

All data taken at Pacific Northwest National Laboratory (PNNL)

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Composite spectrum for HF_5T

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

Equivalent concentration x path-length of composite spectrum: 8.237×10^{-7} grams/liter-meter

Cell windows replaced with unwedged BaF₂ windows to avoid reaction with sample. Unwedged windows produce fringing that will often increase apparent noise in spectra. In addition, BaF₂ windows limit spectral region to $\sim 700 \text{ cm}^{-1}$.

Sample Conditions-

- Chemical name and CAS number: Hydrogen fluoride, etching acid, HF A, fluoric acid, Antisal 2B, fluorohydric acid, HF : [7664-39-3]
- Physical properties: fw=20.006 g/mole, fp=-83.55° C, bp=19.5° C
- Supplier and stated purity: Matheson, 99.9% (!?). Contains approximately 0.83% SiF₄
- Sample class: III (PNNL scale). Extremely reactive/corrosive, narrow absorbance features
- Temperature of sample: $4.96 \pm 0.02 \text{ C}$
- Diluent: Sample back filled with ultra high purity nitrogen to $760 \pm 5 \text{ Torr}$
- Individual samples at 0.1075, 0.2622, 0.3560, 0.1595, 0.4470, 0.2121 and 0.7200 Torr. Path length = 19.96 cm. Final data is a composite spectrum.
- Preparation: Multiple freeze-thaw cycles at 77 K to remove air.

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: $6,500 \text{ to } 900 \text{ cm}^{-1}$ (1.534 to 11.111 microns)
- 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: $15798 \text{ to } 0 \text{ cm}^{-1}$

Post Processing and Related Parameters-

- Non-linearity detector correction (Bruker proprietary) applied to interferogram ($\tau = 0.90$, $\tau = 500$)
- 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^2 (transmission squared), all absorbance values > 1.6 are given zero weight
- Calculated and estimated errors: Type A = 2.6%, Type B = 10%
- Frequency correction (already applied): $V(\text{corrected}) = V(\text{instrument}) * 0.999998 + 1.287 \times 10^{-4}$
- Axis units: X=wavenumbers (cm^{-1}), Y=Absorbance (base-10)

- Trace carbon dioxide, HCl and SiF₄ features removed via spectral subtraction
- Baseline correction via 7th order polynomial subtraction