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Cavity ringdown spectroscopy of $^{13}$C$_2$H$_2$ in the 12900–13400 cm$^{-1}$ region

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Abstract

We have utilized an acetylene gas sample to assess the performance of a newly constructed cavity ring-down laser absorption (CRDS) spectrometer at the Arkansas Center for Laser Applications and Science (ArCLAS). During this assessment process, four overtone combination bands were observed for the $^{13}$C$_2$H$_2$ species, three of which have not been previously reported in the literature. For two of these previously unreported bands, a total of 85 rovibrational transitions (over 40 in each band) have been assigned using ground state combination difference theory. The data have been fit to standard energy expressions, and a set of molecular constants for each overtone combination band have been obtained. Here we present a brief description of the ArCLAS CRDS instrument along with the complete rovibrational analysis of these two combination overtone bands.

1. Introduction

Spectroscopic interest in acetylene is due, in part, to the ubiquitous nature of the molecule itself. For example, acetylene is found in stellar and interstellar atmospheres [1,2], plays a central role in the combustion chemistry of hydrocarbons [3], and is also an important species in diamond chemical vapor deposition (CVD) chemistry [4]. Modern spectroscopic studies of acetylene date back to the early 20th century [5–7]. Since that time, acetylene, in all of its isotopic variations, has been subjected to countless spectroscopic investigations by researchers employing numerous instrumental techniques.

Acetylene possesses a linear equilibrium molecular geometry with $D_{xy}$ symmetry. There are five normal modes, two of which are infrared active [8]. Limiting the spectroscopic discussion solely to the ground electronic state, a number of combination bands have been observed across the mid-infrared region [8] and literally dozens of combination-overtone bands have been recorded and cataloged from 4000–24000 cm$^{-1}$ (see for example Herman et al. and references therein [9,10]). For example, Romanini and coworkers, utilizing a variant of the cavity ringdown absorption technique, recently observed an overtone band of acetylene corresponding to 8 quanta in the CH stretch [11]. All of these vibrational bands generally possess distinct rovibrational structures which have been analyzed, assigned, and fit to extract sets of molecular constants [8,11–40].

These high quality spectroscopic measurements have played a role either in the development of potential energy surface(s) [9] or have served as rigorous benchmarks for surfaces generated via $ab$ initio methods [41,42]. From a molecular dynamic perspective, acetylene has been used as a prototypical system for examining local mode behavior and intramolecular vibrational [32]. Again, the spectroscopic data have proven invaluable to those trying to probe and understand these important dynamical processes [34,43–45]. Despite the extensive body of data on acetylene and its isotopically labeled variants generated to date, these molecules continue to be a focus for many theoretical and spectroscopic investigations.

As part of the ArCLAS spectral signatures effort, a cavity ringdown laser absorption spectroscopic (CRDS) instrument has been assembled and brought online at Arkansas State University. In order to access spectrometer performance, a series of shakedown experiments were conducted on several spectrally well characterized molecular systems including acetylene. For the isotopically labeled $^{13}$C$_2$H$_2$ species, three overtone bands were observed which we believe have not been previously recorded and analyzed. In this report, we briefly describe the spectrometer, the set of isotopically labeled acetylene shakedown experiments, and the subsequent analysis of two of these bands.

2. Experiment details

The ArCLAS cavity ringdown spectrometer shares design features with a number of CRDS spectrometers previously reported in literature [46]. A schematic of the ArCLAS instrument is shown in Fig. 1. Briefly, tunable radiation from a Nd:YAG pumped dye...
laser (Lambda Physik ScanMate Pro C-400) is sent into a 0.5 m quartz lined CRLAS cell from Los Gatos Research (LGR, Inc.). A set of highly reflective mirrors (also from LGR, Inc.), with a maximum reflectivity of 99.995% at 765 nm (13072 cm⁻¹), are mounted on the cell. Light exiting the cavity was collected using a photomultiplier tube (PMT; Oriel 77341) and recorded on a PC using a set of LabVIEW VI's developed in-house. Absolute frequency calibration was achieved by directing ≈2% of the laser light into a wavelength meter (High Finesse Angstrom-WS Ultimate 10). For the measurements described here LDS-759 dye (Exciton), was used to produce the tunable laser light. Initially, a broad survey scan over the entire operational range of the dye was completed using a 1 cm⁻¹ step size. Then, for each region of interest, a series of additional scans were recorded at a higher level of spectral resolution corresponding to a step size of ≈0.05 cm⁻¹.

Because the US Department of Transportation now prohibits the shipping of undissolved acetylene, isotopically pure ¹³C₂H₂ was synthesized in house following a standard literature prep [47,48]. Essentially, calcium shot (Strem Chemicals) first is reacted with powdered amorphous carbon (99%¹³C from Icon Isotopes) under high heat to form calcium carbide. The labelled Ca¹³C then was reacted with 100 ± 10 mbar of the synthesized ¹³C₂H₂ gas. Based on preliminary work with AA grade acetylene, adding additional sample beyond this pressure did not appear to increase the signal to noise ratio, but did appear to have an effect on the observed FWHM of the rovibrational lines. Assuming a nominal pressure broadening coefficient of ≈10 MHz/torr, the pressure broadening at 100 mbar is estimated to be Δν₁₀ = 0.025 cm⁻¹ or about one fourth of the observed FWHM. Therefore the measured FWHM (ΔFWHM ≈ 0.1 cm⁻¹) probably represents an instrumental limitation because the spectral resolution of the dye laser is approximately this same value.

3. Results and discussion

Broad survey scans for ¹³C₂H₂ in the 12900 and 13425 cm⁻¹ region, were obtained with the ArCLAS CRDS instrument. A representative spectrum is shown in Fig. 2. The reflectivity of the CRD mirrors varies over the scan range which tends to create a sloping baseline in the spectra. Baselines were corrected using standard routines available in most data analysis software. There are a number of molecular bands in the figure including the ¹³C₂H₂ 3υ₃ + υ₃ band at 12960 cm⁻¹ [49]. The intense set of rovibrionic transitions, directly to the blue of this band, can be assigned to the (0,0) band from the forbidden b′Σ⁺ → X′Σ⁻ system of molecular oxygen. The doublet ⁸P, ⁶Q and ⁴R, ⁴Q structure is clearly visible and the line positions have been verified from literature [50]. Parenthetically, oxygen is an impurity observed in all of the ¹³C₂H₂ samples produced with this prep and is probably generated during the Ca¹³C + H₂O → ¹³C₂H₂ step.

Beginning just beyond the oxygen (0–0) bandhead region are three previously unreported bands belonging to the ¹³C₂H₂ species. Given the weak intensity of these bands, it is not surprising that they previously have not been reported. One of these weak bands actually overlaps the oxygen ⁴R, ⁴Q structure in frequency space to the point that we were unable to perform a full rovibrational analysis (only the R branch is clearly visible), the other two bands proved more amenable to such an analysis and will be discussed in detail.

In Fig. 3, a higher resolution (0.1 cm⁻¹) scan of the 13300–13400 cm⁻¹ region is shown. Centered near 13365 cm⁻¹ is a Σ → Σ type band observed only when ¹³C₂H₂ is present in the system of molecular oxygen. The ⁴P, ⁴Q and ⁴R structure in frequency space of the ¹³C₂H₂ step.
Table 1
Quantum number assignments and observed rovibrational transitions (cm⁻¹) for the (Σ − Σ) band of \(^{13}\text{C}_2\text{H}_2\) centered near 13365 cm⁻¹.

<table>
<thead>
<tr>
<th>P(J)</th>
<th>Observed</th>
<th>Obs-calc</th>
<th>R(J)</th>
<th>Observed</th>
<th>Obs-calc</th>
</tr>
</thead>
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<td>20</td>
<td>13400.27</td>
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</tr>
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Table 2
Molecular constants (in cm⁻¹) for the \(^{13}\text{C}_2\text{H}_2\) \(\Sigma − \Sigma\) and \(\Pi − \Sigma\) type bands in the 12900−13400 cm⁻¹ region.

\[
\begin{array}{cccc}
\Sigma & \Sigma & \varepsilon & \Gamma \\
0 & 1.3634 & 94 & (3) \\
\varepsilon & 1.0922 & (9) \\
\end{array}
\]

\[
\begin{array}{cccc}
\Pi & \Sigma & \varepsilon & \Gamma \\
0 & 1.3302 & 53 & (20) \\
\varepsilon & 1.0003 & (23) \\
\end{array}
\]

\[
\begin{array}{cccc}
\varepsilon & 1.097 & (6) \\
\varepsilon & 0.17 \\
\end{array}
\]

All of the entries for the states of the fully substituted carbon-13 species are red shifted, as they should be. The largest shift is observed for the band terminating in the \((013\Sigma^0\Pi)\) state for which the difference is \(\approx 105\) cm⁻¹. The magnitude of this shift seems rather large for a carbon-13 substitution, although it should be pointed out that the \(v_2\) mode does involve a symmetric C=C stretch. Interestingly, a shift of \(\approx 86\) cm⁻¹ is predicted for this set of combination overtone bands within the harmonic approximation. While such a crude approach is perhaps qualitative at best, the same type of approximation yields a shift of \(\approx 148\) cm⁻¹ for the unassigned \(^{13}\text{C}_2\text{H}_2\) \(\Sigma − \Sigma\) band from Fig. 3 if a \((023\Sigma^0\Pi)\) vibrational assignment is assumed for the upper state. Certainly, a Global fit, incorporating this new band into the existing vibrational spectroscopic assignment database, represents the most reliable method for confirming vibrational state assignment [9,10]. Nevertheless, we have tentatively assigned the upper state for this \(\Sigma − \Sigma\) band as \((023\Sigma^0\Pi)\).

There is another previously unreported band in Fig. 2 which is centered near 13302 cm⁻¹. Even in the broad survey scan, the overall band contour appears a bit different than the \(\Sigma − \Sigma\) structure highlighted in Fig. 3. For example, there does appear to be a strong central feature to the band which becomes more evident at higher spectral resolution. This region of interest, 13260−13335 cm⁻¹, was also collected at a 0.1 cm⁻¹ instrumental resolution, and a representative higher resolution scan for this band is shown in Fig. 5.
An analysis, similar to that described for the \( \Sigma - \Sigma \) band, was also performed on this \( ^{13} \text{C}_2\text{H}_2 \) band. Again, the method of ground-state combination differences were used to assign a total of 28 rovibrational including \( P(J = 2-15) \) and \( R(J = 0-13) \). Using these assignments, 14 Q branch lines were predicted, identified in the observed spectra and subsequently included in the fit. While there is often some uncertainty associated with \( Q \) branch assignments, particularly when \( \ell \)-type doubling effects are large, we will point out that shifts in \( J \)-numbering here do result in substantially larger obs–calc values (note, a shift of \( J = 2 \) is necessary to reproduce the expected intensity alternation pattern).

A graphical representation of the \( J \) quantum number assignments are indicated by the hash marks at the top of Fig. 5. A tabulated listing of these assignments, to include spectral frequencies and obs–calc values, is found in Table 3. Assigning the band in Fig. 3 to a \( \Sigma - \Sigma \) symmetry type was based on the overall shape of the band, specifically the absence of a strong central Q branch. The situation with this rovibrational band is a bit different. Both \( \Pi - \Sigma \) and \( \Pi - \Pi \) vibrational bands can exhibit Q branch rovibrational structures, although the Q branch intensity falls off rapidly in the case of \( \Pi - \Pi \) type bands. However it is unlikely that the band shown in Fig. 3 is a \( \Pi - \Pi \) type band. Not only would a \( \Pi - \Pi \) assignment represent a hot band, given the relatively small \( \ell \)-type doubling, the intensity alternation would be different [8]. Finally, it would be hard to conceive how ground state combination differences could confirm spectral assignments if the lower state possessed \( \Pi \) symmetry. Thus we have assigned this particular band as a \( \Pi - \Sigma \) type.

An iterative fit was also performed on this set of spectroscopic assignments using appropriate energy expressions for \( P \)- and \( R \)-branch transitions from Smith and Winn [45] viz

\[
Y(J') = v_0 + B(J' - J' - 1) - D(J' - J' - 1) - E; \quad B' - D' - J' - J' - 1 - E
\]

In Eq. (2), \( v_0 \) is the vibrational band origin while the rotational and centrifugal distortion constants for the ground and excited vibrational states are given by \( B, D, B', D' \) respectively. The rotational and vibrational angular momentum quantum numbers are indicated by \( J, J' \) and \( J, J' \) respectively. The corresponding \( Q \)-branch transitions of the \( \Pi - \Sigma \) band were fit to Eq. (3) [45]:

\[
Y(J) = v_0 - B(J^2 + (B' - B)(J + 1))
\]

The molecular constants from this analysis are included in Table 2. Again, while attempts were made to determine and upper state distortion constant, \( D' \), the uncertainty was sufficiently large to suggest that the value itself could not be determined.

### Table 3

Quantum number assignments and observed rovibrational transitions (cm\(^{-1}\)) for the \( \Pi - \Sigma \) band of \( ^{13} \text{C}_2\text{H}_2 \) centered around 13302 cm\(^{-1}\).

<table>
<thead>
<tr>
<th>( P(J) )</th>
<th>Observed</th>
<th>Obs–calc</th>
<th>( R(J) )</th>
<th>Observed</th>
<th>Obs–calc</th>
</tr>
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### 4. Conclusion

In summary, three previously unreported overtone combination bands of \( ^{13} \text{C}_2\text{H}_2 \) have been observed with a recently assembled AR-CLAS CRDS spectrometer. Rovibrational structure for two of these bands have been analyzed and associated with \( \Sigma - \Sigma \) and \( \Pi - \Sigma \) type symmetry, respectively. Approximately, 40 rotational quantum number assignments have been identified for each band and the assignments, where appropriate, have been confirmed using ground state combination differences. From these assignments a set of molecular constants have been determined for the excited states. In the case of the \( \Sigma - \Sigma \) band, the upper or excited state has been tentatively assigned as the \( 0230_{00}^{(0)} \) state. We have not identified the excited state associated with the \( \Pi - \Sigma \) band.

### Acknowledgments

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### References