

All data taken at the Pacific Northwest National Laboratory

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**Composite spectrum for:** 3-Bromo-1-propyne (propargyl bromide) in toluene

- First Column: Position in wavenumber ( $\text{cm}^{-1}$ )
- 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  $2\text{ cm}^{-1}$ , Absolute Integrated Intensities, and Dipole Moment Derivatives of Methanol at  $25^\circ\text{C}$ . *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: 3-Bromo-1-propyne (propargyl bromide),  $\text{C}_3\text{H}_3\text{Br}$ , [106-96-7]
- IUPAC name: 3-Bromoprop-1-yne
- Synonyms: Propargyl bromide; Propyne, 3-bromo-; 1-Bromo-2-propyne; 2-Propynyl bromide
- Physical properties: FW = 118.96 g/mole; mp =  $-61.1^\circ\text{C}$ ; bp =  $89^\circ\text{C}$ ;  $\rho = 1.579\text{ g/cm}^3$
- Supplier and stated purity: Sigma-Aldrich, 80% in Toluene (Lot # WXBC6076V)
- Temperature of sample:  $26^\circ\text{C}$  ( $\pm 1^\circ\text{C}$ )
- Individual samples were measured at the following path lengths: MIR: 3.36, 4.19, 6.24, 7.98, 10.4, 28.2, 39.4, 117, 201 and  $508\text{ }\mu\text{m}$ ; NIR: 119, 203, 508, 1024 and  $3040\text{ }\mu\text{m}$ . Final data are a composite of these spectra.
- Sample cell window material was potassium bromide (KBr) except the 4.19 (MIR), 508 (MIR), 508 (NIR) and 1024 (NIR) cell windows were potassium chloride (KCl).
- Preparation: None.

**NIR Instrument Parameters:**

- Bruker Vertex 70, purged with UHP nitrogen
- Spectral range: 10,000 to  $3,000\text{ cm}^{-1}$  (1.0 to 3.33 microns)
- NIR source: Quartz tungsten bulb
- Beamsplitter: Broadband Potassium bromide (KBr)
- Detector: DLTGS at room temperature
- Aperture: 3 mm
- Folding limits: 31601 to  $0\text{ cm}^{-1}$

**MIR Instrument Parameters:**

- Tensor 27, purged with UHP nitrogen
- Spectral range: 7800 to  $400\text{ cm}^{-1}$  (1.282 to 25 microns)
- IR source: Silicon carbide glow bar
- Beamsplitter: Broadband Potassium bromide (KBr)
- Detector: DLTGS at room temperature
- Aperture: 3 mm
- Folding limits: 15802 to  $0\text{ cm}^{-1}$

### NIR/MIR Instrument Parameters:

- Instrument resolution:  $2.0\text{ cm}^{-1}$
- Number of interferograms averaged per single channel spectrum: 128
- Apodization: Norton-Beer, Medium
- Phase correction: Mertz
- Scanner velocity: 10 kHz
- Interferogram zerofill: 4x
- Spectral interval after zerofilling:  $0.4823\text{ cm}^{-1}$

a)



b)



Figure 1: The Bruker Vertex 70 FTIR (a) and Tensor 27 FTIR (b).

### Measured Refractive Index:

The refractive index for 3-Bromo-1-propyne (propargyl bromide) was measured at  $10\text{ }^{\circ}\text{C}$  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  $1550\text{ nm}$ . The temperature was controlled to match that in the sample compartment of the FTIR using a heated circulating bath.

480 nm: $n = 1.5127$	486 nm: $n = 1.5117$	546 nm: $n = 1.5044$
589 nm: $n = 1.5010$	644 nm: $n = 1.4981$	656 nm: $n = 1.4969$
1550 nm: $n = 1.4768$		

The refractive index,  $n$ , vs. wavelength in microns,  $\lambda$ , 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. After extrapolation, the  $n(7800\text{ cm}^{-1})$  and  $n(10,000\text{ cm}^{-1})$  results were corrected for a  $17\text{ }^{\circ}\text{C}$  increase in temperature to match the FTIR measurements by using an estimate of  $-0.00045$  per degree ( $17\text{ }^{\circ}\text{C}$  difference is equal to a decrease in value by  $0.00765$ ). For 3-Bromo-1-propyne (propargyl bromide), the results were

$$\begin{aligned} n(7800\text{ cm}^{-1}) &= 1.472 \text{ at } 27\text{ }^{\circ}\text{C} \text{ (1.4792 at } 10\text{ }^{\circ}\text{C) for MIR data and} \\ n(10,000\text{ cm}^{-1}) &= 1.4762 \text{ at } 27\text{ }^{\circ}\text{C} \text{ (1.4836 at } 10\text{ }^{\circ}\text{C) for NIR and merged data.} \end{aligned}$$

## Post Processing and Related Parameters:

For the MIR, a composite spectrum was created from 10 absorbance spectra (base-10) taken at 10 path lengths: 3.36, 4.19, 6.24, 7.98, 10.4, 28.2, 39.4, 117, 201 and 508 micrometers ( $\mu\text{m}$ ). For the NIR, a composite spectrum was created from 5 absorbance spectra (base-10) taken at 5 path lengths: 119, 203, 508, 1024 and 3040  $\mu\text{m}$ . The same cells for the 100, 200 and 500  $\mu\text{m}$  path lengths were used for both spectral ranges. 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 KBr windows and the measured refractive index at  $7800\text{ cm}^{-1}$  for the MIR data and  $10,000\text{ cm}^{-1}$  for the NIR data.
- 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  $\geq 2.5$  are given zero weight. For the MIR, five composite vectors were created and merged by hand.
  - a) The first  $k$  vector used the results from the 201 and 508  $\mu\text{m}$  cells. This  $k$  vector determined the final values for the range from  $7800$  to  $6100\text{ cm}^{-1}$ .
  - b) The second  $k$  vector used the results from the 117 through 508  $\mu\text{m}$  cells. This  $k$  vector determined the final values for the range from  $6100$  to  $4450\text{ cm}^{-1}$ .
  - c) The third  $k$  vector used the results from the 28.2 through 508  $\mu\text{m}$  cells. This  $k$  vector determined the final values for the range from  $4450$  to  $3750\text{ cm}^{-1}$  and  $2800$  to  $1230\text{ cm}^{-1}$ .
  - d) The fourth  $k$  vector used the results from the 3.36 through 117  $\mu\text{m}$  cells. This  $k$  vector determined the final values for the range from  $3750$  to  $2800\text{ cm}^{-1}$  and  $1230$  to  $560\text{ cm}^{-1}$ .
  - e) The fifth  $k$  vector used the results from the 7.98 through 28.2  $\mu\text{m}$  cells. This  $k$  vector determined the final values for the range from  $560$  to  $400\text{ cm}^{-1}$ .
- 3) A frequency correction was applied to the resulting composite MIR  $k$  vector.
  - a) Frequency correction (already applied):  $\tilde{\nu}(\text{corrected}) = [\tilde{\nu}(\text{instrument}) * .999848 + .010722]$  as determined by comparing measured atmospheric spectral lines ( $\text{H}_2\text{O}$  and  $\text{CO}_2$ ) to values from the Northwest Infrared Spectral Library Database.
- 4) For the NIR, two composite vectors were created and merged by hand.
  - a) The first  $k$  vector used the results from the 1024 and 3040  $\mu\text{m}$  cells. This  $k$  vector determined the final values for the range from  $10000$  to  $6800\text{ cm}^{-1}$ .
  - b) The second  $k$  vector used the results from the 119 through 3040  $\mu\text{m}$  cells. This  $k$  vector determined the final values for the range from  $6800$  to  $4500\text{ cm}^{-1}$ .
- 5) A frequency correction was applied to the resulting composite NIR  $k$  vector.
  - a) Frequency correction (already applied):  $\tilde{\nu}(\text{corrected}) = [\tilde{\nu}(\text{instrument}) * .999869 + .0158818]$  as determined by comparing measured atmospheric spectral lines ( $\text{H}_2\text{O}$  and  $\text{CO}_2$ ) to values from the Northwest Infrared Spectral Library Database.
- 6) Finally, the 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 to generate a final composite  $k$  vector across the entire spectral range. The NIR data were used exclusively above  $4900\text{ cm}^{-1}$ , and only the MIR data were used below  $4730\text{ cm}^{-1}$ . A weighted average, with the weight of the MIR vector increasing linearly from 0 to 100% between  $4900$  and  $4730\text{ cm}^{-1}$  was used in the overlapping spectral region. The resulting composite  $k$  vector and the refractive index at  $10,000\text{ cm}^{-1}$  were used to create the final  $n$  vector using the Kramers-Kronig relation, as per Bertie's program "LZZKTB."

NOTE: This liquid is sold by Aldrich as a solution: 80% in toluene. The toluene is included in the final spectrum.

**Photograph of Sample 3-Bromo-1-propyne (propargyl bromide):**



Figure 2: 3-Bromo-1-propyne (propargyl bromide) solution in Sigma-Aldrich container.