

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

Composite spectrum for: 7.5% H₂O₂ in water

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

Modifications to the standard experimental procedure were required for the H₂O₂ solution due to both its aqueous nature and reactivity. Salt cells such as KBr or KCl could not be utilized, and zinc selenide (ZnSe) cells also proved to be problematic. The high refractive index of ZnSe led to strong fringing caused by the cell-liquid interfaces so that collecting data with high fidelity at all path lengths and across the entire spectral region was difficult. Moreover, H₂O₂ reacted if left in the cell for an extended period of time leading to the formation of bubbles and causing the transmitted intensity to vary significantly. 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: Hydrogen peroxide solution, H₂O₂ in H₂O, [7722-84-1]
- IUPAC name: Hydrogen peroxide
- Synonyms: Dihydrogen dioxide
- Physical properties: FW = 34.01 g/mole; mp = -0.43 °C; bp = n/a; ρ = 1.11 g/cm³
- Supplier and stated purity: Sigma-Aldrich, 30 wt. % in H₂O (Lot # MKBB0397)
- Temperature of sample: 27 °C (+/-1 °C)
- Individual samples were measured at the following path lengths: 76, 197 and 504 micrometers (μ m). Final data from 7500 to 3800 cm⁻¹ are a composite of these spectra.
- Data obtained from 5000 to 690 cm⁻¹ were taken in a horizontal ATR accessory.
- Sample cell window material is ZnSe. HATR crystal is Ge.
- Preparation: The 30% by wt. H₂O₂ stock solution was diluted 1:4 by weight with H₂O.

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: 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: 4 mm

Measured Refractive Index:

The refractive index for 7.5% H_2O_2 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:	$n = 1.3414$	486 nm:	$n = 1.3409$	546 nm:	$n = 1.3386$
589 nm:	$n = 1.3374$	644 nm:	$n = 1.3358$	656 nm:	$n = 1.3350$
1550 nm:	$n = 1.3200$				

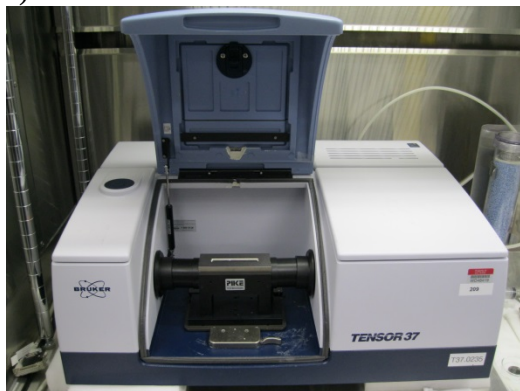
The refractive index, n , vs. wavelength in microns, λ , was fit to an equation similar to that of Sellmeier:

$$n(\lambda) = \{a + b/(\lambda^2 - c)\}^{1/2}$$

The resulting best-fit equation was used to find the refractive index at the highest energy data point in our experimental spectra. For calculations using the ZnSe cells and the HATR accessory, $n(7500\text{cm}^{-1})$ and $n(5000\text{cm}^{-1})$ were used, respectively. For 7.5% H_2O_2 solution, the results were

$$\begin{aligned}n(7500\text{ cm}^{-1}) &= 1.3220 \text{ at } 27\text{ }^\circ\text{C} \\n(5000\text{ cm}^{-1}) &= 1.3174 \text{ at } 27\text{ }^\circ\text{C}.\end{aligned}$$

a)



b)



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

Post Processing and Related Parameters:

A composite spectrum was created from 3 absorbance spectra (base-10) taken at 3 path lengths: 76, 197 and 504 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 or k vector from 7500 to 3800 cm^{-1} 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 ZnSe windows.
- 2) A composite k vector was 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.
- 3) 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.
- 4) The two k vectors were matched between 5000 and 4000 cm^{-1} with a slight baseline shift of the HATR data, and then simply appended to each other. The k vector and the refractive index at 7500 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 0.2% .
 - b) Frequency correction (already applied): $\tilde{\nu}(\text{corrected}) = [\tilde{\nu}(\text{instrument}) * .99977 + .13186]$ 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: $X = \text{Wavenumbers (cm}^{-1}\text{)}$; $Y = \text{Absorbance (base 10)}$.

Photograph of Sample H_2O_2 :



Figure 2: Hydrogen peroxide, 30 wt. %, in Sigma-Aldrich container.