

Accuracy limits for simple molecular absorption based wavelength references

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Abstract: We present limitations on the characterization and use of molecular absorption lines for wavelength calibration purposes. These limits assume a Doppler and pressure-broadened absorption spectrum obtained by transmitting light through a simple gas cell. Attempting to define the line centers to ever-higher accuracy reveals limits associated with effects of cell pressure uncertainty, weak features in the spectrum, increasing complexity in the line profile model, and accuracy limits of wavelength meters.

Introduction: Absorption line based wavelength references have gained widespread acceptance as calibration references throughout the near infrared wavelength region. Introduced to the optical telecommunications industry for instrument calibration [1], these references have also proven useful in fields such as optical sensing and spectroscopy. A typical reference consists of a short gas filled cell that is optical fiber-coupled for attachment to a light source and the instrument being calibrated [Fig. 1]. This format offers reliable service while remaining simple to use. Typical line center uncertainties range from

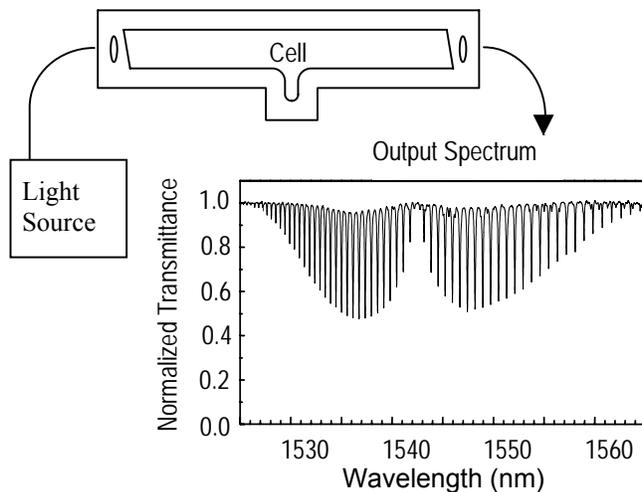


Figure 1: Molecular absorption wavelength reference. The source may be an LED and the output spectrum displayed on a spectrum analyzer, or the source could be a tunable laser and the spectrum measured by a photodiode.

about ± 0.1 pm to ± 1 pm, and linewidths are of order 5 to 50 pm, making these references ideal for calibrating measurement apparatus such as optical spectrum analyzers, tunable lasers, and wavelength meters. The need for higher accuracy references, driven by development of high density wavelength division multiplexed (WDM) systems, fiber Bragg grating sensor systems, and sophisticated swept wavelength test and measurement apparatus, has prompted NIST to investigate the suitability of absorption lines to meet these needs. We found that, for simple references of the format described above, an uncertainty limit of about 0.01 pm is reached where the line centers become difficult to define and measure without abandoning the simplicity and resorting to significantly more complex apparatus and measurement techniques, such as Doppler-free spectroscopy.

Absorption line characterization: At very low temperature and gas pressures, an absorption line has a narrow “natural” linewidth and a well-defined and essentially invariant line center [2]. At room temperature this line is Doppler broadened to about 3.5 pm (~ 450 MHz) for the molecules typically used as wavelength references in the 1550 nm region. The line is also collision (pressure) broadened linearly with increasing pressure. This collisional broadening, described by a Lorentzian profile, is convolved with the Gaussian Doppler profile to yield the Voigt profile that closely represents a typical absorption line. Often a wavelength reference will be tailored to have a specific linewidth by adjusting the gas pressure to obtain the desired collisional broadening. Additionally, the line center shifts slightly with pressure [1]. Characterization of an absorption spectrum for use as a wavelength reference typically involves measuring the line center and width at several pressures and extrapolating to zero pressure to obtain the shift and broadening coefficients, as well as the zero-pressure line centers.

Effect of pressure shift and adjacent small lines: The pressure shift of absorption lines is significant for high accuracy applications; it is as large as 0.5 pm for some $H^{13}C^{14}N$ lines at a pressure of 3.3 kPa (25 Torr). If these HCN lines were used for calibration with an intended uncertainty of 0.01 pm, the pressure shift coefficient for that line and the absolute pressure within the cell would need to be known with an uncertainty of better than 2 %. Alternatively, a lower pressure cell, or lines with a smaller pressure shift coefficient could be used.

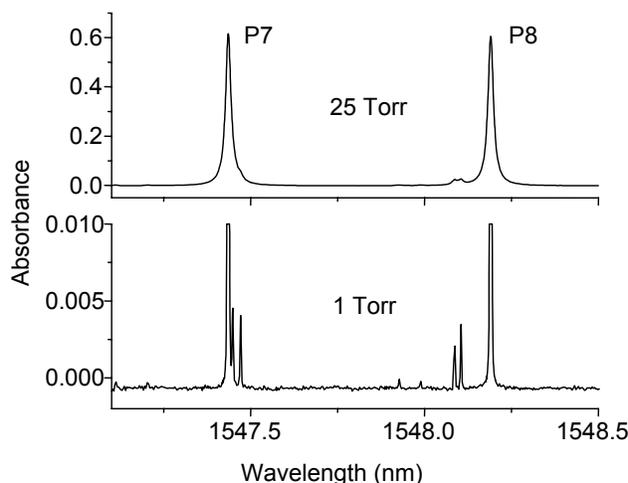


Figure 2: $H^{13}C^{14}N$ lines P7 and P8, showing adjacent small features. The lower trace is expanded 70 \times and the main lines are truncated. Features visible at 0.13 kPa (1 Torr) are blended into line P7 in the 3.3 kPa (25 Torr) spectrum.

of the adjacent feature, we find that only a very few lines in the spectrum are shifted by more than 0.005 pm. This points out to the need for a thorough understanding of the spectrum, including all weak features, and the need for careful fitting, when attempting to obtain high accuracy results from molecular reference spectra. The $^{12}C_2H_2$ spectrum, another commonly used wavelength reference, suffers from hot-band transitions that are stronger than those in the HCN spectrum, and even more care needs to be taken when using this reference at high accuracy.

Subtle effects on line shape: Figure 3 shows $H^{13}C^{14}N$ line P16 at a pressure of 3.3 kPa (25 Torr), and a Voigt fit to this line. Although the fitting function appears indistinguishable from the data, examination of the fit residuals shows a systematic difference between the data and fit function and indicates potential errors in the linewidth and center returned by the fit. This difference is an indicator of other contributions to the line profile, chief among which is collisional narrowing. This is best explained as a narrowing of the Doppler width caused by collisions between the absorbing molecule and other molecules during the interaction time of a photon and the absorbing molecule [3]. A simple Galatry function accounts for this collisional narrowing and better represents the data. Furthermore,

Adjacent weak features common in most molecular spectra introduce line center errors for many reference lines due to their inclusion under the collision broadened line profile. These adjacent features consist primarily of “hot-band” transitions and traces of different isotopic species of the reference molecule. Figure 2 shows the effect of such features on two HCN lines. Our study of effect of adjacent weak features on the HCN spectrum revealed that, for a pressure of 3.3 kPa (25 Torr) and a Voigt fit over about 5 times the linewidth, most lines in the spectrum are shifted by more than 0.005 pm due to adjacent features. Approximately half of the lines are shifted by up to 0.05 pm, and some by more than 0.1 pm. However, if the fit is constrained to the central portion of the line, excluding the body of any adjacent weak feature, and the fit accounts for any linear slope given by the tail

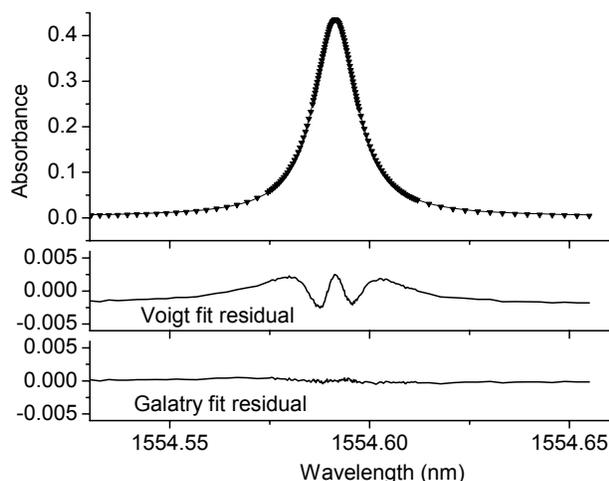


Figure 3: $H^{13}C^{14}N$ line P16. Residuals for both Voigt and Galatry fits are shown on expanded scales.

asymmetry in the residuals points to an asymmetric line shape; fitting such a shape with a symmetric Voigt or Galatry function leads to an ambiguity in the line center. This asymmetry arises from a correlation between the velocity changing collisions responsible for collisional narrowing, and the state perturbing collisions that result in collisional (pressure) broadening. Generalized versions of the Galatry functions, which include a complex velocity-changing frequency term, account for this asymmetry and include a parameter that defines the line center shift with increasing pressure. Using these functions, however, requires a deep understanding of the molecular collision dynamics so that several parameters may be initialized to values specific to the line number and state conditions. Furthermore, subtle offsets and distortions in the detection of light transmitted through the cell can give structure in the residuals that can mask or be confused with effects of collision dynamics.

In both the characterization and use of molecular absorption based wavelength references it is valuable to have a fitting function that returns useful information under a variety of conditions without the undue burden on the user, such as the need to recalculate initial parameters for each set of conditions. The Voigt function satisfies this, at the expense of increasing the uncertainty somewhat on parameters such as the line centers and broadening. We estimated the line center error caused by using a Voigt function to fit an asymmetric line shape by fitting an absorption line using a Voigt function over different widths, and observing the shift in line center. Performing this operation on a high precision scan of a typical molecular reference line, $\text{H}^{13}\text{C}^{14}\text{N}$ line P16 at 25 Torr, revealed a shift of -0.007 pm as the fitted portion was decreased from 5 times to 0.4 times the linewidth. A similar shift is seen for this line at a pressure of 1 Torr. Line P9 showed a shift of $+0.005$ pm, while lines R23 and P24 at 25 Torr showed shifts of only -0.003 pm and $+0.002$ pm, respectively, indicating the variation in behavior of different lines within the same spectrum.

Wavelength meter errors: Of the different means of characterizing molecular absorption spectra, the combination of a tunable laser and a wavelength meter (WLM) remains the most versatile. Here, a laser is stepped across an absorption line, and for each step the transmittance of the absorbing gas and the laser's wavelength are measured. Difference frequency methods, based on the measurement of the difference frequency between a laser locked to a reference line and a second laser locked to a fundamental reference such as a rubidium line [4], offer the highest accuracy but tend to be complicated, and a stable optical frequency comb is required to perform measurements over a molecular band. Fourier transform spectroscopy offers good signal-to-noise ratio, but mitigation of offset and linearity errors requires a set of accurately known calibration lines. Grating based spectrometers suffer these same problems and additional resolution limits. The laser/WLM combination offers measurement bandwidths limited only by the tunable laser's bandwidth, often about 100 nm, and accuracy limited by the WLM.

Wavelength meters of the swept Michelson interferometer variety [5] work by comparing an interference fringe count of a measurand light source with that of a known-wavelength reference source as the interferometer's path difference is swept. Since the fringe count increases with the length of the swept path difference, increasing the interferometer's size will increase the WLM's resolution. A swept path difference of two meters will, at a reference wavelength of 633 nm, give about 6×10^6 fringes per sweep. The resolution is often further increased through splitting the fringe count by up to 100. With fringe splitting, the resulting resolution will be $633 \text{ nm} \div 6 \times 10^8$, or around 0.001 pm at this wavelength. If the WLM is operated in ambient atmosphere, the fringe counts are corrected for the air's refractive index n_{air} at their respective wavelengths, using either the Ciddor or Edlen equation [6], to obtain the wavelength in vacuum. The WLM fractional uncertainty due to this correction is approximately the index uncertainty δn_{air} . Stone [6] gives a $(2\sigma) \delta n_{air}$ of 2×10^{-8} , independent of λ , for air under laboratory conditions. Ciddor [7], claims δn_{air} can be as high as 5×10^{-8} (1σ), and furthermore cautions that infrared absorption bands of H_2O and CO_2 have not been included in any refractive index analysis. Our observations of WLM reading shifts vs. humidity are outside of what would be explained by δn_{air} given in Ref. 6 but within that given by Ref. 7, lending credence to the ambiguity of the uncertainty on n_{air} , especially with respect to the

humidity correction. Operation of the wavelength meter under vacuum would eliminate errors caused by ambient air, but such apparatus are complicated to construct and inconvenient to use, and a limit where errors dominated by optics alignment and aperture interference would soon be reached. Overcoming these error sources leaves the reference laser as the dominant contribution to the WLM's uncertainty. Simple polarization-stabilized helium-neon lasers [8], including commercially available models, offer stability limited to about one part in 10^8 , resulting in a WLM uncertainty of about 0.02 pm at 1550 nm. Iodine-stabilized reference lasers offer stability of better than one part in 10^{10} , but are expensive and complicated to operate. When using a WLM to accuracies greater than about 1 part in 10^6 , periodic calibration with a known reference near the measurand's wavelength is advisable. We frequently calibrate our NIST-built WLM against a 1560 nm rubidium-stabilized laser, thereby correcting for instabilities of the WLM reference laser, any changes in index of refraction due to atmospheric conditions, and alignment errors. This calibration step reduces our standard uncertainty to 0.004 pm (about 0.5 MHz) at 1560 nm. We verified that this accuracy was maintained at nearby wavelengths by measuring a series of $^{12}\text{C}_2\text{H}_2$ lines between 1528 nm and 1538 nm and comparing our results with values given in Ref. 4.

Conclusion: Expending only reasonable effort, the line center of a pressure broadened line typical of a molecular absorption wavelength reference cannot be defined to better than about ± 0.01 pm. This might be improved slightly by using apparatus such as vacuum wavelength meters and sophisticated fitting routines. While these approaches may be appropriate under some laboratory settings, they are time consuming and expensive where entire spectra need to be evaluated. Even if the line centers were to be defined to ± 0.001 pm, careful application of complicated fitting functions, which may lie beyond the means of the reference's user, would be needed to realize this accuracy in a practical setting. Fortunately, recent advances in frequency combs have increased their bandwidths to over 100 THz, making them an attractive alternative to the molecular absorption wavelength reference for high accuracy needs. Where high accuracy is desired and cost is less important, the comb itself can be used as a wavelength reference, or more appropriately an optical frequency reference. Molecular spectra would still satisfy the need for moderate accuracy references, but reevaluating the spectra against a frequency comb would remove any errors associated with the wavelength meter, and give the line centers unambiguously in frequency units. In fact, this reporting of optical spectra directly in frequency units skirts entirely the complications associated with the dependence of wavelength measurements on local refractive indices, and is expected to usher in a new era of optical spectral measurement.

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