

All data taken at Pacific Northwest National Laboratory (PNNL)  
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Composite spectrum for AcetCl\_25T

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

Equivalent concentration x path-length of composite spectrum:  $3.232 \times 10^{-6}$  grams/liter-meter

### Sample Conditions-

- Chemical name and CAS number: Acetyl chloride, ethanoyl chloride,  $\text{CH}_3\text{COCl}$  : [75-36-5]
- Physical properties: M.W. 78.50 amu, F.P.  $-112$  C, B.P.  $52$  C
- Supplier and stated purity: Aldrich, 99+%
- Sample class: III (PNNL scale). Sample exhibited decomposition (hydrolysis) to acetic acid and HCl. Partial pressures corrected ( $\sim 0.3\%$ ) to reflect decomposition products.
- Temperature of sample:  $25.02 \pm 0.02$  C
- Diluent: Sample back filled with ultra high purity nitrogen to  $760 \pm 5$  Torr
- Individual samples at 1.16345, 1.05784, 2.1165, 6.4344, 10.9186, 1.8642, 0.73583, 4.3555, 20.815 and 43.13 Torr. Path length = 19.96 cm. Final data is a composite spectrum.
- Preparation: Multiple freeze-thaw cycles at  $0$  C 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:  $6,500$  to  $550$   $\text{cm}^{-1}$  (1.534 to 18.182 microns)
- Instrumental resolution based on maximum interferometer displacement is  $0.112$   $\text{cm}^{-1}$
- Spectral interval after 2X zero-filling interferogram and FFT:  $0.06$   $\text{cm}^{-1}$
- 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  $0$   $\text{cm}^{-1}$

### Post Processing and Related Parameters-

- Non-linearity detector correction (Bruker proprietary) applied to interferogram ( $\tau = 0.85$ ,  $\nu = 530$ )
- 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  $T^2$  (transmission squared), all absorbance values  $> 1.6$  are given zero weight
- Calculated and estimated errors: Type A = 0.64%, Type B = 10%
- Frequency correction (already applied):  $V(\text{corrected}) = V(\text{instrument}) * 0.999997 + 5.18 \times 10^{-4}$
- Axis units: X=wavenumbers ( $\text{cm}^{-1}$ ), Y=Absorbance (base-10)
- Trace acetic acid,  $\text{CO}_2$  and HCl features removed via spectral subtraction. Some residual features are still observed in composite spectrum.
- Baseline correction via 4<sup>th</sup> order polynomial subtraction