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

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

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

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: $2.303K = 4 \pi \tilde{\upsilon} k$

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. *Applied Spectroscopy, 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 formate, $C_2H_4O_2$, [107-31-3]
- IUPAC name: Methyl formate
- Synonyms: Formic acid methyl ester; Methyl methanoate
- Physical properties: FW = 60.05 g/mole; mp = -100 °C; bp = 32-34 °C; $\rho = 0.974$ g/cm^3
- Supplier and stated purity: Sigma-Aldrich, ≥ 99.8% (Lot # BCBN3126V)
- Temperature of sample: 26 °C (+/-1 °C)
- Individual samples were measured at the following path lengths: 1.53, 1.68, 2.48, 2.95, 3.92, 4.13, 15.8, 37.8, 98.3, 206, 523 and 1096 micrometers (μm). Final data are a composite of these spectra.
- Sample cell window material is potassium bromide (KBr).
- Preparation: None.

Instrument Parameters:

- Bruker Tensor 27 FTIR, purged with UHP nitrogen
- Spectral range: 7800 to 400 cm^{-1} (1.282 to 25 microns)
- 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
- Folding limits: 15802 to 0 cm^{-1}
- Interferogram zerofill: 4x
- Spectral interval after zerofilling: 0.4823 cm^{-1}
- IR source: Silicon carbide glow bar
- Beamsplitter: Broadband potassium bromide (KBr)
- Detector: DLTGS at room temperature
- Aperture: 3 mm

Measured Refractive Index:
The refractive index for Methyl formate was measured at 15 °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 InGaAs camera 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. (15 °C was used rather than 27 °C because of the chemical's fast evaporation rate.)

480 nm: n = 1.3492	486 nm: n = 1.3468	546 nm: n = 1.3452
589 nm: n = 1.3441	644 nm: n = —	656 nm: n = 1.3422
1550 nm: n = 1.3307		

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 point in our experimental spectra. For Methyl formate, the result was

$$n(7800\ cm^{-1}) = 1.3323 \text{ at } 15\ °C.$$

The dependence of refractive index with increasing temperature (dn/dT) for many organic liquids is approximately -0.00049/°C; this gives an estimated value of

$$n(7800\ cm^{-1}) = 1.327 \text{ at } 27\ °C.$$

a) b)

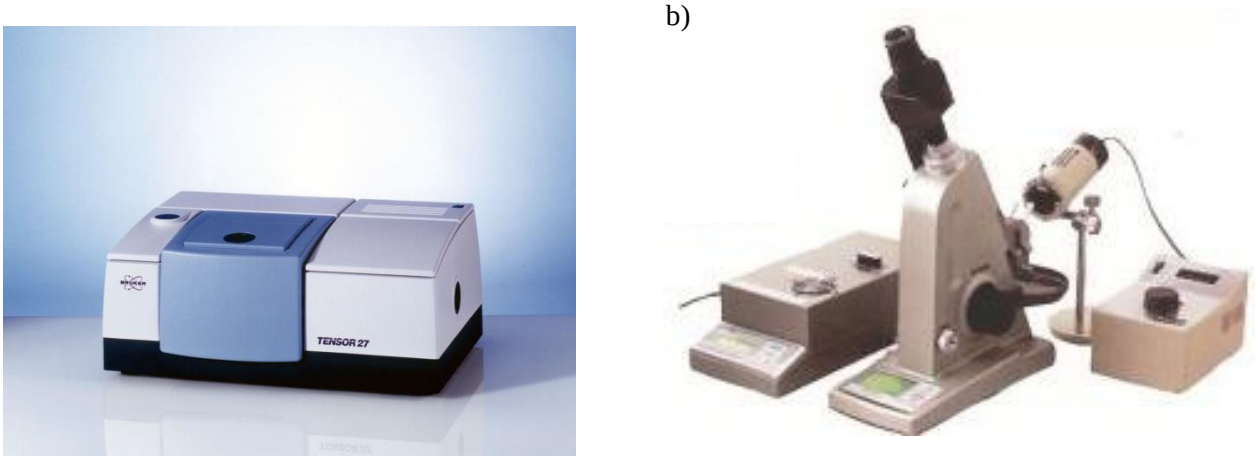

Figure 1: The Bruker Tensor 27 FTIR (a) and Abbe refractometer (b).

Post Processing and Related Parameters:
A composite spectrum was created from 12 absorbance spectra (base-10) taken at 8 path lengths: 1.53, 1.68, 2.48, 2.95, 3.92, 4.13, 15.8, 37.8, 98.3, 206, 523 and 1096 micrometers (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.

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. Four composite vectors were created and merged by hand.

a) The first *k* vector used the results from the 1096 and 523 μm cells. This *k* vector determined the final values for the range from 7800 to 3479 cm^{-1}, 3402 to 3216 cm^{-1} and 612 to 400 cm^{-1}.
b) The second *k* vector used the results from the 206 and 98.3 μm cells. This *k* vector determined the final values for the range from 3479 to 3402 cm^{-1}, 3216 to 3051 cm^{-1} and 757 to 612 cm^{-1}.
c) The third *k* vector used the results from the 37.8 and 15.8 μm cells. This *k* vector determined the final values for the range from 3051 to 1773 cm^{-1} and 765 to 757 cm^{-1}.
d) The fourth *k* vector used the results from the 4.13, 3.92 and 2.95 μm cells. This *k* vector determined the final values for the range from 1773 to 765 cm^{-1}.
e) The results from the 2.48, 1.68 and 1.53 μm cells were not used.

3) The resulting composite *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) Calculated and estimated errors: Type A = 0.7%.
   b) Frequency correction (already applied): $\tilde{\nu}$(corrected) = [$\tilde{\nu}$(instrument) * .99977 - .01872] as determined by comparing measured atmospheric spectral lines (H_2O and CO_2) to values from the Northwest Infrared Spectral Library Database.
   c) Axis units: X = Wavenumbers (cm^{-1}); Y = Absorbance (base 10).

Photograph of Sample Methyl formate:

Figure 2: Methyl formate in Sigma-Aldrich container.