All data taken at the Pacific Northwest National Laboratory
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Data Analysis: Russell Tonkyn

Composite spectrum for: 14% HNO_3 in water

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

Modifications to the standard experimental procedure were required for HNO_3 solution due to both its aqueous nature and reactivity. Salt cells such as KBr or KCl could not be utilized, and ZnSe cells were too reactive with HNO_3. Our spectra were instead obtained using a germanium (Ge) horizontal attenuated reflection (HATR) accessory, which covered the range from 5000 to 690 cm^{-1}. Bertie's program "PKREF" was used to determine the *k* vector. The number of optical reflections or "bounces" in the ATR accessory was calibrated using pure water by adjusting the value until agreement with Bertie's reference spectrum was achieved. The *n* vector was calculated from the *k* vector using Bertie's program "LZZKTB." For information on the use of ATR to obtain optical constants, see reference 3. The FORTRAN programs are available on Bertie's website along with a discussion of their use.

See the following references for a detailed description of terms and units and modified procedures:

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
3) Bertie, J. E., & Lan, Z. (1996). An accurate modified Kramers–Kronig transformation from reflectance to phase shift on attenuated total reflection. *The Journal of Chemical Physics, 105*(19), 8502-8514. doi:10.1063/1.472635
4) John Bertie's Download Site. (n.d.). Retrieved January, 2017, from https://sites.ualberta.ca/~jbertie/JBDownload.HTM.

Sample:

- Chemical name, formula and CAS number: Nitric acid solution; HNO_3 in H_2O, [7697-37-2]
- IUPAC name: Nitric acid
- Synonyms: Aqua fortis; Spirit of niter
- Physical properties: FW = 63.01 g/mole; mp = n/a; bp = 120.5 °C; ρ = 1.413 g/cm^3
- Supplier and stated purity: Sigma-Aldrich, 70% by weight (Lot # SHBB0195)
- Temperature of sample: 27 °C (+/-1 °C)
- Data obtained from 4400 to 690 cm^{-1} were taken in a horizontal ATR accessory.
- HATR crystal is Ge.
- Preparation: The 70% by wt. HNO_3 stock solution was diluted 1:5 by weight with H_2O.

Instrument Parameters:

- Bruker Tensor 37 FTIR, purged with UHP nitrogen
- Spectral range: 7800 to 690 cm^{-1} (1.282 to 14.4 microns)
- Instrument resolution: 2.0 cm^{-1}
- Number of interferograms averaged per single channel spectrum: Varied
- 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: 4 mm

Measured Refractive Index:

The refractive index for 14% HNO_3 solution was measured at 27 °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.

480 nm: n = 1.3569	486 nm: n = 1.3558	546 nm: n = 1.3524
589 nm: n = 1.3506	644 nm: n = 1.3490	656 nm: n = 1.3486
1550 nm: n = 1.3289		

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 14% HNO_3 solution, the result was

$$n(5000\ cm^{-1}) = 1.3323 \text{ at } 27\ °C.$$

a) b)

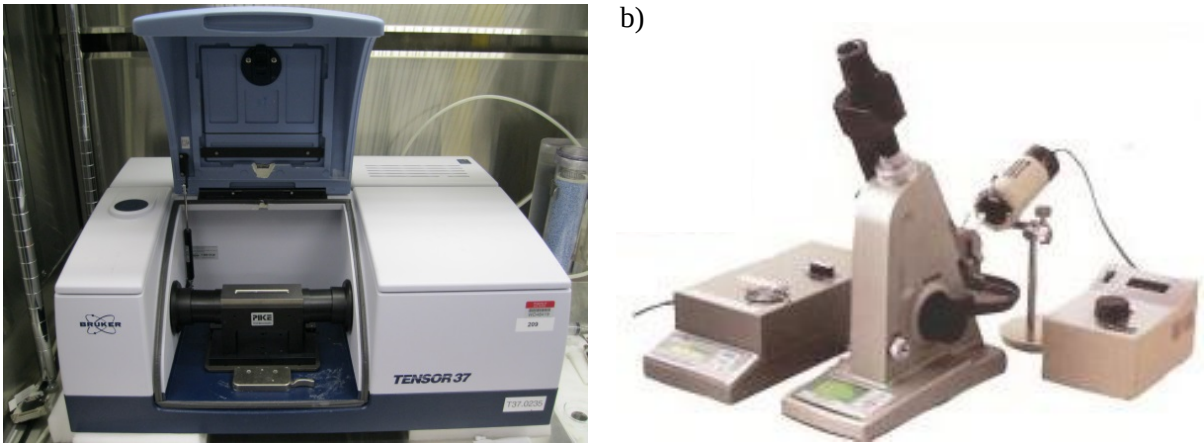

Figure 1: The Bruker Tensor 37 FTIR with HATR accessory (a) and Abbe refractometer (b).

Post Processing and Related Parameters:

1) A *k* vector covering the range from 5000 to 690 cm^{-1} was obtained using a horizontal ATR accessory equipped with a Ge crystal cut at 45 degrees. The number of bounces was calibrated using pure water by comparison to Bertie's reference data. Bertie's program "PKREF" was used.
2) The resulting *k* vector and the refractive index at 5000 cm^{-1} were used to create the real or *n* vector using the Kramers-Kronig relation, as per Bertie's program "LZZKTB."
   a) The errors due to the HATR measurement are hard to quantify, but after calibrating the number of bounces to optimize agreement with Bertie's water spectrum, two integrated band areas agreed to within 1%.
   b) Frequency correction (already applied): $\tilde{\nu}$(corrected) = [$\tilde{\nu}$(instrument) * .99977 + .13186] 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 HNO_3:

Figure 2: Nitric acid 70% in Sigma-Aldrich container.