

All data taken at Pacific Northwest National Laboratory (PNNL)

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Composite spectrum for NO₂_25T

Effective burden of composite spectrum: 1 part-per-million-meter (ppm-meter) at 296 K

Equivalent concentration x path-length of composite spectrum: 1.8941x10⁻⁶ grams/liter-meter

Sample produced by injection of liquid N₂O₄, kept at -2.3° C. Syringe is temperature stabilized by placing in a thermostatic jacket. Sample impurities include NOCl [0.48%], NO [0.33%], HNO₃ [0.15%] and H₂O [0.13%]. Partial pressures of individual NO₂ samples corrected to reflect equilibrium between monomer (NO₂) and dimer (N₂O₄) at temperature of sample. See H. K. Roscoe and A. K. Hind, J. of Atmospheric Chemistry **16**, pp 257-276 (1993). Composite spectrum rescaled to reflect impurities.

Sample Conditions-

- Chemical name and CAS number: Nitrogen dioxide, nitrogen peroxide, NO₂: [10102-44-0]
- Physical properties: M.W. 46.0055 amu, F.P. -11° C, B.P. 21.2° C, Density (-2.3° C) 1.518 g/cm³
- Supplier and stated purity: Matheson, 99.5+%
- Sample class: I (PNNL scale).
- Temperature of White cell (815.76 cm optical path length) 25 ± 2 C
- Diluent (high purity nitrogen) flowed at 25.20 liter/min (21.1° C), ambient atmospheric pressure 760 ± 5 Torr.
- Samples flowed at 2.000, 1.000, 0.500, 2.000, 5.000, 10.000, 1.000, 0.100, 0.250, 25.000, 0.500, 0.100, 0.300, 0.400 and 0.600 microliters/minute
- Individual samples at equivalent pressures of 0.047580, 0.023801, 0.011903, 0.047314, 0.118303, 0.236357, 0.023687, 0.002370, 0.005930, 0.590031, 0.011873, 0.002372, 0.007132, 0.009511 and 0.014266 Torr. Final data is a composite spectrum.
- Preparation: Condensation and purification via multiple freeze-thaw cycles. Liquid N₂O₄ kept at 0° C during storage.

Instrument Parameters-

- Bruker-66V FTIR, evacuated optics bench.
- Modified to include second aperture, between interferometer output and White cell. This substantially reduces both “ghosting” and warm aperture effects.
- Spectral range: 6,500 to 600 cm⁻¹ (1.538 to 16.667 microns)
- Cell windows: Silver chloride (AgCl)
- Instrumental resolution based on maximum interferometer displacement is 0.112 cm⁻¹
- Spectral interval after 2X zero-filling interferogram and FFT: 0.06 cm⁻¹
- Interferogram zero-fill: 2X
- Apodization: Boxcar
- Phase correction: Mertz
- Beam splitter: Potassium bromide (KBr)
- IR source: Carbide glowbar (22 V)
- Scanner velocity: 60KHz (HeNe crossing frequency)
- Number of interferograms averaged per single channel spectra: 256
- Detector: Mid-band HgCdTe, photoconductive, 77K operation

- Folding limits: 15798 to 0 cm^{-1}

Post Processing and Related Parameters-

- Non-linearity detector correction (Bruker proprietary) applied to interferogram ($\alpha=0.90$, $\epsilon=500$)
- Composite spectrum created from 15 individual absorbance (base-10) spectra via classical least squares fit: Intercept=0, slope is fitted, individual absorbance values weighted by T^2 (transmission squared), all absorbance values ≥ 1.6 are given zero weight
- Calculated and estimated errors: Type A = 1.11%, Type B $\leq 7\%$
- Frequency correction (already applied): $V(\text{corrected}) = V(\text{instrument}) * 0.9999965 + 2.87506e-3$
- Axis units: X=wavenumbers (cm^{-1}), Y=Absorbance (base-10)
- Baseline correction via 7th order polynomial subtraction
- Due to large amount of dimer, the 25° C composite spectrum has been rescaled to match that of the 50° C composite spectrum. Specifically, the integrated area under the 1498-1685 cm^{-1} band has been normalized to 1457.33 $\text{cm}^{-2} \text{atm}^{-1}$ (base-e).