the inner coils' current to that of the outer coils. This condition ensures that the magnetic field decreases fast enough with radial distance from the scattering centre so that it does not affect the performance of the electron spectrometer. The magnetic field at a distance of 40 mm from the centre is equal to 0.1% of its value at the centre (1.2 mT). Additionally, the conical shape of the coils allows for the efficient pumping of the target gas from the target region.

The electron spectrometer is housed in a μ-metal shield in a stainless steel vacuum chamber of about 80 l volume. It is pumped down to 10^{-7} mbar by a 2000 l s^{-1} diffusion pump.

In the present work, electron energy loss spectra have been measured in molecular oxygen at an electron incident energy of 10 eV and at scattering angles from $15°$ to $180°$ in $10°$ steps. The background contributions to these spectra which are due to electrons not scattered from the molecular beam have been measured by removing the molecular beam and introducing the target gas directly into the vacuum chamber by a side valve. The gas pressure in the vacuum chamber then was the same as during the collection of the energy loss spectra. These contributions have been subtracted from the measured spectra. The variation of the analyser transmission with electron energy in the range 9–10 eV, which corresponds to the energy loss range 0–1 eV, has been investigated by observing excitation of the 2^3S state in helium in the incident energy range 28.8–29.8 eV. A comparison with the calculated excitation cross sections of Fon *et al* [14] showed that the analyser transmission is constant to within $\pm5\%$, and no transmission correction has been applied to the obtained spectra. From the spectra, the intensities of the energy loss peaks corresponding to the excitation of the $v = 1-4$ vibrational levels of the $X^3\Sigma_g^-$ ground state of oxygen have been determined with respect to the intensity of the elastic peak using a peak fitting procedure. The absolute differential cross sections for the above vibrational levels have been derived by normalizing the relative vibrational intensities to the elastic differential cross sections which have been measured using the relative flow technique. This is a technique which determines relative gas density in the scattering region from the measurements of the gas flow through the gas line. Here, for normalization in the $15°-90°$ range the latest, most accurate elastic cross sections of Sullivan *et al* [15] have been selected, while for the $100°-180°$ angular range we relied on our recent measurements of Linert *et al* [12]. The uncertainties in the present differential cross sections are estimated to be 22%, 25% and 30% for the $v = 1$, $v = 2$ and $v = 3, 4$ differential cross sections, respectively. This total uncertainty results from contributions of uncertainties in the elastic differential cross section used for normalization (10%), in the transmission of an electron analyser (5%) and in the determination of the vibrational to elastic intensities ratio ($\leqslant15\%$ depending on the vibrational level). The total uncertainty is taken to be equal to the sum of the above contributions.

The scattering angle scale has been calibrated by observing at the energy of 10 eV the position of a minimum in the elastic differential cross section of argon at $117.5°$ [16]. The uncertainty in the angular scale calibration is $3°$. It includes the uncertainty of $1.5°$ introduced by the change of the deflection angle of the scattered electrons in the magnetic field with their final energies over the 1 eV energy loss range of vibrational excitation in measurements with a fixed position of the electron analyser. The electron energy is calibrated against the observed position of the ^{2}P$_{3/2}$ resonance in argon at 11.098 eV [17] with an uncertainty of 30 meV. The energy resolution of the spectrometer in the present measurements of energy loss spectra is estimated from the observed width of the energy loss peaks which was typically about 60 meV (FWHM) (see figure 2).
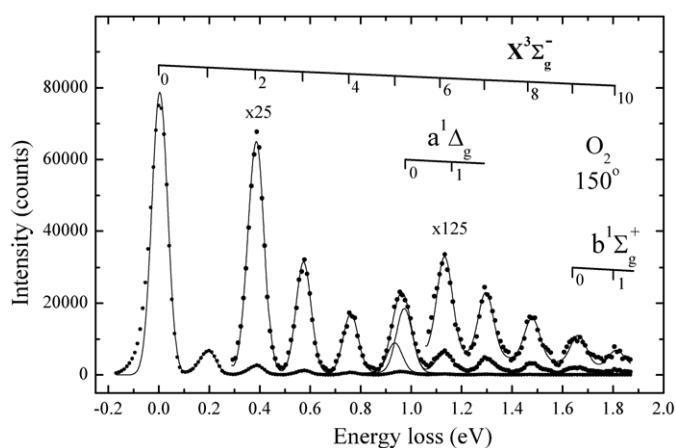
Figure 2. Energy loss spectrum measured in molecular oxygen at an incident electron energy of 10 eV and at a scattering angle of $150°$. The energy loss peaks corresponding to the excitation of vibrational levels of $X\,^3\Sigma_g^-$ and a $^1\Delta_g$ states of oxygen were fitted with Gaussian curves shown by full lines.

3. Results and discussion

The electron energy loss spectrum obtained at a scattering angle of $150°$ is shown in figure 2. The background contribution has been removed from the measured spectrum as it is explained above. In the spectrum, vibrational excitation of the $X\,^3\Sigma_g^-$ ground state of oxygen is clearly identified up to the $v = 10$ level. The excitation of the $v = 0$ level of a $^1\Delta_g$, the first excited state of oxygen, overlaps with that of the $v = 5$ level of the ground state and is shown by a peak of increased width and enhanced intensity as seen in figure 2. The excitation of the $v = 0$ level of the b $^1\Sigma_g^+$ state, the second excited state of oxygen, strongly overlaps with that of the $v = 9$ level and is hardly discernible in the corresponding energy loss peak due to its low excitation cross section for scattering angles at and above $150°$ [7, 18]. The observed elastic and energy loss peaks have been fitted with Gaussian profiles to determine their intensities. It has been found in the fitting procedure that the widths of peaks corresponding to single levels in the obtained spectra for a given scattering angle remained constant to within 5%. We do not have a reasonable explanation for a 'foot' visible on the left of the elastic peak.

Differential cross sections obtained at 10 eV incident energy for the $v = 1–4$ vibrational levels of the $X\,^3\Sigma_g^-$ state are presented in figures 3(a)–(d) and are listed in table 1. The current results are shown (figure 3) together with previous measurements of Brunger *et al* [9] carried out in the $10°–90°$ angular range and those of Shyn and Sweeney [10] performed in the $12°–156°$ range. The results of Wong *et al* [11] at $25°$ and Allan [8] at $90°$ are also included in the figures. Our cross sections for the measured vibrational levels show broad minima centred at about $90°$ which are consistent with the pσ wave of the $^4\Sigma_u^-$ resonance. They are in agreement with the results of Shyn and Sweeney with respect to the overall angular dependence. In each of the cross sections for $v = 1$ and 2 and to a lesser extent in those for $v = 3$, there is additionally a weak maximum at $90°$. This observation is in agreement with the earlier measurement at 9 eV of the angular dependence of the $v = 1$ differential cross section made by Allan [8]. To explain this weak maximum, he invoked a contribution from a second d-wave resonance. Considering the magnitude of measured differential cross sections, our
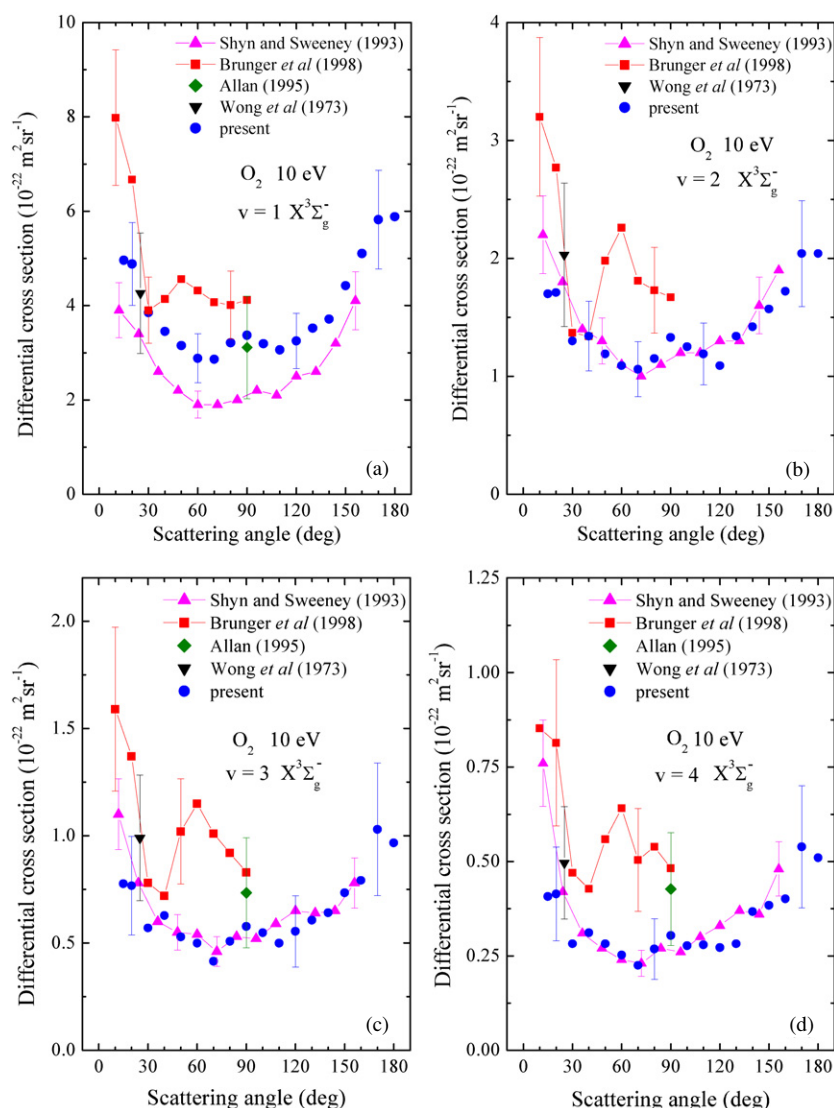
Figure 3. Differential cross sections for excitation of the vibrational levels of the $X^3\Sigma_g^-$ ground state of oxygen measured at an incident electron energy of 10 eV: (a) $v = 1$, (b) $v = 2$, (c) $v = 3$ and (d) $v = 4$.

$v = 1$ cross section is higher than that of Shyn and Sweeney and at $90°$, it appears between their result and that of Brunger *et al*. However, it agrees very well with the value reported at $90°$ by Allan. Our $v = 2$, 3 and 4 cross sections, on the other hand, coincide with the results of Shyn and Sweeney in the region of their overlap. At $90°$ our $v = 3$ and 4 cross sections are lower than those of Allan, but this disagreement appears within the given experimental uncertainties of both measurements.

We have also obtained integral cross sections for excitation of the $v = 1$–4 vibrational levels at the energy of 10 eV. Here, we have extrapolated our differential cross sections down

Table 1. Differential cross sections in units of 10^{-22} m^2 sr^{-1} for excitation of vibrational levels $v = 1, 2, 3, 4$ of the X$^3\Sigma_g^-$ ground state of oxygen at an incident electron energy of 10 eV.

Scattering angle (degree)	Vibrational level			
	$v = 1$	$v = 2$	$v = 3$	$v = 4$
15	4.96	1.70	0.776	0.407
20	4.88	1.71	0.767	0.414
30	3.85	1.30	0.570	0.282
40	3.45	1.34	0.628	0.311
50	3.15	1.19	0.528	0.282
60	2.88	1.09	0.499	0.252
70	3.06	1.17	0.475	0.225
80	3.21	1.15	0.508	0.268
90	3.37	1.33	0.577	0.304
100	3.19	1.25	0.548	0.277
110	3.06	1.19	0.499	0.279
120	3.25	1.09	0.554	0.272
130	3.52	1.34	0.606	0.282
140	3.71	1.42	0.641	0.367
150	4.42	1.57	0.734	0.384
160	5.10	1.72	0.792	0.401
170	5.82	2.04	1.03	0.539
180	5.88	2.04	0.967	0.510

Table 2. Integral cross sections in units of 10^{-22} m^2 for excitation of vibrational levels $v = 1, 2, 3, 4$ of the X$^3\Sigma_g^-$ ground state of oxygen at an incident electron energy of 10 eV.

Vibrational level	Present	Shyn and Sweeney (1993)	Noble *et al* (1996)
$v = 1$	44.0	31.2	53.63
$v = 2$	16.3	16.5	25.52
$v = 3$	7.30	7.5	11.45
$v = 4$	3.77	4.0	6.53

to 0° and then performed integration in the total scattering angle range. In the extrapolation, an angular dependence similar to that observed for high scattering angles, 160°–180°, has been taken assuming symmetry of the cross section at about 90° (the pσ wave of the $^4\Sigma_u^-$ resonance). The present integral cross sections are listed in table 2 where they are compared with the experimental cross sections of Shyn and Sweeney [10] and Noble *et al* [19]. The present $v = 1$ result is in good accord with the experimental cross section of Noble *et al* while the cross section of Shyn and Sweeney is lower than both these results. Our $v = 2$–4 results, as may be expected from a comparison in figures 3(b)–(d), coincide with the results of Shyn and Sweeney. Both results are lower than those of Noble *et al*. In figure 4, our $v = 1$ result at 10 eV and the $v = 1$ experimental integral cross sections of Shyn and Sweeney [10] and Noble *et al* [19] (as given in [2]) obtained in the 5–15 eV energy range are compared with the theoretical R-matrix cross section of Noble *et al* [19]. The calculated cross section which reproduces well the resonance broad peak of the vibrational excitation lies below the existing experimental cross sections. This tendency of the theoretical cross sections of Noble *et al* in the 5–15 eV energy range proceeds to the $v = 2$–4 vibrational levels.
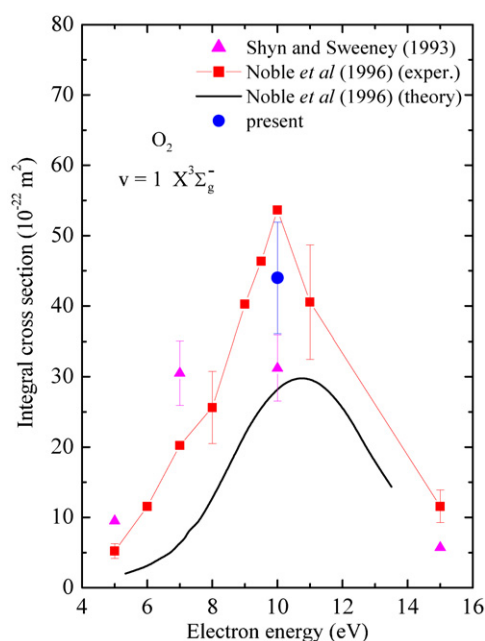
Figure 4. Integral cross sections for excitation of the $v = 1$ vibrational level of the $X^3\Sigma_g^-$ ground state of oxygen.

4. Conclusions

We have presented differential cross sections for excitation of the $v = 1$–4 vibrational level of the ground $X^3\Sigma_g^-$ state of molecular oxygen measured in a wide scattering angle range, $15°$–$180°$, that includes the whole range of backward scattering. The present studies have been carried out using a recently constructed double hemispherical electron spectrometer which employs the magnetic angle-changing technique. The previous measurements of Shyn and Sweeney [10] for the $v = 2$–4 vibrational levels coincide with our results, but for the $v = 1$ level are somewhat below our measured cross section. Our results resolve differences existing among previously published cross sections of Brunger *et al* [9] and Shyn and Sweeney [10] and confirm the angular dependence of the differential cross section obtained by Shyn and Sweeney. The measurements carried out over a wide scattering angle range have also allowed the integral cross sections for excitation of the above vibrational levels to be determined.

Acknowledgments

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