

The rotational spectrum of CN^-

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The rotational spectrum of the molecular negative ion CN^- has been detected in the laboratory at high resolution. The four lowest transitions were observed in a low pressure glow discharge through C_2N_2 and N_2 . Conclusive evidence for the identification was provided by well-resolved nitrogen quadrupole hyperfine structure in the lowest rotational transition, and a measurable Doppler shift owing to ion drift in the positive column of the discharge. Three spectroscopic constants (B , D , and eQq) reproduce the observed spectrum to within one part in 10^7 or better, allowing the entire rotational spectrum to be calculated well into the far IR to within 1 km s^{-1} in equivalent radial velocity. CN^- is an excellent candidate for astronomical detection, because the CN radical is observed in many galactic molecular sources, the electron binding energy of CN^- is large, and calculations indicate CN^- should be detectable in IRC+10216—the carbon star where C_6H^- has recently been observed. The fairly high concentration of CN^- in the discharge implies that other molecular anions containing the nitrile group may be within reach. © 2007 American Institute of Physics. [DOI: 10.1063/1.2737442]

Negative molecular ions (anions) are important in many areas of chemistry, and material and environmental science.¹ CN^- is a unique molecular anion because neutral CN has one of the highest known electron affinities [3.86 eV (Ref. 2)], is observed under a wide range of terrestrial conditions, and because this closed-shell molecule is structurally and spectroscopically quite simple, making it amenable to both laboratory detection and high-level quantum chemical calculations.

Although CN^- has been studied by photoelectron spectroscopy,² no high-resolution spectra have been reported. Recently we observed the rotational spectrum of the carbon chain anion C_6H^- in the laboratory and in two astronomical sources,³ and subsequently the spectra of C_2H^- , C_4H^- , and C_8H^- .^{4,5} Here we report the laboratory rotational spectrum of CN^- . The spectroscopic data are now in hand to conduct a sensitive radio search for CN^- in the interstellar gas and other astronomical sources.

The transitions of CN^- were observed with the same free space millimeter-wave spectrometer in which the carbon chain anions were recently detected.^{3–5} The four lowest transitions were observed in a low pressure dc discharge (25 mA) through a flowing mixture of cyanogen (C_2N_2 , 75%), and argon or nitrogen (25%) at a pressure of about 10 mTorr. To increase the sensitivity, the discharge cell was cooled to 200 K. Cyanogen was used as the starting organic vapor fed into the discharge, because studies have shown that CN^- is formed by dissociative electron attachment to cyanogen with a much higher yield than for other organic molecules containing the nitrile group.⁶

The search for CN^- was guided by recent high-level molecular structure calculations.^{7–9} Because of the closed-shell $^1\Sigma$ electronic ground state, rotational transitions are very closely harmonic in frequency—i.e., simple multiples of the fundamental ($J=1-0$) transition at 112 GHz. To find these

transitions, a frequency range of roughly $\pm 500 \text{ MHz}$ (or $\pm 0.1\%$ about the theoretical predictions) was covered for the successive transitions at 224 GHz ($J=2-1$) and 336 GHz ($3-2$). A discharge current of 100 mA was maintained during the search, as that yielded the most intense lines of acetylenic C_{2n}H^- anions in previous experiments with the same spectrometer. Many background lines were encountered during this search; for example, the CN^- line at 224 GHz is very close in frequency to an intense line of CN in the first excited ($v=1$) vibrational state,¹⁰ but harmonic lines of CN^- were readily picked out, because theoretical estimates of the centrifugal distortion constant (D) allow prediction of successive transitions to less than a linewidth. Following the identification of the lines at 224 and 336 GHz, lines at higher and lower frequencies were then detected. Nitrogen quadrupole hyperfine structure (hfs) was well resolved in the lowest transition at 112 GHz (Fig. 1), and partially resolved in the next lowest transition at 224 GHz.

The highest concentration of CN^- was observed at a somewhat lower discharge current (25 mA) than that which best produces CN (100 mA). At that current, the line near 336 GHz was about 300 times weaker than that of CN, summed over all hyperfine components. There is no net enhancement of CN^- line intensities relative to those of CN owing to the partition function and the dipole moment (see Ref. 4), yet lines of CN^- were detected with good signal to noise in a few minutes integration (e.g., ~ 35 in 2 min at 336 GHz). The concentration of CN^- in our discharge ($2 \times 10^9 \text{ cm}^{-3}$), corresponding to a mole fraction of 5×10^{-6} [for an assumed dipole moment of $\mu=0.65 \text{ D}$ (Refs. 7 and 9)], is about 100 times less than that of CN, but is quite high for a molecular ion in the positive column of a glow discharge.

In all, seven lines of CN^- in the four lowest rotational transitions were measured (Table I). The frequencies are re-

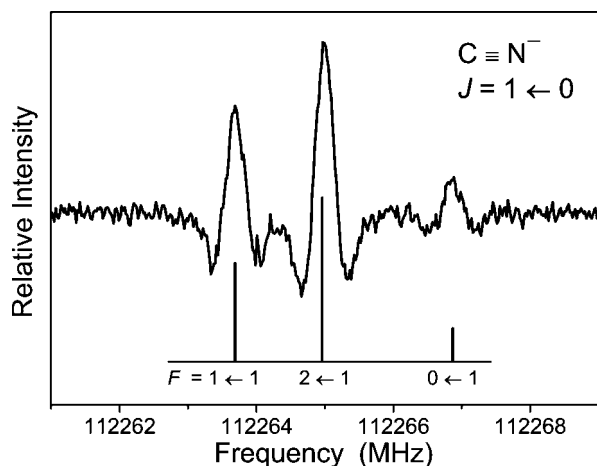


FIG. 1. The $J=1 \leftarrow 0$ line of CN^- with resolved ^{14}N quadrupole hyperfine structure. Shown beneath the observed spectrum is a stick diagram of the classic triplet hyperfine pattern predicted by the spectroscopic constants in Table II. Owing to the modulation and detection scheme employed, the instrumental line shape is approximately the second derivative of a Lorentzian. The integration time was 74 min.

produced to a rms of only 13 kHz (or about 1% of the pressure broadened linewidth) with three spectroscopic constants: the rotational constant B , the centrifugal distortion constant D , and the quadrupole coupling constant eQq (Table II). With these three constants and the sixth-order centrifugal distortion constant H calculated theoretically [$H=0.241$ Hz (Ref. 7)], the entire rotational spectrum can now be predicted to two parts in 10^6 at 2 THz, allowing for deep searches well into the far IR in essentially all astronomical sources.

The evidence that the assigned lines are from CN^- is overwhelming. The close harmonicity and the absence of fine structure confirm that the carrier has a closed-shell $^1\Sigma$ ground state. The large rotational constant indicates that the carrier is almost certainly a light diatomic molecule. Hfs in the $1-0$ transition with relative intensities in the theoretical ratio of 5:3:1 (Fig. 1) and the quadrupole coupling constant (eQq) within 10% of that of HCN [-4.71 MHz (Ref. 11)] demonstrates that the molecule contains a nitrogen atom. The carrier must also contain a carbon atom because C is the only other element in our $\text{C}_2\text{N}_2/\text{N}_2$ discharge, and B differs by only 1% from that of CN. Any additional constituent other than C would result in a rotational constant that is too small. These considerations force the conclusion that we are observing either CN^- or CN^+ .

The spectroscopic constants provide decisive evidence against the positive ion. The rotational constant is within 0.1% of the most recent quantum theoretical estimates for

TABLE I. Laboratory frequencies of CN^- .

Transition		Frequency ^a (MHz)	$O-C^b$ (kHz)
$J'-J$	$F'-F$		
1-0	1-1	112 263.694	-4
	2-1	264.997	28
	0-1	266.865	-11
2-1	2-2	224 523.894	-12
	1-0	523.894	-12
	2-1	525.123	8
	3-2	525.123	8
	1-1	[527.175] ^c	...
3-2	2-1	336 776.410	-4
	3-2	776.410	-4
	4-3	776.410	-4
4-3	3-2	449 014.351	2
	4-3	014.351	2
	5-4	014.351	2

^aEstimated 1σ uncertainties are 20 kHz. The derived frequencies are unaffected by ion drift because in normal operation the millimeter-wave radiation makes two passes in opposite directions through the discharge cell.

^bCalculated from the spectroscopic constants in Table II. Except for the fully resolved $J=1-0$ transition, calculated frequencies are weighted averages of the unresolved hyperfine components.

^cCalculated frequency; this line is blended with the $(N,J,F)=(2,3/2,1/2-1,1/2,3/2)$ component of CN in the first excited ($v=1$) vibrational state at 224 528.713 MHz (Ref. 10).

CN^- , which our measurements of four C_{2n}H^- anions suggest is the typical accuracy of high-level (coupled cluster) calculations of small closed-shell molecular anions. Similarly, the measured values of D and eQq for CN^- are in excellent agreement with those expected (see Table II). On the other hand, B deduced from the electronic spectrum of CN^+ is 0.8% too high¹² and eQq for CN^+ is about 20% too high.¹³

Determination of the charge state of the carrier provides conclusive confirmation of CN^- . Ions are accelerated in the positive column of the discharge plasma owing to the axial electric field [typically 5–15 V/cm (Ref. 14)]. When the millimeter-wave radiation makes a single pass through the discharge cell, a measurable Doppler shift is observed from the ion drift. As Fig. 2 shows, the sign of the observed shift changes when the cathode and anode potentials are reversed, as predicted for a negative ion.

We demonstrated previously that the rotational spectra of the C_{2n}H^- anions were observable in the same laboratory discharge in which the corresponding radicals had previously been detected.³⁻⁵ Now that CN^- has been detected in the

TABLE II. Spectroscopic constants of CN^- (in MHz).

Constant	Measured (this work)	Theoretical			
		Ref. 7	Ref. 8	Ref. 9	Ref. 20
B	56 132.7504(35)	56 062	56 109	56 152	...
D	0.185 79(15)	0.186	...	0.185	...
$H \times 10^6$...	0.241
eQq	-4.238(32)	-4.25	-4.250

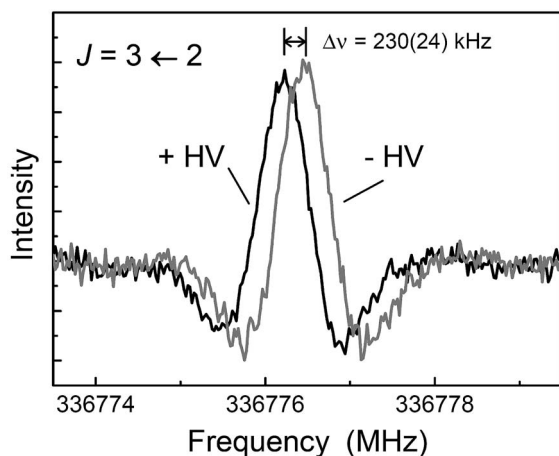


FIG. 2. The $J=3 \leftarrow 2$ line of CN^- observed in single pass absorption with either positive or negative high voltage (HV) applied to the electrode near the radiation source; the electrode near the detector was maintained at ground potential. The integration time for each spectrum was approximately 25 min. The frequency shift derived from five pairs of measurements similar to those here (115 ± 12 kHz) corresponds to an ion drift velocity of 100 ± 10 m s⁻¹.

same discharge as CN, other molecular anions containing the nitrile group such as C_3N^- , C_5N^- , H_2CCN^- , etc. may be detectable by the present technique. Many are of potential astrophysical interest, and all are probably produced under certain laboratory conditions.

The work here may aid the identification of CN^- in the IR. In addition to providing accurate rotational and centrifugal constants for the ground vibrational state, our detection establishes the discharge conditions and approximate concentration under which to observe it.

Owing to the difficulty in observing molecular anions by high-resolution spectroscopy, quantum theorists have attempted to calculate spectroscopic constants that are sufficiently accurate to aid the assignment of rotational spectra.^{7,8,15,16} Molecular structure calculations of anions are more difficult than those of neutral molecules and cations,¹⁵ yet rotational constants obtained from coupled cluster calculations are in surprisingly good agreement with experiment. Theoretical rotational constants of CN^- in the ground vibrational state⁷⁻⁹ agree to better than 0.1% with our measured value here (Table II), and a nearly comparable level of accuracy in the calculations is achieved for the C_{2n}H^- anions.³⁻⁵ This agreement between theory⁷⁻⁹ and experiment for CN^- is gratifying, but a more critical assessment will require additional measurements of new molecular ions such as C_3N^- , etc. Specifically, it remains to be established whether the same theoretical methods applied to OH^- and CN^- (Refs. 7-9 and 15) predict accurate spectroscopic constants for larger molecular anions and nonlinear ones.

The production of CN^- in our discharge is not fully understood. Two possible routes are (i) dissociative attachment to C_2N_2 to produce CN^- and CN (Ref. 6) or (ii) radiative electron attachment to CN which is produced at a fairly high concentration in the discharge. Because it is a one-step process from the abundant precursor, dissociative attachment might account for the fairly high observed concentration of CN^- . Mass spectrometric measurements have shown that the

cross section for dissociative attachment is a maximum at about 3 eV (Ref. 6)—i.e., comparable to the electron energies in our low pressure glow discharge.¹⁷ These measurements also show that the yield of CN^- by dissociative attachment to other molecules containing the nitrile group (e.g., CH_3CN and $\text{C}_6\text{H}_5\text{CN}$) is several orders of magnitude lower.^{6,18} Comparison of the abundances of CN^- in discharges through CH_3CN , $\text{C}_6\text{H}_5\text{CN}$, etc. might help establish whether this is the dominant process for the formation of CN^- here. The CN radical is also observed in discharges through precursor gases that do not contain the nitrile group (e.g., CO and N_2 , or CH_4 and N_2). Detection of CN^- in these discharges, with concentrations proportional to that of CN, might indicate whether CN^- is formed by direct radiative electron attachment rather than by dissociative attachment to stable precursors. Now that CN^- has been detected, the work here suggests a way to find yet other molecular anions. For example, laboratory experiments show that C_3N^- is formed by dissociative attachment to HC_3N ,¹⁹ so by analogy with formation of CN^- from C_2N_2 , the rotational spectrum of C_3N^- may be detectable in a discharge through HC_3N .

The CN^+ cation may also be detectable in our C_2N_2 discharge. The rotational spectrum of CN^+ has not been observed directly in the $^1\Sigma$ ground state, but B was derived from the electronic spectrum.¹² The high abundance of CN^- in our discharge and the larger polarity of CN^+ [1.2 D (Ref. 20) versus 0.65 D] imply that CN^+ is a good candidate for detection by the present technique. If CN^+ is detected, it would be one of the few cases in which a molecular radical, anion, and cation are observed in the same source by high-resolution spectroscopy. CN^+ , however, is probably a poor candidate for detection in the interstellar gas, because it reacts with the dominant H_2 in a very fast bimolecular reaction.²¹

The CN^- anion has long been suggested as an interstellar molecule,²²⁻²⁴ because CN is very abundant in galactic sources^{25,26} and its electron affinity is high. If CN^- is detected in the interstellar gas, it might be feasible to derive the electron concentration (fractional ionization) from its measured abundance provided the formation and destruction processes are understood.²⁴ The rotational spectrum of CN^- is very sparse, with transitions in the radio band only every 112 GHz, so not many lines are accessible to existing radio telescopes. Petrie predicts on the basis of chemical model calculations²⁴ that CN^- may be detectable in the circumstellar envelope of the late-type carbon rich star IRC+10216, and there is already tentative evidence for the 2-1 line of CN^- in this source.²⁷ Now that precise line frequencies are in hand, sensitive searches for CN^- in a variety of astronomical sources are appropriate.

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