

Quantitative Vapor-Phase Infrared Spectrometry of Ammonia

LIMIN SHAO, PETER R. GRIFFITHS,* PAMELA M. CHU, and THOMAS W. VETTER

Department of Chemistry, University of Idaho, Moscow, Idaho 83844-2343 (L.S., P.R.G.); and National Institute of Standards and Technology, 100 Bureau Drive, Gaithersburg, Maryland 20899

Reference spectra of ammonia from four sources are compared. Low-resolution spectra (i.e., spectra for which the spectrometer resolution is numerically greater than the full-width at half-height of the rotational lines) were obtained from the Environmental Protection Agency (EPA) web site and from Infrared Analysis, Inc. High-resolution (0.12 cm^{-1}) spectra were obtained from the National Institute for Standards and Technology (NIST) and Pacific Northwest National Laboratory (PNNL). Two protocols were used to validate the EPA and Infrared Analysis spectra, with one requiring that Beer's law be obeyed by the low-resolution spectrum and the other that Beer's law be obeyed by the high-resolution spectrum. In all cases, the second protocol gave a significantly better spectral match. It is shown that the path-integrated concentrations for the low-resolution reference spectra were in error by as little as 4% to as much as an order of magnitude, presumably because of the effect of adsorption on the cell walls. Measured absorptivities of the NIST and PNNL spectra were different by $\approx 2.6\%$ and it is believed that the effect of adsorption on these spectra is small. When the same protocols were used to test the reference spectrum of methane, the calculated path-integrated concentration was only $\sim 2\%$ different from the one that was calculated from the NIST reference spectrum, suggesting that the data processing protocols provide accurate data.

Index Headings: Reference spectra; Vapor phase; Ammonia; Methane; Beer's law; Resolution.

INTRODUCTION

The accuracy of quantitative determinations of gases by Fourier transform infrared (FT-IR) spectrometry depends on two factors: the accuracy of the reference spectra and whether Beer's law is obeyed under the experimental conditions. In this paper, we examine these two factors, with emphasis on the determination of ammonia in open-path (OP) FT-IR spectrometry.

Every multivariate analytical technique used in quantitative infrared spectrometry gives more accurate results if Beer's law is obeyed, i.e., if the measured absorbance varies linearly with the concentration of each analyte. For condensed-phase samples, Beer's law behavior can be affected by chemical interactions between the analyte molecules and the matrix; however, such interactions rarely affect vapor-phase measurements. There are several instrumental factors that affect the linear range of Beer's law for spectra measured on FT-IR spectrometers, especially resolution and apodization. Ramsay¹ defined the *resolution parameter*, ρ , as the ratio of the full-width at half-height (FWHH) of the triangular slit function of a grating monochromator to the FWHH of a Lorentzian band measured at infinitely high resolution (i.e., the true FWHH of the measured band). He investigated the relationship between the apparent (measured) peak absorbance, A_{peak}^a , and the true peak absorbance, A_{peak}^t , as a function of ρ and found that when $A_{\text{peak}}^t < 0.7$, Beer's law is obeyed (i.e., A_{peak}^a is proportional to A_{peak}^t) provided that $\rho \leq 0.2$, where A_{peak}^t and A_{peak}^a are the base 10 absorbances.

In 1975, Anderson and Griffiths² made a similar investigation for FT-IR spectra computed with either boxcar truncation or triangular apodization, where the nominal resolution was defined as the reciprocal of the maximum optical path difference of the interferogram. In this paper, we define resolution in the same way. For boxcar truncation, they found Beer's law was obeyed either when ρ or A_{peak}^t was small, but there were significant deviations when $\rho > 1$. With triangular apodization, the resolution parameter must be much lower ($\rho < 0.1$) if Beer's law is to be obeyed by strong spectral features. Subsequently, Zhu and Griffiths³ investigated the effects of several other apodization functions, including the Norton-Beer (NB) functions,⁴ on the linearity of Beer's law. They found that a wider range of concentrations could be accommodated by using the NB functions than by either boxcar truncation or triangular apodization. By using the NB "medium" apodization function, they found that Beer's law is obeyed when $A_{\text{peak}}^t < 5$, provided that ρ is no larger than about 0.2. It should be noted, however, that the photometric accuracy of most FT-IR spectrometers is limited by the accuracy to which the zero-energy value under intense bands can be estimated, and few FT-IR spectrometers are able to measure bands with $A_{\text{peak}}^a > 3$ correctly.⁵

In all cases, the linear range of Beer's law in quantitative FT-IR spectroscopy is dependent on the resolution at which the spectrum is measured. As a general rule, for intense bands, the higher the resolution, the wider the linear range. However, for relatively weak bands ($A_{\text{peak}}^t < 0.5$), Beer's law is invariably obeyed for all values of ρ and all apodization functions. There is often a benefit to low-resolution measurements because low-noise spectra can be measured rapidly and instruments are small and inexpensive.

While most condensed-phase spectra and the vapor-phase spectra of large molecules (for which the spacing of the rotational lines is less than the linewidths) can be readily measured with $\rho < 1$, this is not the case for the vapor-phase spectra of small molecules. The typical pressure-broadening coefficient for an isolated line in the vibration-rotation spectrum of a small molecule in air at a pressure of 101.3 kPa (1 atm) is $1\text{--}3 \times 10^{-3}\text{ cm}^{-1}/\text{kPa}$ ($0.1\text{--}0.3\text{ cm}^{-1}/\text{atm}$). For example, the true FWHH of most lines in the vibration-rotation spectrum of ammonia at 101.3 kPa (1 atm) pressure is $\approx 0.22\text{ cm}^{-1}$. Measuring such lines with $\rho \leq 0.2$ would require a resolution better than 0.05 cm^{-1} , which would lead to excessively long measurement times if an acceptable noise level is to be achieved.

Figure 1 shows a plot of $\log A_{\text{peak}}^a$ against $\log A_{\text{peak}}^t$ for a Lorentzian band computed with triangular apodization with $\rho = 0$ (infinitely high resolution, upper curve) and $\rho = 1$ (lower curve). Beer's law is obeyed when the slope of this plot is equal to unity. If the true peak absorbance (proportional to concentration) of the reference is at point a , Beer's law is obeyed whether the spectrum is measured with $\rho = 0$ or 1. On the other hand, for any value of A_{peak}^t above b , Beer's law is not

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* Author to whom correspondence should be sent. E-mail: pgriff@uidaho.edu.

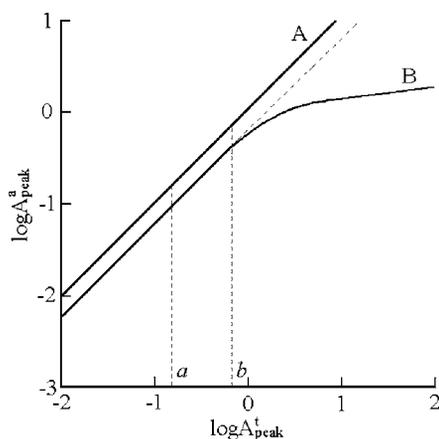


FIG. 1. Plot of $\log A_{\text{peak}}^a$ vs. $\log A_{\text{peak}}^t$ (base 10) for spectra computed with triangular apodization: (A) $\rho = 0$; (B) $\rho = 1.0$.

obeyed and severe quantitative errors are encountered if linear Beer's law behavior is assumed in any calibration made under this circumstance.

This type of consideration has led to a considerable controversy as to the resolution at which OP/FT-IR spectra of small molecules with readily resolvable rotational fine structure should be measured.^{6–12} We have been interested in OP/FT-IR measurements of ammonia, and we will use this molecule to illustrate some of the problems associated with quantitative spectroscopy of gases at low resolution.

REFERENCE SPECTRA

Large collections of air-broadened vapor-phase infrared reference spectra are available from several sources. Data from the U.S. Environmental Protection Agency (EPA) were measured by Entropy Environmentalists Inc. using a cell with a path length of 3 m.¹³ This collection contains the interferograms for 99 compounds from which spectra with a nominal resolution of 0.25 cm^{-1} may be calculated. For most of the compounds, four interferograms are available, two measured with the sample at high concentration in 101.3 kPa (1 atm) of nitrogen (typically $500 \mu\text{mol mol}^{-1}$ (ppm), i.e., a path-integrated concentration of $\approx 1500 \mu\text{mol mol}^{-1} \text{ m}$ (ppm-m)) and two at lower concentration (path-integrated concentration of $\approx 300 \mu\text{mol mol}^{-1} \text{ m}$ (ppm-m)). Even lower concentration samples were used for molecules of very high absorptivity. The stated concentrations for the reference spectra of ammonia in the EPA database were (500, 500, 99.8, and 99.9) $\mu\text{mol mol}^{-1}$ (ppm).¹³ When these interferograms were used in our work, spectra were calculated with the Norton–Beer “medium” apodization function.

Another large collection of vapor-phase reference spectra was measured by Infrared Analysis, Inc. (IA) (QASoft 4.0 Database). This library contains duplicate reference spectra of over 200 compounds measured at nominal resolutions of 0.5 cm^{-1} and 1 cm^{-1} . The path-integrated concentration of ammonia was $100 \mu\text{mol mol}^{-1} \text{ m}$ (ppm-m). Nitrogen was added to raise the pressure to 101.3 kPa (1 atm) and the cell was held at 25°C . Two absorption spectra of the same sample were supplied at resolutions of 0.5 cm^{-1} and 1 cm^{-1} and with a zero-filling factor of 2. The interferograms had been transformed with a triangular apodization function. After the spectra had been converted to a linear absorbance format, they

were further smoothed by a Fourier smoothing function,¹⁴ although this is not stated in the software manual. For the purpose of this comparison, the concentrations of ammonia in the EPA or IA reference spectra will be referred to as unknowns. All spectra in the Infrared Analysis and EPA databases were measured with the sample at 25°C .

Additional collections of very high quality vapor-phase reference spectra are also available from the National Institute of Standards and Technology (NIST)¹⁵ and the Pacific Northwest National Laboratory (PNNL).¹⁶ The spectra in both these collections were measured at a nominal resolution of $\sim 0.125 \text{ cm}^{-1}$ and are unapodized. Both collections provide reference spectra with path-integrated concentrations of $1 \mu\text{mol mol}^{-1} \text{ m}$ (or 1 ppm m) at 296 K and 101.3 kPa. The PNNL spectra were measured with the sample at 25°C and the NIST spectra were measured at 24.5°C for NH_3 and 23.4°C for CH_4 . The differences between these temperatures and 25°C , at which all the other reference spectra were measured, was found to be insignificant and was neglected.

For our investigation, a NIST sample interferogram was obtained from a gravimetrically prepared NH_3 in high-purity nitrogen mixture purchased from a commercial specialty gas supplier. The calculated gravimetric concentration of ammonia was $(39.95 \pm 0.2) \mu\text{mol mol}^{-1}$ (ppm). All reported 2σ uncertainties are provided to the 95% confidence level. The background interferogram was obtained using ultra-high purity nitrogen. The FT-IR measurements were made with a Ni coated stainless-steel sample cell with a path length of $(2.01 \pm 0.01) \text{ m}$, a temperature of $(24.5 \pm 0.1)^\circ\text{C}$, and a pressure of $(99.6 \pm 2) \text{ kPa}$. The nominal resolution was 0.125 cm^{-1} and the interferograms were not apodized. Under these conditions the measured absorbance (which at this value of ρ is approximately equal to A_{peak}^t) for the strongest NH_3 peak was 0.24.

In light of the reactive nature of NH_3 , the capability of delivering a known quantity of these species to the FT-IR sample cell was a concern. While the gravimetric preparation process should provide an accurate measure of the material that is initially introduced into the gas cylinder, adsorption to the wall of the gas cylinder, regulator, sample lines, and FT-IR cell may reduce the capability to deliver a known NH_3 concentration. Comparison of absorbance spectra for 14 gravimetrically prepared NH_3 in nitrogen mixes allows the quality of the NH_3 data to be assessed from a quantitative perspective. A linear regression comparing the integrated absorbance over 950 cm^{-1} to 980 cm^{-1} to the theoretical gravimetric values resulted in an r -squared value $r^2 = 0.99985$. These results suggest that the FT-IR measurements were well correlated with the theoretical gravimetric values. The data were examined with regard to the likelihood that all of the analyte was delivered to the FT-IR sample cell by noting any time-dependent changes in the absorbance spectra. Under the sampling conditions used for these measurements, the signal change over the course of the one-hour measurement was only a 0.3%, without any corrections for any background shifts. Additionally, the background spectra obtained both before and after the analyte spectra were examined for residual analyte absorption features that could bias the final absorption spectra and indicate a problem of material being retained in the sample cell.

Finally, a further measure was taken for spectra measured at NIST. The concentration of the NH_3 in nitrogen mixture was analyzed by trapping the NH_3 as the gas sample is introduced into a dilute boric acid solution, and then measuring the amount

of NH_3 collected by titrating the solution with hydrochloric acid. The mole fraction of NH_3 in the delivered gas mixture was calculated based on the amount of NH_3 captured coupled with the measured flow rate and time that the sample gas was passed through the trap.¹⁷ This titrimetric analysis indicated that $(37.47 \pm 0.26) \mu\text{mol mol}^{-1}$ NH_3 was delivered from the gas cylinders compared to the $(39.95 \pm 0.2) \mu\text{mol mol}^{-1}$ calculated gravimetric values that report the amount of material placed into the cylinder. The reported uncertainties represent the expanded uncertainty or 2σ values associated with the Type A or random uncertainties for the measurements. The titration results, which measured the material delivered from the gravimetric cylinder, potentially more accurately reflect the ammonia concentration delivered to the FT-IR sample cell. Based on this assumption, the NIST NH_3 spectrum has been scaled to the concentration obtained from the titrimetric analysis. It is important to note that a systematic bias may be present in the titration results, as well. Perhaps a reasonable estimate for the current uncertainty of delivering and measuring NH_3 concentrations is obtained from the 6% difference between the theoretical gravimetric concentrations and the titration results.

DATA PROCESSING

The NIST spectrum of ammonia was compared with the EPA and IA spectra in two ways. In each approach, the NIST spectrum was converted to absorbance, scaled, and subtracted from the unknown spectrum. The magnitude of the residual spectrum, as estimated by the value of the sum of the squares of the data points in the region between 1250 cm^{-1} and 750 cm^{-1} , was used as a measure of how closely the scaled NIST spectrum matched the unknown spectrum.

In the first approach, referred to as Protocol A, sample and reference interferograms that had been measured at NIST were truncated to the same optical path difference used for the measurement of the EPA or IA reference spectrum. The truncated interferograms were then multiplied by the same apodization function used for the unknown spectrum. The single-beam spectra measured with the sample present and absent were then calculated and ratioed, and the resulting transmittance spectrum was converted to absorbance. This spectrum was scaled and subtracted from the EPA or IA reference spectrum. The scaling factor, k , was selected by a least-squares criterion so that the quantity Q , equal to $(A_U - kA_{\text{NIST}})^2$ over all points in the spectrum between 1250 cm^{-1} and 750 cm^{-1} , was minimized, where A_U is the absorbance of the unknown spectrum and A_{NIST} is the absorbance of the NIST spectrum converted to a lower resolution. This approach relies on Beer's law being obeyed under the conditions of the measurement of the EPA or IA reference spectrum.

The second approach, referred to here as Protocol B, does not rely on the assumption that the peak absorbance, A_{peak}^a , of each line in the EPA or IA spectrum (for which $\rho \sim 4$) obeys Beer's law. Instead, the assumption is that the line intensities in the NIST spectrum that had been measured at a resolution of 0.125 cm^{-1} , for which $\rho \sim 0.5$, obey Beer's law. Here the high-resolution NIST spectrum (linear in absorbance) is first multiplied by a scaling factor. The ratio of the path-integrated concentration of the EPA or IA reference spectrum and that of the NIST spectrum is used as the initial estimate of the scaling factor. The scaled absorbance spectrum was then converted to transmittance. The fast Fourier transform (FFT) of the trans-

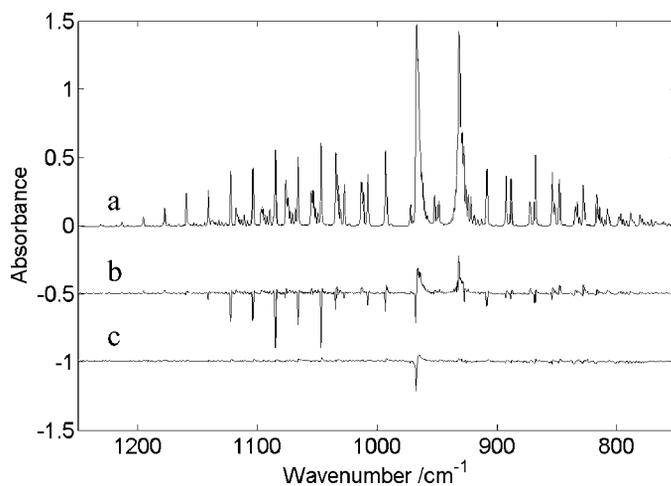


FIG. 2. (a) Absorbance spectrum of ammonia from EPA at a resolution of 1 cm^{-1} calculated with Norton-Beer medium apodization; path-integrated concentration specified = $1500 \mu\text{mol mol}^{-1} \text{ m}$. (b) Difference between spectrum (a) and the NIST reference spectrum using Protocol A, scaling factor = 15.6. (c) Difference between spectrum (a) and the NIST reference spectrum calculated using Protocol B, scaling factor = 20.8. Curves (b) and (c) were displaced for clarity.

mittance spectrum was then calculated and the resulting array was truncated and apodized to make the resolution and instrument line shape function equal to that of the EPA or IA spectrum. The inverse FFT of this array was then calculated to give the transmittance spectrum at the resolution of the unknown spectrum and this array was then converted to absorbance. In the event that the concentration specified for the EPA or IA reference spectrum was not correct, the scaling factor was adjusted and the process was repeated iteratively until the sum of the squares of all points in the difference spectrum between 1250 cm^{-1} and 750 cm^{-1} was minimized. By scaling the high-resolution NIST spectrum rather than the NIST spectrum after truncating the interferogram to lower resolution, this procedure minimizes the effect of resolution errors on Beer's law linearity.

All manipulation of spectra and data processing was done using MATLAB 7.0.1 (The MathWorks Inc., Natick MA) on Windows 2000.†

RESULTS AND DISCUSSION

To evaluate the effect of deviations from Beer's law on the EPA and IA reference spectra of ammonia, these spectra were subtracted from the NIST reference spectrum after conversion to a lower resolution and appropriate scaling using Protocol A. The standard deviation of the difference spectrum was used as a measure of the similarity of the unknown and the lower resolution reference spectrum. In several cases, the lines in the difference spectrum had the appearance of the first derivative, indicating that the wavenumber scale of the two spectra was slightly different. In this case, the wavenumber scale of the unknown spectrum was adjusted to minimize the standard deviation of the difference spectrum.

† Certain equipment, instruments, or software products 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 products identified are necessarily the best available for the purpose.

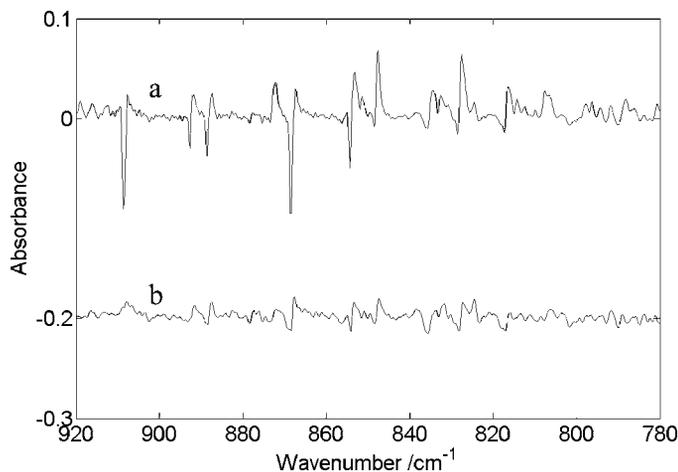


FIG. 3. Expanded regions of spectra shown in Figs. 2b and 2c. Curve (b) was displaced for clarity.

EPA Spectra. Figure 2a shows one of the EPA reference spectra for which the path-integrated concentration of the sample was $1500 \mu\text{mol mol}^{-1} \text{ m}$. The difference between this spectrum and the NIST reference spectrum after treatment according to Protocol A is shown in Fig. 2b. The optimum scaling factor was 15.62, whereas the ratio of the stated path-integrated concentrations was 19.86, indicating that either Beer's law is not obeyed by the low-resolution spectrum or that the concentration of ammonia in either the EPA or the NIST spectrum was incorrect. The difference spectrum with the smallest residual is shown in Fig. 2b and an expanded plot is shown in Fig. 3a. The least squares residual, Q , when Protocol A was applied was 3.5×10^{-2} .

The features in the difference spectrum with the smallest residual do not have the appearance of the first derivative of Lorentzian lines, suggesting that the wavenumber scales of the two spectra are similar. The fact that the strongest line in the spectrum is the least well compensated indicates that the primary reason for the non-zero difference spectrum is deviation from Beer's law.

When Protocol B was applied, the difference spectrum was significantly smaller, as shown in Figs. 2c and 3b. The difference over the region from 1250 cm^{-1} to 750 cm^{-1} is very close to zero except for a spike at 967.6 cm^{-1} , which corresponds to the strongest line in the 0.25 cm^{-1} resolution ammonia spectrum. Comparison with other spectra of ammonia at the same resolution suggested that the intensity of this feature in this particular spectrum was anomalous. This behavior can be explained by the fact that this feature is a dense array of lines in a Q branch; thus, its shape may be expected to be quite pressure and temperature dependent. When the difference spectrum was calculated according to protocol B, the value of Q was reduced to 1.1×10^{-2} . If the assumption is made that the path-integrated concentration given for the NIST spectrum ($75.4 \mu\text{mol mol}^{-1} \text{ m}$) is correct, the path-integrated concentration given for the EPA spectrum is calculated to be $1565 \mu\text{mol mol}^{-1} \text{ m}$. This comparison suggests that the actual concentration is $\sim 4.3\%$ higher than the stated value of $1500 \mu\text{mol mol}^{-1} \text{ m}$, which is within the estimated 6% uncertainty of delivering and measuring NH_3 . The results obtained using the other EPA reference spectrum of ammonia for which the path-integrated concentration was also $1500 \mu\text{mol mol}^{-1} \text{ m}$ were essentially identical to the ones described

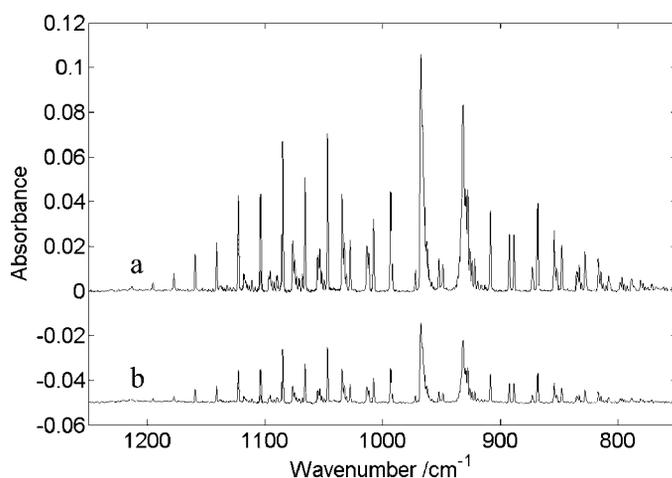


FIG. 4. Spectra of ammonia from EPA database measured at 1 cm^{-1} resolution; the specified path-integrated concentrations for these spectra were specified to be (a) $299.4 \mu\text{mol mol}^{-1} \text{ m}$ and (b) $299.7 \mu\text{mol mol}^{-1} \text{ m}$. Curve (b) was displaced for clarity.

above. Note that these comparisons were not adjusted for the different sample pressures, since the actual sample pressure was not noted for the EPA spectra.

There was an obvious problem with the two EPA reference spectra where the path-integrated concentration was specified to be $\approx 300 \mu\text{mol mol}^{-1} \text{ m}$, since the lines in one of these spectra are about three times more intense than the corresponding lines in the other spectrum, as shown in Fig. 4. Figures 5a and 5b show the difference spectra that were obtained for the weaker spectrum by applying Protocols A and B, respectively. For the difference spectrum shown in Fig. 5a, the scaling factor required to give the minimum value of Q (4.4×10^{-4}) was 0.379. The amplitude of the residual features in this spectrum was small but perceptible. For the difference spectrum obtained using Protocol B, for which the scaling factor was 0.374, the residual features were vanishingly small ($Q = 4.0 \times 10^{-4}$). It is not surprising that the scaling factors and Q values that were obtained with the two protocols are so similar, because Beer's law is always obeyed well when $A_{\text{peak}}^t < 0.5$. However, the

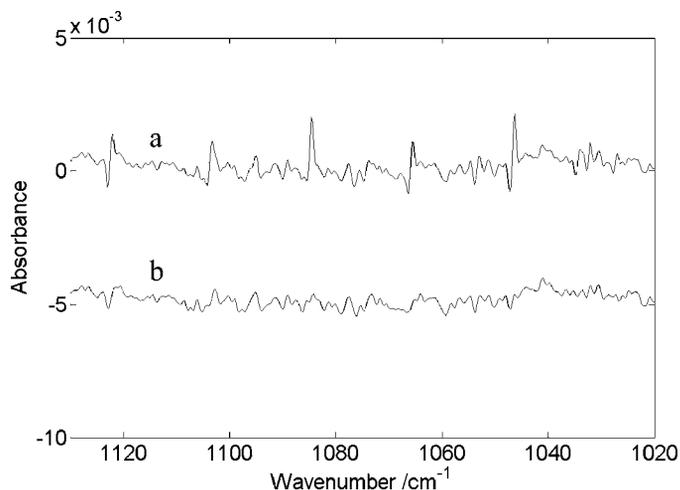


FIG. 5. Differential spectra between the lower spectrum shown in Fig. 4 of ammonia from EPA at a resolution of 1 cm^{-1} and the NIST reference spectrum calculated by (a) Protocol A and (b) Protocol B; the scaling factors were 1.116 and 1.122, respectively. Curve (b) was displaced for clarity.

TABLE I. Quantitative analysis results for the spectra of ammonia obtained from the EPA web site.

Spectrum analyzed	Q (Protocol A/Protocol B)	Scaling factor (Protocol A/Protocol B)	Predicted path-integrated concentration (Protocol A/Protocol B) ($\mu\text{mol mol}^{-1} \text{ m}$)	Reported path-integrated concentration ($\mu\text{mol mol}^{-1} \text{ m}$)
EPA #1	$3.5 \times 10^{-2}/1.1 \times 10^{-2}$	15.62/20.78	1177/1565	1500
EPA #2	$3.5 \times 10^{-2}/1.1 \times 10^{-2}$	15.55/20.66	1171/1556	1500
EPA #3	$4.4 \times 10^{-4}/4.0 \times 10^{-4}$	0.3787/0.3741	28.5/28.2	299.4
EPA #4	$7.2 \times 10^{-4}/5.0 \times 10^{-4}$	1.116/1.122	84.0/84.5	299.7

ammonia path-integrated concentration that is calculated for this spectrum is about $\approx 30 \mu\text{mol mol}^{-1} \text{ m}$, a full factor of ten less than the value of $\approx 300 \mu\text{mol mol}^{-1} \text{ m}$ that is given for this spectrum.

Slightly larger values of Q were found for the corresponding sample that was specified to be at a path-integrated concentration of about $300 \mu\text{mol mol}^{-1} \text{ m}$ but for which the absorbance of the lines was about three times stronger ($Q = 7.2 \times 10^{-4}$ for Protocol A and 5.0×10^{-4} for Protocol B), indicating that adherence to Beer's law was slightly worse than for the previous spectrum. In this case, the calculated path-integrated concentration was about $90 \mu\text{mol mol}^{-1} \text{ m}$, still very different from the specified value of $300 \mu\text{mol mol}^{-1} \text{ m}$. The values of all the specified and calculated parameters are shown in Table I.

It is likely that the actual concentration of ammonia in the cell was reduced by adsorption, because ammonia is known to adsorb strongly on many metal surfaces. If, for example, Spectrum #3 was the first to be measured and ammonia was admitted to the cell before the walls had been previously exposed to ammonia, the ammonia concentration would be greatly reduced by adsorption onto the fresh metal surface. If the walls were partly saturated by ammonia when the sample was admitted for Spectrum #4, less ammonia would have been adsorbed and hence the absorbance of the ammonia lines would be greater. We have no explanation as to why the concentration of ammonia would be calculated to be higher than the value specified, as it was for Spectra #1 and #2, unless the ammonia sample was prepared inaccurately.

Spectra from Infrared Analysis®. The reference spectra from Infrared Analysis® Inc. were analyzed in a similar way to the EPA spectra. In this case, however, the interferograms were unavailable. The spectra were available at resolutions of 0.5 cm^{-1} and 1 cm^{-1} and had been calculated using triangular apodization. Since the path-integrated concentration was low, we expected Beer's law to be obeyed, in which case Protocols A and B would give similar results. In practice, the reference spectrum that had been measured at a resolution of 1 cm^{-1} was best matched ($Q = 1.3 \times 10^{-3}$ with Protocol A and 1.2×10^{-3} with Protocol B) after the wavenumber scale had been adjusted to match that of the NIST spectrum. However, the difference spectra in either case showed residual features that had the appearance of the second derivative of each line (see Figs. 6a and 6b). The path-integrated concentration calculated for this spectrum using Protocol A was $101 \mu\text{mol mol}^{-1} \text{ m}$ and using Protocol B it was $102 \mu\text{mol mol}^{-1} \text{ m}$. However, second-derivative-shaped residual features could always be seen in the difference spectrum obtained from the reference spectrum measured at a resolution of 1 cm^{-1} , suggesting that the IA spectrum had either been measured at a lower resolution or the interferogram had been weighted with a stronger apodization function.

Even when the same procedures were carried out with the IA reference spectrum that had been measured at a resolution of

0.5 cm^{-1} , similar features were seen in the difference spectra. In this case, $Q = 1.2 \times 10^{-3}$ with Protocol A and 1.1×10^{-3} with Protocol B after the wavenumber scale had been adjusted to match that of the NIST spectrum. The path-integrated concentration calculated for this spectrum using Protocol A was $107 \mu\text{mol mol}^{-1} \text{ m}$ and using Protocol B it was $108 \mu\text{mol mol}^{-1} \text{ m}$. On contacting Infrared Analysis,¹⁴ we were told that the IA reference spectra had actually been smoothed after the absorbance spectrum had been calculated, using the Fourier domain smoothing function in the GRAMS/AI™ software package developed by Galactic Industries (now Thermo Electron Informatics Division, Salem, NH).¹⁸ The result of applying any smoothing function is to reduce the peak intensity and increase the width of sharp lines in the spectrum, so that lines in the difference spectrum obtained when an unsmoothed spectrum is subtracted from a smoothed spectrum have the appearance of a second derivative.

We were able to simulate the procedure used by Infrared Analysis by truncating an interferogram of ammonia measured at NIST at various points to yield a nominal resolution (reciprocal of the maximum retardation) numerically greater than the reported resolution of 1.0 cm^{-1} and applying a triangular apodization function to the remaining data points. After calculating the absorbance spectrum, a Fourier domain smoothing procedure was applied. The Fourier transform of the absorbance spectrum was calculated and a triangular weighting function was applied to the Fourier domain array. The reverse transform gave the smoothed absorbance spectrum. Using this

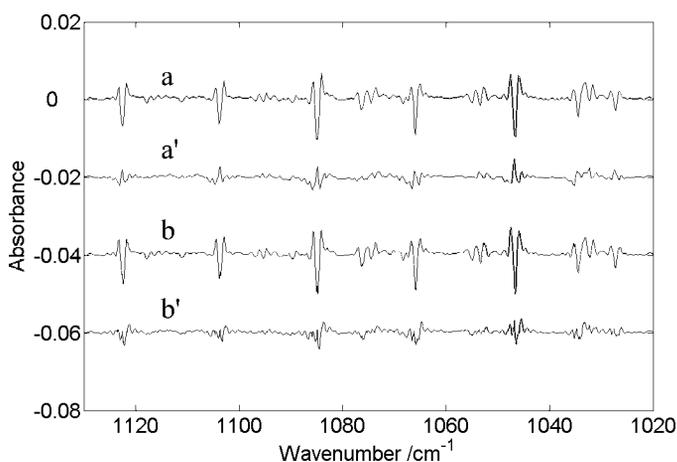


FIG. 6. (a) Difference between the spectrum of ammonia from Infrared Analysis® Inc. at a resolution of 1 cm^{-1} and the reference spectra from NIST calculated by Protocol A without smoothing the NIST spectrum after it had been converted to absorbance. (a') Corresponding spectrum after truncating the interferogram to a nominal resolution of 1.2 cm^{-1} and applying a triangular apodization function to the NIST spectrum. (b and b') Corresponding difference spectra calculated by Protocol B. Curves (a'), (b), and (b') are displaced for clarity.

procedure, the value of the nominal resolution that yielded the lowest value of Q was found to be 1.2 cm^{-1} . Of course, the value of Q will depend on the noise level of the spectrum, but the noise level of the reference spectra we have investigated is sufficiently low that spectral residuals remaining after subtraction are the main contributor to Q . Q could also be affected by the diameter of the Jacquinot stop; we are assuming that the database vendors have always set the Jacquinot stop to an appropriately small diameter. In this case, $Q = 0.78 \times 10^{-3}$ with Protocol A and 0.71×10^{-3} with Protocol B, with the calculated concentrations being $109\text{ }\mu\text{mol mol}^{-1}\text{ m}$ and $107\text{ }\mu\text{mol mol}^{-1}\text{ m}$, respectively. The IA ammonia spectrum that was measured at a resolution of 0.5 cm^{-1} was also smoothed and had to be treated in the same manner with the nominal resolution being 0.55 cm^{-1} . In this case, $Q = 1.0 \times 10^{-3}$ with Protocol A and 1.0×10^{-3} with Protocol B; note that if the difference spectrum only contained noise, the value of Q should be $\sqrt{2}$ times greater than the value of Q calculated for the 1 cm^{-1} spectrum because the number of data points is twice as high. The calculated concentrations were $109\text{ }\mu\text{mol mol}^{-1}\text{ m}$ and $110\text{ }\mu\text{mol mol}^{-1}\text{ m}$, respectively, in acceptable agreement with the values found from the IA spectrum that had been measured at a resolution of 1 cm^{-1} , but still 10% different from the specified path-integrated concentration of $100\text{ }\mu\text{mol mol}^{-1}\text{ m}$. It is important to note that some of this discrepancy may be attributed to the 6% uncertainty of delivering and measuring NH_3 samples. Of course, to achieve a good match between the spectrum of an unknown and any reference spectrum of a small molecule with resolvable fine structure, the two spectra must be treated in an identical manner. We strongly recommend that the exact instrumental conditions used for the measurement of reference spectra of small molecules (resolution, apodization function) be given and that spectra should not be smoothed after the measured interferogram is apodized and transformed into the single-beam spectrum. We were surprised that the calculated concentration was higher than the specified concentration, but learned that an assumed adsorption factor had been used in the analysis of the ammonia data.¹⁴

To verify that the data processing approach that we had developed was valid, we treated the IA reference spectrum of methane that had been measured at a resolution of 1 cm^{-1} in the same way that the 1 cm^{-1} reference spectrum of ammonia was treated. In this case, we found that the resolution of the NIST reference spectrum of methane had to be degraded to 1.7 cm^{-1} before the IA reference spectrum was accurately matched. When the IA spectrum was matched in this way, the path-integrated concentration of methane was found to be $98.9\text{ }\mu\text{mol mol}^{-1}\text{ m}$, in good agreement with the stated value of $100\text{ }\mu\text{mol mol}^{-1}\text{ m}$. When the IA reference spectrum that had been measured at 0.5 cm^{-1} was treated in an analogous way, it was found that the resolution had to be degraded to 1.1 cm^{-1} before the spectra could be matched using Protocol B. In this case, the calculated concentration of methane was $100.1\text{ }\mu\text{mol mol}^{-1}\text{ m}$. These results suggest that our methodology provides reliable reference data and that methane is not adsorbed to the cell walls.

Spectra from Pacific Northwest National Laboratory. When a vapor-phase reference spectrum is used quantitatively, there is always a concern as to its accuracy. In the work described above, we made the assumption that the path-integrated concentration for the NIST reference spectrum of ammonia is accurate to within known uncertainties. The fact that the line intensities in the two low-resolution spectra of

ammonia obtained from the EPA database were so different, and were inconsistent with the intensities of the spectra run at higher concentration, raises question about the quality of these data. Similarly, the fact that the concentration of ammonia listed with the reference spectrum from Infrared Analysis had been adjusted by an assumed factor to compensate for the effect of adsorption on the cell walls suggests that this data is unlikely to yield concentration measurements with acceptable uncertainties. To check on the quality of the NIST spectrum, it was compared to an independently measured reference spectrum of ammonia obtained from Pacific Northwest National Laboratory (PNNL). The NIST and PNNL spectra had been run at approximately the same resolution and neither was apodized. After correction for the wavenumber scale and the different path lengths, concentrations, and sample pressures used by NIST and PNNL, the absorptivities of the lines in the NIST spectra were found to be about 2.6% higher than those of the corresponding lines in the PNNL spectra and agree within the composite expanded uncertainty (2σ) estimate of 3.2% for the NIST and PNNL infrared database projects.¹⁸ This result suggests that the NIST and PNNL data are in better agreement than the reference spectra obtained from either the EPA web site or from Infrared Analysis. It is difficult to judge whether the NIST or PNNL spectrum have unidentified biases, although if any adsorption onto the cell walls had taken place in either case, the concentration would be reduced below the stated value.

CONCLUSION

This investigation suggests several recommendations for the acquisition and use of reference spectra of small molecules in moderate-pressure gaseous matrices:

- (1) Reference spectra of gases should always be prepared at a low enough path-integrated concentration that the true absorbance of every line in the spectrum (i.e., the absorbance that is measured at infinitely high resolution) is less than 0.5; otherwise considerable deviation from Beer's law may occur.
- (2) If conditions are favorable, the reference spectrum should always be measured at the highest resolution available. It is always possible to degrade the resolution of a reference spectrum.
- (3) A reference spectrum should never be treated with any smoothing or noise-removing algorithm in the wavenumber domain. Such algorithms typically distort the reference spectrum and force users to treat their measured spectrum in exactly the same way.
- (4) When comparing low-resolution spectra for small molecules against quantitative reference spectra, Protocol B, which scales the high-resolution reference spectrum, gives a significantly more accurate result than Protocol A, which scales the low-resolution reference spectrum, but takes longer to implement.
- (5) When obtaining quantitative reference spectra for reactive species, care should be taken to verify the concentration of the species in the sample cell.

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