

LETTER TO THE EDITOR

Laboratory detection of the negative molecular ion CCH⁻

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ABSTRACT

Aims. This paper reports the laboratory detection of the rotational spectrum of the acetylide anion, CCH⁻.

Methods. Five successive rotational transitions have been measured to high accuracy in a dc discharge with a free space millimeter-wave spectrometer in the frequency range 83–417 GHz.

Results. Precise spectroscopic constants have been obtained for CCH⁻ and transition rest frequencies can now be calculated to better than 1 km s⁻¹ in equivalent radial velocity far into the terahertz region, allowing for deep astronomical searches for this anion in space. The highly stable and fairly polar CCH⁻ anion is a likely candidate for radio astronomical detection, its neutral analogue CCH being among one of the most abundant molecules in a wide variety of astrophysical sources.

Key words. line: identification – molecular data – astrochemistry – methods: laboratory – ISM: molecules – radio lines: ISM

The search for negative molecular ions (anions) in astronomical sources has recently advanced in an unexpected way, driven by new laboratory results. In the radio band, we recently obtained the laboratory spectra of three carbon chain anions, C₆H⁻, C₄H⁻, and C₈H⁻, and showed that the first is the carrier of the unidentified series of astronomical lines discovered by Kawaguchi et al. (1995) in the molecular envelope of IRC+10216 (McCarthy et al. 2006; Gupta et al. 2007). With good rest frequencies in hand, astronomical searches for C₄H⁻ and C₈H⁻ are now underway. The purpose of the present Letter is to describe the laboratory detection of a fourth molecular anion, CCH⁻, the shortest in the sequence of carbon chain anions with a closed-shell electronic ground state, and to give the rest frequencies required for a radio astronomical search for this polar, astronomically plausible molecule.

Neutral CCH was one of the first reactive molecules identified in space before its radio spectrum was observed in the terrestrial laboratory (Tucker et al. 1974). Since its initial detection in several star-forming regions and a circumstellar shell, its rotational spectrum has been studied in detail in the laboratory at millimeter and submillimeter wavelengths (Sastry et al. 1981; Gottlieb et al. 1983; Müller et al. 2000).

The CCH radical has been found to be one of the most abundant interstellar molecules in standard galactic sources. For example, in TMC-1, Orion A, and Sgr B2, its abundance is 10–15 times higher than that of the three-membered ring *c*-C₃H₂ and is only 2–3 times lower than that of formaldehyde (H₂CO). In addition to the standard molecular sources, CCH is also observed in many other types of galactic sources including cold dust clouds (Wootten et al. 1980), planetary nebula (NGC 7027; Hasegawa & Kwok 2001), photon-dominated regions (PDRs; Teyssier et al. 2004), diffuse clouds (Lucas & Liszt 2000), and protoplanetary disks (Dutrey et al. 1997). In most astronomical sources the abundance of CCH is greater than that of *c*-C₃H₂,

thereby confirming that, like *c*-C₃H₂, the CCH radical is also ubiquitous in our galaxy (Lucas & Liszt 2000).

Because the lowest frequency transition of CCH⁻ is at 83 GHz, well above the range of our very sensitive Fourier transform microwave spectrometer, we have only been able to study this anion with our less sensitive free space millimeter-wave spectrometer (Gottlieb et al. 2003). Five successive rotational transitions have been detected in a dc discharge (150 mA) through a flowing mixture of acetylene (85%) and argon (15%) at a pressure of <15 mtorr when the discharge cell was cooled to 120 K, the same conditions under which C₄H⁻ and C₆H⁻ were observed (see Fig. 1). Lines of CCH⁻ were about a factor of 25 less intense than the strongest hyperfine component of the corresponding rotational transition of CCH observed under the same conditions. Nevertheless, lines of CCH⁻ were observed with a fairly high signal-to-noise ratio (Fig. 2), allowing frequencies to be measured to an accuracy of about 20 kHz (Table 1). In the laboratory, the abundance of the anion is about 0.1% that of the neutral radical. For spectroscopic confirmation, three lines in both singly substituted ¹³C species were observed when an isotopically enriched (50% H¹³CCH) sample was substituted for normal acetylene.

In much the same way as the anions in our previous papers were identified (McCarthy et al. 2006; Gupta et al. 2007), the lines in Table 1 can be assigned to CCH⁻ with great confidence, because (i) they are closely harmonic in frequency, without evidence of hyperfine structure, as expected for the closed-shell configuration of CCH⁻ (Ervin & Lineberger 1991; Mladenovic et al. 1998); (ii) the rotational constant derived from the data is very close (within 0.01%) to the published ab initio value for CCH⁻ ($B_0 = 41\,636(20)$ MHz; Mladenovic et al. 1998) and to that derived from our calculations (see Table 2); and (iii) the elemental composition of the discharge in which the lines are observed indicates that the carrier is a hydrocarbon or a pure carbon molecule, but the latter is ruled out by the disappearance

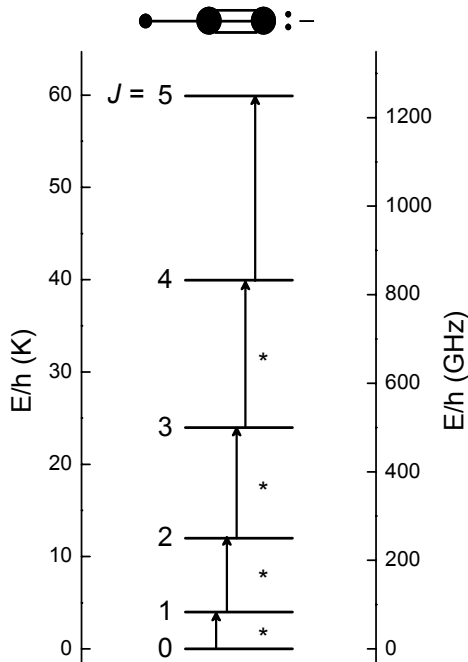


Fig. 1. Lower rotational energy levels of CCH⁻. The measured rotational transitions are indicated by arrows. Transitions that have been covered by published spectral line surveys towards various astronomical sources are marked with an asterisk.

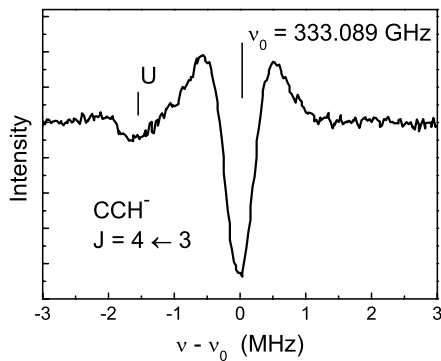


Fig. 2. The $J = 4 \leftarrow 3$ rotational transition of CCH⁻ observed with the free space millimeter-wave spectrometer in an observation of 10 min. Owing to the modulation employed, the instrumental line shape is approximately the second derivative of a Lorentzian. The weak feature marked U, which is produced by the discharge along with CCH⁻, is unidentified.

of the lines when D replaces H in the discharge; and finally, (iv) conclusive quantitative confirmation of the assignment is provided by detection of the two single-carbon-13 isotopic species at exactly the expected isotope shifts and with the predicted centrifugal distortion (see McCarthy et al. 1995).

The spectroscopic constants of CCH⁻ (Table 2) allow for accurate calculation of transition frequencies far into the terahertz region. The sixth-order centrifugal distortion constant H was not determined in the measurements here, but kept fixed at the theoretical value of Botschwina & Sebald (2006); its contribution to the calculated line frequencies is less than 1 km^{-1} in equivalent

Table 1. Rotational frequencies of CCH⁻.

$J' - J''$	Frequency (MHz)	O-C ^a (kHz)
1-0	83 278.094	9
2-1	166 553.865	22
3-2	249 824.940	-7
4-3	333 089.049	-21
5-4	416 343.896	11

Note. Estimated 1σ uncertainties in the measured line frequencies are 20 kHz. ^a Calculated from the spectroscopic constants in Table 2.

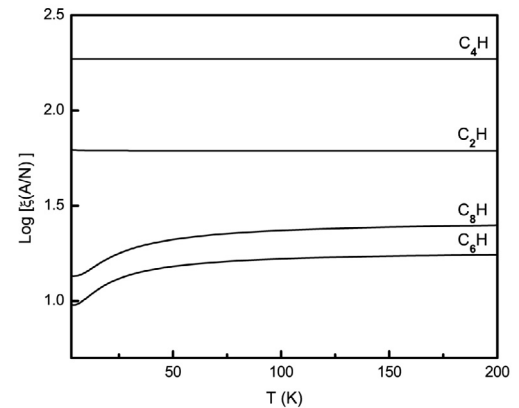


Fig. 3. Enhancement (ξ) in the line intensity of the anion (A) relative to the corresponding neutral radical (N). Plotted is the ratio of the square of the dipole moments divided by the partition functions. The ratio is independent of temperature for CCH and C₄H owing to the $^2\Sigma$ ground state of the neutral species, but depends on temperature for C₆H and C₈H in the $^2\Pi$ ground state.

radial velocity for frequencies below 2 THz, comparable to the calculated uncertainty of the predictions. The present work now allows for deep searches for CCH⁻ in essentially all astronomical sources.

As for the longer carbon chain anions, line intensities of the closed-shell CCH⁻ benefit from the collapse of fine and hyperfine structure, and from the nearly four-fold larger dipole moment than that of the CCH radical (3.09 D for the anion (Mladenovic et al. 1998); versus 0.77 D for the neutral (Woon 1995)). As a result, lines of CCH⁻ are roughly 50 times stronger than those of CCH per unit abundance, an effect that is largely independent of the rotational temperature of the source, as shown in Fig. 3, and facilitates the detection of the anion in space.

The CCH⁻ anion seems to be a particularly good candidate for astronomical detection because of its high stability against photo detachment, owing to the high electron affinity of $\sim 3 \text{ eV}$ of neutral CCH (Rienstra-Kiracofe et al. 2002), but also because it fails to react with molecular hydrogen, the most abundant molecule in space. Gas phase reaction rate measurements by Barckholtz et al. (2001) yield upper limits of only $k < 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ for the reaction of CCH⁻ (and longer carbon chain anions) with H₂, making this reaction a negligible destruction process for CCH⁻.

Recently Morisawa et al. (2005) performed a dedicated search for CCH⁻ towards the cold dark cloud L134N and the star-forming region Sgr B2 (M) with the Nobeyama 45 m and the IRAM 30 m telescopes. Although their search was centered on a frequency calculated from the theoretical structure (Mladenovic et al. 1998), the $J = 1-0$ line (83 278.1 MHz, Table 1) lies

Table 2. Spectroscopic constants (in MHz) and dipole moment (in Debye) of CCH⁻.

Constant	CCH ⁻			¹³ CCH ⁻		C ¹³ CH ⁻	
	Laboratory	Theoretical		Laboratory	Theoretical ^a	Laboratory	Theoretical ^a
		This work ^a	Previous work ^b				
B	41 639.237(4)	41 636.1	41 636	40 111.413(7)	40 108.4	40 637.441(5)	40 635.1
$10^3 D$	96.97(9)	93	96.3	90.0(2)	87	92.6(2)	89
$10^6 H$	[0.13] ^c	–	0.13				
μ		–3.1	–3.1				

^a From a quantum calculation (at the CCSD(T)/cc-pCVQZ level), corrected for vibration-rotation effects.

^b From variational calculations (with the CCSD(T)/250 cGTO potential energy surface) (Mladenovic et al. 1998), H was calculated with the same PEF by Botschwina & Sebald (2006).

^c Constrained to the theoretical value.

Table 3. Column density limits on CCH⁻.

Source	Frequency (MHz)	E_{up}/k (K)	$\mu^2 S$ (D ²)	T_r^* (mK)	Δv (kms ⁻¹)	T_{rot} (K)	N_{lim} (10 ¹² cm ⁻²)	Telescope	Ref.
L134N	83 278	4	9.6	63	0.6	5	0.09	Nobeyama 45 m	Morisawa et al. (2005)
Sgr B2 (M)	83 278	4	9.6	240	13	100	40	Nobeyama 45 m	Morisawa et al. (2005)
	249 825	24	28.7	100	20	100	3.0	SEST 15 m	Nummelin et al. (1998)
	333 089	40	38.3	200	20	100	4.0	CSO 10.4 m	Sutton et al. (1991)
IRC +10216	83 278	4	9.6	5	30	20	0.4	IRAM 30 m	Cernicharo (2006) ^a
	166 554	12	19.1	100	30	20	3.0	IRAM 30 m	Cernicharo et al. (2000)
	333 089	40	38.3	200	30	20	6.0	CSO 10.4 m	Groesbeck et al. (1994)
Orion KL	83 278	4	9.6	50	5	10	0.4	NRAO 11 m	Turner (1991)
	333 089	40	38.3	500	5	10	9.5	CSO 10.4 m	Schilke et al. (1997)

^a Corresponds to published data by Cernicharo et al. (2004).

within their bandwidth. Our laboratory measurements show that the weak feature that Morisama et al. observed towards L134N is not CCH⁻: the frequency of this astronomical line differs from the measured frequency by ~ 7 MHz, or 60 times the linewidth in this source. From the noise level at the CCH⁻ line position we estimate that the anion/neutral ratio is $<0.2\%$ in L134N on the assumption that $N(\text{CCH}) = 5 \times 10^{13} \text{ cm}^{-2}$ (Dickens et al. 2000). Similarly, the upper limit for this ratio in Sgr B2 (M) is $<5\%$ for $N(\text{CCH}) = 7.8 \times 10^{14} \text{ cm}^{-2}$ (Sutton et al. 1991).

We found no evidence of CCH⁻ in published spectral line surveys of standard molecular galactic sources. Limits on the column densities of CCH⁻ are summarized in Table 3. In Sgr B2 (M), a better constraint on the anion-to-neutral ratio of $<0.4\%$ is obtained from an upper limit for the 3–2 transition of <100 mK (Nummelin et al. 1998): $N(\text{CCH}^-) < 3.0 \times 10^{12} \text{ cm}^{-2}$. Lines of C₆H⁻ are quite strong in IRC+10216, so we also examined published surveys of this source (Cernicharo et al. 2000; Groesbeck et al. 1994; Cernicharo et al. 2004). The best limit for CCH⁻ is the one obtained from the 1–0 transition (Cernicharo 2006; Cernicharo et al. 2004), which yields $N(\text{CCH}^-) < 4 \times 10^{11} \text{ cm}^{-2}$. The ratio of the anion to the neutral in IRC+10216 of $<0.01\%$ (for an assumed column density of CCH of $5 \times 10^{15} \text{ cm}^{-2}$; Cernicharo et al. 2000), is more than two orders of magnitude smaller than that found for C₆H⁻. Unfortunately there is no survey data above 50 GHz in TMC–1, the other source in which C₆H⁻ has been found. In Orion A, the CCH radical is quite abundant ($N(\text{CCH}) = (3\text{--}4) \times 10^{14} \text{ cm}^{-2}$; Ziurys et al. 1982), so the spectral line surveys were examined for possible evidence of CCH⁻. The 1–0 and 3–2 transitions of CCH⁻ were covered in two separate surveys of Orion KL (Turner 1991; Schilke et al. 1997). On the assumption that CCH⁻ is present in the same extended region as CCH, we estimate that $N(\text{CCH}^-) < 4 \times 10^{11} \text{ cm}^{-2}$ and the anion/neutral ratio

is $<0.1\%$. From the published spectra in L134N, Orion KL, and Sgr B2 (M), our limit for the ratio of CCH⁻ to CCH is $<(0.1\text{--}0.4)\%$, which is about 10 times higher than that derived for IRC+10216.

In conclusion, we find anion-to-neutral ratios for CCH⁻ in all investigated sources of more than one order of magnitude lower than found for the longer chain C₆H⁻, which is about a few percent in IRC+10216 and TMC-1. This result is consistent with a simple set of assumptions about the formation of these two anions, specifically: (i) both CCH⁻ and C₆H⁻ result from the competition between electron attachment to the parent neutral molecule and subsequent photodetachment; (ii) the photodetachment rates for CCH⁻ and C₆H⁻ do not much differ, because the electron affinities for CCH (2.969 eV) and C₆H (3.809 eV) are not very different (Rienstra-Kiracofe et al. 2002); and (iii) the electron attachment rate for CCH, however, is much lower than that for C₆H, because of the much lower density of excited vibrational states. To clarify this simple picture, or to rule it out, much better astronomical observations than those now available are needed. Radio surveys of a variety of molecular sources at the frequencies given here are an obvious place to start. Deep integrations should improve the present limits by half an order of magnitude or more, or may ultimately yield the detection of CCH⁻ in space.

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