

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet PNOx4

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NO₂ + hv → products

Primary photochemical transitions

Reaction		$\Delta H^\circ/\text{kJ mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
NO ₂ + hv → NO + O(³ P)	(1)	301	398
→ NO + O(¹ D)	(2)	490	244

Absorption cross-section data

Wavelength range/nm	Reference	Comments
300-500	Merienne, Jenouvrier, and Coquart, 1995 ¹	(a)
400-500	Coquart, Jenouvrier, and Merienne, 1995 ²	(b)
380-830	Vandaele <i>et al.</i> , 1996 ³	(c)
200-300	Jenouvrier, Coquart, and Merienne, 1996 ⁴	(d)
350-585	Harder <i>et al.</i> , 1997 ⁵	(e)
360-470	Yoshino, Esmond, and Parkinson, 1997 ⁶	(f)
200-400	Merienne <i>et al.</i> , 1997 ⁷	(g)
238-1000	Vandaele <i>et al.</i> , 1998 ⁸	(h)
231-794	Burrows <i>et al.</i> , 1998 ⁹	(i)

Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
ϕ_1	295-445	Jones and Bayes, 1973 ¹⁰	(j)
ϕ_1	375-420	Harker, Ho, and Ratto, 1977 ¹¹	(k)
ϕ_1	390-420	Davenport, 1978 ¹²	(l)
ϕ_1	334-404	Gardner, Sperry, and Calvert, 1987 ¹³	(m)
ϕ_1	388-411	Roehl <i>et al.</i> , 1994 ¹⁴	(n)

Comments

- (a) Cross-sections were measured at 293 ± 0.3 K with NO_2 concentrations of $(3-9) \times 10^{14}$ molecule cm^{-3} . A conventional spectrometer was used with a multipass cell giving a total path length of 60.7 m. The spectral bandwidths were < 0.01 nm at $\lambda > 400$ nm and < 0.15 at $\lambda < 400$ nm. Cross-sections were measured at 0.01 nm intervals with a wavelength accuracy of 0.01 nm. Corrections were made for the presence of N_2O_4 and for adsorption on the cell walls. Averaged cross-sections over 5 nm intervals were given for the range 305-425 nm.
- (b) Technique as in (a). Data were obtained at 0.01 nm intervals at 220 and 240 K. Averaged data are also given at 1 nm intervals at 293, 240 and 220 K over the range 400-500 nm. Features in the spectrum sharpen with decrease in temperature but there are no significant changes in the cross-sections at this resolution.
- (c) Cross-sections were measured at 293 K with dilute NO_2 - O_2 mixtures at a total pressure of 1 bar in a cell of 5.15 cm path length. A Bruker FT spectrometer was used and spectra were measured at resolutions of 0.02 nm and 0.3 nm. Effects of NO_2 adsorption on cell walls and of N_2O_4 formation were checked and corrections made.
- (d) Technique as in (a). Data were obtained at 293 K, at NO_2 concentrations of $(0.4-1.5) \times 10^{14}$ molecules cm^{-3} . Measurements were made at 0.01 nm intervals at bandwidths in the range 0.016-0.065 nm.
- (e) Cross-sections of 84.1 ppmv mixtures of $\text{NO}_2/\text{N}_2\text{O}_4$ in air at total pressures in the range 0.13-0.79 bar were measured at 217 K, 230 K, 239 K and 294 K using a FT spectrometer employing path lengths of 418.2 cm and 1220.6 cm and having a resolution of 0.15 cm^{-1} . Corrections for absorption by N_2O_4 were made using literature values of the equilibrium constant and values obtained in this study. The data are compared with data from other studies and a detailed analysis of potential sources of instrumental error is given.
- (f) Cross-sections were measured at 293 K using a conventional vacuum grating spectrometer with a resolution of 0.003 nm and optical path length of 42.3 cm. Measurements were made at several NO_2 pressures and the values extrapolated to zero pressure to obtain the cross-section at each wavelength. Results agree extremely closely with those of Merienne *et al.*¹
- (g) This study is an extension of the low temperature measurements of Coquart *et al.*² into the 200-300 nm wavelength range. The technique was as in (b) but measurements were made only at 220 K, the optical path length was reduced to 20.8 m, and measurements were made at several pressures of $\text{NO}_2/\text{N}_2\text{O}_4$ in the range 0.0026-0.098 mbar to allow corrections to be made for N_2O_4 absorption.
- (h) This study combines the high resolution FT technique of Vandaele *et al.*³ (Comment c) with the long path cell technique of Merienne *et al.*^{1,2,4,7} (Comments a, b, d, g). Cross-sections were measured at 294 K over the pressure range 0.013-1.3 mbar and at 220 K over the pressure range 0.009-1.3 mbar. Measurements were made using a Bruker FT spectrometer equipped with a multi-pass cell having a path length of 60 m and at a resolution of 2 cm^{-1} . At 294 K contributions from N_2O_4 absorption are less than 0.1% but at 220 K measurements were made over a range of pressures to correct for the N_2O_4 contribution. A significant pressure effect was observed in the visible at both temperatures but it may also be present in other spectral regions since only low pressures were used. Careful comparisons were made with a number of other studies.
- (i) Relative cross-sections of NO_2 -air mixtures were measured at temperatures of 221 K, 241 K, 273 K, and 293 K using a four-channel Si-diode array spectrometer at a resolution of 0.2 nm below 405 nm and about 0.3 nm above 405 nm. The optical path length was varied between 985 cm and 1465 cm. Relative cross-sections were put on an absolute basis by measuring the spectrum at 293 K on a Bruker FT spectrometer over the range 400-550 nm. Corrections for

N_2O_4 were made by measurements made at several NO_2 partial pressures. Comparisons are made with several other studies.

- (j) Relative quantum yields for NO production were measured using mass-spectrometric detection of the NO, and were normalized to literature values at 313 nm and 366 nm. Measurements were made at 5 or 10 nm intervals in the range 295-445 nm and at 492 nm, 546 nm, and 579 nm.
- (k) Quantum yield for NO_2 photodissociation by pulsed dye laser measured at 1 nm intervals. The change in $[\text{NO}_2]$ was obtained by absorption spectroscopy using absorption cross-sections measured in the same study. The absorbed quanta were calculated from measurements of the light intensity with joulemeters calibrated by ferrioxalate actinometry.
- (l) Quantum yield for NO production measured relative to NO production from NOCl photolysis at six wavelengths for $T = 300$ K and 223 K.
- (m) The primary quantum yield, ϕ_1 , was derived from measurements of (1) quantum yield of NO_2 loss (optical absorption), (2) quantum yield of NO formation (mass spectrometry), (3) quantum yield of O_2 formation (mass spectrometry). Light intensity was measured by NOCl actinometry. ϕ_1 was found to be close to unity for wavelengths less than 395 nm. At 404 nm measurements were also made for 273 K to 370 K. The results were found to be in qualitative agreement with the simple theory that for $\lambda > 395$ nm the energy deficiency for dissociation is made up from internal rotational and vibrational energy of the NO_2 molecules. On the basis of later experiments in the same laboratory by Calvert *et al.*¹⁵ in which the absorption cross-section at 404.7 nm was measured from 273 K to 370 K, the authors concluded that vibrationally excited molecules absorb more strongly than the unexcited molecules. They were thereby able to derive a reasonable fit to the variation of primary quantum yield with temperature for photodecomposition in the energy-deficient region at 404.7 nm.
- (n) The quantum yield for NO production from dye laser photodissociation of NO_2 was measured at 248 K and 298 K relative to NO production from NOCl photolysis. Quantum yields were measured at high resolution (0.001 nm).

Preferred Values

Absorption cross-sections of NO₂ at 298 K and 220 K.

λ/nm	$10^{20}\sigma/\text{cm}^2$		λ/nm	$10^{20}\sigma/\text{cm}^2$		λ/nm	$10^{20}\sigma/\text{cm}^2$	
	298 K	220 K		298 K	220 K		298 K	220 K
205	33.81	34.29	305	16.04	15.85	405	57.68	56.17
210	44.51	42.46	310	18.82	18.70	410	61.53	60.82
215	48.87	45.80	315	21.64	21.96	415	58.92	57.53
220	46.72	44.03	320	25.42	24.94	420	59.50	58.43
225	39.04	36.96	325	28.79	27.53	425	56.70	55.22
230	27.65	26.11	330	31.88	29.82	430	54.04	52.95
235	16.53	14.57	335	35.87	33.62	435	55.54	55.09
240	8.30	7.54	340	40.20	37.81	440	48.42	47.33
245	3.75	3.29	345	41.75	39.11	445	48.84	47.77
250	1.46	1.14	350	46.10	43.71	450	48.13	48.61
255	1.09	0.84	355	49.82	47.55	455	41.24	39.68
260	1.54	1.04	360	50.77	49.24	460	42.97	42.76
265	2.18	1.96	365	55.01	54.18	465	40.87	40.54
270	2.92	3.00	370	56.07	55.93	470	33.56	31.97
275	4.06	4.16	375	58.88	58.96	475	38.49	37.95
280	5.27	5.33	380	59.24	58.33	480	33.44	32.52
285	6.82	6.73	385	59.42	58.97	485	25.18	23.33
290	8.64	8.79	390	62.00	62.20	490	30.74	30.17
295	10.64	10.64	395	59.20	58.01	495	29.30	28.63
300	12.99	12.82	400	63.85	63.20			

Quantum Yields at 298 K and 248 K

λ/nm	ϕ		λ/nm	ϕ	
	298 K	248 K		298 K	248 K
300-398	1.00	1.00	407	0.26	0.18
399	0.95	0.94	408	0.22	0.14
400	0.88	0.86	409	0.18	0.12
401	0.75	0.69	410	0.15	0.10
402	0.62	0.56	411	0.13	0.08
403	0.53	0.44	412	0.11	0.07
404	0.44	0.34	413	0.09	0.06
405	0.37	0.28	414	0.08	0.04
406	0.30	0.22	415	0.06	0.03

Comments on Preferred Values

Since our previous evaluation, IUPAC, 1997,¹⁶ there have been several studies, mostly at high resolution, of the NO₂ spectrum at temperatures ranging from 298 K to 220 K.³⁻⁹ The most extensive study is that of Vandaele *et al.*⁸ covering the wavelength range 238-1000 nm at 220 K and 294 K. It is in excellent agreement with a number of other high resolution studies. At temperatures close to 298 K the data of Vandaele *et al.*,^{3,8} Merienne *et al.*,¹ and Yoshino *et al.*⁶ all lie within $\pm 2\%$ over most of the wavelength range covered by their measurements. All of

the studies appear to be less reliable at the extremes of the wavelength range covered by each of them but there is sufficient overlap for this group of studies to provide a set of reliable cross-section data for the range 300-600 nm. The study of Burrows *et al.*⁹ also gives values within ~2% of these studies and provides reliable medium resolution data for the 300-600 nm range. At shorter wavelengths (200-300 nm) there are studies of Bass *et al.*¹⁷ Jenouvrier *et al.*,⁴ Merienne *et al.*,⁷ and Schneider *et al.*¹⁸ The studies of Jenouvrier *et al.*⁴ and Merienne *et al.*⁷ are in excellent agreement with the high resolution studies at longer wavelengths where they overlap and are preferred for the 200-300 nm range. There are uncertainties in the wavelength calibration of Schneider *et al.*¹⁸ but the older data of Bass *et al.*¹⁷ are in reasonable agreement. Our recommended values for cross-sections are those given in the studies just described¹⁻⁹ and are preferred to those in the older studies of Schneider *et al.*,¹⁸ Harwood and Jones,¹⁹ and Davidson *et al.*²⁰ which were the basis of our previous recommendations, IUPAC, 1997.¹⁶ The recommended spectra are too detailed for cross-sections for an extensive listing here but 5 nm averaged cross-sections are given, taken from the studies of Mérienne *et al.*^{1,7} Coquart *et al.*² and Jenouvrier *et al.*⁴ These studies^{1,2,4,7} suffer a little from undersampling at high resolution but are in good agreement with the recommended high resolution studies. For more detailed spectra the original papers¹⁻⁹ should be consulted; in most cases detailed spectra are available from the authors.

Studies at temperatures down to 220 K^{2,5,7,8,19} have shown that the effect of lowering the temperature is to increase the sharpness of the structural features of the spectrum. There are no shifts in wavelength observed and those reported by Schneider *et al.*¹⁸ and Davidson *et al.*,²⁰ may have been due to small calibration errors. At 220 K the data of Vandaele *et al.*,⁸ Coquart *et al.*,² and Merienne *et al.*⁷ agree to within ~ 2.5% in the regions where they overlap. The data of Harder *et al.*⁵ are in good agreement with these other studies over most of their wavelength range but show large deviations at longer wavelengths (> 500 nm). The data of Harwood and Jones¹⁹ are lower by between 5% and 10 % over most of their range but up to 20% lower at long wavelengths.

A significant pressure effect on the spectrum has also been observed in pure NO₂ (0.026-1.3 mbar)⁸ and in highly dilute NO₂/N₂ mixtures (6.6-790 mbar).⁵ The publications of Vandaele *et al.*⁸ and Harder *et al.*⁵ should be consulted for details.

The preferred values of the quantum yields in our previous evaluation, IUPAC, 1997,¹⁶ were those derived by Gardner *et al.*¹³ based on their own data and a critical assessment of the earlier studies of Jones and Bayes,¹⁰ Davenport,¹² and Harker *et al.*¹¹ The measurements of Roehl *et al.*¹⁴ are in agreement with these recommendations. Since these studies Troe²¹ has corrected the values of Gardner *et al.*¹³ and Roehl *et al.*¹⁴ for small, but significant effects of secondary reactions and fluctuations of the specific rate constant. The values presented by Troe²¹ are adopted as our preferred values.

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