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Cavity ringdown spectroscopy of $^{13}C_2H_2$ in the 12 900–13 400 cm^{-1} region

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ABSTRACT

We have utilized an acetylene gas sample to assess the performance of a newly constructed cavity ringdown 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 $^{13}C_2H_2$ 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 $D_{\infty h}$ 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 4000–24 000 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 labelled $^{13}C_2H_2$ 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

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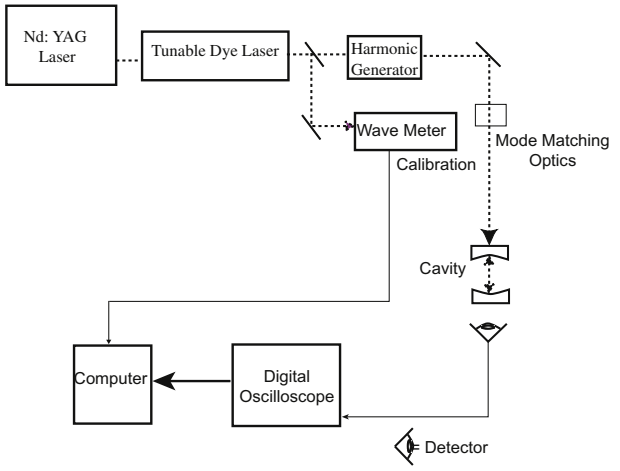

Fig. 1. The ArCLAS CRLAS spectrometer.

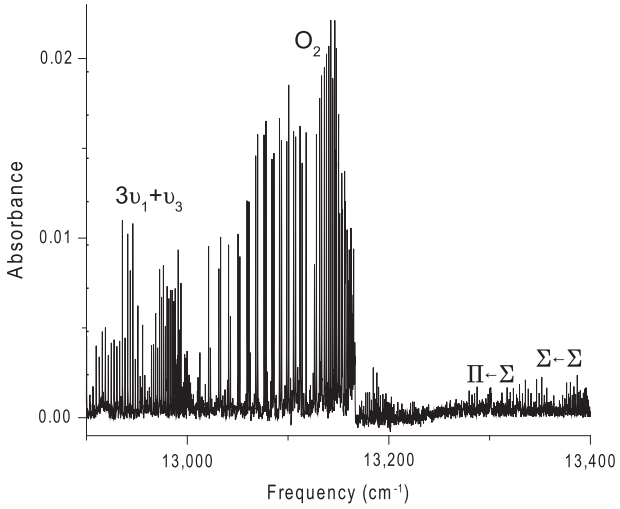

Fig. 2. Spectra of $^{13}C_2H_2$ between 12900 and 13425 cm^{-1} recorded using the ArCLAS CRDS spectrometer. The $3\nu_1 + \nu_3$ band assignment previously was made by Hall [49]. Other combination-overtone band assignments are discussed in the text.

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 $^{13}C_2H_2$ was synthesized in house following a standard literature prep [47,48]. Essentially, calcium shot (Strem Chemicals) first is reacted with powdered amorphous carbon (99% ^{13}C from Icon Isotopes) under high heat to form calcium carbide. The labelled $Ca^{13}C_2$ then was reacted with water to produce acetylene gas. A series of pump-freeze cycles was used to help isolate and purify the $^{13}C_2H_2$ once the reaction was complete. The purity of the synthesized acetylene was checked and verified using FTIR spectroscopy.

For the CRDS measurements described here, the cavity was filled with 100 ± 10 mbar of the synthesized $^{13}C_2H_2$ 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 $\Delta\nu_{PB} = 0.025$ cm^{-1} or about one fourth of the observed FWHM. Therefore the measured FWHM ($\Delta\nu_{FWHM} \approx 0.1$ 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 $^{13}C_2H_2$ 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 $^{13}C_2H_2$ $3\nu_1 + \nu_3$ band at 12960 cm^{-1} [49]. The intense set of rovibronic transitions, directly to the blue of this band, can be assigned to the (0,0) band from the forbidden $b^1\Sigma_g^+ \leftarrow X^3\Sigma_g^-$ system of molecular oxygen. The doublet ^PP, ^PQ and ^RR, ^RQ structure is clearly visible and the line positions have been verified from literature [50]. Parenthetically, oxygen is an impurity observed in all of the $^{13}C_2H_2$ samples produced with this prep and is probably generated during the $Ca^{13}C_2+H_2O \rightarrow {}^{13}C_2H_2$ step.

Beginning just beyond the oxygen (0–0) bandhead region are three previously unreported bands belonging to the $^{13}C_2H_2$ 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 ^RR, ^RQ 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 $\Sigma \leftarrow \Sigma$ type band observed only when $^{13}C_2H_2$ is present in the

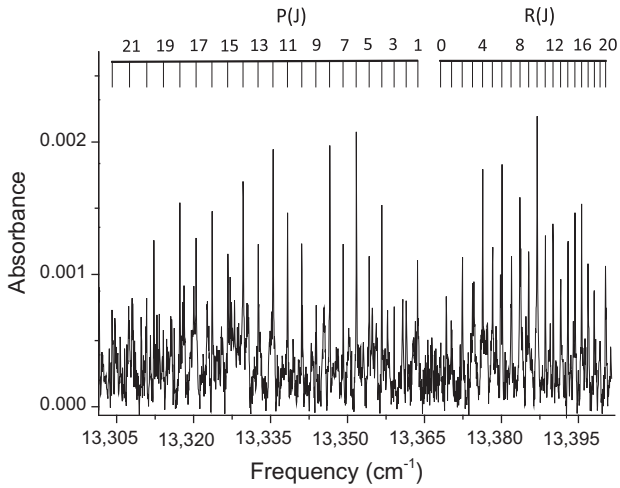

Fig. 3. A $\Sigma \leftarrow \Sigma$ type band of $^{13}C_2H_2$ centered around 13365 cm^{-1}.