Re-evaluation of ortho-para-dependence of self-pressure broadening in the \( v_1 + v_3 \) band of acetylene

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Measurements of self-pressure broadened line profiles of the R(8)–R(13) lines in the \( v_1 + v_3 \) band of acetylene near 1.52\( \mu \)m are reported. The analysis of the data found no evidence for a previously reported [Iwakuni et al. Phys. Rev. Letts. 117, 143902(5) 2016] systematic alternation in self-pressure broadened line widths with the nuclear spin state of the molecule. The present work brought out the need for a careful accounting of weak background absorptions due to hot-band and lower abundance isotopomer lines as well as the requirement for the use of an accurate line profile model. The data were adequately fit using the quadratic speed-dependent Voigt profile model, and parameters describing the average and speed dependent broadening and shift, and line strengths were determined for each line. Smaller contributions to the full HTP including the rate of velocity-changing collisions and the correlation between velocity- and state-changing collisions were only marginally determined and did not significantly improve the overall quality of the line profile fitting. The results of Iwakuni et al. derived from the use of an approximate (Voigt) line profile model combined with data taken in a regime where peak transmission was very small and pressure effects accounted for only a fraction of the observed line widths.

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I. INTRODUCTION

The absorption spectra of molecules in a gaseous sample are broadened by a combination of the Doppler effect due to the Maxwell-Boltzmann distribution of velocities, and the lifetimes of the states involved in the spectroscopic transition. For spectra in the infrared region, the natural lifetimes of the states involved are normally very long and state lifetimes are limited by intermolecular collisions that alter the phase of the absorption or cause the molecule to transition to another rotational quantum state. As sample pressures are increased, so are the collision rates, and the widths of the Doppler limited lines observed at low pressures are found to broaden and the line shape function changes. Understanding the variation of the shapes and widths of spectral lines as a function of pressure and composition is critical for remote sensing and other analytical applications and much effort has been expended in both measurement, calculation and modeling of observed line profiles.1–5

Given our understanding of the phenomenon, it was therefore a surprise when, in 2016, Iwakuni et al.6 measured the well-studied \( v_1 + v_3 \) vibrational combination band of acetylene using a new instrument based on a dual frequency-comb7–12 spectrometer and reported a large (≈ 10%) alternation in the measured self-pressure broadening coefficients with rotational quantum number. Transitions involving \textit{ortho-} acetylene molecules apparently showed a greater self pressure broadening than \textit{para-} ones. In the ground state of acetylene, \textit{ortho-} nuclear spin symmetry is associated with odd rotational quantum number \((J)\) levels, while \textit{para-} are associated with even \(J\) levels, hence correlating with the alternation in line widths with rotational quantum number in the spectrum.

The observations were explained by the following arguments. Since the \textit{ortho-} spin arrangement is statistically favored 3:1 to the \textit{para-} one, \textit{ortho-} \textit{ortho-} collisions are more probable than \textit{para-} \textit{para-} ones, so that efficient resonant collisional energy transfer processes are more probable among \textit{ortho-} molecules than \textit{para-} ones. If the collisions that cause lifetime broadening are dominated by resonant energy transfer ones, then \( \Delta J = \pm 2 \) rotational energy transfer between molecules with common nuclear spin symmetry will be more efficient than other inelastic interactions. Having a light molecule where the rotational intervals are large compared to translational energies helps to see the effect because
the “elastic” $|\Delta J| = 2$ resonant collisions, become more probable than inelastic for large rotational energy spacings. The general idea was first described by Anderson in 1949.\textsuperscript{13} It is well documented in gaseous $\text{H}_2$, from rotational Raman spectra,\textsuperscript{14–16} but $\text{H}_2$ is a special case due to its huge rotational energy level spacings. There have been reports of analogous effects in $\text{HCl}$\textsuperscript{17–19} where the rotational energy spacings are also large, resulting in a peak in the pressure broadening coefficient at low $|\Delta J|$, and an oscillatory behavior in broadening at high $|\Delta J|$, but there had been no subsequent convincing demonstration of the effect in molecules with larger moments of inertia such as acetylene.

The reported effects\textsuperscript{6} are comparable to or greater than the limits of the precision of data recorded using conventional Fourier Transform Infrared (FTIR) spectrometers, and so it was surprising that previous experimental measurements and analyses had missed the differences. The report was immediately controversial and theoretical calculations and analysis by Lehmann\textsuperscript{20} suggested that effects of quadrupole-induced $|\Delta J| = 2$ resonant energy transfer could not explain the size of the measured differences. Separately, Hartmann and Tran\textsuperscript{21} suggested that the use of an approximate Voigt profile (VP) model in the original analysis was at fault because fits of the measured transmission spectra were made, and the more strongly absorbing ortho- lines lead to systematically increased apparent widths compared to the less strongly absorbing para- lines due to the model deficiencies. But no experimental study has yet been reported to confirm or deny the experimental results or to investigate the effects of using approximate line profile models on experimental data.

In this work, we report measurements of the $R(8) - R(13)$ rotational lines in the $v_1 + v_3$ band of pure acetylene gas in question. These lines showed the strongest ortho- para- pressure broadening differences in the original report.\textsuperscript{6} The data were all recorded at (measured) ambient temperatures (295-300K) and over a pressure range from 0.50 – 150 torr (0.067 – 20 kPa). Different length absorption cells were used to ensure optimum absorption strengths over the range of pressures used, that is, peak absorption values were below 60%. Most of the data were recorded using a free-running extended cavity diode laser as the spectroscopic source, but several measurements were made with the same laser locked to a component of a frequency comb resulting in absolute frequencies and long-term optical frequency stability good to a few parts in $10^{11}$. To interpret the measurements a variety of line profile models
were used in the analyses, from a simple Voigt convolution through two speed-dependent models to a full Hartmann-Tran profile.\textsuperscript{22,23} We also found it necessary to account for the presence of many weak underlying hot band and lower abundance isotopomer lines, but the detailed analysis of the data showed no evidence for a systematic ortho-para- variation in pressure-broadening. The most likely explanation for the original observations is that suggested by Hartmann and Tran.\textsuperscript{21} The large absorbances in the original work combined with the use of an approximate, Voigt, line profile in the transmission representation to analyze the data caused a systematic over-estimate of widths for the stronger absorbing ortho- lines.

II. EXPERIMENTAL DETAILS

A. Non-Comb Measurements

The output from a tunable external cavity diode laser (ECDL) (Sacher Lasertechnik TEC 500), centered at 1550 nm, was passed through an electro-optical amplitude modulator (Newport 4104), driven by a high voltage amplifier (Newport 3211) with a 1.6 $V_{pp}$ synthesized sine wave of 50 kHz (SRS, model SG382). A Glan-Taylor Prism at 90$^\circ$, was used as an analyzer resulting in a 50 kHz amplitude modulated beam. Neutral density filters were used to reduce the laser light intensity to ensure a linear electronic response from the detectors. The light was split using a 50:50 polarizing beamsplitter: half the light was focused on a detector acting as a reference ($I_0$) while the other half passed an absorption cell and was focused on to the other (signal) detector ($I_t$). The two detectors were based on matched Hamamatsu InGaAs photodiodes. Their output signals were analyzed with two lock-in amplifiers (SRS, model SR830) controlled by LabView code over a GPIB bus. A sample of the, unmodulated, laser output was used to continuously record the wavelength of the light using a Bristol model 621 wavemeter. Optical frequency measurement accuracy and precision in this configuration was typically $\approx \pm 30$ MHz.

A purified sample of acetylene gas was loaded into one of two absorption cells at the desired pressure. The two cells were a 1.085 cm cell machined from solid copper with CaF$_2$
windows that was used previously,\textsuperscript{12,24} and a 3.612 cm cell of similar construction. Total pressure in the cell and its temperature was monitored and recorded at the beginning and end of each scan. Three different pressure gauges were used in this work to optimize measurements in different pressure regimes: two MKS-398HD with certified accuracy of better than 0.08\%, and a MKS-622C11TAD with certified accuracy of better than 0.15\%. Temperatures were measured with a Omega Micromega readout using a T-type thermocouple, with a maximum error of 0.4°C. The experiment was conducted under ambient, measured, temperatures, and the temperature never changed by more than 0.2°C over the course of a scan. Scan conditions are summarized in table I. The maximum peak absorption of the recorded lines was limited to the range between \(\approx 1\%\) and 60\%. This was controlled by the selection of pressures and cell path length used for the measurements.

### Table I. Pressures (in torr, 1 torr = 0.13329 kPa) for each rotational line measurement, with pressure gauge and cell length used.

| Line Label | 1.085 cm + MKS398-01000 | 1.085 cm + MKS398-00100 | 3.753\(a\) cm + MKS622 |
|------------|-------------------------|-------------------------|-------------------------|
| R(8)       | 156.032, 120.362        | 100.167, 67.902, 40.526, 20.432 | 9.940, 5.011, 1.996, 1.016, 0.523 |
| R(9)       | -                       | 99.646, 70.367, 40.296, 19.130, 10.074 | 9.921, 5.021, 1.999, 1.013, 0.503 |
| R(10)      | 151.545, 115.393        | 100.558, 70.036, 40.075, 20.312 | 9.937, 5.009, 1.992, 1.016, 0.498 |
| R(11)      | -                       | 99.506, 69.675, 40.506, 20.322 | 9.982, 4.999, 1.998, 0.993, 0.506 |
| R(12)      | 166.36                  | 97.643, 70.577, 38.302, 21.494 | 9.937, 5.008, 2.001, 0.994, 0.506 |
| R(13)      | -                       | 100.979, 70.777, 39.875, 20.352, 10.124 | 9.934, 5.007, 2.006, 1.001, 0.500 |
| R(11) with comb | -                     | -                       | 7.960, 5.001, 2.003, 1.068, 0.492 |
| R(12) with comb | -                     | -                       | 8.052, 4.974, 2.092, 0.991, 0.523 |

\(a\). 3.612 cm cell with probe beam passing through at an angle.

Data acquisition was controlled by a LabView program which averaged the measurements from the two lock-in amplifiers for one second (time constant was 3 ms), at each wavelength step. The laser wavelength was stepped by adjusting the laser cavity length piezo actuator. After a wavelength step, the system paused for 300 ms to allow the laser frequency output to stabilize before acquiring the next data point. A single scan typically contained \(\approx 400 – 500\) points. At the end of each scan, the pressure in the cell was decreased to the next value. The measured leak and/or outgassing rate of the cell was constant and minimal for each scan, but was approximately accounted for by taking the mean of values recorded at the beginning and end of the scan. Tests, carried out by bringing the cell back to vacuum before proceeding to the next pressure, showed no significant differences. By making all the
pressure measurements for one line at a time rather than moving from line to line at a given pressure, the laser frequency was more stable, because no coarse frequency adjustments were needed except at the start of the measurement sequence.

FIG. 1. Comparison of comb-locked and non-comb-locked data for R(11) at a pressures of 2 torr (0.27 kPa) at 297.85 K, with a pathlength of 1.085 cm.

B. Comb Locked Measurements

A few later measurements, as detailed in table I, were made with the diode laser phase locked to a Menlo Systems FC1500 frequency comb in a configuration similar to that used previously.\textsuperscript{12,24} Scanning of the diode laser was achieved by stepping the comb repetition frequency by a few Hz. Adjustment of the piezo actuator of the diode laser caused its optical frequency to follow that of the comb tooth to which it was locked. In all other aspects operation of the comb-referenced spectrometer was identical to that described above. With the current comb-referenced system, continuous scans over an entire Doppler and pressure-broadened line were easily achieved. The offset frequency between the diode laser and the comb tooth was nominally set to 30 MHz, but it, and its variance, were recorded continuously using a frequency counter (SRS, model SR620) permitting real time measurement of the optical frequency. Optical frequency accuracy and precision in this configuration was typically better than ±20 kHz.

Data recorded at pressures of less than ~2 torr (0.27 kPa) show very little collisional
broadening, as the Lorentzian contribution is a small fraction of the Gaussian, and fit well to the calculated, and fixed, Doppler broadened Gaussian lineshape. The low pressure data do not show any broadening over and above the expected Gaussian, indicating negligible laser source broadening. The free-running laser stability under the experimental conditions was also confirmed by monitoring its output frequency stability using the frequency comb. Short-term deviations were of the order of 1 MHz, while longer term drifts were of the order of 10 MHz over periods of minutes.

III. ANALYSIS

A. Absorption Line Modeling

Global fits of the sets of data corresponding to the same vibration-rotational transition at varying pressures (in table I) were performed. A suite of Python programs, described in the Appendix and available as Supplementary Data for this paper, were written to read the data files, collate files by transition, fit the data to a normalized line shape function, and present the resulting line profile parameters. Absorption per centimeter path length was calculated using Beer-Lambert law, equation (1).

\[
\text{Transmission} = \frac{I_t}{I_0} (\nu - \nu_0) = e^{-Amp \times l_{\text{path}} \times \epsilon(\nu - \nu_0)}
\]

thus

\[
\text{Absorbance} = Amp \times \epsilon(\nu - \nu_0) = \frac{\ln(\frac{I_0}{I_t} (\nu - \nu_0))}{l_{\text{path}}}\quad (1)
\]

with

\[
Amp = S^N_\nu \ast N\quad (2)
\]

Where \(I_t\) and \(I_0\) are the intensity of light on the transmitted and reference detectors respectively, \(S^N_\nu\) is the spectral line intensity, \(N\) is the number density of the gas, \(l_{\text{path}}\) is the optical pathlength through the gas, and \(\epsilon\) is the area normalized line profile function for the molecular absorption. Typically, pathlength is combined with the amplitude scalar, \(Amp\); however, to ensure that data from several different cells could be compared, it was required to determine the absorption per pathlength. Fits using both the Transmission and Absorbance representations of the current data were tested for realistic line profile functions (i.e. beyond the VP) and found to be equivalent. In the final analyses described
below, the Absorbance representation was used as Hartmann and Tran\textsuperscript{21} showed that this eliminates systematic problems at large absorption strengths when the VP model is used in the transmission representation. However, at the relatively low peak absorbances and higher pressures used in this work compared to those used by Iwakuni et al\textsuperscript{6} even the VP fitting data in the Transmission representation did not show the large systematic ortho-para- broadening variation they reported.

The amplitude, $Amp$ in equation 2, consists of the spectral line intensity, $S_N^\nu$, and the density of the absorbing gas, $N$. The density was calculated assuming the ideal gas law, such that $N = p/(k_B T)$, with units of molecules per cm$^3$. HITRAN\textsuperscript{1} reports $S_N^\nu$ at a reference temperature of 296 K, and it was converted to other temperatures by using equation (3)\textsuperscript{25}.

$$S_N^\nu(T) = S_N^\nu(T_{ref}) \frac{Q_{tot}(T_{ref})}{Q_{tot}(T)} e^{-c_2 E_1(1/T-1/T_{ref})} \left[ \frac{1 - e^{c_2 \nu/T}}{1 - e^{c_2 \nu/T_{ref}}} \right]$$

(3)

with the partition function\textsuperscript{26}:

$$Q_{tot}(T) = -8.3088 + 1.4484 T - 2.5946 \times 10^{-3} T^2 + 8.4612 \times 10^{-6} T^3,$$

(4)

where $h$ is the Planck constant, $c$ is the speed of light, and $k_B$ is the Boltzmann constant. The energy of the lower level of the transition, $E_1$, and $S_N^\nu$ reported in HITRAN can also be found in table II. $S_N^\nu(T)$ was allowed to vary in the line profile fits, see below.

| TABLE II. Relevant Line Parameter Values |
|-----------------------------------------|
| Line | Transition Energy $^{27}$ | Transition Energy $^1$ | Line Intensity ($S_N^\nu(T = 293K)$) | $E_1$ |
|------|---------------------------|------------------------|----------------------------------------|-------|
| R(8) | 6576.4816594              | 6576.481658            | 4.46x10$^{-21}$                       | 84.710|
| R(9) | 6578.5758953              | 6578.575894            | 1.34x10$^{-20}$                       | 105.885|
| R(10)| 6580.6440273              | 6580.644023            | 4.38x10$^{-21}$                       | 129.411|
| R(11)| 6582.6860309              | 6582.686025            | 1.264x10$^{-20}$                      | 155.289|
| R(12)| 6584.7018607              | 6584.701861            | 3.977x10$^{-21}$                      | 183.517|
| R(13)| 6586.6914933              | 6586.691493            | 1.107x10$^{-20}$                      | 214.096|

Equation (1) shows how the data is related to the molecular line shape, $\epsilon$, using the Beer-Lambert law, and this parameter is an area normalized lineshape function. Since the
IUPAC (International Union of Pure and Applied Chemistry) recommended\textsuperscript{23} the adoption of the line shape proposed by Ngo et al.\textsuperscript{22} in 2014, and named it the Hartmann-Tran Profile (HTP), it has increasingly become the lineshape model of choice in high resolution spectroscopy. A line profile fitting code written previously\textsuperscript{31} was translated to Python and used the built-in Faddeeva function\textsuperscript{32}. Fitting to the full set of parameters of the HTP requires very high signal-to-noise ratio data, however the HTP has the advantage of being able to be reduced to several simpler line profile models\textsuperscript{22} by nulling specific parameters. The Doppler-broadening, Gaussian, contribution for all profile models was calculated for the given temperature, and was not varied.\textsuperscript{33}

As previously noted, Iwakuni et al\textsuperscript{6} used a Voigt Profile to fit their data. It can be obtained by eliminating all but the average broadening ($\gamma_0$) and shift ($\delta_0$) coefficients in the HTP. Adkins et al.\textsuperscript{34} showed that the smaller HTP parameters are sensitive to different noise characteristics in the data and we experimented using two intermediate profile functions: the quadratic Speed Dependent Voigt Profile (QSDVP) and the Speed-dependent Nelkin-Ghatak Profile (QSDNGP), also known as Speed-dependent Rautian Profile. The same HTP code was used in all the data modeling to different profiles by varying the non-zero parameters used in the fitting, see below for details.

\textbf{B. Baseline and Hot-Band Corrections}

As in our previous work\textsuperscript{31}, small experimental baseline drifts were included in the profile fitting function. A second-order polynomial function allowed for a realtime fitting of the data without additional data manipulation and is added directly to our absorption equation (1) to give equation (5).

$$\frac{\ln \left( \frac{I_0}{I_t}(\nu - \nu_0) \right)}{l_{path}} = Amp \times \epsilon(\nu - \nu_0) + (b_0 + (\nu - \nu_0) \times b_1 + (\nu - \nu_0)^2 \times b_2)$$ \hspace{1cm} (5)

The effects of weaker hot band and low abundance isotope lines lying close to the transitions of interest are not negligible. A background spectrum for a specific region, pressure and temperature was generated by combining Voigt profiles using parameters from HITRAN\textsuperscript{1}, and included in Supplementary Data for this paper. The frequencies from the data were
FIG. 2. The influence of hot band transitions near R(12). The calculated hot band spectrum on the lower plot, broadens the line of interest, as seen in the zoomed in region (highlighted).

then used as the frequency variable for the appropriate background function. This resulted in a one-to-one ratio of points to background making background subtraction much simpler. This was a vital part of the data analysis since many weaker transitions lie near or underneath the transition of interest, and have absorptions of $\approx 1\%$. Figure 2 shows the results for the R(12) transition where the neglect of the background transitions causes a strong distortion in the profile. The procedure worked well except for the R(8) line where there is a moderately strong background line not in the HITRAN$^1$ list. Adjustments were made to empirically correct for the feature, as detailed in the Supplementary data.

Finally in combining the comb data and the earlier measurements, we noted a systematic shift in the absolute wavenumber recorded by the wavemeter compared to the frequency comb measurement. The average was $25.7(3.7)$ MHz, with one standard deviation in parenthesis, with small deviations from this value for each line. These offsets were applied to the frequency scale of the non-comb-referenced data before the analysis.
IV. RESULTS

A. Data Fitting

An example of a sequence of pressure scans is shown in Figure 3. The signal-to-noise ratio of the measured absorbance data is dependent on the intensity of the peak which is proportional to, $S_N^\nu$, increases with pressure and how long any given point is averaged. At low pressures, a compromise between signal-to-noise ratio (SNR) and collection time was balanced by pressure variation during the scan due to some combination of outgassing and leak rate of the cells which compromised the pressure measurement accuracy. Averaging data points for one second resulted in low pressure data with an acceptable SNR and reasonable compromise in the pressure variations. Beyond the obvious pressure broadening, a pressure dependent line frequency shift is also present, but is small enough that it is difficult to see in the overview spectra in Figure 3.

FIG. 3. Absorbance data for R(9) at a series of pressures.

As a typical example, Figure 4 illustrates the results of fits to the data for R(11) near 60 torr (8.00 kPa). Fitting a line recorded at intermediate pressures such as this to the VP (bottom panel of the figure) results in a “W” shaped residual due to the absence of a collisional (speed-dependent) narrowing contribution to the model profile in this case. The estimated broadening coefficient from such a fit is systematically smaller than it is in reality,
due to a partial accommodation of the model deficiency by a reduction in the size of the broadening parameter. However, changes in the function’s shape are still limited, and thus wings are observed in the residual between observed and calculated profiles as seen in the bottom panel. This gross systematic deviation is not found for the more accurate functions as is evident in the figure.

Overall, the QSDVP was found to be adequate to fit the data. While the QSDNGP and HTP produced marginally better fits, as can be seen in figure 4, but the additional parameters incorporated in them were poorly determined and correlated with other parameters. The QSDVP includes parameters describing the speed-dependent collisional broadening and shift but neglects the velocity-changing collision rate (included in the QSDNGP and HTP) and correlation between phase-changing and velocity-changing collisions, included in the full HTP.

Table III presents the fitted parameters for the VP and QSDVP fits. As expected, the VP pressure broadening parameter, $\gamma_0$, is systematically smaller than that of the QSDVP’s for the reason discussed above. There is a decreasing trend in the average broadening $\gamma_0$ with rotational quantum number, $J$, which is expected as rotational energy intervals increase. The results show reasonable agreement with published empirical fits$^{35,36}$ of multiple published results to smooth functional forms, that are effectively the same as included in HITRAN, as is highlighted in Figure 5. Importantly, there is no evidence for the kind of systematic reduction in the average broadening parameter for para- lines compared to ortho- ones reported by Iwakuni et al. This disagreement is most likely due to the reasons outlined by Hartmann and Tran$^{21}$; the use of an approximate Voigt profile lineshape function combined with fitting transmission data at very high absorbances.

The $\gamma_0$ results for R(8) and R(9) do show some deviations from the overall trend. There are two major reasons: their relative intensities are small compared to the higher J lines which lie near the peak of the Boltzmann population at this temperature, and the underlying hot band spectra, particularly as issue for R(8). $J = 11$ is the most populated rotational state at ambient temperature, and thus R(11) is the strongest line of those studied here. The intensity of the lines decreases quickly with quantum number below this value and, as a result, the hot bands in the background spectra near R(8) and R(9) have a proportionally
greater effect than in the more intense lines. However, it is also expected on theoretical
grounds that the broadening coefficient for the most populated level(s) show a slight increase
over the general trend because the effects of resonant $\Delta J = |2|$ transitions are the largest
for these most populated levels.$^2,^{20}$

Table IV compares the numerical results for the average broadening parameter $\gamma_0$. 

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TABLE III. Results of the line profile modeling.

| Line Label | Voigt Profile | SDV Profile |
|------------|---------------|-------------|
|            | $\gamma_0$ | $\delta_0$ | $S_N^N$ Correction | $\gamma_0$ | $\delta_0$ | $\gamma_2$ | $\delta_2$ | $S_N^N$ Correction |
| R(8)       | 0.15150 (22) | -0.00729 (3) | 0.867 (37) | 0.16585 (32) | -0.00609 (3) | 0.03425 (3) | 0.00357 (9) | 0.843 (42) |
| R(9)       | 0.14405 (22) | -0.00845 (3) | 0.900 (37) | 0.15095 (32) | -0.00861 (3) | 0.01558 (3) | 0.00076 (9) | 0.890 (42) |
| R(10)      | 0.14492 (22) | -0.00843 (3) | 0.972 (37) | 0.15151 (32) | -0.00870 (3) | 0.01815 (3) | 0.00158 (9) | 0.959 (42) |
| R(11)      | 0.14097 (22) | -0.01022 (3) | 0.948 (37) | 0.15030 (32) | -0.01082 (3) | 0.02034 (3) | -0.00232 (9) | 0.933 (42) |
| R(12)      | 0.14126 (22) | -0.01093 (3) | 1.026 (37) | 0.14610 (32) | -0.01147 (3) | 0.01501 (3) | -0.00228 (9) | 1.017 (42) |
| R(13)      | 0.13400 (22) | -0.009920 (3) | 0.952 (37) | 0.13897 (32) | -0.00951 (3) | 0.01181 (3) | -0.00164 (9) | 0.944 (42) |

a. Units are cm$^{-1}$/atm, except for the $S_N^N$ correction, which is dimensionless

b. Uncertainties are derived from Monte Carlo estimates of the combined systematic measurement uncertainties, see section IV B

FIG. 5. Average pressure broadening parameter, $\gamma_0$, comparisons.

B. Error Estimates

A Monte Carlo simulation was used to better model the error propagation, since the statistical estimates of errors from least squares fitting of large amounts of high precision data tend to underestimate the true parameter uncertainties because of the neglect of systematic errors. To implement the Monte Carlo error estimation, the HTP function was used to generate simulated data and a file that resembled a standard experimental data set. Parameter values, were set to rounded values, close to the actual ones, but were similar enough to avoid any bias in the results of the error estimate.

This synthetic data file was read, and a constant error to a single specified condition (pressure, temperature, etc.) added via an argument in the modified version of the analysis.
TABLE IV. Comparison of $\gamma_0$ from Iwakuni et al.,\textsuperscript{6} Empirical Function Fitting\textsuperscript{35,36} and Present Results

| line label | Iwakuni\textsuperscript{6} | Empirical\textsuperscript{b} | This work VP | This work QSDVP |
|------------|-----------------|------------------|-------------|--------------|
| R(8)       | 0.1426          | 0.1548           | 0.1515      | 0.1659       |
| R(9)       | 0.1545          | 0.1514           | 0.1441      | 0.1510       |
| R(10)      | 0.1489          | 0.1480           | 0.1449      | 0.1515       |
| R(11)      | 0.1492          | 0.1449           | 0.1410      | 0.1503       |
| R(12)      | 0.1328          | 0.1418           | 0.1413      | 0.1461       |
| R(13)      | 0.1433          | 0.1388           | 0.1340      | 0.1390       |

a. Units are cm$^{-1}$/atm
b. References\textsuperscript{20,35,36}

program. A wrapper program was constructed, generating a random collection of these errors, in a Gaussian distribution about the estimated size of the error in the condition under consideration and running the analysis software 1000 times. The program would null-out any values that were outside the chosen fit function. All other initial parameters were set to that of the simulated line's values. Only one parameter was analyzed at a time. The only other change to the analysis program was a simplified output that was concatenated to a file, so that the wrapper would output an average error distribution as shown in figure 6, for the error in the (here) $\gamma_0$ parameter of the VP and QSDVP fits. The total parameter errors derived from these procedures are in table III.

Errors in the background spectra corrections due to weak lines were tested in a similar fashion. An additional line was added to the simulated line slightly offset and with an intensity 1% of that of the main signal. Deviations in intensity or center frequency were added to the hot band list, changing the generated background spectra. This can be a relatively large contributor to the error budget, if the background line is strongly overlapping.

However, in general, the largest error contribution is the pressure measurement uncertainty. A combination of three pressure gauges were used for the analysis, but the conservative choice was made to use the (largest) MKS-622’s 0.15% margin of error for the error analysis.
C. Influence of Comb-Referenced Measurements

Since the original work of Iwakuni et al.\textsuperscript{6} used a dual-comb spectrometer, measurements were made to verify that the findings made using the free-running ECDL were unbiased. The R(11) and R(12) transitions were re-recorded at low pressures (see table I) using the modified, comb-referenced instrument. A comparison of R(11) is shown in figure 1. Efforts were taken to match the pressures and temperatures of the two scans as closely as possible.

The comb-referenced data had slightly improved signal-to-noise ratios and more accurate frequency scales, but its inclusion in the global fits did not change the resulting parameters outside the error estimates.

D. Voigt Profile in the Strong Absorption Regime

Hartmann and Tran\textsuperscript{21} provided evidence that the VP is an unreliable line shape model when applied to transmission spectral data recorded under conditions where at peak absorbances approach unity, especially at low pressures. It is noticeable that in Figure 5 and table IV the VP broadening parameters determined here, while differing strongly from
those determined by fitting the same data to more complete profile models, do not show
the systematic ortho- / para- behavior seen by Iwakuni et al. Additional simulations were
therefore carried out to better understand the results in their report. Modeling suggested
that under the pressure conditions and cell path lengths used in that work, the larger mag-
nitude ortho- transitions were near 0% transmission at peak. We used the same analysis
codes to model increasingly weak peak transmission by varying the simulated path length,
and fitted the simulated data to a Voigt profile model. As path lengths (and therefore peak
absorption/minimum transmission) were increased, the “saw-tooth” affect in the pressure
broadening vs. the rotational quantum number, J, graph becomes easily recognizable, as
shown in figure 7.

FIG. 7. Simulations of VP fits (pressures 10 to 100 torr, 1.33 to 13.3 kPa) showed a sawtooth
affect on pressure broadening as path length (and thus absorption) was increased.

E. Conclusions and Summary

Iwakuni et al.\textsuperscript{6} reported an alternation in the self-pressure broadening coefficients in
the \( v_1 + v_3 \) band of acetylene correlating with the nuclear spin state of the protons in
the molecule whilst demonstrating a new dual frequency-comb spectrometer. In a careful
study of self-broadening of lines in this spectrum that apparently showed the largest effects,
we did not reproduce this behavior. We show that multiple effects, such as weaker back-
ground absorptions due to hot band lines, contribute to the apparent line profile parameters
determined from modeling the measurements, but do not lead to the kind of systematic
alternation reported. The largest effect that does result in this behavior is a result of the use of an approximate Voigt profile model combined with the fitting to the transmission representation of the data in the strong absorption regime in the original work, as suggested by Harmann and Tran. The present measurements and analysis have provided the most accurate and detailed line profile parameters available for the lines in question.

V. SUPPLEMENTARY MATERIAL

See supplementary material for information regarding hot bands subtraction and the line parameters used for the simulated line in Monte Carlo simulations.

VI. DATA AVAILABILITY STATEMENT

The experimental data that supports the findings of this study is available from the corresponding author upon reasonable request. The data analysis programs are available in the Gitlab repository as detailed in the Appendix.

VII. ACKNOWLEDGEMENTS

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VIII. APPENDIX

Copies of the programs described below are available on a GitLab repository, https://gitlab.com/Eiceman/pbroadgfit 10.5281/zenodo.3672083
A.  \textit{pBroad.py}

The Python program \textit{pBroad.py} purpose was to gather the relevant data from the LabView data acquisition program’s output files. Options were set through a configuration file, which would contain several options, including a file path option, and a tab separated list giving data file names, pressure, temperature and cell length. The files in the configuration file were would be opened, and the in-phase and quadrature values of the two lock-ins were imported into an array, where their magnitudes were calculated. The laser frequency imported was either the wavemeter measurement or the calculated comb-corrected value, depending on the file type option set. The temperature was expanded to an array of the same length as the data of each file, however an option was included to linearly interpolate this array between two given points, which was never used. Pressure was also treated a non-changing over the course of the data recorded. This is valid since the partial pressure of Acetylene could never increase, and air only contributes a small amount to broadening. However, pressure was handled either by calculating the partial pressure of each scan (pressure was only lowered to that of the next scan), or assuming the given partial pressure was originally given (vacuumed between each scan, see Section II for details).

Once the data was organized, \textit{pBroad.py} would carry out the calculations in Equation 1, concatenate all the data files together in one large array, and export the data as a ROOT\textsuperscript{39} TTree Framework.

B.  \textit{gFit.py}

The Python program \textit{gFit.py} was our global fitting program. The data was read from a ROOT\textsuperscript{39} TTree Framework exported from \textit{pBroad.py}. A background spectrum was generated for each pressure using the data found in the supplementary data table, and subtracted for the file. The MINUIT function minimizer was used using the Python package\textsuperscript{38}. The \textit{HTP.py} contained the program of the function to minimize, equation 5 The fixed variable, and thus the fitting function was determined by command line argument, the baseline was set in the program as it often didn’t change. Once the function was minimized, the fit parameters, $\chi^2$ value, and several other fitting specific values were written to a text file. Fits, residuals, and other plots helpful in debugging were also saved to a file. If the function was not minimized, the best result was given, and the plots were still generated, so the user could decide the meaning of the non-valid fit.
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