LABORATORY AND ASTRONOMICAL IDENTIFICATION OF THE NEGATIVE MOLECULAR ION C_6H^-

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ABSTRACT

The negative molecular ion C_6H^- has been detected in the radio band in the laboratory and has been identified in the molecular envelope of IRC +10216 and in the dense molecular cloud TMC-1. The spectroscopic constants derived from laboratory measurements of 17 rotational lines between 8 and 187 GHz are identical to those derived from the astronomical data, establishing unambiguously that C_6H^- is the carrier of the series of lines with rotational constant 1377 MHz first observed by K. Kawaguchi et al. in IRC +10216. The column density of C_6H^- toward both sources is 1%–5% that of neutral C_6H. These surprisingly high abundances for a negative ion imply that if other molecular anions are similarly abundant with respect to their neutral counterparts, they may be detectable both in the laboratory at high resolution and in interstellar molecular clouds.

Subject headings: ISM: molecules — line: identification — molecular data — molecular processes — radio lines: ISM

The importance of negative ions (anions) in astronomy was demonstrated nearly 70 years ago by Wildt (1939a, 1939b), who showed that H^- is the major source of optical opacity in the solar atmosphere and therefore the material that one mainly sees when looking at the Sun and similar stars. It is remarkable that in the many years since, during which nearly 130 neutral molecules and 14 positive molecular ions have been found in astronomical sources, no molecular anion has been identified. More than 1000 molecular anions have now been studied in the laboratory at low resolution by photoelectron spectroscopy (Rienstra-Kiracofe et al. 2002), but almost none have been produced at sufficiently high density to study at the high spectral resolution required for an astronomical search (Hirota 1992; Owrutsky et al. 1987), and it is only for two, OH^- (Liu & Oka 1986; Liu et al. 1987; Matsushima et al. 2006) and SH^- (Civiš et al. 1998), that rotational spectra have been obtained. The purpose of this Letter is to report the laboratory detection in the radio band of the large carbon chain anion C_6H^-, the measurement of its rotational spectrum to high accuracy, and its identification in two well-known astronomical sources: the molecular shell of the evolved carbon star IRC +10216 and the rich molecular cloud TMC-1 in the Taurus complex of dark nebulae. In IRC +10216, our identification solves the puzzle of the unidentified harmonic sequence of lines discovered over 11 years ago by Kawaguchi et al. (1995) and designated B1377 because it is apparently from a closed-shell linear molecule with a rotational constant B of 1377 MHz.

The rotational constant of the C_6H radical, one of the most abundant molecules in IRC +10216, is 1391 MHz (Pearson et al. 1988), only 1% larger than that of B1377, but this open-shell molecule with fine and hyperfine structure and lambda doubling is clearly not the carrier of B1377. Attachment of an electron to form the anion C_6H^-, however, suppresses this structure and yields the required closed-shell ground state (Fehér & Maier 1994). Aoki (2000) has shown from a theoretical quantum calculation that the rotational constant of this anion is also within 1% of that observed—as might be expected because

electron attachment is a small perturbation on the geometrical structure of the molecule, generally resulting in a slight decrease in the rotational constant.

In the laboratory, we have now observed rotational lines of C_6H^- in both the centimeter-wave and millimeter-wave bands at frequencies in precise agreement with those measured in space. Those in the millimeter-wave band were observed first in absorption with a free-space spectrometer (Gottlieb et al. 2003) used previously to detect seven carbon-chain radicals, C_2H through C_8H, under conditions similar to those that produce strong lines of C_6H: a DC discharge through a flowing mixture of argon (15%) and acetylene (85%), a total pressure of ≤10 mtorr when the cell walls were cooled to 150 K, but with a somewhat lower discharge current (~150 mA) than that which produces the most intense lines of C_6H (~400 mA). Under these conditions, lines of C_6H^- are about 20 times less intense than those of C_6H, but these were still observed with a signal-to-noise ratio of 10 or more in 1 hr of integration, allowing line frequencies to be measured to about 40 kHz or better. The C_6H^- line frequencies are unaffected by ion drift because the millimeter-wave radiation makes two passes in opposite directions through the discharge cell. The concentration of C_6H^- in our discharge (7×10^5 cm^{-3}), corresponding to a mole fraction of about 10^{-9}, is about 200 times less than that of C_6H.

Rotational lines of C_6H^- have also been observed in the centimeter band by Fourier transform microwave spectroscopy of a supersonic molecular beam, using a spectrometer (McCarthy et al. 2000) in which the cavity mirrors and first-stage amplifier are cooled to 77 K. The anion was produced by a 600 V low-current (~20 mA) gas discharge synchronized with a gas pulse 330 μs long (yielding a flow of 25 cm^3 minute^{-1} at standard temperature and pressure), the gas sample consisting of either acetylene or diacetylene (0.10%) heavily diluted with Ne at a stagnation pressure of 2.5 ktorr behind the pulsed valve of the nozzle. Diacetylene produces the stronger lines, but because DCCD was readily available, that was the precursor used for C_6D^-. The optimum discharge voltage for both C_6H^- and C_6D^- is considerably lower than that which produces the strongest lines of the neutral (1000 V), and the polarity of the discharge is reversed with respect to the neutral as well, but these conditions are nearly identical to those used to measure the photoelectron spectrum of C_6H^- using a similar discharge

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TABLE 1
LABORATORY ROTATIONAL FREQUENCIES OF C_6H^-

Transition	Frequency (MHz)	$O - C$[a] (kHz)
3–2	8261.174(2)	0
4–3	11014.896(2)	0
5–4	13768.612(2)	−2
6–5	16522.329(2)	1
7–6	19276.038(2)	1
8–7	22029.740(2)	−1
53–52	145928.242(43)	30
54–53	148680.850(43)	24
56–55	154185.988(31)	59
57–56	156938.411(28)	−5
58–57	159690.889(19)	30
59–58	162443.214(39)	−42
60–59	165195.588(15)	−20
61–60	167947.947(25)	34
62–61	170700.161(20)	−9
64–63	176204.535(18)	−6
68–67	187212.655(30)	−23

NOTE.—Here and in the other tables, the 1 σ uncertainties (in parentheses) are in units of the last significant digit.

[a] Calculated from the spectroscopic constants in Table 2.

nozzle (Taylor et al. 1998). Under favorable conditions, the strongest lines of C_6H^- were observed with a signal-to-noise ratio of 20 in 20 minutes of integration, about 15% the intensity of the C_6H lines observed under the same conditions. On the basis of line intensities relative to those of the stable molecule OCS at a known fractional abundance (i.e., 1% OCS in Ne), we estimate ~10^8 C_6H^- per gas pulse, a few percent that of C_6H.

A total of 17 lines of C_6H^- and five of C_6D^- have been measured to an accuracy approaching 0.1 parts per million (see Table 1); two are shown in Figure 1 to indicate the sensitivity achieved in the laboratory in a few tens of minutes of integration, along with the same lines that we have now observed in the astronomical source TMC-1 with the NRAO 100 m Green Bank Telescope (GBT) on 2006 July 16 and 21. As Table 2 shows, the spectroscopic constants derived from the laboratory and astronomical data—seven lines in IRC +10216 and two in TMC-1—are identical, and there is no question that the laboratory and astronomical molecules are the same.

The evidence that this new molecule is the hexatriyne anion C_6H^- is extremely strong. A linear chain of six carbon atoms terminated by a single H (Fig. 1), neutral or ionized, is the only molecule that is consistent with the elemental composition of the hydrocarbon precursors that yield B1377, the rotational constant, and the isotopic shift observed on deuteration. The
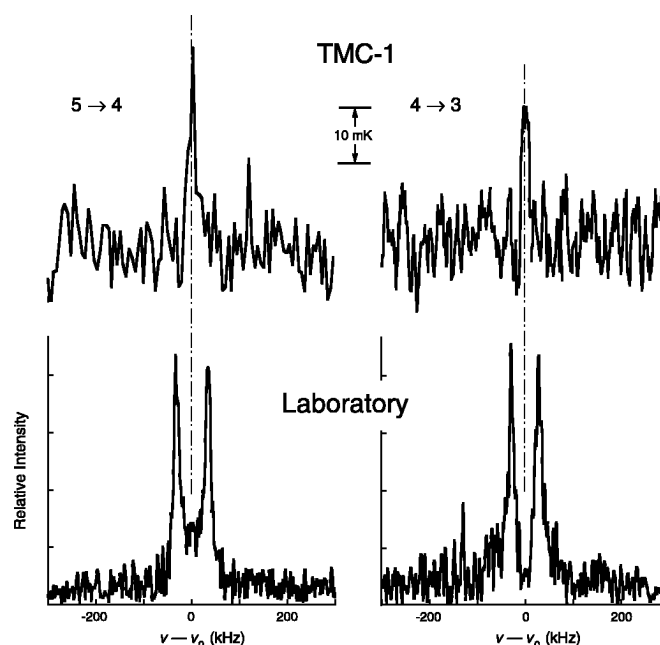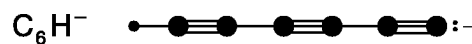

FIG. 1.—Two rotational transitions of C_6H^- in the laboratory and in TMC-1. Frequencies are relative to the laboratory rest frequencies (Table 1), assuming the standard mean radial velocity of 5.80 km s^{-1} for TMC-1. The geometrical structure of C_6H^-, the hexatriyne anion, obtained by removing H$^+$ from triacetylene, is shown on top. According to the theoretical calculation of Aoki (2000), the bonds are accurately represented as triple and single bonds as drawn; the two dots on the terminal carbon denote the approximate location of the paired electrons. The double-peaked laboratory line shape, obtained in 20 minutes of integration, is instrumental in origin, the result of the Doppler shift of the fast-moving supersonic molecular beam relative to the two traveling waves that compose the confocal mode of the Fabry-Pérot cavity; the rest frequency of the transition is the average of these two components. The TMC-1 spectra were obtained by position-switching for 12 hr. Owing to the extremely low line density in TMC-1, the probability that either line is due to a chance coincidence is ≤10^{-2}; the joint probability is <10^{-4}, indicating that a misidentification is highly improbable. The astronomical lines agree in frequency with those measured in the laboratory to 4 kHz, i.e., roughly one-half of the 6 kHz channel width used for the TMC-1 observations.

lines of B1377 disappear when the precursor gas is deuterated, ruling out a pure carbon molecule, and the rotational constant requires a chain with six and only six carbon atoms—one more or less yields a constant too low or high by more than 40%. The large deuterium shift (4.53%) is nearly identical to that found for neutral C_6H (4.55%; Linnartz et al. 1999), thus re-

TABLE 2
SPECTROSCOPIC CONSTANTS OF C_6H^- AND C_6D^- (IN UNITS OF MHz)

| CONSTANT | C_6H^- | | | C_6D^- | |
	Laboratory	Astronomical	Theoretical[a]	Laboratory	Predicted
B	1376.86298(7)	1376.86248(294)	1376.9	1314.47424(22)	1314.4[b]
$10^6 D$	32.35(1)	33.35(993)	27	36.04(223)	29.5[c]

NOTE.—The laboratory constants for C_6H^- are derived from a least-squares fit to 17 rotational transitions between 8 and 187 GHz (Table 1), for C_6D^- from five transitions between 10 and 22 GHz, and the astronomical constants from seven lines in IRC +10216 between 30 and 50 GHz (Kawaguchi et al. 1995), and two lines in TMC-1.

[a] B_e from a CCSD(T)/cc-pVTZ calculation; the vibration-rotation correction (−1 MHz) and D were calculated at the CCSD(T)/cc-pVDZ level of theory (H. Gupta & J. F. Stanton 2006, private communication).

[b] Scaled by the ratio of the theoretical rotational constants for C_6H^- and C_6D^- to that measured for C_6H^-.

[c] Scaled from D for C_6H^- by the square of the ratio of the rotational constants.

quiring a single H atom at one end of the carbon chain. From these facts alone, there are only three possible carriers for B1377: neutral C_6H or one of its two ions.

The crucial observational evidence for C_6H^- is the closed-shell $^1\Sigma$ electronic ground state of B1377, which has been established beyond any reasonable doubt from the absence of any detectable fine or hyperfine structure in the lower rotational laboratory lines at high spectral resolution (see Fig. 1) and because these lines are fairly insensitive to an applied magnetic field. Both neutral C_6H ($^2\Pi$) and C_6H^+ can be ruled out because they lack the required closed-shell symmetry. The ground state of C_6H^+ is predicted (Fehér & Maier 1994) and observed on the basis of electronic spectroscopy in neon matrices (Shnitko et al. 2006) to be $^3\Sigma$, not $^1\Sigma$. As a result, its rotational spectrum—like that of C_6H—should be far more complicated than that observed in the laboratory or in space, owing to hyperfine structure from the hydrogen nucleus and the triplet fine structure from the two unpaired electrons. The calculated rotational constant of C_6H^+ is also predicted (Fehér & Maier 1994) to be larger than that of neutral C_6H by roughly 0.5%, the opposite shift to that observed.

Circumstantial evidence that an ion is the carrier of B1377 is provided by the somewhat larger widths (~50%) of the low-J laboratory lines relative to those of H_2C_6 and other closed-shell neutral molecules, a broadening presumably caused by the larger collisional cross sections of ions via dipole-induced-dipole interactions (Buffa et al. 1994). Lines in the millimeter-wave band are also broader (~30%) than those of C_6H presumably for the same reason, but also because the line shape consists of two Doppler components owing to the axial drift velocity of the ion in the discharge plasma (Cazzoli & Puzzarini 2005). Finally, the calculation of Aoki (2000) is welcome confirmation of the assignment, one that we have checked in an independent calculation (see Table 2). Because of the large number of its lines unambiguously assigned and the extremely precise match to our laboratory data, C_6H^- can be considered one of the most securely identified astronomical molecules.

On the assumption that the dipole moment of C_6H^- is 8.2 D (Blanksby et al. 2001), the column density of C_6H^- toward IRC +10216 is found to be 4×10^{12} cm^{-2}, or 1%–5% of C_6H depending on the rotational partition function assumed for the neutral species. From the intensities of the two lines in TMC-1 (Table 3), assuming a rotational temperature of 5 K, the C_6H^- column density is 1×10^{11} cm^{-2}, about 2.5% that of C_6H in this source (4×10^{12} cm^{-2}; Bell et al. 1999). These are surprisingly high abundances for a negative ion, and therefore of considerable general interest, because if other molecular anions are similarly abundant relative to their neutral counterparts, they should be detectable both in the laboratory at high resolution and in astronomical sources. According to Lepp & Dalgarno (1988b), anions that abundant may also produce a significant source of heating in molecular clouds.

The C_6H^-/C_6H ratios derived here for TMC-1 and IRC +10216 are consistent with our understanding of ion-molecule processes and the ionization equilibrium in molecular clouds and circumstellar shells (Millar et al. 2000), but the theoretical ratio is quite uncertain, ranging from 1% to 10% (Herbst 1981). The values derived here for two rich astronomical sources may serve as a useful constraint on cloud models.

It might seem paradoxical that the first molecular anion in space is larger than nearly all the neutral molecules that have been found and larger than all the cations. But size confers stability, and the cross section for electron radiative attachment increases with size to favor the formation of large ions (Lepp

TABLE 3
LINES OF C_6H^- IN TMC-1

Transition	Frequency (MHz)	T_A (mK)	v_{LSR} (km s^{-1})	Δv (km s^{-1})
4–3	11014.896	25(3)	5.80(2)	0.38(4)
5–4	13768.612	24(3)	5.80(11)	0.44(7)

NOTE.—Line parameters are derived from a least-squares fit of a single Gaussian profile to the spectra shown in Fig. 1. $\alpha(1950.0) = 04^h38^m38^s.6$, $\delta(1950.0) = +25°35'45''.0$.

& Dalgarno 1988a, 1988b). Recent calculations (Terzieva & Herbst 2000) on small carbon chains C_n indicate that electron attachment becomes highly efficient once a critical size of about six carbon atoms is reached. Another crucial factor favoring C_6H^- is its unusual stability. This anion possesses an exceptionally high electron binding energy, i.e., the electron affinity of the corresponding neutral, 3.8 eV according to Taylor et al. (1998), which strongly favors electron attachment. As discussed by Blanksby et al. (2001), C_6H^- and other even-numbered $C_{2n}H^-$ anions have closed-shell electronic ground states, in which the lone electron pair of the anion occupies a tightly bound σ-orbital of very high s character on the terminal carbon atom—a configuration of the valence electrons that is highly stable.

There are also spectroscopic factors not previously appreciated that favor detection of linear anions similar to C_6H^-. Neutral C_6H is a $^2\Pi$ free radical, with fine and hyperfine structure and lambda doubling from the unpaired electron, all of which spreads the intensity of its rotational spectrum across many lines. Electron attachment collapses this structure and reduces the spectrum to that of a simple linear $^1\Sigma$ molecule, with lines systematically stronger by a factor of 4–8 (the exact amount depending on the temperature). Electron attachment yields a further improvement of nearly two in line intensities, because the dipole moment of the anion is calculated to be significantly larger than that of the neutral (8.2 vs. 5.6 D for C_6H; Woon 1995). Together the smaller partition function and the larger dipole moment enhance the lines of the anion relative to those of the neutral radical by as much as an order of magnitude. Such gain in spectroscopic symmetry on electron attachment is not specific to C_6H^- but instead applies to many molecules and may help detection of new anions.

The present work strongly suggests that a variety of other molecular anions may now be detectable. Those structurally similar to C_6H^- are particularly promising, starting with C_4H^- and C_8H^-, whose neutral counterparts are observed in IRC +10216 and TMC-1. (The odd-numbered chains $C_{2n+1}H^-$ such as C_5H^- are poor candidates because they are somewhat less stable [Pan et al. 2003] and because they possess triplet $^3A''$ ground states with significant rotational dilution.) These chains have very high electron binding energies and dipole moments that are calculated (Blanksby et al. 2001) to increase with chain length. C_8H^-, for example, possesses an even higher density of states, binding energy (4.0 eV; Taylor et al. 1998), and dipole moment (10.4 D; Blanksby et al. 2001) than C_6H^-, all factors that promote electron attachment. In addition, C_7H^- and longer hydrocarbon anions are known (Barckholtz et al. 2001) to be produced efficiently by the reaction $C_n^- + H \rightarrow C_nH^-$ at high density in a selected ion flow tube apparatus, so it is possible that C_8H^- may be formed in space with a higher fractional abundance relative to the neutral than has been found for C_6H^-. The isoelectronic nitrogen analogs, $C_{2n+1}N^-$, may also be good candidates for detection. The few astronomical searches for molecular anions that have been done in the radio band (Mor-

isawa et al. 2005) have unfortunately been almost entirely dedicated to those that may be too small for efficient electron attachment, and the same appears to be true in the laboratory— a likely explanation as to why the rotational spectrum of C_6H^- has now been measured when detection of smaller anions by similar techniques has failed.

In both the laboratory and in astronomical sources, the identification of C_6H^- may prove a significant turning point in the high-resolution study of molecular anions. In the laboratory, it should lead to emphasis on the rotational spectra of large anions with six or more atoms, the approximate size at which electron attachment becomes efficient, with particular attention devoted to those that possess high binding energies, large dipole moments, and $^1\Sigma$ electronic ground states. The present work suggests that some of these may be considerably easier to detect than one might suppose. Most of our C_6H^- laboratory lines were detected with a conventional free-space millimeter-wave spectrometer, an instrument whose sensitivity has not been fundamentally improved in over 15 years.

The strategy adopted in the search for molecular anions in space—to the extent that there has been one—seems to have been to start with anions for which good laboratory data existed and to attempt to find these not in the molecular clouds rich in neutral molecules and molecular cations but instead in objects such as diffuse clouds (McCall et al. 2001) where these species are not particularly conspicuous. In light of the present work, the best strategy to follow may instead be to look for large anions in the standard rich molecular sources.

Finally, the present work illustrates once again one of the main general findings of molecular astrophysics: dense clouds in space contain an astonishingly rich collection of both familiar and exotic molecules in various states of ionization and excitation, and molecules difficult to produce in the terrestrial laboratory are often conspicuous there.

A full account of the present work, including a complete list of line frequencies and a description of the many experimental details omitted here, will appear elsewhere.

Note added in manuscript.—While this Letter was being submitted, C_8H^-, the next ion in the series, was detected here— a crucial confirmation of the present identification. Details will be presented elsewhere. An astronomical search is underway.

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Note added in proof.—A third member in the series, C_4H^-, has now been detected in the laboratory at centimeter and millimeter wavelengths. A full account of this work will be presented elsewhere.