

All data taken at Pacific Northwest National Laboratory (PNNL)

Operators: Steven W. Sharpe, Timothy J. Johnson and Robert L. Sams : sw.sharpe@pnl.gov

Version 1.0, February, 03

Both H₂O (20.6%) and D₂O (31.4%) spectral features removed by spectral subtraction and the composite spectrum rescaled to account for partial pressures of H₂O and D₂O.

Composite spectrum for HDO_25T

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

Equivalent concentration x path-length of composite spectrum: 7.8312x10⁻⁷ grams/liter-meter

Sample Conditions-

- Chemical name and CAS number: Water-d1, HDO, HOD, DOH : [14940-63-7]
- Physical properties: M.W. 19.0213 amu, F.P. na, B.P. na, Density (estimated, 20 C) 1.053 g/cm³
- Supplier and stated purity: Made by mixing equal volumes of H₂O and D₂O, ~50%
- Sample class: I (PNNL scale).
- Temperature of White cell (792.0 cm optical path length) 25 ± 2 C
- Diluent (high purity nitrogen) flowed at 24.90 liter/min (296 K), ambient atmospheric pressure 770 ± 5 Torr.
- Samples flowed at 20.000, 1.000, 5.000, 2.000, 10.000, 50.000, 0.500, 75.000, 3.000, 7.000 and 15.000 microliters/minute
- Individual samples at equivalent pressures of 0.811122, 0.040524, 0.202861, 0.081091, 0.405293, 2.039877, 0.020407, 3.061024, 0.122441, 0.285771 and 0.612044 Torr. Final data is a composite spectrum.
- Preparation: None

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: 7,500 to 550 cm⁻¹ (1.333 to 18.1818 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 to 0 cm⁻¹

Post Processing and Related Parameters-

- Non-linearity detector correction (Bruker proprietary) applied to interferogram (=0.90, =500)
- Composite spectrum created from 11 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 = 0.83%, Type B = 7%
- Frequency correction (already applied): $V(\text{corrected}) = V(\text{instrument}) * 0.999998 + 1.566836e-04$
- Axis units: X=wavenumbers (cm^{-1}), Y=Absorbance (base-10)
- Baseline correction via 7th order polynomial subtraction