DETECTION OF C₅N⁻ AND VIBRATIONALLY EXCITED C₆H IN IRC +10216

J. Cernicharo,² M. Guélin,² M. Agúndez,³ M. C. McCarthy,⁴ and P. Thaddeus⁴

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ABSTRACT

We report the detection in the envelope of the C-rich star IRC +10216 of four series of lines with harmonically related frequencies: B1389, B1390, B1394, and B1401. The four series must arise from linear molecules with mass and size close to those of C₆H and C₅N. Three of the series have half-integer rotational quantum numbers; we assign them to the ³Δ and ³Σ⁻ vibronic states of C₆H in its lowest (ν₁₁) bending mode. The fourth series, B1389, has integer J with no evidence of fine or hyperfine structure; it has a rotational constant of 1388.860(2) MHz and a centrifugal distortion constant of 33(1) Hz; it is almost certainly the C₅N⁻ anion.

Subject headings: circumstellar matter --- ISM: molecules --- radio lines: ISM --- stars: AGB and post-AGB --- stars: individual (IRC +10216)

Online material: color figures, machine-readable table

1. INTRODUCTION

The dusty envelope of the carbon star IRC +10216 is a rich radio source where at least 70 molecules have been observed (see, e.g., Cernicharo et al. 2000). Particularly rich in long linear carbon chains, it is the source where the polyacetylenic radicals C₃H (n = 4, 6, 8; see Guélin et al. 1987; Cernicharo & Guélin 1996) and C₅N (n = 3, 5; see Guélin et al. 1998) were first detected and identified. The butadiynyl radical C₄H has been observed there in rotational lines of the ground and several vibrationally excited states. The excited-state lines are strong, owing to perturbation by the low-lying A'''' electronic state (Yamamoto et al. 1987). Notably poor in cations, IRC +10216 has turned out to be the richest source of anions in the sky. All known interstellar anions, C₃H⁻, C₅H⁻, C₆H⁻, and C₅N⁻ (Thaddeus et al. 2008 and references therein), have been identified there, where they are fairly abundant. The presence of carbon chain negative ions in space was predicted long ago (see, e.g., Cernicharo et al. 2000). Particularly rich in long carbon chain negative ions in space was predicted long ago (see, e.g., Cernicharo et al. 2000). Particularly rich in long carbon chain negative ions in space was predicted long ago (see, e.g., Cernicharo et al. 2000). Particularly rich in long carbon chain negative ions in space was predicted long ago (see, e.g., Cernicharo et al. 2000). Particularly rich in long carbon chain negative ions in space was predicted long ago (see, e.g., Cernicharo et al. 2000).

2. OBSERVATIONS

The astronomical observations presented here are mainly from a spectral line survey of IRC +10216 done with the IRAM 30 m telescope between 1995 and 2008 (Cernicharo et al. 2000; J. Cernicharo et al. 2008, in preparation). The 3 mm part of this survey covers the 80–115 GHz band with an rms noise of 0.3–2 mK per 1 MHz wide channel. Data were taken with the secondary nutating by 90°–120°, an arrangement which produced very flat spectral baselines. Two SIS 3 mm receivers, with orthogonal polarizations and system temperatures of 100–130 K, were used simultaneously. Pointing and focus were regularly checked on planets and on the strong nearby quasar OJ 287. In Figures 1 and 2 the intensities are given in T_{A^*}, the antenna temperature corrected for atmospheric absorption and rear spillover losses, by means of the ATM code (Cernicharo 1985). A few complementary observations at 22 GHz were carried out in 2008 March with the MPIfR Effelsberg telescope, both on IRC +10216 and on TMC-1. Derived line parameters are given in Table 1.

3. RESULTS: VIBRATIONALLY EXCITED C₆H

During the survey, about 1500 lines in the 80–115 GHz band were observed, most from known molecules. A few hundred escaped identification; among these, the four harmonic series with either integer or half-integer quantum numbers in Figures 1 and 2 stand out; for one series, B1394, the lines are split into doublets (see Tables 1 and 2). Since the B and D values are very close to those of C₆H and C₅N (B = 1391.2 MHz, D = 51 Hz, and B = 1403.1 MHz, D = 50 Hz, respectively), the carriers of the four series must be linear molecules of weight and size similar to that of these two radicals. C₆H is a linear radical with a ⁴Π ground electronic state (Cernicharo et al. 1987). It has 6 stretching modes, ν₁–ν₅, and 5 bending modes, ν₆–ν₁₁. The modes ν₁ and ν₁₁ have the lowest energies, =210 and =93 cm⁻¹, respectively, according to ab initio calculations by Cao & Peyerimhoff (2001); the next mode ν₆ is at about 400 cm⁻¹.

Even though excited vibrational states of long carbon chains are susceptible to infrared fluorescence excitation in IRC +10216, vibrational temperatures remain low; e.g., 40–50 K for the ν₁ mode of HC₆N and the ν₁₁ mode of HC₅N (Cernicharo et al. 1987; J. Cernicharo et al. 2008, in preparation). Only the lowest bending mode of C₆H (ν₁₁) is therefore expected to be sufficiently populated to detect. The first excited electronic state of C₆H, ³Σ⁻, is known to lie very close in energy to the ⁴Π ground state (Murakami et al. 1987). Owing to coupling between the vibrational bending modes and the electronic orbital motion of the molecule (the Renner-Teller effect), each bending mode of C₆H is split into one ³Δ (with half-integer quantum numbers) and two ³Σ vibronic states (³Σ⁻ and ³Σ⁺ with integer quantum numbers). According to Herzberg (1966), the splitting
Fig. 1.—Spectra of IRC +10216 observed with the IRAM 30 m telescope, showing lines from the B1389 series assigned here to C5N. The marginal weak line U83278 is worth noting, because it is within 0.1 MHz of the J = 1–0 line of CCH (see text). [See the electronic edition of the Journal for a color version of this figure.]

Table 1

| Transition | Obs. Freq. (MHz) | Cal. Freq. (MHz) | T_dv (K km s\(^{-1}\)) | v_exp (km s\(^{-1}\)) |
|------------|------------------|------------------|-------------------------|---------------------|
| B1389 (C5N\(^-\)) |                  |                  |                         |                     |
| J = 29–28  | 80550.7(4)       | 80550.7          | 0.30(3)                 | 14.6(8)             |
| J = 30–29  | 83328.0(3)       | 83328.0          | 0.23(3)                 | 15.3(7)             |
| J = 32–31  | 88883.1(10)      | 88882.7          | 0.20(3)                 | 14.5**              |
| J = 33–32  | 91660.0(6)       | 91660.0          | 0.25(3)                 | 15.4(7)             |

Notes.—Numbers in parentheses are 1\(\sigma\) uncertainties in units of the last digits. A superscript "a" indicates that the line width parameter \(v_\text{exp}\) has been fixed. Table 1 is published in its entirety in the electronic edition of the Astrophysical Journal. A portion is shown here for guidance regarding its form and content.

Fig. 2.—Spectra of IRC +10216 observed with the IRAM 30 m telescope showing selected lines pertaining to the series B1390, B1394, and B1401. These three series of lines are assigned to vibronic states of the bending \(n_{11}\) mode of C6H.

Table 2

| Series   | B (MHz)     | \(D\) (Hz) | \(N_{\text{max}}\) | J-Range |
|----------|-------------|------------|---------------------|---------|
| B1389    | 1388.860(2) | 33(1)      | 13                  | 8, 29–40 |
| B1390    | 1389.878(7) | −35(3)     | 9                   | 59/2–79/2 |
| B1394    | 1394.609(10)| 32(4)      | 22                  | 29–41\(^a\) |
| B1401    | 1401.559(26)| 139(7)     | 7                   | 59/2–75/2 |

Note.—Number in parentheses are 1\(\sigma\) uncertainties in units of the last digits.

\(^a\) B1394 corresponds to a \(\Sigma^+\) vibronic state with \(\gamma = 15.2(13)\) MHz and \(\gamma = −1.53(35)\) KHz.
the lowest of the two \( ^2\Sigma \) ladders of the \( \nu_1 \) state, the \( ^2\Sigma^- \) ladder. We note that we have found no other series of line doublets of comparable or greater intensity that could match this ladder, would B1394 pertain to another vibrational state.

With the assignment of B1394 and B1390/B1401 series to the \( ^2\Sigma^- \) and the \( ^3\Delta \) ladders of \( \nu_1 \), we can derive from relations (1) through (5) a set of rovibrational parameters that give a good fit to the data: \( B_0 = 1395.72 \) MHz, \( A_{\text{eff}} = 11.13 \) cm\(^{-1}\), \( \epsilon_0 = 0.352, A_C \approx 145.0 \) cm\(^{-1}\), and \( \omega \approx 120 \) cm\(^{-1}\), a value compatible with that calculated for \( \nu_1 \) by Cao & Peyerimhoff (2001). Therefore, under the assumption that relations (1) through (5) apply to C_{5N}, the \( ^2\Sigma^- \), \( ^3\Delta \), and \( ^2\Sigma^+ \) vibronic states lie \( 68, 173, \) and \( 277 \) K above the ground state. The \( ^2\Sigma^- \) vibronic state will have a rotation constant \( (B') \) so close to that of the \( ^2\Sigma^- \) state \( (B^-) \), and a doublet separation so similar \( (\gamma^- = \psi^-) \) that its rotational lines will be blended in IRC +10216 with those of \( ^2\Sigma^+ \) up to very high \( J \) (where lines are probably too weak to detect). The column densities derived for the \( \nu_1 \) vibronic states are \( N(\Sigma^-) = 1.4 \times 10^{12} \) cm\(^{-2}\). Both vibronic states have a rotational temperature of \( 45 \) K—somewhat higher than that measured for the ground vibrational state \( (31 \pm 2 \) K; Cernicharo et al. 2007). The column density in the ground state is calculated to be \( 6.6 \times 10^{11} \) cm\(^{-2}\), indicating that about 20% of C_{5N} is in the \( \nu_1 \) state.

Recent laboratory measurements at both millimeter and centimeter wavelengths confirm that B1390, B1401, and B1394 arise from \( ^3\Delta \) and \( ^2\Sigma \) components of a low-lying vibrationally excited state of C_{5N} (Gottlieb et al. 2006). The \( ^2\Sigma \) component has been observed over a wide range of rotational excitation \( (N = 5–85) \), under experimental conditions which optimize lines of ground state C_{5N}. To reproduce the observed spectrum, an effective Hamiltonian with several higher order terms in the spin-rotation constant is required. Although weaker by a factor of 3 or more relative to B1394, the high-lying \( ^3\Delta \) component has also been observed in the same laboratory discharge. The spectroscopic constants derived from the astronomical data agree to within 1 \( \sigma \) with those derived from the larger and more precise set of laboratory data for both the \( ^3\Delta \) and \( ^2\Sigma \) components. A complete account of the laboratory observations will be given elsewhere.

There is so far no laboratory evidence for the remaining astronomical series B1389 under conditions where lines of ground state and vibrationally excited C_{5N} or ground state C_{5N}^- are observed.

4. ASSIGNMENT OF B1389 TO C_{5N}^- 

The remaining series, B1389, has integer \( J \) and exhibits no evidence of hyperfine or other structure (see the \( J = 35–34 \)

line in Fig. 1). For this reason, and because of the strength of these lines, it cannot be assigned to any of the bending modes of C_{5N}. Its carrier is almost certainly a new linear molecule with a \( ^3\Sigma^- \) ground electronic state, and a molecular weight close to that of C_{5N} and C_{5N}^-.

The most obvious candidates are the ions C_{5N}^-, C_{5N}^+, and C_{5N}^-^- C_{5N}^- has already been detected in the laboratory and in IRC +10216 (McCarthy et al. 2006), and is immediately ruled out. Linear C_{5N}^- has a \( ^1\Sigma^- \) ground electronic state (according to Fehér & Maier 1994), and only a fraction of its rotational transitions will be harmonically related with \( B = 1340 \) MHz. Moreover, only one cation, HCO^+, has so far been detected in IRC +10216, and it has a very low abundance. We therefore conclude that C_{5N}^- is not the carrier of B1389.

Finally, C_{5N}^- has the right \( ^1\Sigma^- \) ground electronic state and calculated rotational and distortion constants: 1389 MHz and 33 Hz (Botschwina & Oswald 2008; see also Aoki 2000). Botschwina quotes an error as small as 0.5% for the rotational constant. The match with B1389 is perfect, and it is therefore tempting to conclude that C_{5N}^- is our new molecule.

The only reservation we might see to this identification is the intensity of the lines, which in IRC +10216 are about twice as strong as those of the parent species C_{5N}. Supporting the identification, the lines of the anion benefit from a more favorable partition function (no doublets) and from a larger permanent dipole moment: the latter has been calculated by Botschwina & Oswald (2008) to be 5.2 D. Assuming our identification is correct, we derive a rotation temperature of \( 37 \pm 6 \) K and a C_{5N}^- column density of \( 3.4 \times 10^{12} \) cm\(^{-2}\) (see Fig. 3). Neutral C_{5N} has been observed in IRC +10216 by Guélin et al. (1998), who derived a column density of \( 6 \times 10^{12} \) cm\(^{-2}\) for a dipole moment of 3.39 D (Botschwina 1996). The abundance ratio between the neutral and the anion is then only 1.8, the largest relative abundance observed so far for any anion.

A number of clues, however, suggest that we may have underestimated the abundance of neutral C_{5N}. First of all, as noted by Guélin et al. (1998), the abundance decrement C_{5N}/C_{5N}^- is an order of magnitude larger than that of HCN/HCN and C_{3N}/C_{3N}^- in IRC +10216 and in TMC-1, yet all chemical models predict it to be similar. Second, in the laboratory the lines of C_{5N} are far weaker than those of C_{5N}^-, yet the production of both should be similar. P. Valiron (2008, private communication) has recalculated the ground state symmetry and dipole moment of C_{5N} at restricted open-shell Hartree-Fock and coupled cluster level, using augmented correlation consistent Dunning’s basis sets. Using a double zeta set, he derives a \( ^3\Sigma^- \) ground state with a small \( \sim 1 \) D dipole moment, in agreement with the previous calculations of Pauzat et al. (1991); alternatively with a quadrupole zeta set, he finds a \( ^3\Sigma^- \) ground state and a large dipole moment \( \sim 3.4 \) D, in agreement with Botschwina (1996). Valiron concludes that the dipole moment of C_{5N} may well lie between these two values in the case of admixing between the \( ^2\Sigma^- \) and \( ^3\Sigma^- \) states similar to those observed for C_{5N} and C_{5N}^-. A dipole moment twice smaller than that calculated for the unperturbed \( ^3\Sigma^- \) state would raise the \( C_{5N}/C_{5N}^- \) abundance ratio to 8, making it only slightly smaller than the C_{5N}/C_{5N}^- ratio (see Cernicharo et al. 2007).

To further investigate the formation of C_{5N} and C_{5N}^-, we have modeled the chemistry in the external layers of the circumstellar envelope of IRC +10216 with the same time-dependent chemical model we have used to calculate the abundances of C_{5N} and C_{5N}^- (Cernicharo et al. 2007) and C_{5N} and C_{5N}^- (Thaddeus et al. 2008). Figure 4 shows the computed abundances as a function of the distance to the star, R. In these models we have assumed an electron radiative attachment rate.
for C_5N of 2 × 10^{-7} \times (T/300)^{-0.5} \text{ cm}^3 \text{s}^{-1}, close to those adopted for the largest C_H radicals. In the region of interest [R = (3–5) × 10^{-16} \text{ cm}], C_5N is found to be 2–10 times more abundant than C_5N^-, which is in good agreement with our identification of B1389 with C_5N^-.

We note that our spectral survey should have been sensitive enough to detect another series with a rotational constant close to that predicted by Botschwina & Oswald (2008), assuming that B1389 does not arise from this anion and that the dipole moment of C_5N^- is as large as 5.2 D. No such series was found.

Laboratory searches to detect C_5N^- have also been undertaken with the microwave spectrometer at Harvard on the assumption that this anion is the carrier of B1389. No frequency search is required, because the rotational constant derived from the astronomical data is good to a few kHz, and the nitrogen hfs is negligible throughout much of the centimeter-wave band. As for C_H^+, experimental parameters were first optimized to produce strong lines of the corresponding neutral radical, C_HN. A number of searches for C_5N^- were then performed using different discharge voltages (ranging from 1000 to 600 V); still no such series was found.

Among the unidentified lines of Figure 1, we note that U83278 is within 0.1 MHz of the J = 1–0 line of CCH^-.

Assuming the line arises from this anion, we calculate an abundance ratio CCH/CCH = 12,500. The J = 3–2 CCH^- transition would then be strong enough to be detectable; a search for this transition to confirm the present assignment is under way.

Shortly before this Letter was submitted, Pierre Valiron kindly calculated for us the structure of C_5N^-, and gave an estimate of its dipole moment. This was one of his last scientific contributions; he died untimely on August 31. Pierre was a valued colleague and friend, who will be greatly missed. We thank Carl Gottlieb for supporting laboratory frequencies. We acknowledge funding support from Spanish MEC through grants AYA2006-14876 and ESP2004-665, from PRICIT CM project S-0505-ESP-0237 (ASTROCAM), and from FP6 MCTN “The Molecular Universe.” M. Agúndez also acknowledges grant AP2003-4619 from Spanish MEC. The work in Cambridge is supported by NSF grant CHE-0701204 and NASA grant NNX08AE05G.

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