IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet POx1

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$O_2 + h\upsilon \rightarrow$ products

Primary photochemical transitions

Reaction		$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$O_2 + h\nu \rightarrow O(^3P) + O(^3P)$	(1)	494	242
$\rightarrow O(^3P) + O(^1D)$	(2)	683	175
$\rightarrow O(^1D) + O(^1D)$	(3)	873	137
$\rightarrow O(^3P) + O(^1S)$	(4)	898	132

Absorption cross-section data

Wavelength range/nm	Reference	Comment
230-280 nm	Oshima, Okamoto and Koda, 1995[1]	(a)
240-270 nm	Yoshino *et al*., 1995[2]	(b)
205-240 nm	Yoshino *et al*., 1988[3]	(c)
242.2-244.2 nm	Slanger *et al*., 1996[4]	(d)
240-275 nm	Yoshino *et al*., 1999[5]; 2000[6]	(e)

Quantum yield data

Measurement	λ/nm	Reference	Comment
$\Phi[O(^1D)]$	130-175	Nee and Lee, 1997[7]	(f)
$\Phi[O(^3P), O(^1D)]$	159	Lin *et al.*, 1998[8]	(g)
$\Phi[O(^1D)]$	121.2-121.9	Lacoursière *et al*., 1999[9]	(h)

Comments

(a) The effect of pressurized foreign gases on the photoabsorption of O_2 in the Herzberg bands and Herzberg continuum (230-280 nm) was studied. The values of the cross-sections in O_2 and O_2/N_2 mixtures under various pressures were in good agreement with the previous literature.

(b) High resolution FT spectrometry (0.06 cm^{-1}) was used to measure photoabsorption cross-sections of O_2 in the Herzberg I bands (240-270 nm). Precise band oscillator strengths of the (4,0)-(11,0) bands were obtained, which were significantly higher than previous experimental values.

(c) Analysis and combination of data of Cheung *et al*.[10] and Jenouvrier *et al*.[11]

(d) Cavity ring down (CRD) spectroscopy of O_2 in the 40950-41300 cm^{-1} region. Five new bands were observed in addition to many weak lines in the previously observed $\left(A^3\Sigma_u^+ - X^3\Sigma_g^-\right)$ 11-0 band. Intensities given.

(e) FT spectroscopic absorption measurements of the Herzberg II $\left(c^{'}\Sigma_u^- - X^3\Sigma_g^-\right)$ and Herzberg III $\left(A^{'3}\Delta_u - X^3\Sigma_g^-\right)$ bands at 295 K with resolution of 0.06 cm^{-1}. Precise band oscillator strengths obtained by summing the cross sections of individual rotational lines.

(f) $O(^1D)$ produced by O_2 photodissociation in the Schumann-Runge continuum and monitored by fluorescence from $\left(b^{'}\Sigma_g^+\right)$ produced by $O(^1D) + O_2$ reaction. $\Phi[O(^1D)] = 1$ for $139 < \lambda/nm < 175$. At 130-139 nm, $\Phi < 1$, arising from upper state crossing; at $\lambda > 175$ nm $\Phi > 0$ due to rotational energy contribution.

(g) Photodissociation of O_2 at 157 nm by photofragmentation translational spectroscopy. Both energetically available channels (1) and (2) observed.

(h) Tunable laser photolysis of O_2 at spectral resolution of 1 cm^{-1} (1.5 x 10^{-3} nm) $O(^1D)$ yield in the envelope of the H-Lyman $\propto$ feature measure following the emission from O_2 $\left(b^{'}\Sigma_g^+\right)$ at 762 nm produced by the quenching of O('D) by O_2. $\Phi(^1D)$ was strongly wavelength dependent: 1.0 at 121.35 nm decreasing to a minimum of 0.48 near 121.62 nm. Strong temperature dependence found, the minimum yield at 121.62 nm was 0.28 at 84 K.

Preferred Values

Absorption cross-section of O_2 in the 205-240 nm region of the Herzberg continuum

λ/nm	10^{24} σ/cm^2	λ/nm	10^{24}σ/cm^2
205	7.35	223	3.89
207	7.05	225	3.45
209	6.68	227	2.98
211	6.24	229	2.63
213	5.89	231	2.25
215	5.59	233	1.94
217	5.13	235	1.63
219	4.64	237	1.34
221	4.26	239	1.10
		240	1.01

Quantum Yields

$\Phi_1 = 1$ for $242 > \lambda > 175$ nm

$\Phi_2 = 1$ for $175 > \lambda > 139$ nm

$\Phi_2 = 0.44$ for $\lambda = 121.6$ nm

Comments on Preferred Values

The recommended absorption cross-section values for the Herzberg continuum are taken from the study of Yoshino *et al*.,[3] where values are tabulated for every nm from 205-240 nm. These

values were derived from an analysis and combination of the data of Cheung *et al*.[10] and Jenouvrier *et al*.[11] These data are in agreement with the results of Johnston *et al*.,[12] and are consistent with the lower absorption cross-section values inferred from balloon-borne measurements of solar irradiance attenuation in the stratosphere by Frederick and Mentall,[13] Herman and Mentall[14] and Anderson and Hall.[15] Herzberg continuum cross-section values under the S-R bands (< 200 nm) have been determined more accurately by Yoshino *et al*.[16] and are significantly smaller than any previous values. The data from Oshima *et al*.[1], Yoshino *et al*.[2], Slanger *et al*.[4] and Yoshino *et al*.[5,6] relate to the Herzberg bound system in the region beyond the photodissociation threshold for O_2, and do not affect the preferred cross-sections for the photolysis of atmospheric O_2.

In the Schumann-Runge wavelength region (175-200 nm), a detailed analysis of the penetration of solar radiation requires absorption cross-section measurements with very high spectral resolution. Absorption cross-section values for the (0, 0)-(12, 0) S-R bands measured by the Harvard-Smithsonian group[17-25] are the first set of values which are independent of instrumental resolution. Band oscillator strengths for these bands have been determined by direct numerical integration of these absolute cross-section values. Minschwaner *et al*.[26,27] have fitted O_2 cross-sections for the frequency range 49000-57000 cm^{-1} (175-204 nm) with temperature-dependent polynomial expressions for the temperature range 130-500 K using the latest laboratory spectroscopic data. This model provides an efficient and accurate means of determining S-R band absorption cross- sections at 0.5 cm^{-1} resolution. These high resolution calculated values differ from the WMO[28] recommendations by up to 10-20% at some wavelengths. Mean-band parameterizations of O_2 absorption in the S-R bands for calculating UV transmission and photolysis rates have been presented by Murtagh[29] and by Nicolet and Kennes.[30]

The effect on ozone formation in the 214 nm photolysis of oxygen due to O_2 - O_2 collision pairs at high O_2 pressure and the effect of high N_2 pressure has been studied by Horowitz *et al*.[31] Greenblatt *et al*.[32] studied the absorption spectrum of O_2 and O_2 - O_2 collision pairs over the wavelength range 330 - 1140 nm for O_2 pressures from 1 to 55 bar at 298 K. Band centers, band widths, and absorption cross-sections were reported for the absorption features in this wavelength region.[33]

At $\lambda < 242$ nm O_2 dissociates with unit quantum efficiency. Below the threshold for O('D) production (reaction (2)) two ground state O atoms are produced, but above this wavelength both O(^{3}P) and O('D) are produced.[8] The work of Nee and Lee[7] showed that $\Phi(2) = 1$ in the range 175-139 nm based on measuement of O('D) production. This work also confirmed that Φ(O'D) showed sharp variations at shorter wavelengths as observed in earlier work by Lee *et al*.[34], who also reported a value of $\Phi(2) = 0.44 \pm 0.05$ for absorption of Lyman $\propto$ at 121.6 nm. A detailed study[9] of O('D) production over the entire H Lyman $\propto$ profile using a tunable VUV laser source has confirmed that a strong wavelength dependence of O('D) exists in this region.

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