Vibrational Spectroscopy-Based Sensor Systems, ENVIRONMENTAL AND INDUSTRIAL SENSING

Conference 4577
Thursday-Friday 1-2 November 2001
Newton, MA
Proceedings of SPIE Vol. #4577

Creation of 0.10 cm^{-1} Resolution, Quantitative, Infrared Spectral Libraries for Gas Samples

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ABSTRACT

The National Institute of Standards and Technology (NIST) and the Pacific Northwest National Laboratory (PNNL) are independently creating quantitative, ~0.10 cm^{-1} resolution, infrared spectral libraries of vapor phase compounds. The NIST library will consist of approximately 100 vapor phase spectra of volatile hazardous air pollutants (HAPs) and suspected greenhouse gases. The PNNL library will consist of approximately 400 vapor phase spectra associated with DOE's remediation mission.

A critical part of creating and validating any quantitative work involves independent verification based on inter-laboratory comparisons. The two laboratories use significantly different sample preparation and handling techniques. NIST uses gravimetric dilution and a continuous flowing sample while PNNL uses partial pressure dilution and a static sample. Agreement is generally found to be within the statistical uncertainties ($k = 2$, 2σ) of the Beer's law fit and less than 3 % of the total integrated band areas for the 4 chemicals used in this comparison. There does appear to be a small (~1.5 %) systematic difference between the PNNL and NIST data, however. Possible sources of the systematic difference will be discussed as well as technical details concerning the sample preparation and the procedures for overcoming instrumental artifacts.

1. INTRODUCTION

With the advent of commercially available dispersive infrared spectrometers in the 1950s and Fourier-transform infrared (FTIR) spectrometers in the early 1960s, infrared spectroscopy has become an accepted technique for the identification and quantification of many types of samples. While analysis of liquids and solids is by far the largest application of infrared spectroscopy, vapor phase sample analysis is steadily growing. In particular, increased national and international pressure for reduced anthropogenic emissions including hazardous air pollutants, greenhouse gases, and ozone-destroying chemicals has pushed FTIR vapor analysis to new importance. For instance, the Environmental Protection Agency (EPA) has released Method TO-16 for the monitoring of atmospheric gases utilizing long-path, open-path Fourier transform infrared

spectroscopy.[1] Alternatively, EPA Method 320 describes the procedures required for extractive FTIR measurements of vapor phase organic and inorganic emissions.[2] In addition to FTIR techniques, active open-path monitoring has also been performed using a variety of laser based techniques.[3]

Regardless of the technique used for analysis, the success of both open-path and extractive infrared procedures require a comprehensive and accurate set of reference spectra. These reference spectra must fulfill certain minimum criteria to be generally useful including:

- Accurate and statistically meaningful absorbance values
- Accurate frequency values
- Documented sample purity
- Sufficient spectral resolution

There are numerous sources for both hard-copy and digital, vapor-phase, infrared spectral libraries. Some of these libraries are not quantitative, but do use extremely high purity samples such as *The Aldrich Library of FT-IR Spectra of Vapor Phase*.[4] Other spectral libraries are quantitative, but are based on a single absorbance spectrum and not on a Beer's law fit to multiple samples with different concentration path length combinations (burdens).[5, 6, 7] Many of these spectral libraries are acquired at relatively low spectral resolution (*e.g.*, 4 cm^{-1}) and are inadequate for laser based, tropospheric monitoring techniques.

In an effort to develop a comprehensive set of reference spectra useful for general infrared analysis of pressure broadened, vapor phase samples the National Institute of Standards and Technology is in the process of creating *The NIST Quantitative Infrared Database*.[8] In an independent effort the Pacific Northwest National Laboratory has recently been requested by the Department of Energy to create a quantitative spectral library. Early in this effort, it became apparent that laboratory comparisons between PNNL and NIST would be beneficial. In particular, these comparisons resulted in a better understanding of instrumental artifacts that might otherwise compromise the quantitative nature of the resulting spectral data.

2. EXPERIMENT[a]

While both NIST and PNNL use similar vacuum bench FTIR systems (Bruker-66v), sample preparation and the sample delivery methods differ significantly. A continuously flowed White cell with gravimetrically prepared samples is used by NIST. In contrast, PNNL uses a single-pass, static sample cell with number densities based on measured pressure values. The difference in each of the sample handling techniques is necessitated by the type of and number of samples that will be analyzed. Generally, the NIST samples are relatively unreactive species such as Freons, organic alcohols, and aldehydes. In contrast, numerous chemical species for inclusion in the PNNL library are extremely

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[a] *Certain commercial equipment, instruments, or materials are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are the best available for the purpose.*

reactive and undergo hydrolysis or spontaneous combustion or both on contact with air, for example hydrazine or phosphine. While gravimetric sample preparation is a technique for which true number densities can be directly determined, number densities based on measured pressure can be biased by non-ideal gas behavior. For instance, carbon dioxide is known to have a significant deviation[9] from the ideal gas law, $PV=nRT$. In addition, a static gas sample measurement can be biased by sample adsorption onto the sample cell wall as well as sample and contaminant out-gassing from the cell wall. A continuously flowing sample system has less chance of bias from cell wall adsorption or desorption. Despite these shortcomings, the static method is more efficient and reduces opportunities for sample reaction. Although we do not necessarily agree with several of their conclusions, many of the problems encountered in static sample preparation have been discussed in the paper by Richardson and Griffiths.[10] Specifics of both NIST's and PNNL's sample preparation procedures will now be given.

2.1 NIST Specific Procedures

Depending on the phase of the sample at ambient temperature, two different techniques are used for sample preparation. Details related to gravimetric standards preparation have been discussed previously, but will be briefly described below.[11-13]

For liquid samples, an evacuated cylinder is weighed to an accuracy of 0.1 g on a top loading balance with a capacity of 32 kg. The cylinder is fitted with a CGA-350 adaptor that contains a septum and allows injection of the sample directly into the cylinder. Pure sample is drawn into a gas-tight syringe and weighed on a microbalance (100 g capacity) to an uncertainty of 5 µg. To assure complete vaporization of the sample, the septum and valve are heated to 80 °C during sample injection into the evacuated cylinder. Any remaining sample in the syringe is volatilized by gently heating the syringe and allowing the remaining sample to be drawn into the cylinder. The empty syringe is then re-weighed and the sample weight determined by taking the weight difference of the full and empty syringe. Once the sample has been introduced, the cylinder valve is closed and the septum removed. Ultra-high-purity (UHP) nitrogen is then added to the cylinder until a specified pressure is reached. The cylinder is then re-weighed, the amount of nitrogen calculated and the total mole fraction of sample in nitrogen is determined as a micro-mole-fraction, µmol/mol. In general, samples range from 1 µmol/mol to 1000 µmol/mol depending on the IR band strengths and the vapor pressure of the sample. For samples ranging from 50 µmol/mol to 1000 µmol/mol the concentration uncertainty (k = 2) is 0.2 %. Samples with mole fractions up to 50 µmol/mol have an uncertainty of 0.5 %.

Compounds that are gaseous at room temperature require a different preparation procedure: A 150 cm^3 stainless steel cylinder and the cylinder containing the pure gas analyte are connected to a gas manifold. The manifold and all the transfer lines to the cylinders are evacuated. Purging of the system with the pure gas compound is performed several times. An aliquot of pure gas analyte is transferred to the 150 cm^3 stainless steel cylinder which is then weighed a minimum of three times. The aluminum cylinder used for the standard preparation is evacuated and weighed. Both cylinders are connected to the gas manifold and the system evacuated. The analyte is transferred from the 150 cm^3 stainless steel cylinder to the large aluminum cylinder. After closing the valve on the

stainless steel cylinder, the residual in the transfer lines is purged into the aluminum cylinder with pure nitrogen gas. The stainless steel cylinder is removed and weighed a minimum of three times with the resulting difference being the amount of analyte added to the aluminum cylinder. Pure nitrogen gas is then added to the aluminum cylinder to a predetermined pressure which is weighed a final time. The concentration of the compound of interest is calculated from the molar data of the analyte and nitrogen. Using ethylene at 500 µmol/mol as an example, ~2 g of ethylene would be needed to make this concentration in a 30 L cylinder with a final pressure of 12.4 MPa (1800 psi). The uncertainty in weighing this amount of material and the nitrogen, plus the uncertainty in the purity of the analyte and balance nitrogen, would be ± 0.1 % (k = 2). For an ethylene standard at 50 µmol/mol the resulting uncertainty would be ± 0.2 % (k = 2).

Once prepared, each standard is allowed to convectively mix inside the cylinder by placing a heat source at the base of the cylinder. Finally, as a self-consistency check to the gravimetric procedure, each set of standards is analyzed via gas-chromatography (GC) with flame-ionization detection (FID). The results of the GC-FID are then plotted (area versus µmol/mol) and checked for consistency. In general, the GC-FID is found to agree to better than 1 % with the gravimetric procedure. Additionally, the purity of the analytes and UHP nitrogen are verified using a number of techniques including: GC-FID, Karl Fischer methods, and differential scanning calorimetry.

A commercial, variable path, multipass White cell is used with a Bruker-66V FTIR spectrometer. This White cell has a maximum path length of 20 m and a volume of 7.5 L. The exact value of the optical path length is determined by measuring the mirror separations with the cell encasing removed. The single pass distance is found to be 1.356 m ± 0.001 m including the window-to-mirror spacing. The optical path length is verified by comparing band intensities from the FTIR measurements to those obtained by laser studies.[14] The gravimetric standards are flowed continuously at 1 L/min at atmospheric pressure through the White cell. Both sample temperature and pressure are monitored during the data collection using a NIST calibrated thermometer and capacitance manometer. In a similar fashion, background spectra are obtained with UHP nitrogen flowing through the White cell.

2.2 PNNL Specific Procedures

PNNL samples are prepared via pressure dilution on an all metal manifold. The manifold is constructed of stainless steel that has been electro-polished and then gold plated to reduce the chance of sample adsorption or reactions with the manifold surface. Three Baratron type capacitance manometers (NIST traceable) with a full-scale accuracy of 0.05% (k = 2) are connected to the manifold via stainless steel lines. The three MKS Baratrons have full scale pressure of 0.133 kPa, 1.33 kPa, and 133 kPa (1 Torr, 10 Torr and 1000 Torr). The manifold is in turn connected to a single-pass sample cell contained within the spectrometer's sample compartment. The manifold and sample cell can be evacuated to $<10^{-5}$ Torr via a liquid nitrogen trapped diffusion pump. Both the sample cell and pumping system can be independently isolated from the manifold via gate-valves. UHP nitrogen is supplied to the manifold through a computer operated leak valve. Trace water and other condensables are removed from the UHP nitrogen by flowing the

gas through a small bore copper tube immersed in liquid nitrogen. The manifold and all associated plumbing are heated to 60 °C to facilitate sample out-gassing.

The infrared absorption cell is single pass with wedged windows on either end (KBr, ZnSe or NaCl). The length of the sample cell is measured at three points and known to 0.01 cm with a nominal length of 20 cm. Like the manifold, the sample cell is electro-polished and gold plated to reduce sticking and reactions with the samples. The cell is constructed with a 5.1 cm inside diameter and a concentric 7.6 cm outside diameter water jacket. Temperature regulated water is circulated through the outside cell jacket and monitored via a four lead resistance platinum transducer with an accuracy of ± 0.02 °C. To minimize dead volume and the resulting errors during the nitrogen backfill, the cell shut-off valve is located within 1 cm of the cell body. Hence, the dead volume for this 0.64 cm diameter by 1 cm long tube is approximately 0.1 % of the total cell volume.

A sample is prepared by first placing approximately 10 g to 25 g of neat sample into either a 50 cm^3 stainless steel or glass finger. The finger is then mounted to the manifold via an all stainless steel valve and VCR fittings. In the case of gaseous samples, the finger is first cooled to 77 K then several atmospheres of the neat sample are placed into the manifold and allowed to condense into the cooled finger. All samples undergo several freeze-pump-thaw cycles to remove air. In addition, and depending on sample purity, the sample is cooled with a slush bath such that the vapor pressure of the sample is slightly less than 0.133 kPa (1 Torr) and then pumped on for several minutes to remove the more volatile contaminants. If additional purification is required, the sample is distilled to a second cold-finger. In many cases, the samples will have some dissolved trace water and require drying over a desiccant such as $CaSO_4$.

Once purified of air and other impurities, the sample is admitted to the manifold and absorption cell. The pumping system is isolated from the manifold-cell during the sample filling process. Depending on the infrared band strength and vapor pressure of the sample, the manifold and cell are filled to a specified target pressure of sample. The finger is then isolated from the manifold and the pressure allowed to stabilize such that the pressure change is less than 0.5 % in one minute. At this point, a final pressure reading is taken, the cell temperature is noted, and the sample cell is isolated from the manifold. The manifold is then evacuated, purged with UHP nitrogen, and then evacuated again. At this point, the sample cell must be backfilled to 101.3 kPa (1 atm) with UHP nitrogen while avoiding sample backflow from cell to manifold. The backfill process starts by pressurizing the manifold with UHP nitrogen and then opening the manifold-to-sample cell valve when a pressure of ~27 kPa (200 Torr) is reached. The nitrogen flow continues until the manifold and cell pressure reaches approximately 96 kPa (720 Torr), at which point the cell is isolated from the manifold. The manifold is allowed to further pressurize to approximately 103 kPa (770 Torr) and the nitrogen is turned off. The cell is now quickly opened to the manifold for a short duration such that the cell pressure is 101.33 kPa (760 Torr) ± 0.7 %. To avoid much of the tedium and to minimize mistakes, the entire process of backfilling, system purge, and evacuation are performed via a computer interface to the manifold. The gas is allowed to mix and thermally equilibrate in the cell, and the infrared spectrum is recorded as described in Section 2.3. This

process is repeated such that 6 to 12 different concentrations of sample are analyzed per sample at three temperatures, 5 °C, 25 °C, and 50 °C.

The PNNL FTIR spectrometer (Bruker-66V) has undergone modification and a second aperture has been added between the interferometer output and the sample cell.[15] This modification was found necessary to correct two potentially significant instrumental artifacts that plague many commercial FTIR systems when operated in high resolution mode (*e.g.*, < 0.5 cm^{-1}). The first artifact involves double modulation of light reflected off of the back side of the stock aperture (uncoated stainless steel in our case), between the glow-bar source and the interferometer. The second artifact is more serious and involves off-axis radiation entering the interferometer from the warm annulus of the stock aperture. The "warm aperture" effect can degrade both line shapes and intensity measurements by as much as ~10 %. In contrast, the NIST spectrometer appears to be relatively immune to these effects as the White cell appears to act as an effective second aperture.

2.3 Data Acquisition and analysis

Both NIST and PNNL use a similar process for creating the final *composite* spectrum. Each individual absorbance spectrum starts by the acquisition of a single channel spectrum for sample (I) and background (I_0). Absorbance spectra are created via the standard $-log(I/I_0)$. Each single channel spectrum is derived from 256 to 512 averaged interferograms acquired at 0.125 cm^{-1} and 0.112 cm^{-1} resolution for NIST and PNNL, respectively. In both cases, the interferograms are transformed to the spectral domain via the supplied Bruker OPUS software. Boxcar apodization and 2X zerofilling are used to preserve as much information as possible. Both NIST and PNNL use HgCdTe liquid nitrogen cooled detectors, KBr beamsplitters and silicon-carbide glowbars.

Since nonlinearity can be significant for photoconductive HgCdTe detectors, the Bruker supplied correction algorithm is used during the Fourier transform to minimize these effects. Tests indicate that the nonlinearity deviation from Beer's law is approximately 1.5 % for absorbances of 1.6 (base 10). Once a series of absorbance spectra corresponding to different concentrations has been acquired, the set of spectra are fit to a linear equation in concentration at each sampled frequency using classical least squares. (During this process, the NIST spectra are scaled for absolute number density based on the recorded sample temperature and pressure.) Each observed absorbance value is weighted by the transmission squared ($W=T^2$) or zero ($W=0$) for values equal to or above an absorbance of 1.6. The slope of this fit corresponds to the absorption coefficient in the units of $(\mu mol/mol)^{-1}m^{-1}$ for the NIST data. We note that the multiple burden fitting approach is more accurate since the high burdens favor the weak bands whereas the low burdens ensure Beer's law behavior for strong bands. Moreover, any band that does not scale with Beer's law (e.g. impurities) readily manifests itself in the difference spectrum. For the PNNL data the final absorption coefficient data is given in $(\mu Pa\text{-}m)^{-1}$, where the sample number density is calculated from the sample pressure. Using the ideal gas law, the final PNNL absorption coefficients are reported in units of $(\mu mol/mol)^{-1}m^{-1}$ or $(ppm\text{-}m)^{-1}$. The PNNL absorption coefficients should be identical to the NIST data assuming ideal gas behavior. It is interesting to note that the largest source of uncertainty

in this fitting process is due to the detector nonlinearity. One of the benefits to fitting the data to a Beer's law plot is that any impurities that do not scale linearly with the sample concentration manifest as large signatures in the uncertainty vectors.

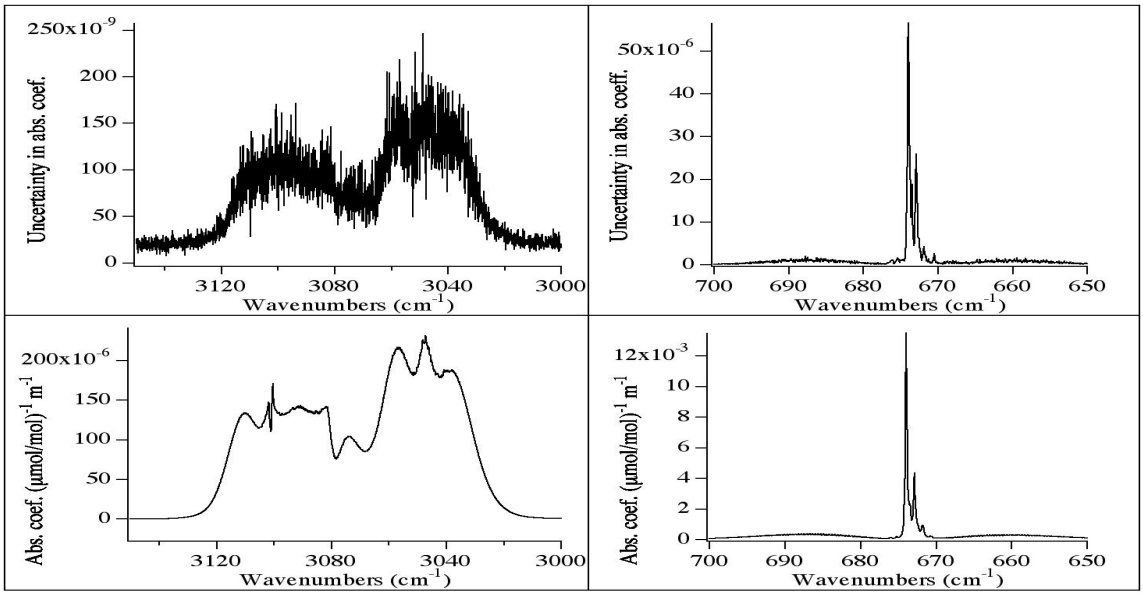

Figure 1. Results (PNNL) for least squares fit to 11 different absorbance spectra for benzene (lower traces). Upper traces contain the corresponding uncertainty in the least squares fit. Note the change in ordinate values.

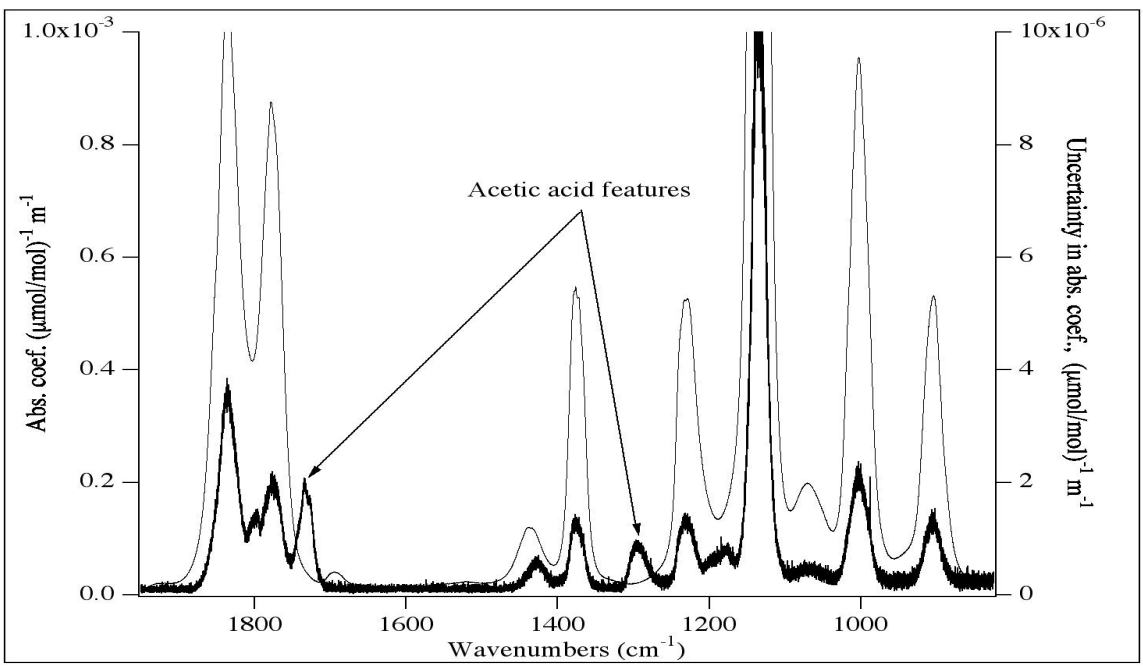

Figure 2. Plot of resulting least squares fit for acetic anhydride (smooth trace) and the associated uncertainty in the fit (noisy trace). PNNL data.

Referring to Figure 1, the relative standard uncertainty in the least squares fit is approximately 0.1 % and 0.42 % for the 3040 cm^{-1} and 675 cm^{-1} features of benzene, respectively. Most of this uncertainty is attributed to residual after correction for nonlinear response of the HgCdTe detector. Partial pressures of benzene ranged from 13.3 Pa to 4.8 kPa (0.1 Torr to 36 Torr). Figure 2 demonstrates the sensitivity of the linear least squares fitting process to the presence of impurities. Specifically, nine individual absorbance files were used to create the composite spectrum for acetic anhydride. The uncertainy trace in Figure 2, shows that acetic acid impurities are easily recognized by their diproportionatly larger values whereas the impurity absorptions are difficult to discern in a single measurement.

2.4 Frequency Calibration

Both NIST and PNNL use similar techniques for frequency calibration. NIST uses 158 specific water lines (3600 cm^{-1} and 1600 cm^{-1} regions) measured by Toth, to generate a linear correction.[16] PNNL uses 165 specific carbon monoxide (4250 cm^{-1} and 2150 cm^{-1} regions) and nitrous oxide (1170 cm^{-1} and 610 cm^{-1} regions) lines measured by Maki and Wells, to generate a linear correction.[17] The root-mean-square (rms) deviation between corrected and reference line positions for NIST and PNNL are 0.0042 cm^{-1} and 0.0018 cm^{-1}, respectively. A plot of the PNNL corrected line positions minus the line positions reported by Maki may be seen in Figure 3.

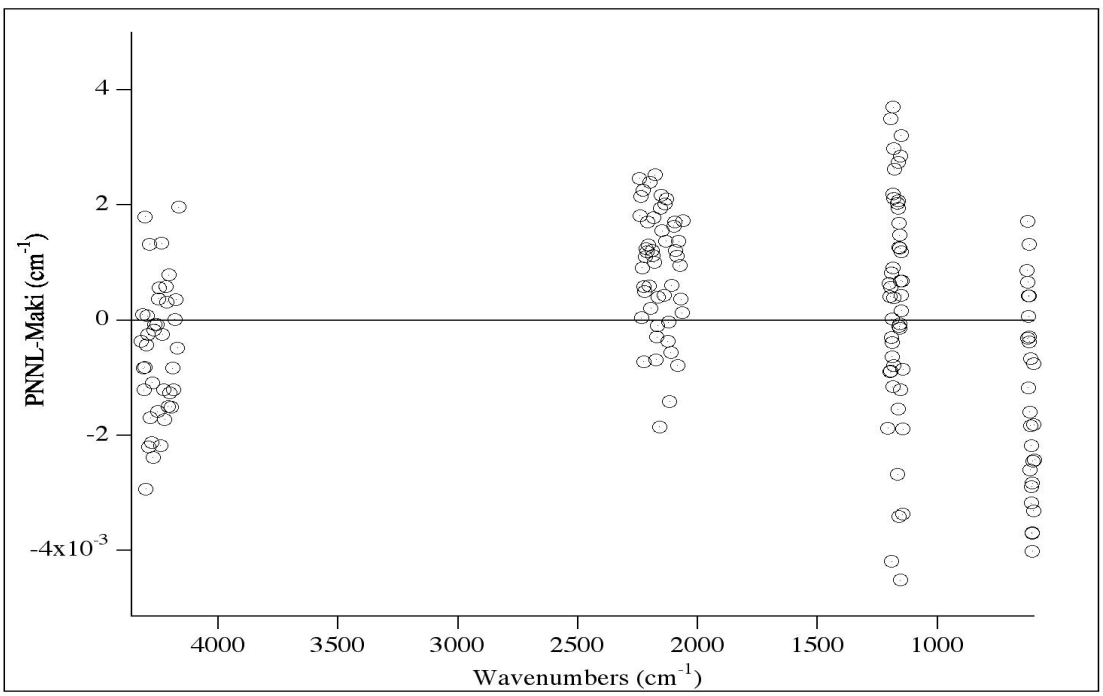

Figure 3. Line position differences (PNNL-Maki) for CO and N_2O. See text for details.

3. RESULTS

Although the NIST and PNNL IR libraries focus on different samples, several chemicals were chosen for comparison purposes. These include ethylene, butane, methanol, and benzene based on their unique spectral and chemical properties. All four compounds are

non-reactive and easy to handle and have large vapor pressures at room temperature. Ethylene and methanol have sharp features spread throughout the MWIR (mid-wave infrared) and LWIR (long-wave infrared) spectral regions. Butane has broad features throughout the MWIR and LWIR region. Benzene has an extremely intense and narrow feature in the LWIR as well as several much weaker features in the MWIR.

There are several ways to compare spectral data and we have chosen to examine the integrated band strengths. In this process one of us (NIST) was tasked to integrate the composite spectra between specific frequency limits. The percent difference is then calculated based on the integrated area as per Equation 1.

$$\%\Delta = [(Area_{NIST} - Area_{PNNL})/Area_{NIST}] \times 100 \qquad (1)$$

Table 1. Comparison of NIST and PNNL integrated band areas for selected compounds.

Sample	Limits (cm^{-1})	NIST	PNNL	%Δ
Ethylene	800-1190	0.01577	0.01552	1.6
	2895-3285	0.007503	0.007365	1.8
Benzene	615-735	0.01880	0.01856	1.3
	2990-3150	0.01328	0.01313	1.1
Butane	1232.6-1558.3	0.005259	0.005276	-0.3
	2502-3460	0.05827	0.05754	1.3
Methanol	885.6-1160	0.01947	0.01924	1.2
	2715.7-3151	0.02264	0.02214	2.2

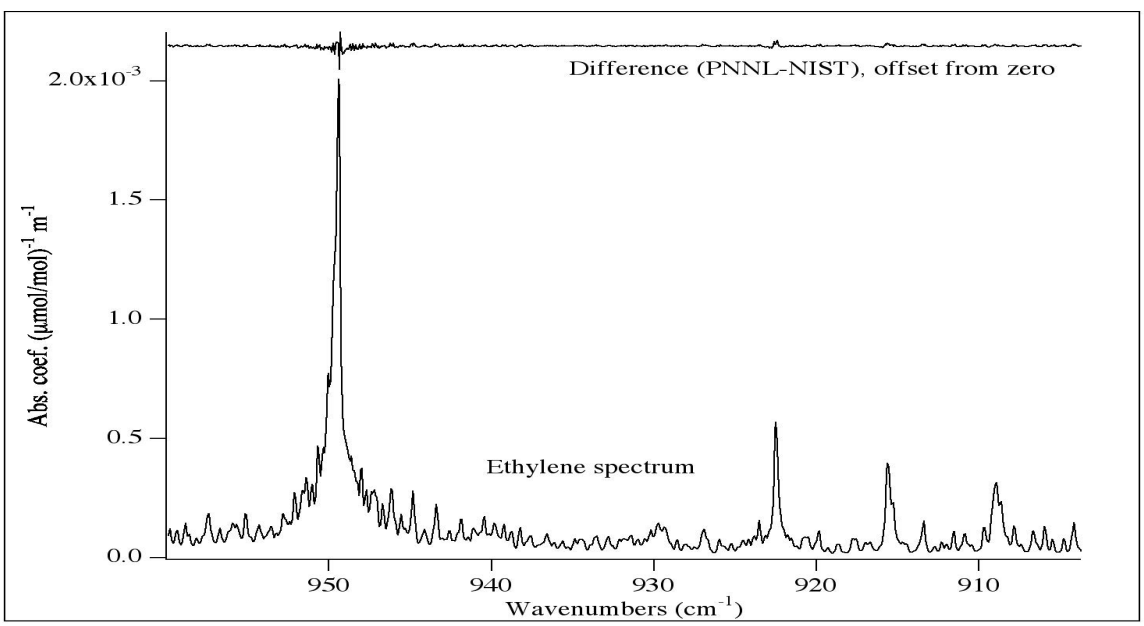

Figure 4. Spectrum of ethylene (lower trace) and offset difference spectrum for PNNL-NIST (upper trace).

Although all integrated areas are well within the expected 3.0 % relative expanded uncertainty limit there does appear to be a trend with the PNNL peak areas being slightly smaller than those of NIST. Alternatively, a graphical representation of the difference between the NIST and PNNL spectra for ethylene and benzene may be seen in Figures 4 and 5. The difference spectra for ethylene and benzene exhibit a derivative shape, thought to be due to slightly different instrumental resolutions and line shapes.

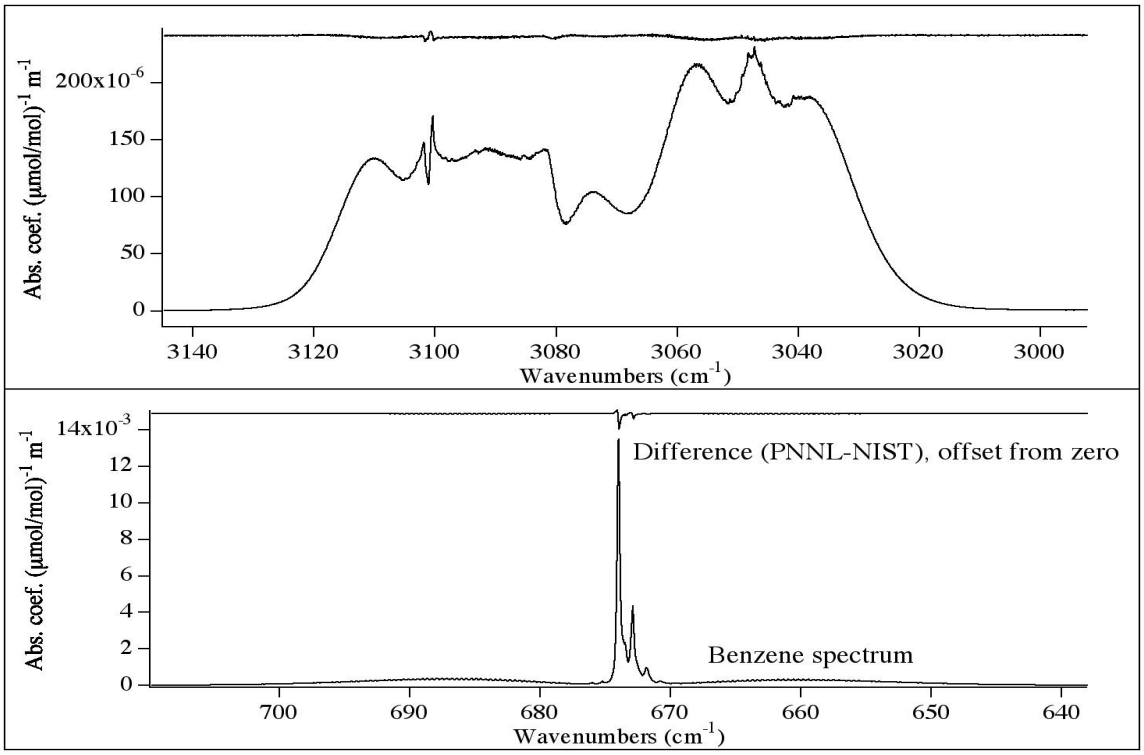

Figure 5. Spectrum of benzene and difference spectrum for PNNL-NIST for the MWIR and LWIR features.

4. DISCUSSION

It is seen that the integrated band intensities for selected NIST and PNNL spectra are in agreement to within the expected relative expanded uncertainty limit (3 %) even though significantly different sample handling procedures are employed. However, there appears to be a small bias between the PNNL and NIST integrated intensities. Specifically, PNNL is ~1.5 % lower than NIST. There may be several explanations for this apparent bias as indicated by the following uncertainty budget analysis.[8]

Table 2. Standard uncertainties due to experimental bias and their estimated magnitudes. See reference 8.

Source	Fractional Value
Optical path length, μ_L	0.001
Sample temperature, μ_T	0.0005
Sample pressure, μ_P	0.001
FTIR drift, μ_P	0.002
HgCdTe nonlineraity, μ_N	0.01

Assuming that these uncertainties are uncorrelated with one-another, the total bias related uncertainties can be written as

$$\mu_{Bias} = k[(\mu_L)^2 + (\mu_T)^2 + (\mu_P)^2 + (\mu_P)^2 + (\mu_N)^2]^{1/2}. \qquad (2)$$

Using the appropriate values from Table 2 with equation (2), the total relative expanded uncertainties due to instrumental bias, μ_{Bias} is found to be 2.1 %. If the NIST and PNNL uncertainties are similar in magnitude and uncorrelated with one another then the uncertainty between the two labs is given by $[\mu_{Bias}(NIST)^2 + [\mu_{Bias}(PNNL)^2]^{1/2} = 3\ \%$. Further investigation is underway to elucidate the apparent 1.5 % bias.

Another potential bias that neither NIST nor PNNL have attempted to correct may be due to optical emission of the sample. The effects of sample emission in FTIR spectroscopy are well known and have been discussed in the literature. Ballard discusses one method for removing such emission errors in FTIR data involving single channel spectra acquired for both sample and background with the glow-bar source turned on and then turned off.[18] The absorbance spectrum is then calculated as per equation (3).

$$A(\upsilon) = -\log\left(\frac{I^{ON} - I^{OFF}}{I_0^{ON} - I_0^{OFF}}\right) \qquad (3)$$

Based on this approach, a corresponding composite spectrum for ethylene was created at PNNL using Ballard's procedure. It appears that sample emission contributes approximately 1 % error to LWIR features (*e.g.*, <1100 cm^{-1}) for 5 ºC to 50 ºC samples. Although, the exact magnitude and sign of the emission effects will depend on the sample temperature.

Another difference noted between the NIST and PNNL data is due to self-broadening effects. In general, the PNNL samples have a significantly higher partial pressure of sample since a single-pass cell is used. The higher sample pressure can cause noticeable self-broadening effects in highly polarizable species such as acetonitrile.

As mentioned in the introduction, there are other sources for IR spectral data. For purposes of comparison a few of these quantitative sources[7,19] are compared against the NIST results and may be seen in Table 3. It should be noted that the EPA data[7] is based on the average of several absorbance spectra. Referring to Table 3, it should be noted the some of the discrepancy between Hitran and NIST is due to the fact that hot bands and combination bands are not included in the line-by-line listing for ethylene. Moreover, many of the Hitran molecules are truncated at higher J-values.

Table 3. Comparison of integrated band areas for several data sources. As before, the percent-change (%Δ) is defined in Equation (1).

Sample	Limits (cm^{-1})	%Δ PNNL	%Δ EPA[7]	%Δ HITRAN[19]
Ethylene	800-1190	+1.6	+1.1	+14.4
	2895-3285	+1.8	+1.4	+18.3
Benzene	615-735	+1.3	+5.2	na
	2990-3150	+1.1	+12.9	na
Butane	1232.6-1558.3	-0.3	na	na
	2502-3460	+1.3	na	na
Methanol	885.6-1160	+1.2	+14.9	na
	2715.7-3151	+2.2	+14.9	na

5. SUMMARY

PNNL and NIST have independently created two separate high-resolution (~0.1 cm^{-1}) databases of digital infrared vapor phase spectra. The two databases serve somewhat different ends, but both are of great use to the vapor phase spectroscopist. The two laboratories used very different methods for sample preparation, namely gravimetrically prepared samples continuously flowed through a long-path cell (NIST) versus a static sample cell with number densities based on pressure measurements (PNNL). Both have taken many measures to avoid the pitfalls associated with gas phase measurements. Fitting of multiple concentrations and path lengths has shown to yield much better Beer's law absorption coefficients as well as eliminating bands due to impurities. Using the two techniques, data from the two labs agree within the 3 % relative expanded uncertainties, but PNNL's integrated absorption bands appear to be systematically ~1.5 % lower than those of NIST. Possible causes of this discrepancy have been discussed and further investigation is currently underway.

ACKNOWLEDGEMENTS

PNNL is operated for the US Department of Energy by the Battelle Memorial Institute under contract DE-AC06-76RLO 1830.

Partial support from NIST Technology Services is greatly appreciated. P. M. Chu thanks W. J. Lafferty for many helpful discussions and P. A. Johnson for the data acquisition.

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