Chemical Physics 170 (1993) 99-109
North-Holland

# Absolute optical oscillator strengths for the photoabsorption of molecular oxygen (5-30 eV) at high resolution

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Received 15 September 1992

Absolute optical oscillator strengths for the photoabsorption of molecular oxygen in the valence shell discrete electronic excitation region have been measured in the energy range 5-30 eV using high resolution dipole (e, e) spectroscopy. Absolute intensities for the Schumann-Runge continuum region and for the discrete bands below the first ionization potential are reported and compared with available experimental and theoretical data.

## 1. Introduction

Since oxygen is the second most abundant species within the earth's atmosphere, an accurate knowledge of absolute oscillator strengths (cross sections) for the photoabsorption of molecular oxygen in the valence discrete region is of great importance in aeronomy and in other areas such as nuclear physics, radiation physics and astrophysics. The dissociation and predissociation of molecular oxygen by the absorption of solar radiation can also be used to determine the oxygen density profile at high altitudes and such processes play an important role in atmospheric phenomena such as aurora and dayglow. Molecular oxygen is also of particular theoretical interest and challenge since it is an open shell system.

The photoabsorption spectrum of oxygen has been studied extensively. Critical reviews and compilations of the spectroscopic data of oxygen can be found in several papers [1-3]. Although Beer-Lambert law photoabsorption methods have often been used to obtain quantitative results for discrete transitions, it has been pointed out [2,4] that absolute oscillator strengths (cross sections) measured by direct absorption of photons may be subject to considerable error because of "line saturation" effects due to the finite resolution (bandwidth) of the optical spectrometer. Such effects can be severe for discrete transitions with very narrow natural linewidth and high cross section. For example, Yoshino et al. [5] have noted that the Schumann-Runge (12, 0) band of $^{18}O_2$ is too sharp for its absolute cross section to be measured by conventional Beer-Lambert law photoabsorption techniques.

The Schumann-Runge band system of molecular oxygen, which involves transitions from the ground $X\,^3\Sigma_g^-$ to the $B\,^3\Sigma_u^-$ state, has been studied extensively by many workers. On the low energy side the system consists of sharp discrete transitions with very low oscillator strength, which have been measured by Lewis et al. [6] using the curve of growth method to allow for bandwidth effects. At higher energy in the 7-9.8 eV region the absorption spectrum of oxygen is dominated by the broad and generally featureless Schumann-Runge continuum, for which many Beer-Lambert law photoabsorption measurements of the absolute cross section have been made [7-16]. Ab initio theoretical calculations have been reported by Buenker and Peyerimhoff [17] and by Allison et al. [18] for the oscillator strengths of the Schumann-Runge continuum region, taking into account the mixing between the valence $B\,^3\Sigma_u^-$ and the Rydberg $E\,^3\Sigma_u^-$ (or $B'\,^3\Sigma_u^-$ in other notation) states. Allison et al. [18] also took into account the contributions from the $1\,^3\Pi_u$ state and reported cross sections and structural features that were consistent with the existing experimental results. Wang et al. [16] performed an experimental absolute photoabsorption measurement of oxygen in the Schumann–Runge continuum region, and by fitting their theoretical calculations to the observed data, they reported potential curves and transition moments for the mixed Rydberg–valence B $^3\Sigma_u^-$ and mixed valence–Rydberg E $^3\Sigma_u^-$ states.

On the high energy side of the Schumann–Runge continuum, there are several diffuse bands. The three prominent peaks at 9.96 eV (longest), 10.28 eV (second) and 10.57 eV (third) have been assigned by Yoshimine et al. [19] and Buenker et al. [20] as transitions to the three lowest vibrational levels of the mixed valence–Rydberg E $^3\Sigma_u^-$ state. Yoshimine et al. [19], Buenker et al. [20] and Li et al. [21] have computed the absolute oscillator strengths for these three bands. Beer–Lambert law-type photoabsorption measurements have also been performed for these diffuse bands [8,10,14], including a recent study by Lewis et al. [22,23], who made measurements on isotopic molecular oxygen ($^{18}O_2$) and for the first time analyzed the data using Beutler–Fano type resonance profiles.

Electron energy loss spectroscopy (EELS) has also been used to study the electronic excitation spectrum of molecular oxygen [24–29] in the valence discrete region. Since electron impact excitation is non-resonant, EELS based methods of determining optical oscillator strengths have the enormous advantage that they are not subject to the limitations of "line saturation" (i.e. bandwidth) effects which cause difficulties in Beer–Lambert law photoabsorption measurements [2,4]. Using measurements of inelastically scattered electrons obtained at a range of scattering angles, absolute optical oscillator strengths for oxygen in the discrete and continuum regions were derived by Lassettre and co-workers [24–26] from extrapolation of the measured generalized oscillator strengths to zero momentum transfer. With the use of extremely high impact energy (25 keV) and small scattering angle, Geiger and Schroder [27] reported a very high resolution electron energy loss spectrum of oxygen in the energy loss region 6.8–21 eV, but only relative intensities (not absolute oscillator strengths) were obtained. Huebner et al. [28] have reported data in the energy region 6–14 eV which were derived from high resolution electron energy loss measurements obtained at an impact energy of only 100 eV and at a small scattering angle (0.02 rad). The measured oscillator strengths are questionable in this case [28] since the experimental conditions correspond to a rather large momentum transfer ($K^2=0.01$ and 0.04 au at 6 and 14 eV respectively). The absolute scale was established by Huebner et al. [28] by normalizing the spectrum to an average optical value [2] at a single point in the Schumann–Runge continuum region where the photoabsorption measurements were mutually in best agreement. An independent TRK sum-rule normalization method was used by Brion et al. [29] to obtain absolute oscillator strengths for the photoabsorption of oxygen in the energy region 5–300 eV from Bethe–Born converted electron energy loss spectra. These latter results [29] were determined directly at negligible momentum transfer using a low resolution ($\Delta E=1$ eV fwhm) dipole (e, e) spectrometer with an impact energy of 8 keV and a mean scattering angle of zero degrees.

In the presently reported work, the recently developed [4,30] high resolution dipole (e, e) method, which has already been applied successfully to measurements for the noble gases [4,30–32] and several small molecules [33–35], has been used to measure directly, at negligible momentum transfer, the absolute oscillator strengths for oxygen in the energy region 6–30 eV at a resolution of 0.048 eV fwhm. The absolute scale has been obtained by normalizing in the smooth continuum at 26 eV to the previously reported absolute oscillator strength value determined by Brion et al. [29] using a low resolution dipole (e, e) spectrometer.

## 2. Experimental method

The experimental procedures employed in the present work are similar to those used for previously reported absolute oscillator strength measurements of the valence shell discrete regions of the noble gases [4,30–33] and small molecules [34,35] using the high resolution dipole (e, e) spectrometer. Details of the construction of this electron energy loss spectrometer can be found in ref. [36]. In brief, an energy-selected electron beam is accelerated to 3 keV and impacted on the gaseous sample molecules in the collision chamber. The inelastically scattered electrons are collected at a mean scattering angle of zero degrees and are energy-analyzed by a hemispherical electrostatic analyzer. Under such experimental conditions the measured electron energy loss spectra are governed by dipole selection rules.

The electron energy loss spectrum of oxygen was measured at a resolution of 0.048 fwhm in the energy region 6–30 eV using the high resolution dipole (e, e) spectrometer. In order to obtain a relative optical oscillator strength spectrum the energy loss spectrum was then multiplied by the Bethe–Born kinematic conversion factor for the spectrometer as determined earlier [4,31]. In the compilation of Gallagher et al. [37], the absolute photoabsorption oscillator strengths reported earlier by Brion et al. [29] for oxygen using low resolution dipole (e, e) spectroscopy are seen to be in very good agreement with directly measured absolute photoabsorption data in the continuum region [38,39]. Therefore, the TRK sum-rule normalized data reported by Brion et al. [29] can confidently be used to normalize the present high resolution relative oscillator strength spectrum in the smooth continuum region at 26 eV. With these procedures the present absolute work is thus completely independent of any direct optical measurements and free of "line saturation" effects. The TRK sum-rule normalization procedures used by Brion et al. [29] avoid the difficulties involved in determining light fluxes and particle densities which are required in conventional absolute photoabsorption measurements.

The small contributions to the spectrum from the background gases at the base pressure of the spectrometer ($\approx 2\times10^{-7}$ Torr) and from non-spectral electrons were removed in the present measurements by subtracting the signal when the oxygen sample pressure was quartered. Calibration of the energy scale was obtained by admitting helium simultaneously with the oxygen sample and referencing to the $1\,^1S\rightarrow2\,^1P$ transition of helium which occurs at 21.218 eV [40]. The oxygen sample was obtained from Medigas and had a stated minimum purity of 99%. No impurities were apparent in the energy loss spectra.

## 3. Results and discussion

The photoabsorption oscillator strengths and spectral assignments of molecular oxygen are conveniently discussed with reference to the ground state molecular orbital, independent particle, valence shell electronic configuration, which may be written as

$$(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^4(3\sigma_g)^2(1\pi_g)^2 .$$

Fig. 1 shows the presently measured absolute differential oscillator strength spectrum of molecular oxygen measured in the energy region 5–30 eV by high resolution dipole (e, e) spectroscopy at a resolution of 0.048 eV fwhm. Several vibrational progressions are clearly visible. The two other sets of data shown in fig. 1 are the low resolution (1 eV fwhm) dipole (e, e) data (open triangles) reported earlier at 1 eV intervals by Brion et al. [29] and the photoabsorption data (open circles) measured by Samson and Haddad [39] using a double ion chamber method. The double ion chamber results [39] are not compared with the present work in the region of the sharp autoionizing structure (12–18 eV) because of significant differences in energy resolution and also because the optical measurements may be subject to "line saturation" effects. Therefore the data of ref. [39] are only shown in fig. 1 in the generally smoother spectral region above 18 eV. It can be seen from fig. 1 that the present results are in very good quantitative agreement with the earlier data of Brion et al. [29] and also those of Samson and Haddad [39] in the smooth continuum region (where the cross section will be effectively independent of resolution). At lower energies the presently obtained high resolution spectrum is seen to be consistent with the data of Brion et al. [29] given the differences in resolution. The total integrated oscillator strengths below 18 eV for both the high and low resolution spectra are in very good agreement with each other, giving values of 1.13 and 1.12 respectively. In the present work, integration of the measured high resolution differential oscillator strength spectrum over a given energy region will give directly the absolute oscillator strength for that region. The uncertainties in the presently reported absolute oscillator strengths are estimated to be ±5%.

Fig. 2 shows an expanded view of fig. 1 in the energy region 6.5–10 eV showing the absolute oscillator strengths for the Schumann–Runge continuum. The weak Schumann–Runge bands below 7 eV which are several orders of magnitude smaller in oscillator strength than the continuum could not be observed

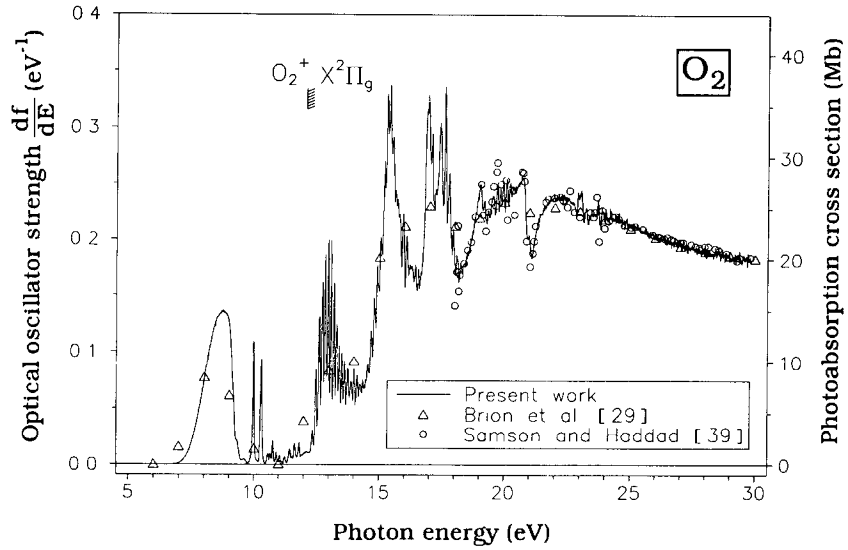

Fig. 1. Absolute oscillator strengths for the photoabsorption of molecular oxygen in the energy region 5–30 eV measured using the high resolution dipole (e, e) spectrometer (fwhm = 0.048 eV).

in the present work. In figs. 2a and 2b the present results are compared with previously published experimental [8–10,12–16,28] and theoretical [16,18] results respectively. Immediately it can be seen from fig. 2a that the present results are in excellent agreement with most of the other experimental data. The data of Ditchburn and Heddle [9] are much higher than all the other experimental data while those of Goldstein and Mastrup [13] are somewhat lower in the energy region around the continuum maximum. For the experimental work shown in fig. 2a only the present high resolution dipole (e, e) measurements and the data of Huebner et al. [28] are derived from electron energy loss spectra. The remainder are Beer–Lambert law photoabsorption measurements [8–10, 12–16] which in this particular energy region should not be subject to "line saturation" effects due to the broad nature of the Schumann–Runge continuum in oxygen. Note that the data of Huebner et al. [28] were normalized at the continuum maximum (8.61 eV) to the average of the optical data [2] which were available at that time and therefore reasonable agreement with the photoabsorption data is not surprising. In contrast, the present high resolution dipole (e, e) spectrum was made absolute using the TRK sum-rule normalized low resolution dipole (e, e) work of Brion et al. [29] in the smooth continuum region at 26 eV, which is ≈ 17 eV above the Schumann–Runge continuum maximum. The Bethe–Born conversion process (see experimental section above) results in a very large change in relative intensity of the two continua between the original electron energy loss data and the relative optical oscillator strength spectrum. Therefore any inaccuracy in the Bethe–Born conversion factor for the spectrometer would produce spurious oscillator strengths. The validity and accuracy of the Bethe–Born conversion factor for the high resolution dipole (e, e) spectrometer used in the present work has previously been confirmed down to ≈ 11 eV by comparison of measurements and highly accurate ab initio calculations for helium [4] and molecular hydrogen [34]. The results for the Schumann–Runge continuum of oxygen now provide a further stringent test of the accuracy with which the Bethe–Born conversion factor for the high resolution dipole (e, e) spectrometer has been determined and in particular in the region down to 7 eV. This is important to establish since the Bethe–Born conversion factor was obtained from a comparison of high and low resolution dipole (e, e) measurements above 22 eV in the ionization continua of helium [4] and neon [31]. The Bethe–Born factor below 22 eV was then obtained by curve fitting the measured quantity above 22 eV and extrapolating to

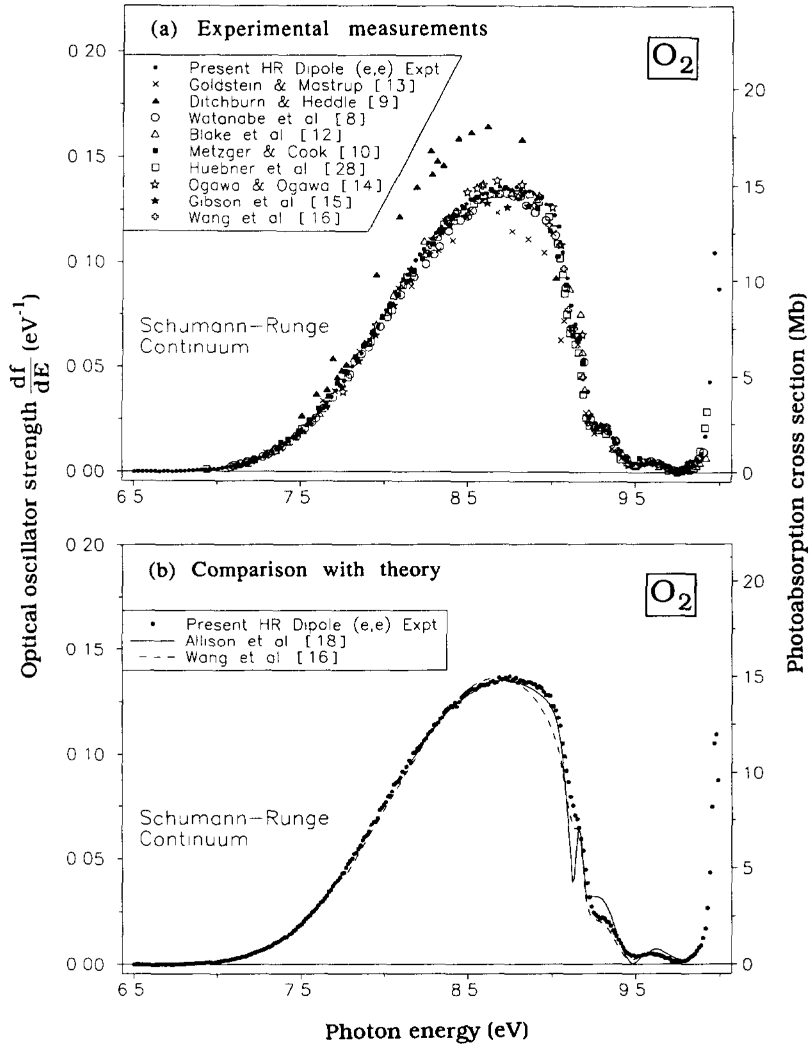

Fig. 2. Absolute oscillator strengths for the photoabsorption of molecular oxygen. Expanded view of fig. 1 in the energy region 6.5–10 eV, showing the Schumann–Runge continuum region. (a) Comparison with previously published experimental data [8–10, 12–16,28]. (b) Comparison with theory [16,18].

lower energies. The excellent agreement of the present work with many previously published photoabsorption measurements of the absolute oscillator strengths in the Schumann–Runge continuum region of oxygen is a very strong indication that the Bethe–Born conversion factor is well characterized for the high resolution dipole (e, e) instrument, even in the low energy loss (photon energy) range.

By extrapolating measured relative generalized oscillator strengths to zero momentum transfer, Lassettre et al. [26] obtained an integrated oscillator strength of 0.179 for the Schumann–Runge continuum region, over the range 6.56–9.46 eV, following correction of their previously published data [24,25]. By integrating the same energy region, the present work gives a slightly lower oscillator strength of 0.169. In the other electron impact based work using low impact energy, Huebner et al. [28] reported an integrated oscillator strength of 0.161 for the Schumann–Runge continuum.

In fig. 2b, the present measurements are compared with the theoretical work reported by Allison et al. [18] and Wang et al. [16]. Both sets of calculated data show reasonable agreement with the present work. However, it must be pointed out that Allison et al. [18] employed a semiempirical method in which the calculated potential curve and the transition moment were adjusted in order to reproduce oscillator strength values and structural features consistent with the experimental results [14]. The theoretical results of Wang et al. [16], on the other hand, were obtained by fitting to their own measurements of the Schumann–Runge continuum region. They then reported potential curves and transition moments for the B $^3\Sigma_u^-$ and E $^3\Sigma_u^-$ mixed Rydberg–valence states, and also the 1 $^3\Pi_u$ valence state, which were obtained from the fitting procedures. Thus, although the existing theoretical absolute oscillator strength values for the Schumann–Runge continuum region appear to show good agreement with the present work, it should be remembered that both of these theoretical results depend for their success on experimental values.

Figs. 3a and 3b show expanded views of fig. 1 in

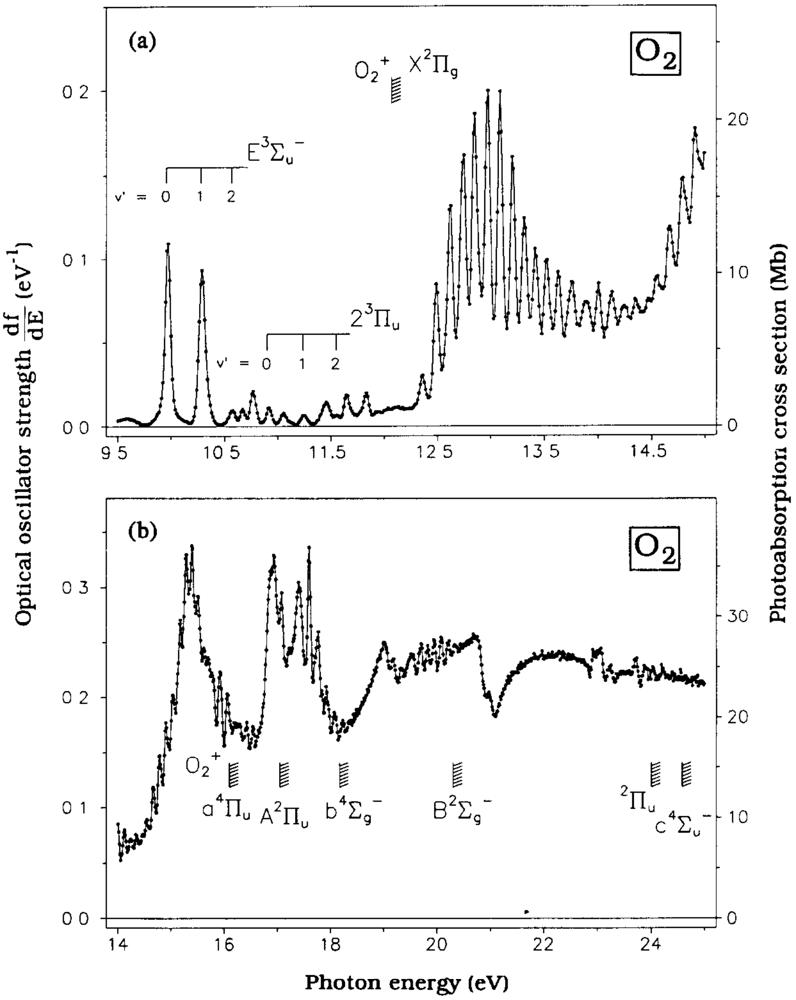

Fig. 3. Absolute oscillator strengths for the photoabsorption of molecular oxygen. The ionization potentials have been obtained from ref. [41]. (a) The energy region 9.5–15 eV. The assignments of the vibrational levels $v'=0$, 1 and 2 of the E $^3\Sigma_u^-$ and 2 $^3\Pi_u$ electronic states are taken from the theoretical work of Buenker et al. [20]. (b) The energy region 14–25 eV.

the energy regions 9.5–15 eV and 14–25 eV respectively. The ionization potentials for the states shown were obtained from the photoelectron work of Edqvist et al. [41]. The first ionization potential due to the ejection of an electron from the $1\pi_g$ orbital occurs at 12.071 eV. In fig. 3a several diffuse bands are observed in the energy region from 9.7 eV to just below the first ionization potential. Due to the diffuse nature of the peaks compared with the relatively narrow bandwidth that can be obtained in optical experiments in this energy region, absolute oscillator strengths (photoabsorption cross sections) for these diffuse bands that have been measured using the Beer–Lambert photoabsorption method are expected to be reasonably accurate [8,10,14,22,23]. The three prominent peaks at 9.96, 10.28 and 10.57 eV, corresponding to the longest, second and third bands respectively, have been assigned [19,20] as transitions to the vibrational levels $v'=0$, 1 and 2 of the mixed valence–Rydberg $E\,^3\Sigma_u^-$ state. The absolute oscillator strengths for the diffuse bands in the energy region 9.7–12.07 eV were determined in the present work and the results are summarized in table 1 along with previously available experimental [14,23,28] and theoretical [19,20,21] data. Column two in table 1 gives the energy regions over which integration was performed in order to obtain the absolute oscillator strength for each diffuse peak. The absolute oscillator strength values reported by Ogawa and Ogawa [14] were obtained by integrating their Beer–Lambert law photoabsorption data over the same energy regions. It can be seen from table 1 that the present results are consistent with the photoabsorption work of Ogawa and Ogawa [14]. The recent Beer–Lambert law photoabsorption work of Lewis et al. [23] for the second and third bands is also in good agreement with the present work and with that of Ogawa and Ogawa [14]. For the lowest ($E\,^3\Sigma_u^-$ ($v'=0$)) band, the data reported by Lewis et al. [22] are only for the energy region 9.95–9.98 eV compared with 9.75–10.17 eV for both the present work and that of Ogawa and Ogawa [14]. Hence the data of Lewis et al. [22] cannot be compared directly with the present work in this region. However, as demonstrated in

Table 1
Absolute optical oscillator strengths for the photoabsorption of molecular oxygen in the energy region 9.75–11.89 eV

| Assignment [a] | Energy range (eV) | Absolute optical oscillator strengths | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | experimental measurements | | | | theoretical calculations | | |
| | | electron impact based methods | | Beer–Lambert law photoabsorption methods | | Buenker et al. [20] | Yoshimine et al. [19] | Li et al. [21] |
| | | present work | Huebner et al. [28] | Lewis et al. [23] | Ogawa and Ogawa [14] | | | |
| $E\,^3\Sigma_u^-$, $v'=0$ | 9.75–10.17 | 0.00844 | 0.01024 | | 0.00833 | 0.0136 | 0.0103 | 0.01742 |
| 1 | 10.17–10.44 | 0.00759 | 0.00804 | 0.00705 [b] | 0.00706 | 0.0157 | 0.0124 | 0.00562 |
| 2 | 10.44–10.62 | 0.000827 | 0.00147 | 0.00078 | 0.000770 | 0.007 | 0.00412 | 0.00061 |
| | 10.62–10.71 | 0.000652 | 0.000650 | | 0.000660 | | | |
| | 10.71–10.84 | 0.00146 | 0.00242 | | 0.00140 | | | |
| $2\,^3\Pi_u$, $v'=0$ | 10.84–10.98 | 0.000814 | 0.000900 | | 0.000820 | 0.0009 | | |
| | 10.98–11.17 | 0.000733 | 0.00159 | | 0.000752 | | | |
| $2\,^3\Pi_u$, $v'=1$ | 11.17–11.33 | 0.000606 | 0.00110 | | 0.000497 | 0.0007 | | |
| | 11.33–11.52 | 0.00147 | 0.00210 | | | | | |
| $2\,^3\Pi_u$, $v'=2$ | 11.52–11.59 | 0.000419 | 0.000502 | | | 0.0006 | | |
| | 11.59–11.74 | 0.00169 | 0.00205 | | | | | |
| | 11.74–11.89 | 0.00174 | 0.00163 | | | | | |
| | 11.89–12.07 | 0.00169 | 0.00283 | | | | | |

[a] The assignments were taken from ref. [20].

[b] This value was obtained from the average of the integrated oscillator strengths for $O^{16}O^{18}$ and $^{18}O_2$ in the energy region 10.19–10.35 eV.

the work of Lewis et al. [22], their absolute cross sections in the limited energy region 9.95–9.98 eV are in excellent agreement with the measurements of Ogawa and Ogawa [14] and thus also with the present work. The electron impact based oscillator strength data reported by Huebner et al. [28] are in general higher than the present results and the data of Ogawa and Ogawa [14]. It should be noted that the accuracy of the Bethe–Born factor used by Huebner et al. [28] was not known over a wide energy range. In addition they employed an impact energy of only 100 eV to measure the energy loss spectrum and this is too low an impact energy to obtain a dipole-only spectrum (i.e. the momentum transfer $\boldsymbol{K}$ is too large). Several vibronic bands in the $X\,^3\Sigma_g^- \to \alpha\,^1\Sigma_u^+$ and $X\,^3\Sigma_g^- \to \beta\,^3\Sigma_u^+$ systems in the energy region 9.8–10.6 eV, which are dipole-forbidden transitions, were observed even in direct photoabsorption measurements [3,23]. The intensities of these dipole-forbidden peaks would be expected to be significantly higher in the electron energy loss spectrum of Huebner et al. [28], which would cause higher oscillator strength values for those energy regions involving dipole-forbidden peaks. The present work, using an impact energy of 3000 eV and zero degree scattering angle, does not suffer from this problem.

Ab initio configuration interaction theoretical methods have been used by three groups [19–21] to calculate the absolute oscillator strengths for the vibrational levels $v'=0$, 1 and 2 of the mixed valence–Rydberg $E\,^3\Sigma_u^-$ state. The theoretical calculations reported by Yoshimine et al. [19] and Buenker et al. [20], which assigned the longest, second and third bands as the vibrational levels $v'=0$, 1 and 2 of the mixed valence–Rydberg $E\,^3\Sigma_u^-$ state from the calculated energy levels, give oscillator strength values for these three bands which are much higher than the present and other experimental values. The recent work of Li et al. [21] shows better agreement with the present results for the $v'=1$ and 2 bands while the value reported by Li et al. [21] for $v'=0$ is even higher than that reported by Yoshimine et al. [19] and Buenker et al. [20]. Buenker et al. [20] also assigned three other peaks at energies of 10.90, 11.24 and 11.55 eV as the vibronic bands $v'=0$, 1 and 2 of the mixed valence–Rydberg $2\,^3\Pi_u$ state. The calculated [20] oscillator strengths for these three peaks are only slightly higher than the present results as seen in table 1. The electron impact data reported by Lassettre et al. [26] give an oscillator strength of 0.020 for the energy region 9.46–10.7 eV while the present estimate for the same energy range is 0.0185. The total oscillator strength sum up to the first ionization potential (12.07 eV) was determined to be 0.198 in the present work, which is exactly the same value as was reported by Huebner et al. [28]. However, it should be remembered that the oscillator strength sum below 9.46 eV reported by Huebner et al. [28] is slightly lower than that in the present work, while in the energy region 9.46–12.07 eV their reported value is slightly higher.

In the energy region 12–17 eV most of the bands in the photoabsorption spectrum of oxygen have not been classified, while from 17–25 eV there are many Rydberg series converging on the various ionization limits shown on fig. 3b. The energy positions and the assignments of these Rydberg states can be found in the critical compilation published by Krupenie [3]. Table 2 shows the present integrated oscillator strength values of selected energy intervals in the energy region 12.07–18.29 eV. The electron impact study by Huebner et al. [28] (which like the present work is free of "line saturation" effects) also reported integrated absolute oscillator strength values in the energy region 12.10–14.04 eV. These values [28], also shown in table 2, are in general somewhat higher than the present results. The absolute oscillator strength sum in the energy region 12.10–14.04 eV was estimated to be 0.181 by Huebner et al. [28], while the present result for the same energy region is 0.151. The value reported by Huebner et al. [28] is ≈ 20% higher than the present result which is consistent with the generally higher values reported by Huebner et al. [28] from 9.75–11.89 eV as seen in table 1. In the review paper of Hudson [2], it was pointed out that much of the Beer–Lambert photoabsorption cross section data for oxygen [42–44] in the energy region 12.10–20.66 eV is subject to bandwidth errors (or "line saturation" effects) and also systematic errors. Based on the photoabsorption data reported by Matsunaga and Watanabe [44], the absolute integrated oscillator strength in the energy region 12.07–16.53 eV was estimated to be 0.724 by Berkowitz [45]. However, we find that a reanalysis of the data of Matsunaga and Watanabe [44] gives an integrated absolute oscillator strength value of

Table 2
Integrated absolute optical oscillator strengths for the photoabsorption of molecular oxygen over intervals in the energy region 12.07–18.29 eV

| Energy range (eV) | Integrated absolute optical oscillator strengths | |
|---|---|---|
| | present work | Huebner et al. [28] |
| 12.070–12.240 | 0.00176 | 0.00182 |
| 12.240–12.412 | 0.00325 | 0.00379 |
| 12.412–12.538 | 0.00611 | 0.00725 |
| 12.538–12.673 | 0.0106 | 0.01176 |
| 12.673–12.794 | 0.0134 | 0.01483 |
| 12.794–12.915 | 0.0149 | 0.01724 |
| 12.915–13.026 | 0.0147 | 0.01641 |
| 13.026–13.152 | 0.0147 | 0.01567 |
| 13.152–13.263 | 0.0117 | 0.01390 |
| 13.263–13.369 | 0.00999 | 0.01186 |
| 13.369–13.476 | 0.00861 | 0.00987 |
| 13.476–13.577 | 0.00793 | 0.01033 |
| 13.577–13.684 | 0.00775 | 0.00952 |
| 13.684–13.814 | 0.00925 | 0.01166 |
| 13.814–13.954 | 0.00941 | 0.01424 |
| 13.954–14.056 | 0.00701 | 0.01027 |
| 14.056–14.181 | 0.00852 | |
| 14.181–14.302 | 0.00812 | |
| 14.302–14.408 | 0.00736 | |
| 14.408–14.488 | 0.00573 | |
| 14.488–14.603 | 0.00948 | |
| 14.603–14.728 | 0.0127 | |
| 14.728–14.853 | 0.0160 | |
| 14.853–14.978 | 0.0195 | |
| 14.978–15.092 | 0.0214 | |
| 15.092–15.217 | 0.0294 | |
| 15.217–15.332 | 0.0340 | |
| 15.332–15.472 | 0.0427 | |
| 15.472–15.587 | 0.0310 | |
| 15.587–15.862 | 0.0614 | |
| 15.862–16.006 | 0.0282 | |
| 16.006–16.151 | 0.0266 | |
| 16.151–16.351 | 0.0345 | |
| 16.351–16.481 | 0.0216 | |
| 16.481–16.581 | 0.0164 | |
| 16.581–17.171 | 0.147 | |
| 17.171–17.514 | 0.0897 | |
| 17.514–17.875 | 0.0882 | |
| 17.875–18.287 | 0.0740 | |

0.587. This value we have obtained by digitizing figs. 1 and 2 of ref. [44]. Alternatively we have obtained a value of 0.685 from the reported [44] numerical oscillator strength values in table 1 of ref. [44]. The difference occurs since the tabulated numerical values reported in the paper of Matsunaga and Watanabe [44] only include one third of their actual experimental data. Thus, insufficient data are given to obtain an accurate integration of the spectral area. Therefore, it would seem that Berkowitz [45] made use of the limited tabulated numerical values reported by Matsunaga and Watanabe [44] in order to obtain the integrated oscillator strength in the energy region 12.07–16.53 eV. The present dipole (e, e) work for the same region gives an integrated oscillator strength of 0.578, which agrees well with the presently revised value of 0.587 obtained by digitizing the data in figs. 1 and 2 reported by Matsunaga and Watanabe [44]. Digitizing the figures of other photoabsorption work reported by Huffman et al. [42] for the energy region 12.07–16.53 eV, an integrated oscillator strength of 0.685 was obtained, which is ≈20% higher than the value determined in the present work. This is again consistent with the work of Matsunaga and Watanabe [44] in which they state that the data of Huffman et al. [42] were 20–30% higher than their measured values in this energy region.

## 4. Conclusions

Absolute optical oscillator strengths for molecular oxygen have been measured by high resolution dipole (e, e) spectroscopy in the energy region 5–30 eV, which are free of "line saturation" (bandwidth) effects. Absolute optical oscillator strengths for the broad Schumann–Runge continuum region of oxygen determined in the present work are in excellent agreement with most previously reported experimental results. This gives considerable confidence in the accuracy of the previously determined Bethe–Born conversion factor for the high resolution dipole (e, e) spectrometer used in the present work, when extrapolated down to 7 eV. This in turn lends support to the accuracy of the absolute oscillator strengths previously reported for argon, krypton and xenon [32], hydrogen [34] and nitrogen [35] from this laboratory. The electron impact data reported by Huebner et al. [28] for oxygen are in general higher than the present work for the electronic transitions higher in energy than the Schumann–Runge continuum. This may be due to appreciable contributions from dipole forbidden transitions due to the low impact energy of 100 eV, or alternatively to inaccuracies in the Bethe–Born conversion factor employed by Huebner et al. [28].

For the diffuse discrete bands in the oxygen spectrum in the 9.7–12.071 eV energy region, the presently determined absolute oscillator strengths are in good agreement with the photoabsorption measurements of Ogawa and Ogawa [14]. The present work is also in good agreement with the integrated oscillator strength value reported by Matsunaga and Watanabe [44] in the energy region 12.07–16.53 eV. "Line saturation" effects which have caused severe difficulties in some of the direct Beer–Lambert law photoabsorption measurements in the valence discrete excitation regions of the electronic spectra of hydrogen [34] and nitrogen [35] are not found for the transitions studied in the present work in molecular oxygen. This is probably due to the generally broader nature of the transition peaks in the oxygen spectrum, in contrast to the situation for hydrogen and nitrogen (see refs. [34,35]). Such broadening is to be expected in oxygen above 12.07 eV (the first ionization potential) due to the short lifetimes of the rapidly autoionizing excited states associated with the higher ionization limits.

## Acknowledgement

Financial support for this project was provided by the Canadian National Networks of Centres of Excellence Programme (Centres of Excellence in Molecular and Interfacial Dynamics) and by the Natural Sciences and Engineering Research Council of Canada. One of us (WFC) gratefully acknowledges a University of British Columbia Graduate Fellowship.

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