

All data taken at Pacific Northwest National Laboratory (PNNL)

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Composite spectrum for PACID\_25T

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

Equivalent concentration x path-length of composite spectrum:  $3.0499 \times 10^{-6}$  grams/liter-meter

As with all of the smaller organic acids, propionic acid forms a dimer in the vapor phase. An attempt has been made to correct for the dimer formation by calculating the equilibrium constant and adjusting the partial pressures. In addition, the dimer features (derived from the error vector) have been subtracted from the composite spectrum.

### Sample Conditions-

- Chemical name and CAS number: Propionic acid, metacetic acid, ethylformic acid, carboxyethane, hydroacrylic acid, methylacetic acid, bugle, luprosil, prozoin, grain preservative,  $\text{CH}_3\text{CH}_2\text{C}(=\text{O})\text{OH}$ : [79-09-4]
- Physical properties: M.W. 74.0792 amu, F.P.  $-21.5^\circ \text{C}$ , B.P.  $140.7^\circ \text{C}$ , Density (20 C)  $0.99336 \text{ g/cm}^3$
- Supplier and stated purity: Aldrich, 99.5+%
- Sample class: III (PNNL scale).
- Temperature of White cell (815.76 cm optical path length)  $25 \pm 2 \text{ C}$
- Diluent (high purity nitrogen) flowed at 25.20 liter/min ( $21.1^\circ \text{C}$ ), ambient atmospheric pressure  $760 \pm 5 \text{ Torr}$ .
- Samples flowed at 3.000, 1.000, 0.500, 0.250, 2.000, 4.000, 2.500, 0.750, 1.500, 5.000, 10.000, 15.000, 20.000 and 7.000 microliters/minute
- Individual samples at equivalent pressures of 0.0273955, 0.00970292, 0.0049551, 0.00255894, 0.0187979, 0.0352015, 0.0229628, 0.00732617, 0.0143728, 0.0427924, 0.0759994, 0.103824, 0.12861 and 0.0569928 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:  $7,100$  to  $550 \text{ cm}^{-1}$  (1.409 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 ( $\alpha=0.90$ ,  $\epsilon=500$ )
- Composite spectrum created from 14 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  $\geq 1.6$  are given zero weight
- Calculated and estimated errors: Type A = 4.98%, Type B  $\leq 7\%$
- Frequency correction (already applied):  $V(\text{corrected})=V(\text{instrument}) * 0.9999987 - 4.24224 \times 10^{-4}$
- Axis units: X=wavenumbers ( $\text{cm}^{-1}$ ), Y=Absorbance (base-10)
- Baseline correction via 7<sup>th</sup> order polynomial subtraction