

All data taken at Pacific Northwest National Laboratory (PNNL)  
Operators: Steven W. Sharpe, Timothy J. Johnson and Robert L. Sams : [sw.sharpe@pnl.gov](mailto:sw.sharpe@pnl.gov)  
Version 1.0, March, 02

Composite spectrum for NICO4\_25T

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

Equivalent concentration x path-length of composite spectrum:  $7.0293 \times 10^{-6}$  grams/liter-meter

This compound was done on a “best effort” basis and may have large quantitative errors in the Y-axis. Nickel carbonyl dissociates at room temperature into nickel metal and carbon monoxide. Steps were taken to correct for this dissociation, but large errors were still observed in the data. The absorbance observed is most likely smaller than the real value, giving Ni(CO)<sub>4</sub> one of the largest rovibrational cross-sections in nature.

### Sample Conditions-

- Chemical name and CAS number: Nickel carbonyl, tetracarbonyl nickel, T-4, Ni(CO)<sub>4</sub> : [13463-39-3]
- Physical properties: fw=170.735 g/mole, fp=-25° C, bp=43° C
- Supplier and stated purity: Atomergic Chemicals Corp., 98%
- Sample class: III (PNNL scale). Unimolecular dissociation at room temperature
- Temperature of sample: 25.00 ± 0.02 C
- Diluent: Sample back filled with ultra high purity nitrogen to 760±5 Torr
- Individual samples at 0.55330, 0.36880, 0.1800, 0.1200 and 0.0990 Torr. Path length = 19.96 cm. Final data is a composite spectrum.
- Preparation: Multiple freeze-thaw cycles at 77 K to remove CO and Nitrogen.

### 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 600 cm<sup>-1</sup> (1.534 to 16.667 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 5 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 = 14%, Type “Best effort”

- Frequency correction (already applied):  $V(\text{corrected}) = V(\text{instrument}) * 0.999998 + 1.287 \times 10^{-4}$
- Axis units: X=wavenumbers ( $\text{cm}^{-1}$ ), Y=Absorbance (base-10)
- Significant carbon dioxide features removed via spectral subtraction. Residual still observable in composite spectrum.
- Baseline correction via 7<sup>th</sup> order polynomial subtraction