High-resolution rotational spectroscopy of the carbon chain anions C₃N⁻, C₄H⁻, and C₄D⁻

M. C. McCarthy and P. Thaddeus
Harvard-Smithsonian Center for Astrophysics, 60 Garden Street, Cambridge, Massachusetts 02138, USA and School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts 02138, USA

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The rotational spectra of C₃N⁻, C₄H⁻, and C₄D⁻ have been measured at high-spectral resolution by Fourier transform microwave spectroscopy. For both C₃N⁻ and C₄D⁻, hyperfine structure in the lowest-J transitions has been resolved and measured to better than 0.1 ppm. The quadrupole coupling constants eQq for both anions are close to those of the neutral counterparts C₃N and C₄D, and that of C₃N⁻ is in good agreement with theoretical calculations. Several properties of these anions, including their linewidths, drift velocities, and abundances, are systematically compared to similar-sized neutral molecules. The production of C₄H⁻ with different hydrocarbon precursor and buffer gases is also discussed. © 2008 American Institute of Physics. [DOI: 10.1063/1.2960626]

I. INTRODUCTION

Only about a dozen negative molecular ions have so far been studied by high resolution spectroscopy, although more than 1000 have been detected at low resolution by photoelectron spectroscopy, mainly to determine the electron affinity (i.e., the electron binding energy of the anion). The polyatomic anions studied at high resolution at visible and infrared wavelengths include H₂CCN⁻, H₂CCC⁻, NCO⁻, NCS⁻, and C₄H⁻; among others, but only three diatomic anions, OH⁻, OD⁻, and SH⁻, have been produced at sufficiently high concentration to detect their pure rotational spectra. Within the past two years, however, this number has increased fourfold with the discovery of six new anions, all carbon chains or related molecules. Four are members of the homologous series CₙH⁻ starting at CCH⁻, and the other two are the isoelectronic systems CN⁻ and C₃N⁻. On the basis of the laboratory measurements, there is already conclusive radioastronomical evidence for at least four of these anions, either in the circumstellar shell of the evolved carbon star IRC+10216, the rich molecular cloud TMC-1, or the protostellar dark nebula L1527.

Three of the new anions, C₆H⁻, C₈H⁻, and C₄H⁻, were successfully detected in a supersonic jet by Fourier transform microwave (FTM) spectroscopy, which has been used with considerable success to study radicals, carbenes, and several cations. With recent improvements in anion production, we have now succeeded in detecting the lowest-J rotational transitions of C₆H⁻, and in extending our previous work on C₄H⁻ and C₄D⁻. Because narrow linewidths are routinely achieved in our spectrometer, hyperfine structure (hfs) in both C₃N⁻ and C₄D⁻ has been resolved, and drift velocities of the ions relative to neutral molecules in the beam have been measured. Finally, the production of C₄H⁻—the most readily observed anion—has been studied with different gas mixtures. A remarkable increase in production is observed when a heavy buffer gas (Ne or Ar) is replaced by a light one (H₂ or He).

II. EXPERIMENTAL

The same FTM spectrometer used to detect C₆H⁻, C₈H⁻, and a large variety of other reactive molecules (Ref. 23 and references therein) was used for the work here. Negatively charged molecules such as radicals, carbenes, and protonated cations are created in the throat of a small supersonic nozzle by applying a low-current dc discharge to a short gas pulse from a fast mechanical valve. As we previously found, anion production is sensitive to the voltage and polarity of the discharge. The optimum voltage is considerably lower (500–700 V) than that which yields the best lines of the corresponding neutral molecule (1000 V), and the polarity is also reversed. The negative high voltage electrode is located close to the valve, the ground electrode is further downstream in the expanding gas. Because the rotational lines of anions are typically weak, the cavity mirrors and first-stage amplifier of the spectrometer were cooled to 77 K to improve the sensitivity.

When C₆H⁻ and C₈H⁻ were originally detected, we found that both anions were produced with similar abundances using either acetylene or diacetylene diluted (≤0.1%) in various buffer gases, including He, Ne, and Ar. Most experimental parameters were fairly similar. The discharge voltage was typically 600 V, the total flow rate was about 20 cm³ min⁻¹ at standard temperature and pressure, with a stagnation pressure behind the valve of 2.5 kTorr, and a 6 Hz pulse rate of the nozzle. Diacetylene in Ne produced the strongest lines of C₆H⁻ and C₈H⁻, but only by about 30%.

With this gas mixture, we unsuccessfully attempted to detect the lowest transitions of C₄H⁻ at frequencies predicted from the higher-J millimeter-wave data. Despite extremely...
then observed, with $\text{H}_2$ yielding stronger lines by a factor of much power, these lines, like those of the highly polar rare

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$\text{H}_2\text{C}_4$, 90 min for $\text{C}_3\text{N}^−$, and 2 min for $\text{C}_3\text{N}$.

velocity, represent total integration times of 90 min for $\text{C}_4\text{H}^−$, 8 min for $\text{H}_2\text{C}_4$, 90 min for $\text{C}_3\text{N}^−$, and 2 min for $\text{C}_3\text{N}$.

strong lines of $\text{C}_3\text{H}$ (observed with a signal-to-noise ratio in excess of 500 in 1 min of integration), no lines of the anion were found. Additional experiments using $\text{Ar}$ instead of $\text{Ne}$, and acetylene instead of diacetylene also failed. Finally, we replaced $\text{Ne}$ with $\text{He}$ and then $\text{H}_2$ in the diacetylene mixture even though these buffer gases yield much weaker lines of $\text{C}_3\text{H}$ by an order of magnitude. To our surprise, $\text{C}_3\text{H}^−$ was then observed, with $\text{H}_2$ yielding stronger lines by a factor of 2–3. As shown in Fig. 1, the $2 → 1$ line of $\text{C}_3\text{H}^−$ at 18.6 GHz is now observed with fairly high signal-to-noise ratio.

With better anion production, it has been possible to improve our original line measurements and to detect two higher frequency lines of $\text{C}_3\text{H}^−$. Because the dipole moment of this anion is large (calculated to be 6 $\text{D}$, Ref. 24), care is required to avoid overpolarizing rotational lines of the anion in the high band (25–42 GHz) of our spectrometer. With too much power, these lines, like those of the highly polar rare gas complex $\text{Ar}⋯\text{D}_4^+$ (9 $\text{D}$, Refs. 25–27) and $\text{Ar}⋯\text{D}_2^+$, are not observed. The $\text{C}_3\text{H}^−$ line measurements are given in Table I, and the $\text{C}_3\text{H}^−/\text{C}_3\text{H}$ abundance ratio with various hydrocarbon and buffer gases is summarized in Table II.

Starting with fully deuterated diacetylene $\text{DC}_4\text{D}$, the same four lines of $\text{C}_4\text{D}^−$ have also been measured under conditions that optimize the lines of $\text{C}_4\text{H}^−$. As with $\text{C}_3\text{H}^−$, no frequency search was required because quite precise predictions were achieved by extrapolation from the millimeter-wave data. Lines of $\text{C}_4\text{D}^−$ were typically about one-half the intensity of those of $\text{C}_4\text{H}^−$.

Attempts to detect $\text{C}_3\text{N}^−$ were initially as frustrating as those for $\text{C}_3\text{H}^−$. Despite very strong lines of $\text{C}_3\text{N}$ with either cyanogen (NCCN) or cyanoacetylene ($\text{HC}_3\text{N}$) and various buffer gases (including hydrogen), no lines of $\text{C}_3\text{N}^−$ were detected at frequencies predicted from the millimeter-wave data, assuming the theoretical quadrupole coupling constant $eQg = −3.3 \text{ MHz}$. After a number of failed attempts, a gas mixture of $\text{HC}_4\text{H}$ and $\text{HC}_3\text{N}$ in hydrogen was used, in which, in the absence of $\text{HC}_3\text{N}$, the experimental conditions were optimized to produce strong lines of $\text{C}_4\text{H}^−$; $\text{HC}_3\text{N}$ was then added in equal molar mixture to $\text{HC}_4\text{H}$, and a search for $\text{C}_3\text{N}^−$ undertaken. To our surprise, weak lines of $\text{C}_3\text{N}^−$ were detected under these conditions. If $\text{HC}_4\text{H}$ is removed from the mixture, the $\text{C}_3\text{N}$ lines increase in strength by about a factor of 3, while those of $\text{C}_3\text{N}^−$ decrease by about the same factor, and are only marginally detectable with very long integrations (~2 h). The rational for using $\text{HC}_3\text{N}$ in combination with $\text{HC}_4\text{H}$ is that $\text{C}_3\text{N}$ [4.49(25) eV, Ref. 28] possesses a higher electron affinity than $\text{C}_3\text{H}^−$ [3.53(1) eV, Ref. 29], and thus charge transfer between $\text{C}_3\text{H}^−$ and $\text{C}_3\text{N}$, which is present in high abundance in the expansion, may occur readily.

![FIG. 1. Rotational line profiles of $\text{C}_4\text{H}^−$ and $\text{C}_3\text{N}^−$ compared to those of similarly sized neutral molecules observed in the same discharge by FTM spectroscopy.](image)

| Table I. Measured rotational transitions of $\text{C}_4\text{H}^−$ and $\text{C}_4\text{D}^−$. |
|-----------------|-----------------|-----------------|
| $J' → J$        | $\text{C}_4\text{H}^−$ Frequency $^a$ (MHz) | $O−C$ (kHz)    |
| $J' → J$        | $\text{C}_4\text{D}^−$ Frequency $^a$ (MHz) | $O−C$ (kHz)    |
| 1→0             | 9309.885(2)     | −2.6           | 8648.060$^b$ | 2.5     |
| 2→1             | 18 619.758(2)   | −3.1           | 17 296.064$^b$ | 0.7     |
| 3→2             | 27 929.600(5)   | −6.4           | 25 944.066(5) | 0.4     |
| 4→3             | 37 239.402(5)   | −0.74          | 34 592.031(5) | −1.6    |
| $^a$Estimated (1σ) measurement uncertainties are indicated in parentheses. |
| $^b$Calculated frequencies are derived from the spectroscopic constants in Table III of Ref. 13 or in Table IV. |
| $^c$Centroid of hyperfine-split line from Table III. |

| Table II. Production of $\text{C}_4\text{H}^−$ using different precursor and buffer gases. |
|-----------------|-----------------|-----------------|
| Precursor/buffer gas | $\text{C}_4\text{H}^−/\text{C}_4\text{H}$ abundance Ratio (%) | Number density of $\text{C}_4\text{H}^−$ (10$^9$/pulse) |
| $\text{HC}_4\text{H}/\text{Ne}$ | <0.01 | <1 |
| $\text{HC}_4\text{H}/\text{H}_2$ | 0.3 | 30 |
| $\text{HC}_4\text{H}/\text{He}$ | 0.03 | 3 |
| $\text{HC}_4\text{H}/\text{Ne}$ | <0.004 | <0.4 |
| $\text{HC}_4\text{D}/\text{Ar}$ | <0.01 | <1 |
Owing to the high-spectrum is a synthesis of several settings of the Fabry–Pérot cavity which, 

A. Hyperfine structure

As Fig. 2 shows, deuterium hfs is well resolved in the fundamental rotational transition of C\(_4\)D\(^-\). Because this structure is small and collapses as \(1/J^2\), it is only partially resolved in the 2→1 transition at 17.3 GHz, and it is unresolved in the two higher-\(J\) transitions: 3→2 at 25.9 GHz, and 4→3 at 34.6 GHz. The data are summarized in Tables I and III.

The standard expression for rotational transitions of a closed-shell linear molecule with quadrupole hfs was fit to the measured frequencies. Only three constants are required to reproduce the four lowest rotational transitions to an rms of 3 kHz: the rotational and centrifugal distortion constants \(B\) and \(D\), and the quadrupole coupling constant \(eQq\). After a satisfactory fit was achieved with the FTM data alone, the millimeter-wave data were included in the analysis. The centimeter-wave lines were assigned uncertainties of 5 kHz and the millimeter-wave ones 20 kHz; so each FTM line was given a weight of 16 relative to each of the 11 millimeter-wave lines, these ranging from \(J' = 20\) to 43. The final spectroscopic parameters derived from the combined fit are nearly identical to those calculated from the FTM data alone, but \(D\) is much more accurately determined (to 0.02% vs 7%) and the correlation between \(eQq\) and both \(B\) and \(D\) is significantly reduced. The rms (11 kHz) is comparable to that obtained from the millimeter-wave data alone (14 kHz). Table IV lists the derived spectroscopic constants of C\(_4\)D\(^-\).

Owing to the much larger quadrupole coupling constant of nitrogen, a total of 11 hyperfine components in three rotational transitions have been measured for C\(_3\)N\(^-\): Three in both the 1→0 and 3→2 transitions, and five in the 2→1 transition (see Table III). As the spectrum in Fig. 3 shows, the fundamental rotational transition exhibits the classic nitrogen triplet with the expected 3:5:1 intensity ratio. As for C\(_4\)D\(^-\), fits were first done to reproduce only the FTM data before the previously published millimeter-wave data\(^{16}\) were folded in. The final constants are given in Table IV.

![Fig. 2. Observed (top) and calculated (bottom) spectra for the 1→0 transition of C\(_4\)D\(^-\) showing quadrupole hfs from the deuterium. The observed spectrum is a synthesis of several settings of the Fabry–Pérot cavity which, owing to the high-Q of the cavity (Q ≈ 40,000), differ in frequency by only 0.1 MHz. The integration time was quite long: 16 h for the 0.6 MHz spectrum shown here. Shown beneath the observed spectrum is a calculated stick diagram derived from the constants in Table IV. Synthetic spectra were calculated from the stick diagram with the appropriate Doppler doubling, using linewidths (20 kHz FWHM) equal to those measured.](image-url)
TABLE IV. Spectroscopic constants of C3N− and C4D− (in megahertz).

<table>
<thead>
<tr>
<th>Constant</th>
<th>This worka</th>
<th>Previous workb</th>
<th>Theorb</th>
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</thead>
<tbody>
<tr>
<td>$B$</td>
<td>4851.621</td>
<td>4851.621</td>
<td>4848</td>
</tr>
<tr>
<td>$D \times 10^6$</td>
<td>685.78(9)</td>
<td>685.92(10)</td>
<td>627</td>
</tr>
<tr>
<td>$eQq$</td>
<td>$-3.248(5)$</td>
<td>$\cdots$</td>
<td>$-3.3$</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>0.204(6)</td>
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</tbody>
</table>

1Derived from the measurements in Table I and III, those in Ref. 16, or from unpublished results. Estimated uncertainties (in parentheses) are 1σ in units of the last significant digit.
2Reference 16.
3Reference 6.
4Scaled from the normal isotopic species by the ratio of the measured rotational constant of C4H− to that calculated theoretically for C4N− and C4D−.

The $eQq$ for C3N− and C4D− are fairly close to the values measured for their neutral counterparts, and for C3N−, it agrees well with the ab initio prediction. Electron attachment to C3N decreases $eQq$ by about 25%, from $-4.32(10)$ MHz (Ref. 16) to $-3.248(5)$ MHz, but has no measurable affect on C4D. It is the same for the neutral [0.204(6) MHz; Ref. 30] and the anion [0.197(12) MHz]. The $eQq$ of C3N− is about 25% smaller than that of CN− [$eQq = -4.24(3)$ MHz, Ref. 15].

B. Drift velocities and linewidths

Because fairly strong lines of C4H− and C3N− are now observed, it is possible by comparing the lines of these anions with those of neutral molecules in the same discharge to determine drift velocities and linewidths, as done here in earlier studies on protonated cations.31 As before, line parameters were determined from fits of Lorentzian profiles to several spectra—typically from three to five; quoted uncertainties are 1σ standard deviation. As the bottom Fig. 1 illustrates for the 2→1 transition of C3N− H2C4, a velocity of 2327(10) m s$^{-1}$ is derived for C3H− from the Doppler splittings, while a slightly slower velocity, 2261(10) m s$^{-1}$, is found for H2C4 under the same conditions. The difference between the two, 66 ± 20 m s$^{-1}$, indicates that the anions are moving about 3% faster than the neutrals—the same velocity difference found for the protonated cation HOCS+ relative to OCS. C3N− and C4N (Fig. 1, top) exhibit a similar difference, the anion having a 3% higher drift velocity than the neutral.

Anions and cations possess an additional source of line broadening over neutral molecules. The linewidth of C3H− [740 ± 80 m s$^{-1}$ full width at half maximum (FWHM)] is more than twice that of H2C4 (270 ± 50 m s$^{-1}$), and the difference between the C3N− and C3N linewidths is also significant [500(75) vs 340(40) m s$^{-1}$]. The linewidth (~300 m s$^{-1}$ or about 5 kHz FWHM) of neutrals mainly results from the somewhat divergent molecular beam and the consequent spread in velocity along the axis of the Fabry–Pérot cavity of the spectrometer.

C. Anion production

As Table II and Fig. 4 indicate, the production here of anions relative to their neutral counterparts increases significantly with chain length. While C3H− and C4H− are made at the level of 1%–2%, C5H− is only made at 0.3%. (A ratio three times higher than previously reported15 because H2 alone yields the strongest lines.) With Ne instead of H2, both C5H− and C6H are observed, but not C4H−, yielding an upper limit that is 100 times smaller than that derived with H2: $4 \times 10^{-5}$. For C3N−/C3N, the ratio was found to be about 1%, again with H2 as the buffer gas.

From a comparison of ionic lines with those of neutral molecules, it is possible to determine ionic number densities, first by measuring the ratio of the line intensities for the same rotational transition of the ion and the parent neutral (see Table II) in the same discharge, and then by comparing line intensities of the neutral to those of known molecules (with a calibrated sample of 1% OCS in Ne or H2). If molecular dipole moments are known, and different molecules are distributed similarly in the supersonic beam, abundances so obtained (Table II) are good to an estimated 20%.
particles in our supersonic beam, which in turn increases the Lorentz force of the magnetic field on the Mach 2 charged ions when a permanent magnet is brought near the molecular beam. These ions have diamagnetic closed-shell ground states that a critical size must be reached before REA formation is efficient.

It is worth noting for the present anions that there is a close agreement between the anion/neutral ratios derived in our discharge and in the dark cloud astronomical source TMC-1. As Fig. 4 shows, the agreement is good to a factor of 2, HC2H− and C3H−; C4H− has not yet been observed either in the laboratory under conditions which optimize C2H (or C2H+) nor has it been observed in TMC-1. The similarity between the two hints at a common production mechanism—most likely REA because of the low density and temperature in TMC-1.

Producing enough C3H− and C3N− to detect has been quite difficult, requiring much trial and error. The optimal experimental conditions are highly specific, and quite different from those which yield the corresponding radical. Despite these difficulties, lines of C2H− in particular can be readily observed. In contrast, rotational lines of the two longer carbon chains C6H− and C8H− are quite faint, but their production appears to be more robust with respect to the choice of the hydrocarbon precursor and buffer gas.

The C2H− data here should serve to guide future astronomical observations in cold molecular clouds such as TMC-1 and L1527 where radio lines of C2H− have already been found. The spectroscopic constants in Table IV allow the astronomically most interesting lines in the radio spectrum to be predicted to an uncertainty of 0.2 km s⁻¹ or

IV. DISCUSSION

The data here show that the drift velocities and linewidths of both anions and cations in our discharge are about the same, but distinct differences exist between ions and neutrals—plausibly caused by long-range ion-dipole interactions. Indirect evidence for this is provided by the disappearance of lines of HSCO⁺, C2H⁺, and several other ions when a permanent magnet is brought near the molecular beam. These ions have diamagnetic closed-shell ground states, so the disappearance of their lines is not the result of the Zeeman effect. It probably results instead from the Lorentz force of the magnetic field on the Mach 2 charged particles in our supersonic beam, which in turn increases the collisional cross section and hence linewidth of light ions. For a given charge, the Lorentz force is proportional to mass, so the acceleration of heavier ions such as C6H− and C8H− will be less pronounced, just as observed: Lines of C6H− decrease in intensity by at most 20% in the presence of the same magnetic field.

In our discharge, hydrocarbon anions are plausibly formed in two ways: (1) by radiative electron attachment (REA) to the hydrocarbon C2nH radical and (2) by dissociative electron attachment (DEA) to either polyacetylene HC2nH or its energetic cumulene carbene isomer H2C2n. Although we have little evidence to favor one formation mechanism or the other, the attachment efficiency versus chain length shown in Fig. 4 is consistent with the findings of Herbst and co-workers who conclude on theoretical grounds that a critical size must be reached before REA works effectively. For the C2nH− anions, they claim about six carbon atoms are required, in agreement to what we find; below this size formation is rapidly quenched.

Formation by DEA cannot be ruled out, however, because C4H− can be produced from HC4H at low electron energies (below 3.5 eV, Ref. 35), and the threshold for this process is more than 0.75 eV lower for HC3H (1.94 eV, Ref. 35) than for HC2H (2.74 eV), even though the C–H bond energies of acetylene [≥4.46(15) eV] and longer polyacetylenes [e.g., 4.20(11) eV for HC4H] are similar. Thus, C4H− may be inefficiently formed from HC4H via DEA in our discharge, where typical electron energies are 1–2 eV, but longer chain anions may be more readily produced by the same reaction if threshold energies decrease even more with chain length.

In our discharge, the formation of C4H− is particularly puzzling, because this anion is only detected with diacetylene in either an H2 or He buffer. More than 10% of Ne or Ar markedly quenches anion production, even as the C2H line intensity increases—perhaps according to Pachkov et al. because C4H− is formed by REA not from the ground state, but from the low-lying 2Π state, calculated and measured to lie 100–200 cm⁻¹ above ground. Pino et al. suggest that the 1Π state serves as the “doorway” state to C6H− because it possesses a large dipole moment (4.5 D), favorable for anion formation [the 2Σ ground state is only weaker polar: 0.87 D (Ref. 40)]. Light buffer gases such as H2 and He, which raise the temperature of the Trot ~ 2 K molecular beam and thus populate the 1Π state, enhance anion production, as observed. The addition of heavier buffer gases (Ne and Ar), even in small amounts, lowers the temperature and depopulates the low-lying 2Π state, quenching C4H− production.

One test of this hypothesis is to study C4H− production in pure ortho and para H2 to determine if the energy difference between the two spin symmetries is important in populating the 2Π state. Both C6H and C8H possess 2Π ground states with large dipole moments, which together with the size of these molecules, may explain why anion formation is efficient.

It is worth noting for the present anions that there is close agreement between the anion/neutral ratios derived in our discharge and in the dark cloud astronomical source TMC-1. As Fig. 4 shows, the agreement is good to a factor of 2 for C6H− and C8H−; C4H− has not yet been observed either in the laboratory under conditions which optimize C2H (or C2H+) nor has it been observed in TMC-1. The similarity between the two hints at a common production mechanism—most likely REA because of the low density and temperature in TMC-1.
better, adequate for observations in the sharpest line molecular sources. TMC-1 appears to the more promising of the two because lines of C$_3$H radical are conspicuous there.

With modest improvements in either detection sensitivity or anion production, it should be possible to detect the carbon-13 isotopic species of C$_3$H$^-$ in the laboratory, and derive a precise geometrical structure for this molecule. With an additional factor of 3 or so, the carbon-13 lines should be observable in natural abundance, but if an isotopically enriched sample of statistical carbon-13 diacetylene is used instead, these lines could be detected with present instrumentaton. Determination of the individual C–C bond lengths would be useful to test theoretical calculations, but would also contribute to the comparative study of similar-sized chains such as C$_4$H and H$_2$C$_4$ whose experimental structures$^{40,47,48}$ are already known.

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