

All data taken at the Pacific Northwest National Laboratory

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Data Analysis: Tracy J. Baker

**Composite spectrum for: Methyl undecanoate**

- 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: Methyl undecanoate,  $\text{C}_{12}\text{H}_{24}\text{O}_2$ , [1731-86-8]
- IUPAC name: Methyl undecanoate
- Synonyms: Isopentyl undecanoate; Undecanoic acid methyl ester; Methyl *n*-undecanoate
- Physical properties: FW = 200.32 g/mole; mp =  $-10^\circ\text{C}$ ; bp =  $246\text{--}248^\circ\text{C}$ ;  $\rho = 0.872\text{ g/cm}^3$
- Supplier and stated purity: Sigma-Aldrich, > 98% (Lot # BCCJ6756)
- Temperature of sample:  $25^\circ\text{C}$  ( $\pm 1^\circ\text{C}$ )
- Individual samples were measured at the following path lengths: MIR: 2.56, 5.39, 6.50, 9.50, 18.5, 34.8, 46.2, 86.0, 215 and 508 micrometers ( $\mu\text{m}$ ); NIR: 86.8, 216, 510, 919 and 4135  $\mu\text{m}$ . Final data are a composite of these spectra.
- Sample cell window material: MIR = potassium bromide (KBr); NIR = KBr except potassium chloride (KCl) for the 1988 and 3933  $\mu\text{m}$  cells.
- 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: 31597.6 to  $0\text{ cm}^{-1}$

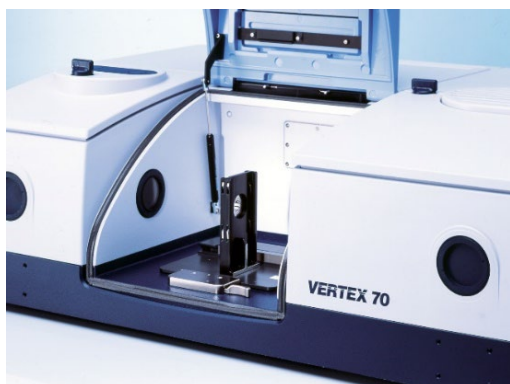
**MIR Instrument Parameters:**

- Tensor II with sample stage rotated 6 degrees, purged with UHP nitrogen
- Spectral range: 7,800 to  $400\text{ cm}^{-1}$  (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: 11664.15 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; 7.5 kHz (MIR)
- Interferogram zerofill: 4x
- Spectral interval after zerofilling:  $0.4822\text{ cm}^{-1}$

a)



b)



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

### Measured Refractive Index:

The refractive index for Methyl undecanoate 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  $1550\text{ nm}$ . The temperature was controlled to match that in the sample compartment of the FTIR using a heated circulating bath.

480 nm: $n = 1.432$	486 nm: $n = 1.4317$	546 nm: $n = 1.4285$
589 nm: $n = 1.4264$	644 nm: $n = 1.4249$	656 nm: $n = 1.4245$
1550 nm: $n = 1.4093$		

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. For Methyl undecanoate, the results were

$$\begin{aligned} n(7,800\text{ cm}^{-1}) &= 1.4115 \text{ at } 25\text{ }^{\circ}\text{C} \text{ for MIR data and} \\ n(10,000\text{ cm}^{-1}) &= 1.4153 \text{ at } 25\text{ }^{\circ}\text{C} \text{ for NIR and merged data.} \end{aligned}$$

### Post Processing and Related Parameters:

For the MIR, a composite spectrum was created from 10 absorbance spectra (base-10) taken at 10 path lengths: 2.56, 5.39, 6.50, 9.50, 18.5, 34.8, 46.2, 86.0, 215 and 508 micrometers ( $\mu\text{m}$ ). These data were collected with the sample stage rotated by  $-6^\circ$  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: 86.8, 216, 510, 919 and 4135  $\mu\text{m}$ . The same cells and liquid fills for the  $\sim 100$ , 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 and/or KCl 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  $\geq 2.5$  are given zero weight. For the MIR, six composite vectors were created and merged by hand.
  - a) The first  $k$  vector used the results from the 86.0 through 508  $\mu\text{m}$  cells. This  $k$  vector determined the final values for the range from 7800 to 3000  $\text{cm}^{-1}$  and 2820 to 1800  $\text{cm}^{-1}$ .
  - b) The second  $k$  vector used the results from 2.56 and 6.50  $\mu\text{m}$  cells. This  $k$  vector determined the final values for the range from 3000 to 2850  $\text{cm}^{-1}$  and 1750 to 1730  $\text{cm}^{-1}$ .
  - c) The third  $k$  vector used the results from the 18.5 through 86.0  $\mu\text{m}$  cells. This  $k$  vector determined the final values for the range from 2850 to 2820  $\text{cm}^{-1}$ , 1800 to 1750  $\text{cm}^{-1}$ , 1730 to 1470  $\text{cm}^{-1}$  and 1100 to 720  $\text{cm}^{-1}$ .
  - d) The fourth  $k$  vector used the results from the 9.50 through 46.2  $\mu\text{m}$  cells. This  $k$  vector determined the final values for the range from 1470 to 1210  $\text{cm}^{-1}$  and 1150 to 1100  $\text{cm}^{-1}$ .
  - e) The fifth  $k$  vector used the results from the 9.50 and 18.5  $\mu\text{m}$  cells. This  $k$  vector determined the final values for the range from 1210 to 1150  $\text{cm}^{-1}$ .
  - f) The sixth  $k$  vector used the results from the 34.8 through 86.0  $\mu\text{m}$  cells. This  $k$  vector determined the final values for the range from 720 to 370  $\text{cm}^{-1}$ .
- 3) A frequency correction was applied to the resulting composite MIR  $k$  vector.
  - a) Frequency correction (already applied):  $\tilde{\nu}(\text{corrected}) = [\tilde{\nu}(\text{instrument}) * 0.99988 + 0.025]$  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, four composite vectors were created and merged by hand.
  - a) The first  $k$  vector used the results from the 4135  $\mu\text{m}$  cell. This  $k$  vector determined the final values for the range from 10,000 to 6000  $\text{cm}^{-1}$  and 5600 to 4500  $\text{cm}^{-1}$ .
  - b) The second  $k$  vector used the results from the 510 through 4135  $\mu\text{m}$  cells. This  $k$  vector determined the final values for the range from 6000 to 5600  $\text{cm}^{-1}$ .
  - c) The third  $k$  vector used the results from the 510 and 919  $\mu\text{m}$  cells. This  $k$  vector determined the final values for the range from 4500 to 3000  $\text{cm}^{-1}$ .
  - d) The fourth  $k$  vector used the results from the 86.8 through 510  $\mu\text{m}$  cells. This  $k$  vector determined the final values for the range from 3000 to 370  $\text{cm}^{-1}$ .
- 5) The resulting composite NIR  $k$  vector and the refractive index at 10,000  $\text{cm}^{-1}$  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 ( $\text{H}_2\text{O}$  and  $\text{CO}_2$ ) to values from the Northwest Infrared Spectral Library Database.
- 6) 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 2992  $\text{cm}^{-1}$ , and only the MIR data were used below 2978  $\text{cm}^{-1}$ . A weighted average, with the weight of the MIR vector increasing linearly from 0 to 100% between 2992 and 2978  $\text{cm}^{-1}$ , 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."

**Photograph of Sample Methyl undecanoate:**

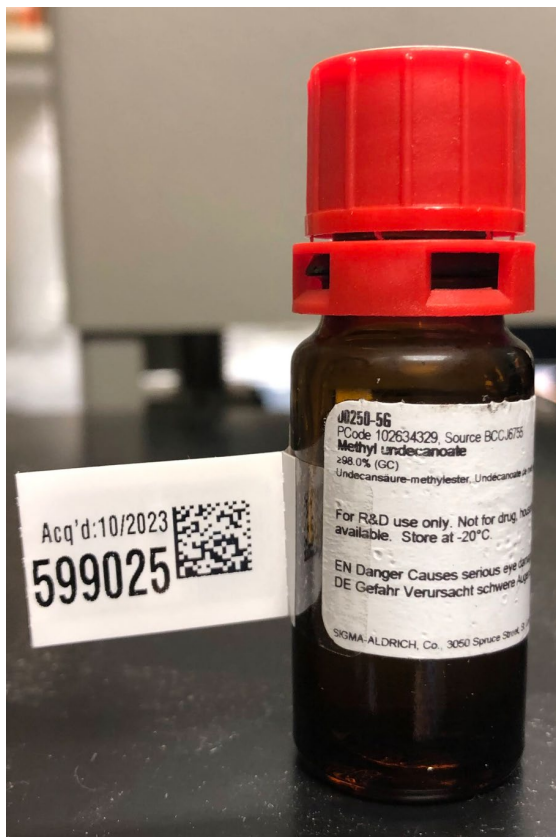


Figure 2: Methyl undecanoate in Sigma-Aldrich container for NIR and MIR measurements.