

All data taken at the Pacific Northwest National Laboratory

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Composite spectrum for: Acetophenone

- 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: Acetophenone, $\text{C}_8\text{H}_8\text{O}$, [98-86-2]
- IUPAC name: 1-Phenylethan-1-one
- Synonyms: 1-Phenylethanone; Methyl phenyl ketone
- Physical properties: FW = 120.15 g/mole; mp = 20°C ; bp = 202°C ; $\rho = 1.03\text{ g/cm}^3$
- Supplier and stated purity: MIR = Fisher, 99% (Lot # 970040); Sigma-Aldrich, 99% (Lot # STBH5416); NIR = Sigma-Aldrich, 99% (Lot # STBH5416)
- Temperature of sample: 27°C ($\pm 1^\circ\text{C}$)
- Individual samples were measured at the following path lengths: MIR = 1.38, 1.97, 4.91, 8.52, 31.1, 52.0, 100 and 500 micrometers (μm); MIR = 3.87, 15.1, 44.5, 110, 209 and 492 μm ; NIR = 130, 207, 529, 2101 and 4005 μm . Final data are a composite of these spectra.
- Sample cell window material: MIR = zinc selenide (ZnSe) except potassium bromide (KBr) for the 3.87 through 492 μm cells; NIR = potassium chloride (KCl) except KBr for the 130 and 207 μm 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: 15801 to 0 cm^{-1}

MIR Instrument Parameters:

- Bruker Vector 22 and Tensor II, purged with UHP nitrogen
- Spectral range: 7800 to 400 cm^{-1} (1.282 to 25 microns)
- MIR source: Silicon carbide glow bar
- Beamsplitter: Potassium bromide (KBr)
- Detector: DTGS at room temperature
- Aperture: 3 mm
- Folding limits: 7899 to 0 cm^{-1} , 11669.8 to 0 cm^{-1}

NIR/MIR Instrument Parameters:

- Instrument resolution: MIR = 1.0 cm⁻¹, 2.0 cm⁻¹; NIR = 2.0 cm⁻¹
- Number of interferograms averaged per single channel spectrum: 128
- Apodization: Norton-Beer, Medium
- Phase correction: Mertz
- Scanner velocity: 10kHz, 7.5kHz (new MIR)
- Interferogram zerofill: MIR = 2x, 4x; NIR = 4x
- Spectral interval after zerofilling: 0.482 cm⁻¹

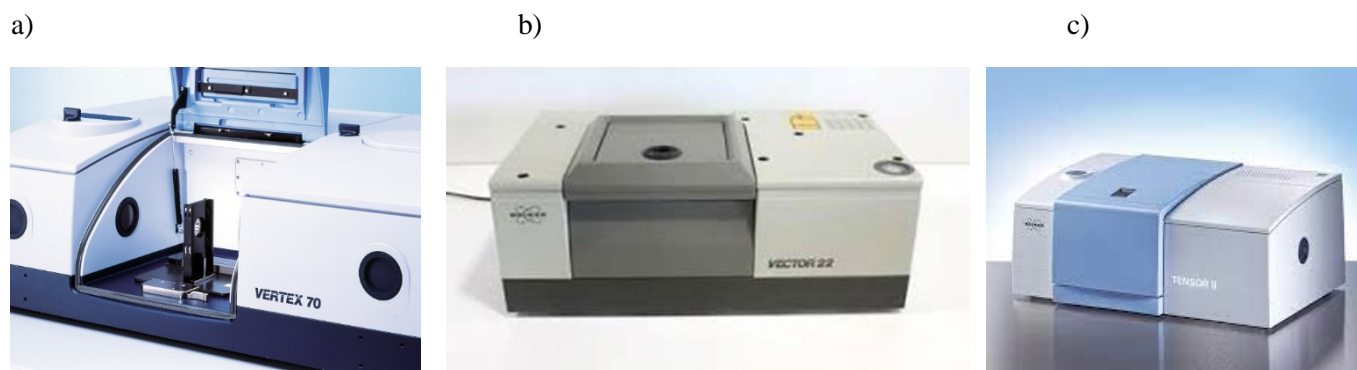


Figure 1: The Bruker Vertex 70 FTIR (a), Vector 22 FTIR (b) and Tensor II (c).

Measured Refractive Index:

The refractive index for Acetophenone was measured at 25 °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: $n = 1.5464$	486 nm: $n = 1.5453$	546 nm: $n = 1.5356$
589 nm: $n = 1.5308$	644 nm: $n = 1.5262$	656 nm: $n = 1.5253$
1550 nm: $n = 1.5028$		

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 Acetophenone, the results were

$$\begin{aligned} n(7,800 \text{ cm}^{-1}) &= 1.5052 \text{ at } 25 \text{ }^\circ\text{C} \text{ for MIR data and} \\ n(10,000 \text{ cm}^{-1}) &= 1.5099 \text{ at } 25 \text{ }^\circ\text{C} \text{ for NIR and merged data.} \end{aligned}$$

Post Processing and Related Parameters:

For the MIR, a composite spectrum was created from 6 absorbance (base-10) spectra taken at 6 path lengths: 4.91, 8.52, 31.1, 52.0, 100 and 500 micrometers (μm). Originally, the data were truncated from 6500 to 500 cm^{-1} to avoid excessive noise in the high energy region and large ZnSe absorbance at the low energy end. Six additional absorbance spectra taken at 6 path lengths (3.87, 15.12, 44.5, 110, 209 and 492 μm) were recorded in the MIR at a later time to extend the spectral range down to 400 cm^{-1} . For the NIR, a composite spectrum was created from 5 absorbance spectra (base-10) taken at 5 path lengths: 130, 207, 529, 2101 and 4005 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 KBr, KCl and/or ZnSe 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, four composite vectors were created and merged by hand.
 - a) The first k vector used the results from the 500 μm cell. This k vector determined the final values for the range from 6500 to 3108, 2958 to 1743 and 560 to 500 cm^{-1} .
 - b) The second k vector used the results from the 100 and 500 μm cells. This k vector determined the final values for the range from 3108 to 2958 cm^{-1} .
 - c) The third k vector used the results from the 4.91 and 8.52 μm cells. This k vector determined the final values for the range from 1743 to 1215 cm^{-1} .
 - d) The fourth k vector used the results from the 8.52, 31.1 and 52.0 μm cells. This k vector determined the final values for the range from 1215 to 560 cm^{-1} .
- 3) A frequency correction was applied to the resulting composite MIR k vector.
 - a) Frequency correction (already applied): $\tilde{\nu}(\text{corrected}) = [\tilde{\nu}(\text{instrument}) * 1.00003 + 0.185411]$ as determined by comparing measured atmospheric spectral lines (H_2O and CO_2) to values from the Northwest Infrared Spectral Library Database.
- 4) From the new MIR data, two composite k vectors were created and merged by hand.
 - a) The first k vector used the results from the 110 through 492 μm cells. This k vector determined the final values for the range from 7800 to 2000 and 580 to 400 cm^{-1} .
 - b) The second k vector used the results from the 3.87 through 492 μm cells. This k vector determined the final values for the range from 2000 to 580 cm^{-1} .
 - c) A frequency correction was applied to the resulting composite MIR k vector.
 - i) Frequency correction (already applied): $\tilde{\nu}(\text{corrected}) = [\tilde{\nu}(\text{instrument}) * 0.999975 + 0.0051]$ as determined by comparing measured atmospheric spectral lines (H_2O and CO_2) to values from the Northwest Infrared Spectral Library Database.
- 5) For the NIR, four composite vectors were created and merged by hand.
 - a) The first k vector used the results from the 2101 and 4005 μm cells. This k vector determined the final values for the range from 10,000 to 6600 cm^{-1} .
 - b) The second k vector used the results from the 529 through 4005 μm cells. This k vector determined the final values for the range from 6600 to 6175 cm^{-1} .
 - c) The third k vector used the results from the 130 through 4005 μm cells. This k vector determined the final values for the range from 6175 to 4100 cm^{-1} .
 - d) The fourth k vector used the results from the 130 through 529 μm cells. This k vector determined the final values for the range from 4100 to 400 cm^{-1} .
- 6) 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): $\tilde{\nu}(\text{corrected}) = [\tilde{\nu}(\text{instrument}) * 0.999748 + 0.00481475]$ as determined by comparing measured atmospheric spectral lines (H_2O and CO_2) to values from the Northwest Infrared Spectral Library Database.
- 7) The original 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 3093 cm^{-1} , and only the MIR data were used below 3089 cm^{-1} . A weighted average, with the weight of the MIR vector increasing linearly from 0 to 100% between 3093 and 3089 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."

- 8) Finally, the k vector from $10,000$ to 500 cm^{-1} (calculated in step 7) was used exclusively above 582 cm^{-1} and merged with the new MIR k vector via a weighted average between 582 and 572 cm^{-1} . 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 Acetophenone:

No photograph available of Acetophenone in Fisher container for previous MIR measurements.



Figure 2: Acetophenone in Sigma-Aldrich container for NIR and recent MIR measurements.