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Letter to the Editor

Astronomical detection of C_4H^-, the second interstellar anion⋆

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ABSTRACT

Aims. Following the recent detection of C_6H^- in the laboratory and in space we have succeeded in studying the microwave spectrum of C_4H^-. We report here the first detection in space of this negative ion.

Methods. We have observed in the envelope of the carbon star IRC +10216 five lines corresponding to the $J = 9-8$, $11-10$, $12-11$, $14-13$ and $15-14$ rotational transitions of C_4H^-. The C_4H^- lines have a cusped shape, denoting that this ion is formed in the outer part of the envelope, like its neutral counterpart C_4H.

Results. The abundance of C_4H^- in IRC+10216 is 1/6 of the abundance of C_6H^- and 1/4200 of that of C_4H.

Conclusions. The detection of C_4H^-, after that of C_6H^-, confirms the theoretical prediction that C-chain anions are abundant in interstellar clouds and yields a first measurement of the electron radiative attachment rates.

Key words. stars: individual: IRC+10216 – stars: carbon – radio lines: stars – astrochemistry – line: identification – stars: AGB and post-AGB

1. Introduction

The presence of negative ions in the interstellar medium was predicted many years ago on general grounds or on the basis of ion-molecule chemical models (see e.g. Dalgarno & McCray 1973; Herbst 1981; Petrie 1996; Millar et al. 2000; Blanksby et al. 2001). It was pointed out that a high electron affinity and a large number of vibrational states increase greatly the sticking coefficient of electrons, so that large, negatively charged carbon chains of the form C_nH^- may be abundant. In particular, Millar et al. (2000) predicted an abundance of C_8H^- as large as 1/4 of that of its neutral counterpart C_8H in the outer envelope of the C-star IRC +10216, a source known to be particularly rich in C-chain molecules. For a long time, however, negative ions escaped detection because of the lack of accurate transition frequencies (see e.g. Morisawa et al. 2005). Recently, McCarthy et al. (2006) have succeeded in studying the microwave spectrum of C_6H^- in the laboratory and identified this species as the carrier of a series of lines observed by Kawaguchi et al. (1995) in the C-rich circumstellar envelope IRC +10216. A few years before, Aoki (2000) already proposed C_6H^- as a possible carrier of these lines on the basis of ab initio calculations. McCarthy et al.'s (2006) identification of C_6H^- in IRC +10216 and their subsequent detection of this species in the cold dark cloud TMC-1 demonstrate that negative ions can indeed be abundant in the interstellar medium. The abundance of C_6H^- derived in these two sources is as high as a few percent of that of C_6H, considerably larger than the abundance of cations relative to their neutral counterparts, e.g. HC_3NH^+ relative to HC_3N. Pursuing their laboratory work, McCarthy and colleagues have measured the rotational spectra of two more polyacetylenic anions, C_8H^- and C_4H^- (Gupta et al. 2007). In this Letter, we report the astronomical detection of the latter species in IRC+10216.

2. Observations

In the course of searches for new molecules, carried out with the IRAM 30-m telescope toward IRC +10216, we have covered a large fraction of the 3-mm spectrum of that source with a high sensitivity. The data revealed a number of spectral lines which could not be assigned to any known molecular species. Three of these unidentified lines (U-lines), with rest frequencies of 83787, 102406 and 111714 MHz and peak intensities of ~10 mK, coincide within the errors in frequency with the $J = 9-8$, $11-10$ and $12-11$ transitions of C_4H^-. The density of lines with intensities $\geq$5 mK in our 3-mm spectral survey being of ~1 per 30 MHz, and the density of unidentified lines at the same level being only 1 per 100 MHz, the evidence for C_4H^- was already compelling.

The 2 mm spectral line survey of IRC +10216 (Cernicharo et al. 2000) is not sensitive enough to show lines with intensities below 10 mK. In order to remove any doubt on the identification of C_4H^- and to further constrain the partition function of the rotational levels, we returned to the 30-m telescope to search for two more C_4H^- transitions: the $J = 14-13$ transition at 130.3 GHz and the $J = 15-14$ transition at 139.6 GHz. The observations were carried out in January 2007 with the 30-m telescope. We observed simultaneously both C_4H^- transitions, using the C and D 2-mm receivers. The backends consisted of two filterbanks with 512×1 MHz-wide channels.

⋆ This work was based on observations carried out with the IRAM 30-m telescope. IRAM is supported by INSU/CNRS (France), MPG (Germany) and IGN (Spain).

Table 1. Number in parentheses are 1σ uncertainties in units of the last digits.

Observed C_4H^- and C_6H^- line parameters

Transition $J' \to J''$	ν_{cal} (MHz)	ν_{obs} (MHz)	$\int T_A^* dv$ (K km s^{-1})	v_{exp} (km s^{-1})
		C_4H^-		
9−8	83787.299	83787.4(10)	0.19(3)^a	14.5^b
11−10	102405.664	102405.7(8)	0.25(2)	14.4(5)
12−11	111714.621	111714.2(10)	0.17(3)^a	14.5(8)
14−13	130332.013	130332.9(8)	0.30(4)	14.8(8)
15−14	139640.420	139640.6(8)	0.16(3)	14.7(7)
		C_6H^-		
29−28	79854.897	79854.9(3)	0.59(4)	13.5(6)
30−29	82608.285	82608.4(2)	0.63(2)	14.2(3)
32−31	88114.991	88114.9(2)	0.59(2)	14.4(2)
33−32	90868.306	90868.2(6)	0.41(4)	14.5^b
34−33	93621.597	93621.2(5)	0.31(3)	14.5^b
35−34	96374.861	96374.5(6)	0.32(3)	14.5^b
36−35	99128.097	99128.0(10)	0.23(2)^a	14.5^b
37−36	101881.306	101880.6(10)	0.25(2)^a	14.5^b
38−37	104634.486	104634.2(8)	0.30(3)	14.5^b
40−39	110140.757	110140.5(1)	0.20(3)	13.7(7)
41−40	112893.846	112893.9(8)	0.15(3)	14.5^b
42−41	115646.903	115645.9(10)	0.22(4)	14.5^b

^{a} denotes a partly blended line and ^{b} indicates that terminal velocity has been fixed to 14.5 km s^{-1}.

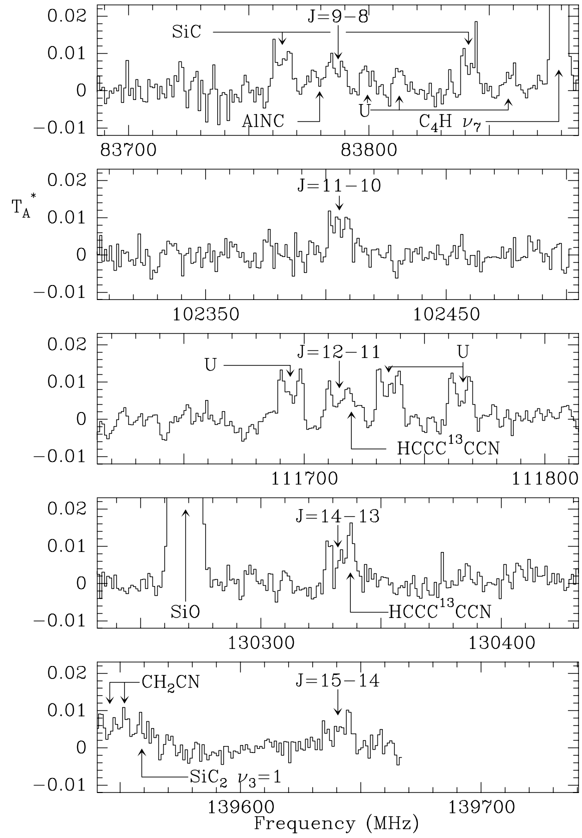

Fig. 1. J = 9−8, 11−10, 12−11, 14−13 and 15−14 lines of C_4H^- toward IRC+10216. The spectral resolution is 1 MHz and the frequency scale (rest frequency) is relative to a systemic velocity of −26.5 km s^{-1}. The positions of the C_4H^- lines are indicated by downward arrows. The lines of $HCCC^{13}CCN$ correspond to its J = 42−41, and 49−48 transitions. The corresponding transitions of $HCC^{13}CCCN$ could be present in the same panels. However, within the S/N of the data these lines are not detected. Spectral intensities are in the antenna temperature scale, T_A^*.

The observing mode, where we wobbled the secondary mirror by ±90″ at a rate of 0.5 Hz, and the dry weather conditions (sky opacity at 225 GHz was below 0.1) ensured flat baselines and low system noise temperatures ($T_{sys} \sim 200$ K). The total ON+OFF integration time was 8 hours per line yielding an rms noise of ~3 mK per 1 MHz channel.

In the 3 mm line survey of IRC+10216 we have also observed 12 lines of C_6H^-. The parameters for these lines are given in Table 1.

3. Results

The 3-mm and 2-mm spectra covering the 5 observed C_4H^- transitions are shown in Fig. 1. Except for the J = 10−9 transition, which falls atop a relatively strong line of C_5H, and the J = 13−12 transition, which lies outside the tunable band of the receivers, all transitions from J = 9−8 to J = 15−14 are detected.

Table 1 gives the parameters for the observed lines of C_4H^- and C_6H^-. The C_4H^- lines show the characteristic cusped shape and sharp edges that are common to all optically thin lines arising from the outer envelope of IRC +10216. Those lines are centered at −26.5 km s^{-1} and have a full width of 29 km s^{-1}, twice the expansion velocity of the envelope. The observed frequencies and widths of the J = 11−10, 14−13 and 15−14 lines agree well with these values. The J = 9−8 and 12−11 lines, although clearly visible, are partly blended with weaker lines of AlNC and $HCCC^{13}CCN$. Thanks to the sharp edges and known widths, their rest frequencies can nevertheless be derived within 1 MHz. The good agreement of the observed and calculated line frequencies and the similarity of the line intensities, which are well accounted for by a single rotation temperature as will be seen below, confirm that we have detected C_4H^-.

As most reactive molecular species, neutral C_4H is concentrated in IRC +10216 inside an hollow shell of radius R = 14″ and thickness $\Delta R \simeq 7''$ (Guélin et al. 1993). The average rotation temperature in the shell is T_{rot} = 35 K and the total column density (twice the radial column density) of C_4H molecules in the ground vibrational state is $N(C_4H) = 3 \times 10^{15}$ cm^{-2} (4/5 of all C_4H, see Cernicharo et al. 2000). Figure 2 shows the averaged spectrum of the 5 lines of C_4H^- in Fig. 1 superimposed on the corresponding average spectrum of C_4H (divided by 100). The strong similarity between the averaged line profiles of both molecules indicates that C_4H and its anion are spatially coexistent. Adopting for C_4H^- a permanent dipole moment μ = 6.2 D (Botschwina, quoted by Blanksby et al. 2001), we derive a rotational temperature $T_{rot}(C_4H^-)$ = 23 ± 2 K, somewhat lower than that of C_4H, and a column density $N(C_4H^-) = 7.1 \pm 2.0 \times 10^{11}$ cm^{-2} (see Fig. 3), which yields $N(C_4H^-)/N(C_4H)$ = 1/4200.

Moreover, once the weak AlNC and $HCCC^{13}CCN$ lines are subtracted, the 5 observed C_4H^- line profiles, and the corresponding ones averaged for the neutral species, can be reproduced very well with a radiative transfer MonteCarlo calculation assuming that C_4H^- and C_4H are co-spatial (details will be given in a forthcoming paper). This definitively shows that C_4H^- has a spatial distribution not very different from that of C_4H. These calculations provide $N(C_4H^-)/N(C_4H) \simeq 1/4400$, i.e., a very similar value to that obtained from the rotational diagrams.

From all observed lines of C_6H^- (see Table 1) we obtain $N(C_6H^-) = 4.1 \pm 1.5 \times 10^{12}$ cm^{-2}, similar to that reported by McCarthy et al. (2006), and T_{rot} = 27 ± 2 K (see Fig. 3). A rotational temperature diagram for the lines of neutral C_6H ($^2\Pi_{3/2}$) observed in our 3 mm line survey (Fig. 3) yields T_{rot} = 31 ± 2 K

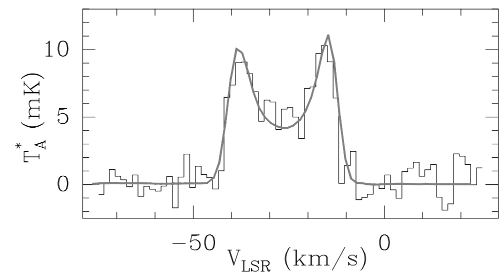

Fig. 2. Averaged spectrum of the J = 9−8, 11−10, 12−11, 14−13 and 15−14 lines of C_4H^- (histogram) and C_4H (thick continuous line). All lines blended with those of C_4H^- have been fitted and removed. The C_4H averaged spectrum has been scaled by a factor 100.

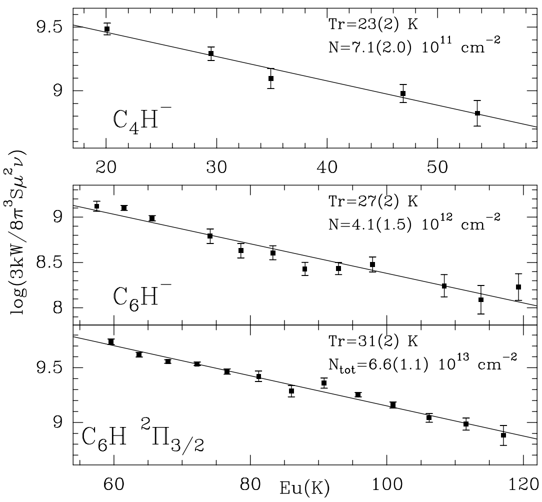

Fig. 3. Rotational diagrams for C_4H^-, C_6H^- and C_6H $^2\Pi_{3/2}$. Main beam integrated intensities (data in Table 1 multiplied by 1.33) have been corrected for beam dilution assuming an uniform source of radius 19″.

and $N(C_6H) = 6.6 \pm 2.0 \times 10^{13}$ cm^{-2}, after including the contribution from the upper $^2\Pi_{1/2}$ spin ladder. Thus, the ratio $N(C_6H^-)/N(C_6H)$ is 1/16 and $N(C_4H^-)/N(C_6H^-)$ = 1/6.

4. Discussion

Herbst (1981) predicted from theoretical considerations that heavy negative ions may be abundant in UV-shielded interstellar and circumstellar clouds. Negative ions A^- form by radiative attachment of electrons on a neutral species A, a 2-step process involving the formation of a complex $(A^-)^*$ and its stabilisation by emission of a photon:

$$A + e^- \rightarrow (A^-)^* \rightarrow A^- + h\nu. \quad (1)$$

They are destroyed mainly through reactions with atomic hydrogen (associative attachment: $A^- + H \rightarrow AH + e^-$), reactions with positive ions (mutual neutralization: $A^- + M^+ \rightarrow B + C$), and photodetachment $A^- + h\nu \rightarrow A + e^-$. In steady state the abundance $[A^-]$ of the anion can be expressed relative to that of its neutral counterpart [A] as:

$$\frac{[A^-]}{[A]} = \frac{k_{\rm ratt} X[e^-]}{k_{\rm aa}[H] + k_{\rm neu}[B^+] + k_{\rm pht}/n(H_2)}, \quad (2)$$

where $[e^-]$ and [H] are the electron and atomic hydrogen abundances, $n(H_2)$ the H_2 volume density, $k_{\rm aa}$, $k_{\rm neu}$, and $k_{\rm pht}$ the rate coefficients for associative attachment, mutual neutralization, and photodetachment reactions respectively, and $k_{\rm ratt}$ is the global rate coefficient of reaction (1).

In the cold dense gas, $k_{\rm ratt}$ should be proportional to the density of vibrational states of A^- at an internal energy equal to the electron affinity EA (Herbst 1981). Thus, $k_{\rm ratt}$ is high for large molecules with a high EA. Among those, the polyacetylenic chain families $C_{2n}H$, which have exceptionally large electron affinities ($EA \geq 3$ eV, Blanksby et al. 2001) and whose smallest members had just been observed in IRC +10216 (Guélin et al. 1978) and in the dark cloud TMC-1 (Guélin et al. 1982), stuck out as the most likely progenitors of large interstellar anions. It is remarkable that with this simple reasoning, Herbst (1981) predicted 26 years ago that C_4H^- and, more generally, $C_{2n}H^-$ ($n \geq 2$) may be abundant in interstellar and circumstellar clouds ($[C_2nH^-]/[C_2nH]$ = 0.1−0.01).

The crucial, yet poorly known parameter controlling the abundance of molecular ions is the radiative attachment rate coefficient $k_{\rm ratt}$. This coefficient is not measured, but only estimated from statistical calculations (Petrie & Herbst 1997; Terzieva & Herbst 2000) or inferred from laboratory three body reaction rate measurements (Herbst 1981). According to Herbst and colleagues, the attachment rate for polyacetylenic radicals with 6 or more C atoms may approach the rate of collisions of heavy neutrals with electrons, $k_{\rm coll} \sim 10^{-6}$ cm^{3}s^{-1} (Petrie & Herbst 1997; Terzieva & Herbst 2000). Adopting a rate that large, Millar et al. (2000) predicted that $[C_8H^-]/[C_8H] \sim 1/4$ in IRC +10216. For smaller species, such as C_4H, the radiative stabilization of the complex, $(A^-)^* \rightarrow A^- + h\nu$, is slower than its detachment, $(A^-)^* \rightarrow A + e$, and $k_{\rm ratt}$ may become much smaller than $k_{\rm coll}$ (Terzieva & Herbst 2000).

Since the physical and chemical conditions in IRC+10216 and the chemical time scales are relatively well known, we can try to derive from the measured $[C_4H^-]/[C_4H]$ and $[C_6H^-]/[C_6H]$ ratios the rates of radiative electron attachment, $k_{\rm ratt}$, for C_4H and C_6H.

Assuming, first, that steady state is a valid approximation for the shell where C_nH and C_nH^- species are present, and neglecting photodetachment (see below), we find from Eq. (2):

$$k_{\rm ratt} = \frac{[A^-]}{[A]}\frac{1}{[e^-]}(k_{\rm aa}[H] + k_{\rm neu}[B^+]). \quad (3)$$

We adopt $k_{\rm neu} = 10^{-7}$ cm^3 s^{-1} (see e.g. Smith & Adams 1979) and $k_{\rm aa}$ from the measurements by Barckholtz et al. (2001). We also take mean values in the R = 14″ shell for the abundance of cations and atomic hydrogen: $[e^-]/[H_2] = [B^+]/[H_2] = 10^{-7}$ (Glassgold et al. 1987) and $[H]/[H_2] = 10^{-4}$ (Glassgold 1996). From our observed values $[C_4H^-]/[C_4H]$ = 1/4400 and $[C_6H^-]/[C_6H]$ = 1/16, we arrive at $k_{\rm ratt}(C_4H) = 2 \times 10^{-10}$ cm^3 s^{-1} and $k_{\rm ratt}(C_6H) = 5 \times 10^{-8}$ cm^3 s^{-1}. The radiative electron attachment rate of C_6H compares well with that calculated for C_6 by Terzieva & Herbst (2000), but the value obtained for C_4H is almost 2 orders of magnitude lower than that of C_4.

With such low rates, however, steady state may not be fullfilled. We have thus performed a time-dependent calculation using the a chemical model of the circumstellar envelope of Agúndez & Cernicharo (2006) to which we included reactions involving the negative ions C_n^- and C_nH^- (n = 4−9). Photodetachment was also included with a rate $\Gamma_{A^-} = 3 \times 10^{-9}\exp(-2\,A_v)$ s^{-1}. In our models, this process is less efficient in destroying anions than the reactions with neutral and cations by more than a factor of 10. Reactions of negative charge exchange, e.g., $A^- + B \rightarrow A + B^-$, are not included in our models as they seem unimportant compared to the other processes. The radiative electron attachment rates of species other than C_4H and C_6H were set to $k_{\rm ratt} = 10^{-7}$ cm^3 s^{-1}, while $k_{\rm ratt}$ for

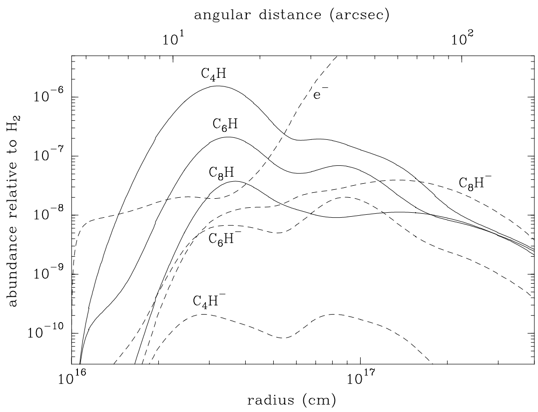

Fig. 4. Abundance profiles of C_nH and C_nH^- given by chemical modelling. Angular distance is given on the top axis for an assumed distance to the star of 150 pc.

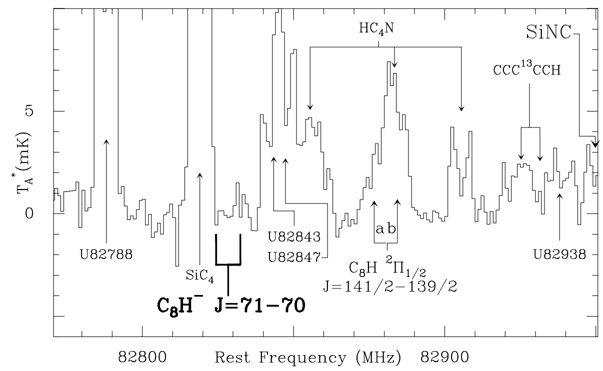

Fig. 5. Spectrum of IRC+10216 covering the J = 71−70 rotational transition of C_8H^-. The upward arrows indicate the position of the edges of the C_8H^- line.

C_4H and C_6H were varied to match the observed $[C_4H^-]/[C_4H]$ and $[C_6H^-]/[C_6H]$ ratios. Fig. 4 shows the abundance profiles obtained from the model for C_nH and C_nH^- for n = 4, 6, 8. Although Fig. 4 shows that steady state is indeed a poor approximation, the values of $k_{\rm ratt}(C_4H)$ and $k_{\rm ratt}(C_6H)$ obtained from the chemical model (1.6×10^{-10} and 4×10^{-8} cm^3 s^{-1}) agree well with those derived just above under this assumption. Our values are somewhat lower than the upper limits $k_{\rm ratt}(C_4H) = 2 \times 10^{-9}$ $(T/300)^{-1/2}$ cm^3 s^{-1} and $k_{\rm ratt}(C_6H) = 6\times10^{-8}$ $(T/300)^{-1/2}$ cm^3 s^{-1} calculated by Herbst (2007, private communication). Our model predicts that anions have a more extended distribution than their neutral counterparts, which is related to the increase of the electron abundance with radius. This behaviour was also predicted by Millar et al. (2000).

The large $[C_6H^-]/[C_6H]$ ratio found in IRC +10216 and the theoretical predictions of large $k_{\rm ratt}$ for increasing molecular size, i.e. increasing $[C_nH^-]/[C_nH]$ for increasing n, suggests that C_8H^- could be detected in IRC +10216 given that C_8H has been already detected (Cernicharo et al. (1996). Our model indicates that $[C_8H^-]/[C_8H]$ is as high as 1/2, while Millar et al. (2000) model predicted it to be 1/4. We have searched for C_8H^- in our IRC +10216 data. Although the low rotational constant of C_8H^- (B = 583 MHz, Gupta et al. 2007) makes that many rotational transitions are covered, the spectral line crowding (which is a serious problem at the 2−3 mK level), and the high level energies (which make it difficult to excite the 3-mm lines), leaves only few transitions that could be reasonably observed in the 3-mm domain. Figure 5 shows the deepest spectrum, which was observed in the course of a search for HC_4N (Cernicharo et al. 2004). The rms noise on this spectrum is 0.7 mK per 1-MHz channel. From this and other spectra we derive a 3-sigma upper limit of $[C_8H^-]/[C_8H] \leq 1/5$, taking into account the difference in permanent dipole moments (6.5 D for C_8H versus 10.4 D for C_8H^-, Blanksby et al. 2001) and the effect of fine structure splitting in C_8H. Our limit is not low enough to set significant constraints on the electron radiative attachment rate on C_8H.

5. Conclusions

Following the identification of C_6H^- by McCarthy et al. (2006) we have detected a second negative ion, C_4H^-, in the C-star envelope IRC +10216. The abundance decrement between the two ions, $[C_4H^-]/[C_6H^-]$ = 1/6, is more than two orders of magnitude smaller than that between their neutral counterparts, $[C_4H]/[C_6H]$ = 45. The two negative ions appear more abundant than their positive ion analogs which, so far, have not been identified.

The detection of C_4H^- and C_6H^- sustains the farsighted prediction of Herbst (1981) and co-workers that carbon-chain anions may be abundant in the interstellar medium. Other negative ions from the same family, such as CN^-, C_3N^-, CCH^- and C_8H^-, are likely to be detectable, although, probably, at lower intensity levels. Some of these species have already been studied in the laboratory and their millimeter rotational frequencies are accurately known, awaiting only of deeper astronomical searches. The observed $[C_4H^-]/[C_6H^-]$ abundance ratio differs significantly from that estimated from statistical calculations of radiative electron attachment. This shows that surprising results are likely in this matter.

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