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

- 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: Diethyl ether, $C_4H_{10}O$, [60-29-7]
- IUPAC name: Ethoxyethane
- Synonyms: Ether; Ethyl ether; Diethyl oxide
- Physical properties: FW = 74.12 g/mole; mp = -116 °C; bp = 34.6 °C; ρ = 0.706 g/cm^3
- Supplier and stated purity: Sigma-Aldrich, ≥99.9% (Lot # SHBG9603V)
- Temperature of sample: 26 °C (+/-1 °C)
- Individual samples were measured at the following path lengths: 3.46, 4.80, 16.1, 38.3, 101, 206, 516 and 1084 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 Diethyl ether was measured at 5 °C and 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. The measurements at 15 °C were as follows:

480 nm: n = 1.3597	486 nm: n = 1.3594	546 nm: n = 1.357
589 nm: n = 1.3551	644 nm: n = 1.3539	656 nm: n = 1.3532
1550 nm: n = 1.3466		

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 Diethyl ether, the result was

$$n(7800\ \text{cm}^{-1}) = 1.3473 \text{ at } 15\ °\text{C}.$$

The change in refractive index with increasing temperature (dn/dT) was estimated to be -0.00069/°C using the measured values from 5 °C and 15 °C. Using this estimate of dn/dT gives a projected value for Diethyl ether of

$$n(7800\ \text{cm}^{-1}) = 1.3390 \text{ at } 27\ °\text{C}.$$

a) b)

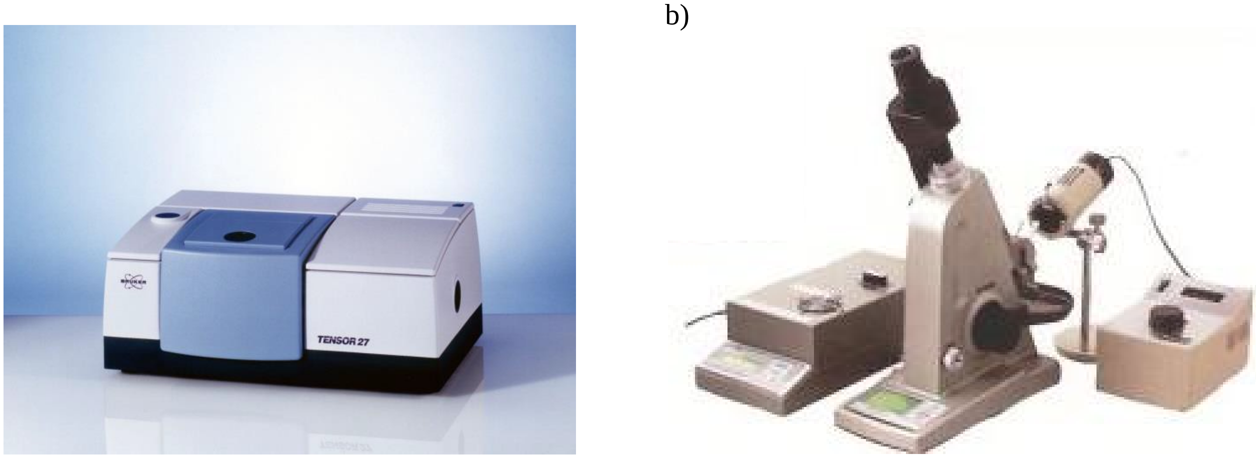

Figure 1: The Bruker Tensor 27 FTIR (a) and Abbe refractometer (b).

Post Processing and Related Parameters:

A composite spectrum was created from 8 absorbance spectra (base-10) taken at 8 path lengths: 3.46, 4.80, 16.1, 38.3, 101, 206, 516 and 1084 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 1084 and 516 μm cells. This *k* vector determined the final values for the range from 7800 to 3036 cm^{-1} and 2678 to 1503 cm^{-1}.

b) The second *k* vector used the results from the 206 and 101 μm cells. This *k* vector determined the final values for the range from 3036 to 3000 cm^{-1}, 1503 to 1448 cm^{-1}, 1348 to 1188 cm^{-1} and 955 to 400 cm^{-1}.

c) The third *k* vector used the results from the 38.3 and 16.1 μm cells. This *k* vector determined the final values for the range from 2772 to 2678 cm^{-1}.

d) The fourth *k* vector used the results from the 4.80 and 3.46 μm cells. This *k* vector determined the final values for the range from 3000 to 2772 cm^{-1}, 1448 to 1348 cm^{-1} and 1188 to 955 cm^{-1}.

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 Diethyl ether:

Figure 2: Diethyl ether in Sigma-Aldrich container.