

All data taken at the Pacific Northwest National Laboratory

FTS Operators: Tracy J. Baker

Data Analysis: Tracy J. Baker

Composite spectrum for: 1,4-Butanediol

- First Column: Position in wavenumber (cm^{-1})
- Second column: Real refractive index $n(\tilde{\nu})$ (dispersion index)
- Third column: Imaginary refractive index, $k(\tilde{\nu})$ (absorption index per unit length in centimeters)

Where the complex refractive index $\hat{n} = n(\tilde{\nu}) + ik(\tilde{\nu})$

Following Bertie (in the references below) we define the absorbance as $A = -\log_{10}(I/I_0)$ and the linear absorption coefficient $K = A/d$, where d is the path length. The connection between the imaginary refractive index and the absorbance coefficient arises from the following: $2.303K = 4\pi\tilde{\nu}k$

See the following references for a detailed description of terms and units:

- 1) Bertie, J. E., Zhang, S. L., Eysel, H. H., Baluja, S., & Ahmed, M. K. (1993). Infrared Intensities of Liquids XI: Infrared Refractive Indices from 8000 to 2 cm^{-1} , Absolute Integrated Intensities, and Dipole Moment Derivatives of Methanol at 25°C . *Appl. Spec.*, 47(8), 1100-1114 doi:10.1366/0003702934067973
- 2) Bertie, J. E., Zhang, S. L., & Keefe, C. D. (1995). Measurement and use of absolute infrared absorption intensities of neat liquids. *Vibrational Spectroscopy*, 8(2), 215-229. doi:10.1016/0924-2031(94)00038-i

Sample:

- Chemical name, formula and CAS number: 1,4-Butanediol, $\text{C}_4\text{H}_{10}\text{O}_2$, [110-63-4]
- IUPAC name: Butane-1,4-diol
- Synonyms: 1,4-Butylene glycol; Tetramethylene glycol
- Physical properties: FW = 90.12 g/mole; mp = 16°C ; bp = 230°C ; vp = 0.01 Torr; $\rho = 1.017\text{ g/cm}^3$
- Supplier and stated purity: Aldrich, $\geq 99\%$ (Lot # MZBH4476V)
- Temperature of sample: 25°C ($\pm 1^\circ\text{C}$)
- Individual samples were measured at the following path lengths: MIR: 2.64, 3.43, 4.97, 8.73, 13.1, 15.28, 15.31, 19.1, 26.7, 27.2, 41.6, 45.8, 98.5, 194 and 461 micrometers (μm); NIR: 99.8, 180, 466, 989 and 2037 μm . Final data are a composite of these spectra.
- Sample cell window material: MIR = Barium fluoride (BaF_2) except zinc selenide (ZnSe) for the 2.64, 13.1, 15.3, 19.1, 26.7 and 41.6 μm cells. NIR = Quartz (Qz).
- Preparation: None

NIR Instrument Parameters:

- Bruker Vertex 70, purged with UHP nitrogen
- Spectral range: 10,000 to 400 cm^{-1} (1.0 to 25 microns)
- NIR source: Quartz tungsten bulb
- Beamsplitter: Broadband potassium bromide (KBr)
- Detector: DLTGS at room temperature
- Aperture: 3 mm
- Folding limits: 31597.6 to 0 cm^{-1}

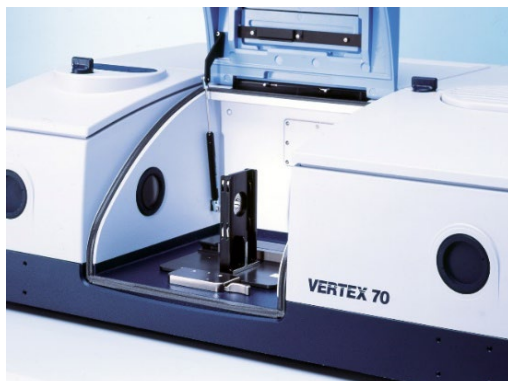
MIR Instrument Parameters:

- Tensor II with sample stage rotated 6 degrees, purged with UHP nitrogen
- Spectral range: 7,800 to 400 cm^{-1} (1.282 to 25 microns)
- IR source: Silicon carbide glow bar
- Beamsplitter: Potassium bromide (KBr)
- Detector: DTGS at room temperature
- Aperture: 3 mm
- Folding limits: 11664.14 to 0 cm^{-1}

NIR/MIR Instrument Parameters:

- Instrument resolution: 2.0 cm^{-1}
- Number of interferograms averaged per single channel spectrum: 128
- Apodization: Norton-Beer, Medium
- Phase correction: Mertz
- Scanner velocity: 10 kHz; 7.5 kHz (MIR)
- Interferogram zerofill: 4x
- Spectral interval after zerofilling: 0.4822 cm^{-1}

a)



b)



Figure 1: The Bruker Vertex 70 FTIR (a) and Tensor II (b).

Measured Refractive Index:

The refractive index for 1,4-Butanediol was measured at $25\text{ }^{\circ}\text{C}$ using an Atago model DR-M2/1550 Abbe refractometer. Notch filters were employed in front of a white light source to make measurements at multiple wavelengths. An infrared viewer from Atago was used to detect signal at 1550 nm . The temperature was controlled to match that in the sample compartment of the FTIR using a heated circulating bath.

480 nm:	$n = 1.4493$	486 nm:	$n = 1.4490$	546 nm:	$n = 1.4462$
589 nm:	$n = 1.4443$	644 nm:	$n = 1.4425$	656 nm:	$n = 1.4421$
1550 nm:	$n = 1.4256$				

The refractive index, n , vs. wavelength in microns, λ , was fit to an equation similar to that of Sellmeier:

$$n(\lambda) = \{a + b/(\lambda^2 - c)\}^{1/2}$$

The resulting best-fit equation was used to find the refractive index at the highest energy data points in our experimental spectra. For 1,4-Butanediol the results were

$$\begin{aligned} n(7,800\text{ cm}^{-1}) &= 1.4282 \text{ at } 25\text{ }^{\circ}\text{C} \text{ for MIR data and} \\ n(10,000\text{ cm}^{-1}) &= 1.4326 \text{ at } 25\text{ }^{\circ}\text{C} \text{ for NIR and merged data.} \end{aligned}$$

Post Processing and Related Parameters:

For the MIR, a composite spectrum was created from 15 absorbance spectra (base-10) taken at 15 path lengths: 2.64, 3.43, 4.97, 8.73, 13.1, 15.28, 15.31, 19.1, 26.7, 27.2, 41.6, 45.8, 98.5, 194 and 461 micrometers (μm). These data were collected with the sample stage rotated by 6° to minimize artifacts resulting from back-reflection into spectrometer (see Johnson et al., *Appl. Spectrosc.*, 76(5) 620-624, 2021). For the NIR, a composite spectrum was created from 5 absorbance spectra (base-10) taken at 5 path lengths: 99.8, 180, 466, 989 and 2037 μm . At each path length several spectra were measured and the results averaged for better signal to noise. The measured cell lengths were adjusted using Beer's law plots in which the NIR and MIR data were analyzed independently.

- 1) The imaginary part of the refractive index, or k vector, was determined for each absorbance file as per Bertie's program "RNJ46A" (see reference above). This takes into account the reflective losses due to the BaF_2 , ZnSe and/or Qz windows.
- 2) A composite k vector is created via a classical, weighted, linear, least squares fit using the output files of program "RNJ46A": Intercept=0, slope is fitted, individual absorbance values weighted by T^2 (transmission squared), all absorbance values ≥ 2.5 are given zero weight. For the MIR BaF_2 data, five composite vectors were created and merged by hand.
 - a) The first k vector used the results from the 98.5 through 461 μm cells. This k vector determined the final values for the range from 7800 to 3800 cm^{-1} .
 - b) The second k vector used the results from the 4.97, 27.2 and 45.8 μm cells. This k vector determined the final values for the range from 3800 to 2400 cm^{-1} and 1100 to 1040 cm^{-1} .
 - c) The third k vector used the results from the 194 and 461 μm cell. This k vector determined the final values for the range from 2400 to 1600 cm^{-1} .
 - d) The fourth k vector used the results from the 45.8 and 98.5 μm cells. This k vector determined the final values for the range from 1600 to 1100 cm^{-1} .
 - e) The fifth k vector used the results from the 27.2 and 45.8 μm cells. This k vector determined the final values for the range from 1040 to 730 cm^{-1} .
- 3) For the MIR ZnSe data, two composite vectors were created and merged by hand.
 - a) The first k vector used the results from the 13.09 through 41.6 μm cells. This k vector determined the final values for the range from 7800 to 1500 cm^{-1} .
 - b) The second k vector used the results from the 26.7 and 41.6 μm cells. This k vector determined the final values for the range from 1500 to 460 cm^{-1} .
- 4) A frequency correction was applied to the resulting ZnSe and BaF_2 composite MIR k vectors.
 - a) Frequency correction (already applied): $\tilde{\nu}(\text{corrected}) = [\tilde{\nu}(\text{instrument}) * 0.99988 + 0.025]$ as determined by comparing measured atmospheric spectral lines (H_2O and CO_2) to values from the Northwest Infrared Spectral Library Database.
- 5) The MIR composite BaF_2 k vector range was extended to 460 cm^{-1} to match the composite MIR ZnSe k vector for a total range of 7800 to 460 cm^{-1} . The two composite k vectors were then merged at 930 cm^{-1} .
- 6) For the NIR, four composite vectors were created and merged by hand.
 - a) The first k vector used the results from the 2037 μm cell. This k vector determined the final values for the range from 10,000 to 5000 cm^{-1} .
 - b) The second k vector used the results from the 989 and 2037 μm cells. This k vector determined the final values for the range from 5000 to 3700 cm^{-1} .
 - c) The third k vector used the results from the 99.8 and 466 through 2037 μm cells. This k vector determined the final values for the range from 3700 to 500 cm^{-1} .
 - d) The fourth k vector used the results from the 99.8 through 466 μm cells. This k vector determined the final values for the range from 3300 to 500 cm^{-1} .
- 7) The resulting composite NIR k vector and the refractive index at 10,000 cm^{-1} were used to create the real or n vector using the Kramers-Kronig relation, as per Bertie's program "LZZKTB."
 - a) Frequency correction (already applied): $\tilde{\nu}(\text{corrected}) = [\tilde{\nu}(\text{instrument}) * 0.99998 - 0.0005]$ as determined by comparing measured atmospheric spectral lines (H_2O and CO_2) to values from the Northwest Infrared Spectral Library Database.
- 8) The composite MIR data were mapped onto the NIR x-axis using an interpolation routine, i.e. the Make Compatible command in OPUS 5.5. Then the composite MIR and NIR k vectors were merged around

3800 cm^{-1} to generate a final composite k vector across the entire spectral range. Absorption increases for ZnSe at wavenumbers below 550 cm^{-1} resulting in increased noise; thus the data were truncated at 500 cm^{-1} . The resulting composite k vector and the refractive index at 10,000 cm^{-1} were used to create the final n vector using the Kramers-Kronig relation, as per Bertie's program "LZZKTB."

Photograph of Sample 1,4-Butanediol:

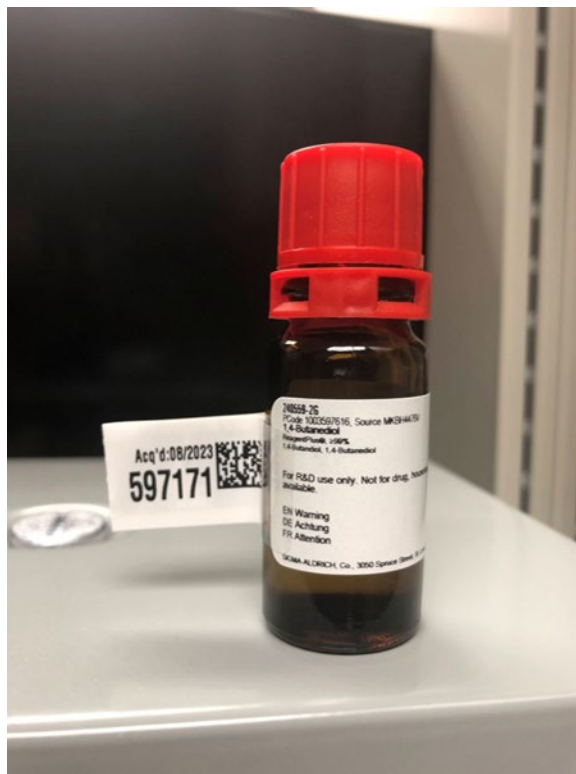


Figure 2: 1,4-Butanediol in Aldrich container for MIR and NIR measurements.