

All data taken at Pacific Northwest National Laboratory (PNNL)  
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Composite spectrum for HNO<sub>3</sub>\_5T

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

Equivalent concentration x path-length of composite spectrum: 3.668x10<sup>-6</sup> grams/liter-meter

Cell windows replaced with unwedged BaF<sub>2</sub> windows to avoid reaction with sample. Unwedged windows produce fringing that will often increase apparent noise in spectra. In addition, BaF<sub>2</sub> windows limit spectral region to ~700 cm<sup>-1</sup>. Individual absorbance spectra corrected and accounted for H<sub>2</sub>O, CO<sub>2</sub>, NO, NO<sub>2</sub>, N<sub>2</sub>O and HCl contamination.

### Sample Conditions-

- Chemical name and CAS number: Nitric acid, HNO<sub>3</sub> : [7697-37-2]
- Physical properties: fw=63.0128 g/mole, fp=-428° C, bp=83° C
- Supplier and stated purity: Home made via KNO<sub>3</sub> + H<sub>2</sub>SO<sub>4</sub>
- Sample class: III (PNNL scale). Extremely reactive. Undergoes rapid decomposition when exposed to heat and reducing agents (*e.g.*, metals, organics,...).
- Temperature of sample: 5.05 ± 0.02 C
- Diluent: Sample back filled with ultra high purity nitrogen to 760±5 Torr
- Individual samples at 1.166, 0.367, 5.4415, 2.278, 0.830, 3.242 and 1.694 Torr. Path length = 19.96 cm. Final data is a composite spectrum.
- Preparation: Multiple freeze-thaw cycles at -80 C to remove air and NO<sub>2</sub>.

### Instrument Parameters-

- Bruker-66V FTIR, temperature controlled environment, evacuated optics bench
- Modified to include second aperture, between interferometer output and sample cell. This substantially reduces both “ghosting” and warm aperture effects.
- Spectral range: 6,500 to 720 cm<sup>-1</sup> (1.534 to 13.889 microns)
- Instrumental resolution based on maximum interferometer displacement is 0.112 cm<sup>-1</sup>
- Spectral interval after 2X zero-filling interferogram and FFT: 0.06 cm<sup>-1</sup>
- 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<sup>-1</sup>

### Post Processing and Related Parameters-

- Non-linearity detector correction (Bruker proprietary) applied to interferogram ( =0.90, =500)
- Composite spectrum created from 7 individual absorbance (base-10) spectra via classical least squares fit: Intercept=0, slope is fitted, individual absorbance values weighted by T<sup>2</sup> (transmission squared), all absorbance values > 1.6 are given zero weight
- Calculated and estimated errors: Type A = 2.5%, Type B “Best effort”
- Frequency correction (already applied): V(corrected) = V(instrument)\*0.999998+1.287x10<sup>-4</sup>

- Axis units: X=wavenumbers ( $\text{cm}^{-1}$ ), Y=Absorbance (base-10)
- Small amounts of  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{N}_2\text{O}$  and  $\text{HCl}$  features removed via spectral subtraction. Residual from subtraction is still observable in composite spectrum.
- Baseline correction via 7<sup>th</sup> order polynomial subtraction