

All data taken at the Pacific Northwest National Laboratory
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Composite spectrum for: Phenylacetaldehyde

- 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: Phenylacetaldehyde, $\text{C}_8\text{H}_8\text{O}$, [122-78-1]
- IUPAC name: 2-Phenylacetaldehyde
- Synonyms: α -Tolylaldehyde
- Physical properties: FW = 120.15 g/mole; mp = -10°C ; bp = 195°C ; $\rho = 1.03\text{ g/cm}^3$
- Supplier and stated purity: Sigma-Aldrich, $\geq 95\%$ (Lot # MKCB0206V)
- Temperature of sample: 26°C ($\pm 1^\circ\text{C}$)
- Individual samples were measured at the following path lengths: MIR: 5.4, 8.7, 10.6, 18.4, 17.0, 30.2, 57.6, 57.7, 122, 221 and $510\text{ }\mu\text{m}$; NIR: 123, 222, 518, 1243 and $3759\text{ }\mu\text{m}$. Final data are a composite of these spectra.
- Sample cell window material is potassium bromide (KBr).
- 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)
- IR source: Quartz tungsten bulb
- Beamsplitter: Broadband Potassium bromide (KBr)
- Detector: DLTGS at room temperature
- Aperture: 3 mm
- Folding limits: 31601 to 0 cm^{-1}

MIR Instrument Parameters:

- Tensor 27, purged with UHP nitrogen
- Spectral range: 7800 to 400 cm^{-1} (1.282 to 25 microns)
- NIR source: Silicon carbide glow bar
- Beamsplitter: Broadband Potassium bromide (KBr)
- Detector: DLTGS at room temperature
- Aperture: 3 mm
- Folding limits: 15802 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
- Interferogram zerofill: 4x
- Spectral interval after zerofilling: 0.4823 cm^{-1}

a)



b)



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

Measured Refractive Index:

The refractive index for Phenylacetaldehyde 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: $n = 1.5547$	486 nm: $n = 1.5540$	546 nm: $n = 1.5459$
589 nm: $n = 1.5417$	644 nm: $n = 1.5378$	656 nm: $n = 1.5371$
1550 nm: $n = 1.5161$		

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 Phenylacetaldehyde, the results were

$$\begin{aligned} n(7800\text{ cm}^{-1}) &= 1.5184 \text{ at } 25\text{ }^{\circ}\text{C} \text{ for MIR data and} \\ n(10,000\text{ cm}^{-1}) &= 1.5229 \text{ at } 25\text{ }^{\circ}\text{C} \text{ for NIR and merged data.} \end{aligned}$$

Post Processing and Related Parameters:

For the MIR, a composite spectrum was created from 11 absorbance spectra (base-10) taken at 11 path lengths: 5.4, 8.7, 10.6, 18.4, 17.0, 30.2, 57.6, 57.7, 122, 221 and 510 micrometers (μm). For the NIR, a composite spectrum was created from 5 absorbance spectra (base-10) taken at 5 path lengths: 123, 222, 518, 1243, and 3759 micrometers (μm). The same cells for the 100, 200 and 500 μm 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.
- 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, five composite vectors were created and merged by hand.
 - a) The first k vector used the results from the 221 and 510 μm cells. This k vector determined the final values for the range from 7800 to 6300 cm^{-1} .
 - b) The second k vector used the results from the 122 through 510 μm cells. This k vector determined the final values for the range from 6300 to 5000 cm^{-1} .
 - c) The third k vector used the results from the 17 through 510 μm cells. This k vector determined the final values for the range from 5000 to 3100 cm^{-1} and 480 to 400 cm^{-1} .
 - d) The fourth k vector used the results from the 5 through 11 μm cells. This k vector determined the final values for the range from 3100 to 2700 cm^{-1} .
 - e) The fifth k vector used the results from the 5 through 58 μm cells. This k vector determined the final values for the range from 2700 to 480 cm^{-1} .
- 3) The resulting composite MIR k vector and the refractive index at 7800 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): $\tilde{\nu}(\text{corrected}) = [\tilde{\nu}(\text{instrument}) * 0.999848 + 0.010722]$ as determined by comparing measured atmospheric spectral lines (H_2O and CO_2) to values from the Northwest Infrared Spectral Library Database.
- 4) For the NIR, three composite vectors were created and merged by hand.
 - a) The first k vector used the results from the 3759 μm cell. This k vector determined the final values for the range from 10000 to 9000 cm^{-1} .
 - b) The second k vector used the results from the 1258 and 3759 μm cells. This k vector determined the final values for the range from 9000 to 6400 cm^{-1} .
 - c) The third k vector used the results from the 122 through 3759 μm cells. This k vector determined the final values for the range from 6400 to 400 cm^{-1} .
- 5) 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): $\tilde{\nu}(\text{corrected}) = [\tilde{\nu}(\text{instrument}) * 0.999869 + 0.0158818]$ as determined by comparing measured atmospheric spectral lines (H_2O and 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 6260 cm^{-1} , and only the MIR data were used below 5195 cm^{-1} . A weighted average, with the weight of the MIR vector increasing linearly from 0 to 100% between 6260 and 5195 cm^{-1} was used in the overlapping spectral region. 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."

A photograph of a small, dark glass vial with a red cap, labeled 'SIGMA-ALDRICH W287407-SAMPLE-K Phenylacetaldehyde 99.5%, FCC, FG'. A white label with a QR code and the number '535841' is placed next to the vial.

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