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A re-examination of the 4051 Å band of C_3 using cavity ringdown spectroscopy of a supersonic plasma

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Abstract

The C_3 molecule is of fundamental interest to chemists, both as the simplest cumulene and as a prototypical nonrigid system. It is also of great importance in astrophysics, as it now serves as a remote diagnostic of the temperature and density of interstellar clouds. However, high resolution astronomical spectra have uncovered a discrepancy between the observed $R(0)$ transition and the laboratory spectrum. We have used cavity ringdown spectroscopy to obtain a high resolution, low temperature spectrum of the 4051 Å band, and have confirmed that the $R(0)$ transition was incorrectly assigned in previous laboratory work.

1. Introduction

The '4050-Å group' of C_3, which consists of a series of bands ranging from 3900 to 4140 Å , has been of considerable interest to both astronomers and laboratory spectroscopists since it was first observed in emission from comet Tebbutt by Huggins [1] in 1881 and subsequently observed in many cometary spectra. The bands were first observed in the laboratory in a Meckler burner flame by Raffety [2] in 1916. In 1951, Douglas [3] performed a study using isotopically substituted ^{13}C and showed that these bands were due to C_3. In a more detailed study of the bands using flash photolysis of CH_2N_2 in 1965, Gausset et al. [4] assigned the bands to the $A^1\Pi_u \leftarrow X^1\Sigma_g^+$ transition and performed a detailed ro-vibrational assignment of many of the bands. Since that time, many of the bands have been revisited using high resolution laser spectroscopy (e.g., [5]), but, to our knowledge, the 000–000 band at 4051.6 Å has never been re-examined.

This band, the strongest one arising from the vibrational ground state of C_3, took on greater importance after its discovery by Maier et al. [6] in absorption in the diffuse interstellar medium towards ζ Ophiuchi, 20 Aquilae, and ζ Persei. It was subsequently detected toward HD 210121 by Roueff et al. [7], and toward χ Ophiuchi and ζ^1 Scorpii by Galazutdinov et al. [8]. Twelve additional detections (rotationally unresolved) were reported this year by Oka et al. [10], and many

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of these have now been observed at higher resolution [11].

The need for a re-examination of the laboratory spectrum of this band became clear following recent observations at the Keck Observatory by a group including two of us (BJM and MÁ). Our high-resolution, high signal-to-noise spectra of C_3 in diffuse clouds [11] revealed an apparent discrepancy in the position of the weak $R(0)$ transition, compared with the laboratory frequency of Gausset et al. [4]. In hindsight, this discrepancy was also apparent in the previous interstellar spectra [6–8], although the low signal-to-noise ratios of the previous work did not exclude the possibility that the $R(0)$ line had simply not been clearly detected. Due to the presence of a perturbation affecting the low J levels of the $A^1\Pi_u$ 000 state, which Gausset et al. attribute to a $^3\Pi_u$ state, this discrepancy cannot be resolved by theoretical analysis, so we must rely on laboratory spectroscopy. Because the $R(0)$ line was only marginally detected in the previous work [4], we decided to obtain a new laboratory spectrum.

2. Experimental method

The 4051 Å band of C_3 was investigated in direct absorption with the use of cavity ringdown spectroscopy [9]. The C_3 was generated using a pulsed supersonic expansion of a discharge in a dilute (<1%) mixture of C_2H_2 in helium through a ∼150 μm slit, 1.5 in. in length. The typical backing pressure used was about 30 psi, although signal was observed over a wide range of backing pressures. A supersonic expansion source was chosen to minimize the rotational temperature and yield the clearest possible detection of the $R(0)$ line, which is comparatively weak in high temperature discharges.

Tunable violet light was generated by focusing the orange (610 nm) output of a Nd:YAG-pumped dye laser (∼10 ns pulse length) into the center of a 53-cm long cell of high pressure (10 atm) hydrogen gas. The output of this Raman shifter was then refocused and sent through the shifter a second time to increase the amount of second anti-Stokes light. The majority of the pump beam was then removed by passing the beam through a 2-cm sample of a saturated aqueous solution of $CuSO_4$. The second anti-Stokes radiation was then isolated by passing the remaining radiation through two bandpass filters centered at 400 nm. Although the anti-Stokes radiation emerges from the Raman shifter with a donut-shaped spatial profile (due to phase-matching conditions), this did not pose a problem for the cavity ringdown measurements. This approach yielded sufficient intensity to perform cavity ringdown laser absorption spectroscopy of the slit source, using a Hamamatsu R928 photomultiplier tube as the detector.

Judging by the observed spectrum, the second anti-Stokes beam appears to contain both a narrow linewidth component (∼0.04 cm^{-1}, the linewidth of the dye laser) as well as a broader component. Because the linewidth of the radiation far exceeded the Doppler width of the C_3 transitions in the slit source, it was necessary to fit the exponential decay of the ringdown signal using only the data close to the very beginning (2–7 μs) of the ringdown: after this time, a substantial fraction of the resonant radiation had decayed away and the apparent absorption strength declined. Because of this effect, we do not consider our absolute intensities to be reliable.

As is typically the case in supersonic plasmas, we observe a nonthermal rotational distribution of C_3. We estimate that the effective rotational temperature of C_3 (for the low J levels observed) is $\lesssim 60$ K, which is consistent with our past experience using these sources. Frequency calibration was achieved by passing a portion of the fundamental beam through a heated (700 K) iodine cell and onto a photodiode. The resulting absorption spectrum was compared with a simulated spectrum (produced using the software package IodineSpec, from Toptica). Our estimated uncertainty in the frequency calibration (which is limited by the signal-to-noise of our iodine spectrum) is approximately 0.05 cm^{-1}.

3. Results and discussion

Our results are summarized in Fig. 1. For comparison, trace (a) shows the spectrum obtained by Gausset et al. [4], as extracted from the repro-

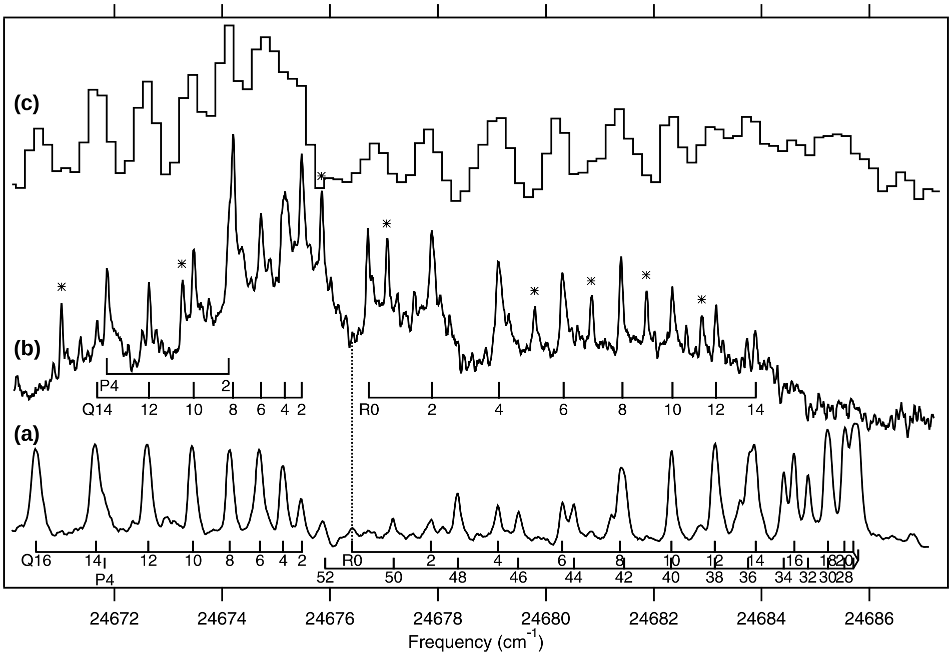

Fig. 1. (a) Spectrum of Gausset et al. [4], digitized from the plate shown in [12]; (b) our observed cavity ringdown spectrum of C_3 in a pulsed supersonic expansion slit source; (c) astronomical spectrum of HD 62542, displayed with absorptions pointing upward for consistency [11]. Note the discrepancy in the position of the $R(0)$ line, which was incorrectly assigned by Gausset et al. The asterisks indicate unassigned transitions in our spectrum.

duction of their plate shown in Herzberg's book [12]. Trace (b) shows our cavity ringdown spectrum along with our assignments, and trace (c) shows the interstellar spectrum of HD 62542 [11] for comparison. The agreement between our laboratory spectrum and the spectrum of HD 62542 seems to be very good, given the resolution and signal-to-noise of the latter.

While most of our lines agree very well with those of Gausset et al., there is a clear discrepancy in the case of $R(0)$, as expected from the astronomical spectra. In defense of Gausset et al., we should point out that the line they assigned to $R(0)$ was extremely weak in their spectrum. In fact, our $R(0)$ line also appears to be present in their spectrum very weakly – in our spectrum, it is greatly enhanced by the lower temperature of our supersonically expanded discharge. Our assignment of the line at 24676.70 cm^{-1} to $R(0)$ is also supported by the presence of an apparently too-strong $Q(8)$ line, which actually is a blend of $Q(8)$ and $P(2)$. Since $P(2)$ and $R(0)$ share the same upper level, the assignments are confirmed by the fact that the seperation between these lines is nearly equal to the energy difference between $J = 0$ and $J = 2$ in the ground state (2.58 cm^{-1}) derived from precise spectroscopic constants [13]. The $P(2)$ line was not assigned by Gausset et al., probably due to its weakness in their higher temperature source. Because of our low temperature and high resolution, we also achieve a good separation of the $P(4)$ and $Q(14)$ transitions. Table 1 summarizes our measured line positions, as well as those of Gausset et al.

Our spectrum also shows many lines that do not match the assigned C_3 lines of Gausset et al. and do not appear in the interstellar spectra. The strongest of these unassigned lines are marked with asterisks in Fig. 1, and their frequencies are given in Table 2. It is striking that the four unassigned lines between $R(4)$ and $R(12)$ of C_3 appear to form a sequence with spacing similar to that of the C_3 R-branch. These lines also appear to be weakly present in the spectrum of Gausset et al., so

Table 1
Observed C_3 frequencies and assignments

Line	Frequency (cm^{-1})	Gausset et al. [4]
R(0)	24676.70	24676.41
R(2)	24677.89	24677.87
R(4)	24679.13	24679.11
R(6)	24680.33	24680.30
R(8)	24681.40	24681.37
R(10)	24682.35	24682.33
R(12)	24683.16	24683.13
P(2)	24674.13	– [a]
P(4)	24671.87	24671.82
Q(2)	24675.48	24675.48
Q(4)	24675.17	24675.13
Q(6)	24674.72	24674.70
Q(8)	24674.21	24674.14[a]
Q(10)	24673.48	24673.46
Q(12)	24672.65	24672.63
Q(14)	24671.68	24671.66

[a] Gausset et al. did not resolve the *P*(2)–*Q*(8) blend.

Table 2
Strong unassigned lines

Frequency (cm^{-1})	Frequency (cm^{-1})
24671.02	24679.80
24673.27	24680.85
24675.85	24681.87
24677.06	24682.90

it may be possible that they belong to another band of C_3, or some other species which is produced both in a C_2H_2 discharge and in the flash photolysis of CH_2N_2.

4. Summary

In summary, we have re-examined the laboratory spectrum of the 000–000 band of the $A^1\Pi_u \leftarrow X^1\Sigma_g^+$ transition of C_3 using cavity ringdown spectroscopy of a supersonic expansion slit discharge of C_2H_2. We have confirmed that the frequency of the *R*(0) line listed by Gausset et al. [4] is incorrect, and our determination of the *R*(0) frequency is more consistent with astronomical observations. We have also detected several strong unassigned lines, and we encourage other groups to revisit this band with higher spectral resolution, given its importance in astrophysics.

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