

All data taken at Pacific Northwest National Laboratory (PNNL)
Operator: Steven W. Sharpe, sw.sharpe@pnl.gov
Version 1.0, January, 2000

Composite spectrum for NO₂_5T

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

Sample Conditions-

- Chemical name and CAS number: Nitrogen dioxide, NO₂ : [10102-44-0]
- Physical properties: M.W. 46 amu, F.P. -11 C, B.P. 21.1 C
- Supplier and stated purity: Matheson., 99.5%
- Sample class: III (PNNL scale).
- Temperature of sample: 24.98 ± 0.02 C
- Diluent: Sample back filled with ultra high purity nitrogen to 760±5 Torr
- Individual samples 0.943659, 0.720366, 1.274446, 2.399003, 6.829579, 14.551040 and 24.026615 Torr (corrected pressure). Path length = 19.96 cm. Final data is a composite spectrum.
- Preparation: Multiple freeze-thaw cycles at 77K to remove air.

Instrument Parameters-

- Bruker-66V FTIR, temperature controlled environment, evacuated optics bench
- Spectral range: 6,500 to 600 cm⁻¹ (1.534 to 16.667 microns)
- Instrumental resolution (interferogram): 0.112 cm⁻¹
- Spectral intervals after 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: 9 (Bruker arbitrary)
- 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 ($\alpha = 0.85$, $\beta = 530$)
- Composite spectrum created from 10 individual absorbance (base-10) spectra via classical least squares fit: Intercept=0, slope is fitted, individual absorbance values weighted by T² (transmission squared), all absorbance values > 1.6 are given zero weight
- Calculated and estimated errors: Type A = 8.5%, Type B = 10%
- Frequency correction: $V(\text{corrected}) = V(\text{instrument}) * 0.9999984669 + 0.005187$
- Axis units: X=wavenumbers (cm⁻¹), Y=Absorbance (base-10)
- Trace water and nitric oxide removed by spectral subtraction
- 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).

- Dimer (N_2O_4) features are at arbitrary concentration. By comparing NO_2 spectra at different temperatures it is possible to recognize the dimer (N_2O_4) features as these will increase at lower temperature and decrease at higher temperature.