LABORATORY OBSERVATION OF THE ROTATION-VIBRATION SPECTRUM OF GAS-PHASE C_5

N. MOAZZEN-AHMADI, A.R.W. McKELLAR and T. AMANO
Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6

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The highest asymmetric stretching fundamental (ν_3) of the gas-phase linear carbon chain C_5 has been detected in the laboratory using a cooled hollow-cathode discharge in C_2H_2+He or C_2H_4+He mixtures with a tunable diode laser spectrometer. Our work was guided by recent matrix-isolation and astronomical observations of this band. We have measured a total of 59 lines with J values ranging from 0 to 72. A small local perturbation is observed to affect upper-state energy levels around $J'=41$. The measurements are analyzed to give accurate values of the band origin and the ground- and excited-state rotational parameters.

1. Introduction

In an elegant demonstration of the power of low-temperature matrix-isolation infrared spectroscopy, Vala et al. [1] very recently established a value of 2164 cm^{-1} for ν_3, the highest asymmetric stretching frequency of the linear carbon chain molecule C_5. The unambiguous assignment to C_5 was made by using an equal starting mixture of ^{12}C and ^{13}C and observing all 20 of the expected isotopomers in the spectrum; this corrected an earlier assignment [2] of the 2164 cm^{-1} feature to C_4. Subsequently, the vibration–rotation band of C_5 corresponding to this same vibration has been observed in the circumstellar shell of the carbon star IRC+10216 by Bernath et al. [3].

Guided by refs. [1,3], we have detected and measured the same spectrum in the laboratory, using a tunable diode laser spectrometer and a cooled hollow-cathode source with a discharge in C_2H_2+He or C_2H_4+He mixtures. Preliminary results of this study are reported here.

C_5 is the next member of the family of odd linear carbon chain molecules that begins with C_3. Although C_3 has long been known spectroscopically, its gas-phase infrared spectrum was not observed until last year. At that time, the asymmetric stretch of C_3 around 2040 cm^{-1} was detected almost simultaneously in the laboratory [4] and in the star IRC+10216 [5]. In some unpublished work at about that same time, we had also observed C_3 around 2040 cm^{-1}. The apparatus and experimental conditions described below were found to give very strong C_3 signals, and we were thus encouraged to search for the analogous nearby band of C_5 under the same conditions.

2. Experimental details

We used a tunable diode laser spectrometer (Laser Analytics Div., Spectra Physics Inc.) as described previously [6]. The positions of the C_5 lines were measured relative to nearby infrared standard lines of N_2O [7] using the fringes from a temperature-stabilized solid Ge etalon. Three infrared detectors and a three-pen recorder were used to record the C_5, reference, and etalon signals simultaneously; the measurement accuracy is about 0.0015 cm^{-1}.

C_5 molecules were generated by discharging a mixture of C_2H_2 (0.015 Torr) and He (1.6 Torr), or of C_2H_4 (0.015 Torr) and He (1.6 Torr), in a hollow-cathode cell [8]. The stainless steel cathode had a diameter of 38 mm and a length of 80 cm. It was cooled to a temperature of from −50 to −80°C by circulating methanol from a dry ice bath or closed-cycle refrigerator; the temperature was not critical. The cell was fitted with multiple traversal mirrors to

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give effective path lengths of 10–20 m in the discharge region. Discharge modulation at a frequency of about 1 kHz with a peak current of about 1 A was used to enhance sensitivity and discriminate in favor of the transient C_5 molecules.

Higher modulation frequencies gave distinctly reduced C_5 signals, implying that the lifetime of the molecule was of the order of 1 ms under these conditions. C_2H_2 or C_2H_4 were found to give approximately equal C_5 signals, and an allene+helium discharge was also approximately the same. However, a methane+helium discharge gave only very weak signals. The spectra of C_5 and C_3 were found to optimize under virtually the same conditions, but the latter is so strong that it could be detected even with conditions far from the optimum.

3. Results

Based on the results of ref. [3], and our previous experience with C_3, we started searching for C_5 signals around 2162 cm^{-1} and immediately found a series of lines with the expected spacing of about 0.4 cm^{-1}. (As in C_3, only even J rotational levels of $^{12}C_5$ are populated in the ground vibrational state and so the line spacing is $\approx 4B$ for a stretching fundamental.) This series corresponded to the fundamental band observed by Bernath et al. [3] in the spectrum of IRC+10216. Our next strongest lines in this region formed a series with a spacing about half that of the fundamental (0.2 $cm^{-1} \approx 2B$), but with a slight staggering between alternate members of the series. This is just the appearance expected for a bending hot band of C_5, with the staggering caused by l-type doubling.

By following the fundamental band series, we were ultimately able to measure a total of 59 lines belonging to it, ranging from P(72) to P(2), and from R(0) to R(70); their measured frequencies are listed in table 1. Low-J (<8) lines were quite weak and often surrounded by stronger unassigned features. However, we were able to observe both P(2) and R(0) and thus establish an unambiguous J-numbering for the band. This numbering agrees with that of Bernath et al. [3], and it was also confirmed by the observation of a small local perturbation in the band structure for J-values of around 40, as discussed below.

The measurements were fitted to a simple linear molecule energy level expression, $E=BJ(J+1)-DJ^2(J+1)^2$, in a least-squares analysis from which transitions judged to be affected by the perturbation were omitted. The parameters resulting from this fit are given in table 2. Table 1 shows the residuals (obs.−calc.) from the fit, and is organized so that transitions with equal values of J' are beside each other. It may be noted that the residuals in the region of the perturbation are approximately equal for the corresponding (equal J') P and R transitions, indicating that it is the upper-state energy levels that are affected by the perturbation. Information contained in the perturbed transitions was utilized by including in the fit six ground-state combination differences that were derived from them.

4. Discussion

The gas-phase band origin obtained here is just 5.4 cm^{-1} higher than the matrix-isolation value of Vala et al. [1]. This is a very good correspondence, though not as close as for C_3, where the gas-phase band origin [4] lies within about 1 cm^{-1} of the matrix value. Recent ab initio predictions of the C_5 frequency include values of 2344 cm^{-1} from Raghavachari and Binkley [9] and 2193 cm^{-1} from Martin et al. [10]. Calculations also indicate that for both C_5 and C_3 the ν_3 bands have unusually large infrared intensities [10,11].

The perturbation noted above appears to be homogeneous (Fermi-type) rather than J-dependent (Coriolis-type), since the transitions return to their expected positions at higher J values above the point of maximum perturbation. However, a more thorough analysis, now in progress, will be required to confirm this supposition. It may even be possible to observe the perturbing levels directly in the spectrum.

The magnitude and negative sign of the change in rotational parameter B upon excitation of the asymmetric stretching vibration in C_5 are found here to be quite normal for a linear molecule, as are the centrifugal distortion parameters D. This is in contrast to the case of C_3, where unusual values [4] for these quantities are reflections of the known [12] quasi-

Table 1
Measured wavenumbers in the spectrum of C_5

	Observed (cm^{-1})	Obs. – calc. (cm^{-1})		Observed (cm^{-1})	Obs. – calc. (cm^{-1})
P(72)	2155.0137	–0.0007	R(70)	2179.3975	–0.0004
P(70)	2155.4732	–0.0002	R(68)	2179.1755	–0.0002
P(68)	2155.9306	0.0015	R(66)	2178.9515	0.0014
P(66)	–		R(64)	2178.7220	0.0008
P(56)	2158.5948	0.0008	R(54)	–	
P(54)	2159.0270	0.0004	R(52)	2177.2745	–0.0025
P(52)	2159.4544	–0.0014	R(50)	2177.0250	0.0005
P(50)	2159.8794	–0.0024	R(48)	2176.7655	–0.0029
P(48)	2160.3009 [a]	–0.0035	R(46)	2176.5060 [a]	–0.0033
P(46)	2160.7178 [a]	–0.0059	R(44)	2176.2411 [a]	–0.0056
P(44)	2161.1218 [a]	–0.0178	R(42)	2175.9646 [a]	–0.0160
P(42)	2161.5753 [a]	0.0230	R(40)	2175.7330 [a]	0.0218
P(40)	–		R(38)	2175.4493 [a]	0.0108
P(38)	2162.3732 [a]	0.0057	R(36)	2175.1686 [a]	0.0063
P(36)	2162.7731 [a]	0.0030	R(34)	2174.8861 [a]	0.0003
P(34)	2163.1717	0.0023	R(32)	2174.6012	0.0014
P(32)	2163.5668	0.0015	R(30)	2174.3148	0.0013
P(30)	2163.9591	0.0012	R(28)	2174.0253	0.0014
P(28)	2164.3488	0.0017	R(26)	2173.7308	0.0000
P(26)	2164.7315	–0.0015	R(24)	2173.4344	0.0001
P(24)	2165.1162	0.0007	R(22)	2173.1352	0.0007
P(22)	2165.4955	0.0008	R(20)	2172.8306	–0.0007
P(20)	2165.8693	–0.0012	R(18)	2172.5252	0.0005
P(18)	2166.2419	–0.0010	R(16)	2172.2145	–0.0002
P(16)	2166.6118	–0.0002	R(14)	2171.9010	–0.0003
P(14)	2166.9788	0.0011	R(12)	2171.5825	–0.0021
P(12)	2167.3396	–0.0004	R(10)	–	
P(10)	2167.6980	–0.0010	R(8)	2170.9421	0.0012
P(8)	2168.0543	–0.0003	R(6)	2170.6131	–0.0009
P(6)	2168.4049	–0.0019	R(4)	2170.2864	0.0027
P(4)	2168.7547	–0.0010	R(2)	–	
P(2)	2169.1010	–0.0001	R(0)	2169.6122	–0.0008

[a] A transition omitted from the least-squares fit due to the perturbation discussed in the text.

Table 2
Fitted parameters for the 2169 cm^{-1} band of C_5 [a]

ν_0 (cm^{-1})	2169.4432(2)
B' (MHz)	2545.01(11)
D' (kHz)	0.16(2)
B'' (MHz)	2557.66(11)
D'' (kHz)	0.17(2)

[a] Uncertainties in parentheses correspond to 1σ from the least-squares fit.

linearity of the molecule. The implication is that C_5 is a more rigidly linear molecule than C_3.

We are informed [13] that R.J. Saykally and coworkers have also observed this band of C_5 in the laboratory. In addition to the transitions assigned here to the fundamental band, numerous other lines were observed in the same region during the course of this work. Many of these are expected to belong to hot bands of C_5, and their analysis is currently in progress.

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