

DETECTION OF C_3N^- AND VIBRATIONALLY EXCITED C_6H IN IRC +10216¹

J. CERNICHAO,² M. GUÉLIN,³ M. AGÚNDEZ,² M. C. MCCARTHY,⁴ AND P. THADDEUS⁴

Received 2008 July 2; accepted 2008 October 8; published 2008 October 29

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 C_6H and C_5N . Three of the series have half-integer rotational quantum numbers; we assign them to the ${}^2\Delta$ and ${}^2\Sigma^-$ vibronic states of C_6H in its lowest (ν_{11}) 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 C_5N^- 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 C_nH ($n = 4, 6, 8$; see Guélin et al. 1987; Cernicharo & Guélin 1996) and C_nN ($n = 3, 5$; see Guélin et al. 1998) were first detected and identified. The butadiynyl radical C_4H 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 $A^2\Pi$ 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, C_6H^- , C_4H^- , C_8H^- , and C_3N^- (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., Sarre 1980; Herbst 1981) on the ground that electron radiative attachment is efficient for molecules with large electron affinities and dense vibrational spectra. The presence of C_3N and C_5N in IRC +10216 and the recent detection of C_3N^- in this source imply that C_5N^- may be present.

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 C_6H

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 C_6H and C_5N ($B = 1391.2$ 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.

C_6H is a linear radical with a ${}^2\Pi$ ground electronic state (Cernicharo et al. 1987). It has 6 stretching modes, ν_1 – ν_6 , and 5 bending modes, ν_7 – ν_{11} . The modes ν_{10} and ν_{11} have the lowest energies, ≈ 210 and ≈ 93 cm^{-1} , respectively, according to ab initio calculations by Cao & Peyerimhoff (2001); the next mode ν_9 is at about 400 cm^{-1} .

Even though excited vibrational states of long carbon chains are susceptible to infrared fluorescent excitation in IRC +10216, vibrational temperatures remain low: e.g., 40–50 K for the ν_7 mode of HC_3N and the ν_{11} mode of HC_5N (Cernicharo et al. 1987; J. Cernicharo et al. 2008, in preparation). Only the lowest bending mode of C_6H (ν_{11}) is therefore expected to be sufficiently populated to detect. The first excited electronic state of C_6H , ${}^2\Sigma$, is known to lie very close in energy to the ${}^2\Pi$ 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 C_6H is split into one ${}^2\Delta$ (with half-integer quantum numbers) and two ${}^2\Sigma$ vibronic states (${}^2\Sigma^+$ and ${}^2\Sigma^-$ with integer quantum numbers). According to Herzberg (1966), the splitting

¹ Based on observations carried out with the IRAM 30 m telescope. IRAM is supported by INSU/CNRS (France), MPG (Germany), and IGN (Spain).

² DAMIR, Instituto de Estructura de la Materia, CSIC, Serrano 121, 28006 Madrid, Spain; cerni@damir.iem.csic.es.

³ Institut de Radioastronomie Millimétrique, 300 rue de la Piscine, 38406 St. Martin d'Hères, France; and LRA-ENS/LERMA, Observatoire de Paris, France.

⁴ Harvard-Smithsonian Center for Astrophysics, 60 Garden Street, Cambridge, MA 02138; and School of Engineering and Applied Sciences, Harvard University, 29 Oxford Street, Cambridge, MA 02138.

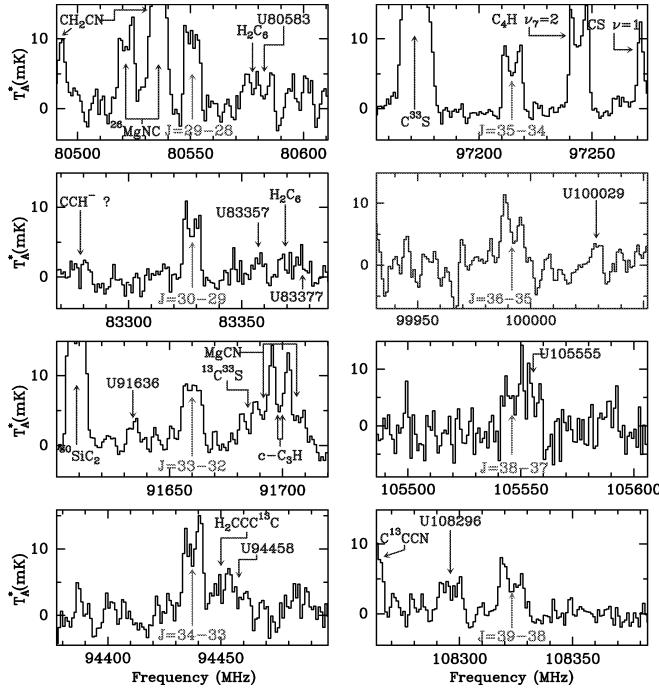


FIG. 1.—Spectra of IRC +10216 observed with the IRAM 30 m telescope, showing lines from the B1389 series assigned here to C_5N^- . The marginal weak line U83278 is worth noting, because it is within 0.1 MHz of the $J = 1-0$ line of CCH^- (see text). [See the electronic edition of the *Journal* for a color version of this figure.]

between the Σ^+ and Σ^- states, A_{Σ} , produced by the Renner-Teller effect is

$$A_{\Sigma} = (A_{SO}^2 + 4\epsilon^2\omega^2)^{1/2}, \quad (1)$$

where A_{SO} is the spin-orbit constant of the ground ${}^2\Pi$ electronic state of C_6H ($A_{SO} = -15.04 \text{ cm}^{-1}$; Linnartz et al. 1999), ϵ is the Renner parameter, and ω is the frequency of the bending

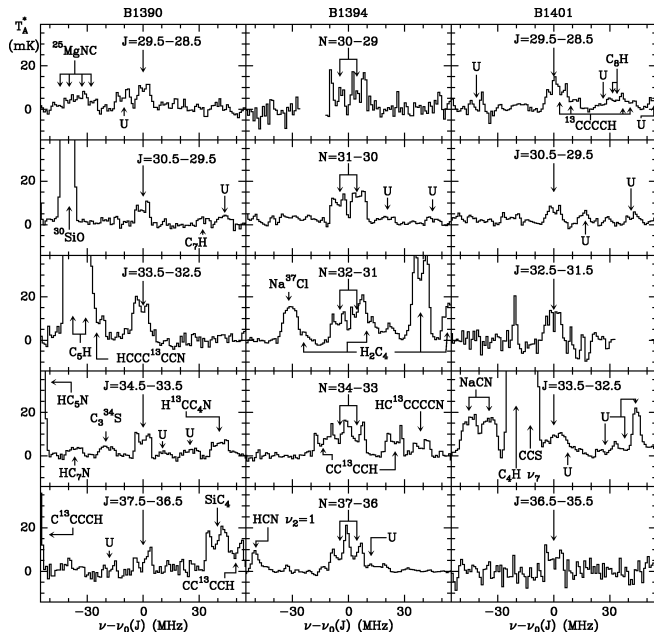


FIG. 2.—Spectra of IRC +10216 observed with the IRAM 30 m telescope showing selected lines pertaining to the series B1390, B1394, and B1401. These three series of lines are assigned to vibronic states of the ν_{11} bending mode of C_6H .

TABLE 1
OBSERVED LINE PARAMETERS IN IRC +10216

Transition	Obs. Freq. (MHz)	Cal. Freq. (MHz)	$\int T_A^* dv$ (K km s $^{-1}$)	v_{exp} (km s $^{-1}$)
B1389 (C_5N^-)				
$J = 29-28$	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 ^a
$J = 33-32$	91660.0(6)	91660.0	0.25(3)	15.4(7)

NOTES.—Numbers in parentheses are 1σ uncertainties in units of the last digits. A superscript “a” indicates that the line width parameter v_{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.

mode. The ${}^2\Sigma^-$ and ${}^2\Sigma^+$ states lie above and below the ${}^2\Delta$ state by $A_{\Sigma}/2$. The values of B and γ for the ${}^2\Sigma^{\pm}$ states, the effective spin-orbit constant for the ${}^2\Delta$ vibronic state, and the effective rotational constants for the two ladders of this state are given by (Herzberg 1966)

$$B_{\Sigma^{\pm}} = B(1 \pm A_{SO}^2 B/A_{\Sigma}^3), \quad (2)$$

$$\gamma_{\Sigma^{\pm}} = 2B(1 - 2\epsilon\omega/A_{\Sigma} \pm A_{SO}^2 B/A_{\Sigma}^3), \quad (3)$$

$$A_{\text{eff}} = A_{SO}(1 - 3\epsilon^2/4), \quad (4)$$

$$B_{\text{eff}\Delta} = B(1 \pm B/A_{\text{eff}}), \quad (5)$$

where B is the unperturbed rotational constant of the bending mode. These expressions have to be taken with caution as additional rovibronic coupling with higher lying vibronic states may introduce significant higher order corrections (see, e.g., Brown 2003).

In view of the close agreement between the rotational constant of C_6H and those of our four new series, it was probable that one or more may be produced by the low-lying ν_{11} bend of C_6H . By analogy with HC_5N , which has a vibrational spectrum similar to that here, C_6H in its ν_{11} bending mode is expected to have a rotational constant 1.004 times larger than that in its vibrational ground state, i.e., close to 1395 MHz. The assignment of B1390 and B1401, both with half-integer quantum numbers and whose average B value is close to 1395 MHz, to the ${}^2\Delta_{3/2}$ and ${}^2\Delta_{5/2}$ ladders of the ${}^2\Delta$ vibronic state of ν_{11} was therefore logical. As discussed below, these assignments have been confirmed in the laboratory (see below).

Because B1394 shows well-resolved doublets with integer rotational quantum numbers (see Fig. 2), this series is almost certainly from a ${}^2\Sigma$ vibronic state. The most likely carrier is

TABLE 2
DERIVED ROTATIONAL CONSTANTS

Series	B (MHz)	D (Hz)	N_{lines}	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 1σ uncertainties in units of the last digits.

^a B1394 corresponds to a ${}^2\Sigma$ vibronic state with $\gamma = 15.2(13)$ MHz and $\gamma_d = -1.53(35)$ KHz.

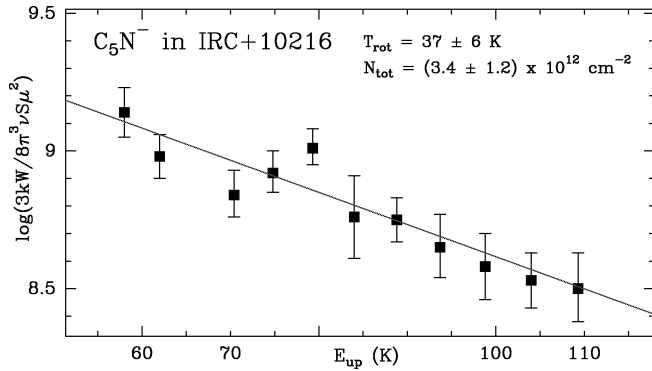


FIG. 3.—Rotational diagram for B1389. The column density has been derived assuming a dipole moment of 5.2 D (see text).

the lowest of the two ${}^2\Sigma$ ladders of the ν_{11} 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 ${}^2\Delta$ ladders of ν_{11} , we can derive from relations (1) through (5) a set of rovibrational parameters that give a good fit to the data: $B_{\Delta} = 1395.72$ MHz, $A_{\text{eff}\Delta} = 11.13$ cm^{-1} , $\epsilon^2 = 0.352$, $A_{\Sigma} \approx 145.0$ cm^{-1} , and $\omega \approx 120$ cm^{-1} , a value compatible with that calculated for ν_{11} by Cao & Peyrimhoff (2001). Therefore, under the assumption that relations (1) through (5) apply to C_6H , the ${}^2\Sigma^-$, ${}^2\Delta$, 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 ($\gamma^+ \approx \gamma^-$) 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 ν_{11} vibronic states are $N({}^2\Sigma^-) \approx 1.4 \times N({}^2\Delta) = 8 \times 10^{12}$ cm^{-2} . Both vibronic states have a rotational temperature of ≈ 45 K—somewhat higher than that measured for the ground vibrational state (31 ± 2 K; Cernicharo et al. 2007). The column density in the ground state is calculated to be 6.6×10^{13} cm^{-2} , indicating that about 20% of C_6H is in the ν_{11} state.

Recent laboratory measurements at both millimeter and centimeter wavelengths confirm that B1390, B1401, and B1394 arise from ${}^2\Delta$ and ${}^2\Sigma$ components of a low-lying vibrationally excited state of C_6H (Gottlieb et al. 2006). The ${}^2\Sigma$ component has been observed over a wide range of rotational excitation ($N = 5\text{--}85$), under experimental conditions which optimize lines of ground state C_6H . 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 ${}^2\Delta$ component has also been observed in the same laboratory discharge. The spectroscopic constants derived from the astronomical data agree to within 1σ with those derived from the larger and more precise set of laboratory data for both the ${}^2\Delta$ 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_6H or ground state C_6H^- 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 $J = 35\text{--}34$

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_6H . Its carrier is almost certainly a new linear molecule with a ${}^1\Sigma$ ground electronic state, and a molecular weight close to that of C_6H and C_5N .

The most obvious candidates are the ions C_6H^- , C_6H^+ , and C_5N^- . C_6H^- has already been detected in the laboratory and in IRC +10216 (McCarthy et al. 2006), and is immediately ruled out. Linear C_6H^+ has a ${}^3\Sigma$ ground electronic state (according to Fehér & Maier 1994), and only a fraction of its rotational transitions will be harmonically related with $B \approx 1340$ 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_6H^+ 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 ± 6 K and a C_5N^- column density of 3.4×10^{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 6×10^{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 HC_3N/HC_5N and C_4H/C_6H , both 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_6H , 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 ${}^2\Pi$ ground state with a small (~ 1 D) dipole moment, in agreement with the previous calculations of Pauzat et al. (1991); alternatively with a quadruple zeta set, he finds a ${}^2\Sigma$ ground state and a large dipole moment (≈ 3.4 D), in agreement with Botschwina (1996). Valiron concludes that the dipole moment of C_5N may well lie between those two values in the case of admixing between the ${}^2\Sigma$ and ${}^2\Pi$ states similar to those observed for C_4H and C_6H . A dipole moment twice smaller than that calculated for the unperturbed ${}^2\Sigma$ state would raise the C_5N/C_5N^- abundance ratio to 8, making it only slightly smaller than the C_6H/C_6H^- 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_4H and C_4H^- (Cernicharo et al. 2007) and C_3N and C_3N^- (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

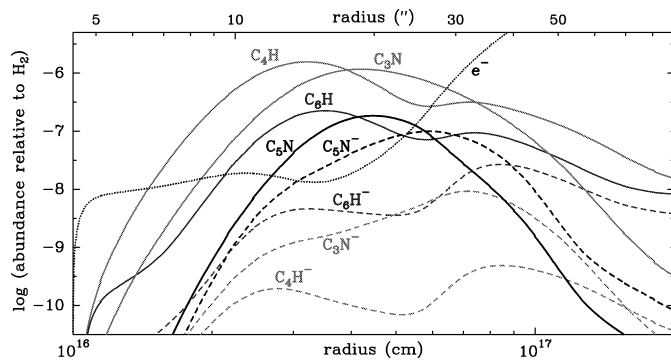


FIG. 4.—Model abundances of the neutral radicals C_nH , C_nN , and their anions in the outer envelope of IRC +10216. [See the electronic edition of the *Journal* for a color version of this figure.]

for C_5N of $2 \times 10^{-7} \times (T/300)^{-0.5} \text{ cm}^3 \text{ s}^{-1}$, close to those adopted for the largest C_nH radicals. In the region of interest [$R = (3\text{--}5) \times 10^{16} \text{ cm}$], 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_6H^- , experimental parameters were first optimized to produce strong lines of the corresponding neutral radical, C_5N . A number of searches for C_5N^- were then performed using different discharge voltages (ranging from 1000 to 600 V); still other searches using a range of concentrations and gas pulses of various lengths were also attempted, all without success. Our failure to detect C_5N^- is not particularly disturbing, because finding C_4H^- and C_3N^- was very difficult (McCarthy & Thaddeus 2008), requiring repeated trial and error. Additional

experiments are needed to find the highly specific conditions which are apparently required to make this anion.

Finally, a number of other candidates for B1389 were considered and rejected, including AICCCN, AINCCC, NaCCCN, and NaNCCC. All have $^1\Sigma$ electronic states, large dipole moments ($\mu_a = 6.2, 4.0, 13.6,$ and 16.6 D , respectively), and about the right mass and size. The calculated rotational constants, however, differ by more than 4% from 1389 MHz, versus an estimated uncertainty of 1% (Petrie 1999)—probably a prohibitive discrepancy. Finally, MgCCCN, whose calculated rotational constant is close to B1389 (1397 MHz; see Petrie 1999), has a $^2\Sigma$ not a $^1\Sigma$ ground electronic state.

With no plausible alternative, we therefore conclude that B1389 is almost certainly C_5N^- . The observation of low- J lines in the cold source TMC-1 would strengthen this conclusion. We have searched for the $J = 8\text{--}7$ transition in TMC-1 with the Effelsberg telescope, and have detected a 3σ feature at the right frequency; a further factor of 2 improvement in sensitivity is required for confirmation. The final proof, however, must await detection of the B1389 lines in the laboratory.

Among the unidentified lines of Figure 1, we note that U83278 is within 0.1 MHz of the $J = 1\text{--}0$ line of CCH^- . Assuming the line arises from this anion, we calculate an abundance ratio $CCH/CCH^- \approx 12,500$. The $J = 3\text{--}2$ 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.

REFERENCES

- Aoki, K. 2000, *Chem. Phys. Lett.*, 323, 55
 Botschwina, P. 1996, *Chem. Phys. Lett.*, 259, 627
 Botschwina, P., & Oswald, R. 2008, *J. Chem. Phys.*, 129, 044305
 Brown, J. M. 2003, *Mol. Phys.*, 101, 3419
 Cao, Z., & Peyerimhoff, S. 2001, *Phys. Chem. Chem. Phys.*, 3, 1403
 Cernicharo, J. 1985, ATM: A Program to Compute Atmospheric Opacity between 0–1000 GHz, IRAM Internal Report
 Cernicharo, J., & Guélin, M. 1996, *A&A*, 309, L27
 Cernicharo, J., Guélin, M., & Kahane, C. 2000, *A&AS*, 142, 181
 Cernicharo, J., Guélin, M., Menten, K. M., & Walmsley, C. M. 1987, *A&A*, 181, L1
 Cernicharo, J., et al. 2007, *A&A*, 467, L37
 Fehér M., & Maier, J. P. 1994, *Chem. Phys. Lett.*, 227, 371
 Gottlieb, C. A., McCarthy, M. C., & Thaddeus, P. 2006, in 61st Ohio State University International Symposium on Molecular Spectroscopy (Columbus: OSU), talk RF07
 Guélin, M., Neisinger, N., & Cernicharo, J. 1998, *A&A*, 335, L1
 Guélin, M., et al. 1987, *A&A*, 175, L5
 Herbst, E. 1981, *Nature*, 289, 656
 Herzberg, G. 1966, in *Molecular Spectra and Molecular Structure*, Vol. 3, (Malabar, FL: Krieger Publishing Company)
 Linnartz, H., et al. 1999, *J. Mol. Spectrosc.*, 197, 1
 McCarthy, M., Gottlieb, C. A., Gupta, H., & Thaddeus, P. 2006, *ApJ*, 652, L141
 McCarthy, M. C., & Thaddeus, P. 2008, *J. Chem. Phys.*, 129, 054314
 Murakami, A., Kawaguchi, K., & Saito, S. 1987, *PASJ*, 39, 189
 Puzat, F., et al. 1991, *ApJ*, 369, L13
 Petrie, S. 1999, *MNRAS*, 302, 482
 Sarre, P. J. 1980, *J. Chim. Phys.*, 77(7-8), 769
 Thaddeus, P., et al. 2008, *ApJ*, 677, 1132
 Yamamoto, S., Saito, S., & Guélin, M. 1987, *ApJ*, 323, L149