

THE ROTATIONAL SPECTRUM OF THE NCO^- ANION

V. LATTANZI^{1,2}, C. A. GOTTLIEB^{1,2}, P. THADDEUS^{1,2}, S. THORWIRTH^{3,4}, AND M. C. MCCARTHY^{1,2}

¹ Harvard-Smithsonian Center for Astrophysics, 60 Garden St., Cambridge, MA 02138, USA

² School of Engineering & Applied Sciences, Harvard University, 29 Oxford St., Cambridge, MA 02138, USA;
vlattanzi@cfa.harvard.edu, cgottlieb@cfa.harvard.edu, pthaddeus@cfa.harvard.edu, mccarthy@cfa.harvard.edu

³ I. Physikalisches Institut, Universität zu Köln, Zùlpicher Str. 77, 50937 Köln, Germany; sthorwirth@ph1.uni-koeln.de

⁴ Max-Planck-Institut für Radioastronomie, Auf dem Hügel 69, 53121 Bonn, Germany

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ABSTRACT

The rotational spectrum of the negative molecular ion NCO^- has been observed both in a supersonic molecular beam and in a low-pressure glow discharge. The identification is ironclad because of the previous infrared detection of NCO^- , the presence of well-resolved nitrogen quadrupole hyperfine structure, and the observation of nine harmonically related transitions in the millimeter band. The spectroscopic constants B and D are three orders of magnitude more accurate than those derived from the earlier IR measurements, and the theoretical eQq is in good agreement with that measured. The entire rotational spectrum can now be calculated well into the THz region to 1 km s^{-1} in equivalent radial velocity or better. NCO^- is an excellent candidate for radio astronomical detection because of its high stability, polarity, and favorable partition function. The fairly high concentration of NCO^- in our laboratory source implies that other molecular anions containing the NCO group may be detectable in the radio band.

Key words: ISM: individual objects (Sgr B2) – ISM: molecules – line: identification – molecular data – molecular processes – radio lines: ISM

Online-only material: color figure

1. INTRODUCTION

During the past three years, the rotational spectra of six carbon-chain anions have been detected in the laboratory, and with our precise laboratory rest frequencies, five of these have now been identified in cold dust clouds and the circumstellar shell of an evolved carbon star (Thaddeus et al. 2008 and references therein; Agúndez et al. 2010). There is also evidence for yet a sixth anion, C_5N^- , in IRC+10216, although the rotational spectrum of this species has not yet been detected in the laboratory (Cernicharo et al. 2008). It now seems clear that other molecular anions should be detectable in the interstellar gas when good rest frequencies are available. One of the most promising candidates is the cyanate anion (NCO^-), a well-known functional group in organic chemistry, that is plausibly tied to the abundant interstellar molecule HNCO with the same heavy-atom backbone.

Isocyanic acid (HNCO) and its isomers have a long and intricate history in organic chemistry. The salts of fulminic acid (HCNO) have been important since the 17th century in the preparation of explosives (Teles et al. 1989). Almost two centuries later, work on the silver salts of fulminic acid and isocyanic acid led to the recognition of isomerization—one of the major advances in chemistry—when chemists realized that in spite of different chemical and physical properties, two different substances could have the same elemental formula (Liebig & Gay-Lussac 1824). Isocyanic acid was one of the earliest polyatomic molecules observed in the interstellar gas (Snyder & Buhl 1972) and has now been found in over 60 galactic sources and nine external galaxies (Martín et al. 2009 and references therein). Recently, strong lines of two of its metastable isomers, cyanic acid (HOCN) and fulminic acid, have been detected in some of the sources in which HNCO is found (Brünken et al. 2009a; Marcelino et al. 2009).

The cyanate ion, first observed spectroscopically in alkali halide host crystals (Smith et al. 1973 and references therein),

has been the subject of extensive astronomical observations and laboratory experiments on interstellar ice analogs. It is thought that OCN^- embedded in a hydrogen-bonded ice environment⁵ is the carrier of the $4.62 \mu\text{m}$ band observed over 30 years ago toward a highly obscured infrared source in W33 A (Soifer et al. 1979) and now observed in over 40 sources, most of which are deeply embedded low-mass young stellar objects (YSOs; van Broekhuizen et al. 2005 and references therein). In hot core regions, gaseous HNCO is correlated with the $4.62 \mu\text{m}$ ice feature (Bisschop et al. 2007), but in many other sources there is considerable uncertainty in the formation of HNCO , its isomers, and its connection with OCN^- in ices (Marcelino et al. 2010).

Here, we report the high-resolution rotational spectrum of NCO^- . The present work improves the accuracy of the radio spectrum by 3 orders of magnitude over that obtained from infrared (IR) measurements (Gruebele et al. 1987), allowing a deep unambiguous search for this simple negative ion in the interstellar gas. Because of its very large electron binding energy (3.609 eV; Bradforth et al. 1993), polarity (1.5 D; Pak et al. 1997), and closed-shell $^1\Sigma$ ground state, NCO^- is an excellent candidate for radio astronomical detection. The measurements here of NCO^- should be of interest in future studies of the CHNO isomers and interstellar ices.

2. LABORATORY MEASUREMENTS AND RESULTS

The fundamental ($J = 1 \rightarrow 0$) rotational transition of NCO^- at 23 GHz was observed in a supersonic beam with our Fourier transform microwave (FTM) spectrometer (McCarthy et al. 2000). The anion was produced in a low-current discharge through HNCO and H_2 in the throat of a small nozzle. The

⁵ Astronomers studying interstellar ices designate the cyanate ion as OCN^- in accordance with the IUPAC convention and Chemical Abstracts Services (CAS: 661-20-1). In the work here, we follow the example of spectroscopists and refer to the cyanate ion as NCO^- (e.g., Smith et al. 1973; Gruebele et al. 1987; Bradforth et al. 1993; and Pak et al. 1997).

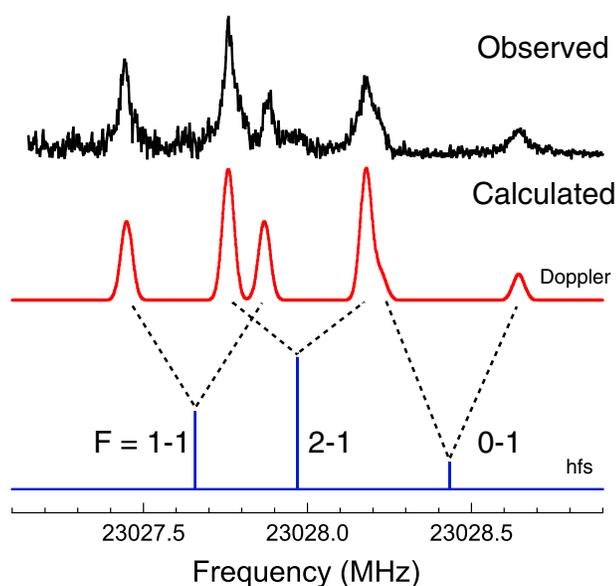


Figure 1. $J = 1 \rightarrow 0$ transition of NCO^- showing the well-resolved triplet nitrogen hfs. The observed spectrum is a composite of four consecutive scans, each 320 kHz wide. The integration time of each was 15 minutes. Shown beneath the observed spectrum is a stick diagram calculated from the constants in Table 2. The double-peaked line shape is instrumental in origin, the result of the Doppler shift of the fast-moving supersonic beam relative to the two traveling waves that compose the confocal mode of the Fabry–Perot cavity. (A color version of this figure is available in the online journal.)

source conditions that produced optimum NCO^- were similar to those used to produce other anions: a 700 V discharge (~ 20 mA) through isocyanic acid (HNCO , 0.02%) heavily diluted in hydrogen, a gas pulse of 250 μs duration (resulting in a flow rate of 35 $\text{cm}^3 \text{min}^{-1}$ at standard temperature and pressure), and a stagnation pressure of 2.5 kTorr behind the nozzle. Isocyanic acid was synthesized by dropwise addition of a saturated aqueous solution of potassium cyanate to concentrated phosphoric acid (85%) in the one-step procedure described by Ashby & Werner (1965). The sample was then diluted in hydrogen and stored at room temperature in a standard gas cylinder.

The laboratory search for the $J = 1 \rightarrow 0$ transition was based on the rotational constant (B) derived from the rotationally resolved IR spectrum (Gruebele et al. 1987). Three closely spaced lines, consistent with a fundamental transition of a closed-shell molecule with nitrogen quadrupole hyperfine structure (Figure 1), were observed about 4 MHz lower in frequency than that predicted from the IR rotational constant. The evidence that NCO^- is the carrier of the observed centimeter-wave line rests on the close (2σ) agreement of the rotational constant with that from the IR measurements, hyperfine splitting (hfs) in the theoretical 3:5:1 ratio for the fundamental transition, and a quadrupole coupling constant (eQq) within a few percent of the value calculated here quantum chemically at the CCSD(T)/aug-cc-pwCV5Z level of theory (Table 2) with the ACES2 suite of programs (Stanton et al. 2005). Additional evidence to support the assignment is the observation that the candidate line is present only in a discharge, the lines are broadened when a permanent magnet is brought near the molecular beam, and the source conditions (i.e., the polarity of the discharge and dilution of the precursor in the H_2 expansion) are consistent with those of other polyatomic anions observed by the same technique (McCarthy & Thaddeus 2008).

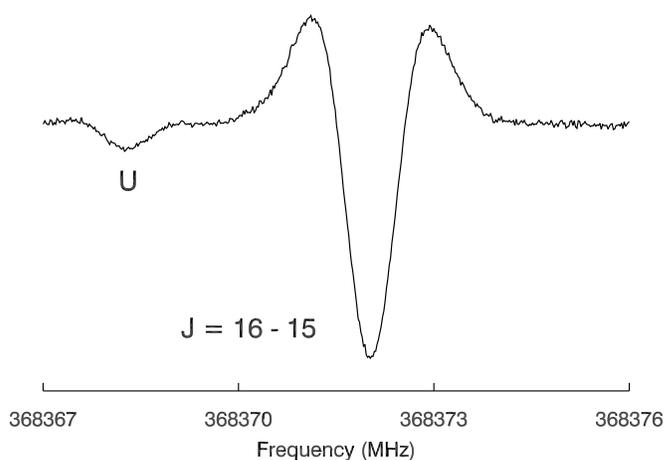


Figure 2. $J = 16 \leftarrow 15$ transition of NCO^- observed in a low-pressure glow discharge, the average of 15 sweeps in the forward and reverse directions. Owing to the modulation and detection scheme employed, the instrumental line shape is approximately the second derivative of a Lorentzian. The weak feature marked “U” is from an unassigned molecule present in the discharge. The integration time was 21 minutes.

On the basis of the rotational constant obtained from the $J = 1 \rightarrow 0$ line and the centrifugal distortion constant (D) from Gruebele et al., we then searched with our free space absorption spectrometer (Gottlieb et al. 2003) for the millimeter-wave transitions of NCO^- in a low-pressure glow discharge. At first, lines of the anion at 322, 345, and 368 GHz were observed within a few MHz of those predicted, under conditions which yield the most intense lines of HNCO and HOCN (Brünken et al. 2009a). Lines of NCO^- were most intense in a room temperature DC discharge (30 mA) through an equimolar mixture of water, cyanogen (NCCN), and argon at a total pressure of 20 mTorr (see Figure 2). Under these conditions, the mole fraction of NCO^- (5×10^{-7}) is 400 times lower than that of HNCO (2×10^{-4}) and 40 times lower than NCO (2×10^{-5}). The anion to radical concentration of 2% is comparable to that of CN^- observed under similar conditions in an earlier experiment (Gottlieb et al. 2007), but the abundance of NCO^- is about 10 times lower than that of CN^- in the respective discharges.

We are uncertain how NCO^- is formed in our millimeter-wave discharge, but if it is produced by dissociative electron attachment to HNCO , by analogy with CN^- it might be possible to produce NCO^- in a higher yield in a discharge through HNCO rather than in the gas mixture used here. Although a significant fraction of a stable molecule introduced directly in our discharge is dissociated, the mole fraction of HNCO might be 10 times higher if it behaves like other stable organic molecules such as HCCCN (Thaddeus et al. 2008).

In all, 10 rotational transitions of NCO^- were observed (Table 1). There were no missing lines, but the transition at 253 GHz was obscured by a line from another species present in our discharge. IR measurements of several bands established that NCO^- is a rigid linear molecule (Gruebele et al. 1987). With two spectroscopic constants (B and D), the calculated frequencies reproduce the measurements of 10 lines to an rms of 13 kHz or 0.5% of the width of a millimeter-wave line (Table 1). The rotational constant B is within 0.02% of that obtained previously in the IR, while the centrifugal distortion constant D is about 1% smaller (Table 2). Detection of a harmonic series of lines with D close to that derived from the IR spectrum provides evidence confirming that we have observed the rotational spectrum of NCO^- .

Table 1
Laboratory Frequencies of NCO⁻

Transition		Frequency ^a	$O - C^b$
$J' - J$	$F' - F$	(MHz)	(kHz)
1-0	1 - 1	23027.659	1
	2 - 1	23027.969	0
	0 - 1	23028.432	0
7-6		161189.304	11
8-7		184214.146	-1
9-8		207238.157	31
10-9		230261.101	-18
12-11		276303.702	-11
13-12		299323.109	14
14-13		322341.060	5
15-14		345357.465	-18
16-15		368372.276	7

Notes.

^a The estimated 1σ uncertainties: 2 kHz for the $J = 1-0$ transition, 20 kHz for the millimeter-wave lines.

^b Calculated from the spectroscopic constants in Table 2.

Among the several theoretical studies performed on this anion, two high level (coupled cluster) calculations of NCO⁻ were reported prior to this work (Botschwina et al. 1995; Pak et al. 1997). The most recent theoretical rotational constant B_0 derived by Pak et al. with vibration-rotation interactions is about 7 MHz ($\sim 0.06\%$) lower than that measured here. In the work here, B_0 (11519.6 MHz) obtained from the theoretical equilibrium structure at the CCSD(T)/aug-cc-pwCV5Z level of theory [$r_e(\text{NC}) = 1.1899 \text{ \AA}$, $r_e(\text{CO}) = 1.2268 \text{ \AA}$] and zero-point vibrational corrections from Pak et al. is only 0.05% higher than the measured B_0 (Table 2). The equilibrium dipole moment calculated at the same level is 1.53 D.

The spectroscopic constants of NCO⁻ (Table 2) allow accurate prediction of transitions well into the THz band. The sixth-order distortion constant H was not determined in the measurements here, but we estimate that its contribution at frequencies near 1.5 THz of about 1 km s^{-1} is comparable to the uncertainties of the predictions on the assumption that H is similar to that of HNCO ($0.730 \times 10^{-9} \text{ MHz}$; Niedenhoff et al. 1995).

3. DISCUSSION

Five molecular anions observed in the interstellar gas contain four or more heavy atoms. It is thought that anions are formed in the interstellar gas by radiative attachment of an electron to a neutral molecule ($A + e \rightarrow A^- + h\nu$), which is apparently an efficient process for molecules containing more than three or four heavy atoms and with electron affinities of 2–3 eV or higher (Herbst & Osamura 2008). Because it is not feasible to measure the electron attachment rates in the laboratory and they are difficult to calculate precisely, there are some significant discrepancies in the predicted abundances. Specifically, the calculated abundances of anions with six or more heavy atoms are in fairly good agreement with the measured abundances, but they are 100–1000 times too high for C_4H^- , 10 times too low for C_3N^- , and more than 10^5 times too low for CN^- (Herbst & Osamura 2008; Agúndez et al. 2010). To better understand the formation of molecular anions in the interstellar gas, observations of more small molecular anions are required.

There are at least three anions with three heavy atoms that are plausible candidates for astronomical detection: H_2CCN^- ,

Table 2
Spectroscopic Constants of NCO⁻ (in MHz)

Constant	Measured		Theoretical	
	This Work	IR ^a	This Work ^b	Previous ^c
B	11513.9683(8)	11516.3(13)	11519.6 ^d	11507
$10^3 D$	4.561(2)	4.62(33)	...	4.47
eQq	-1.0307(37)	...	-1.00	...

Notes. The numbers in parentheses are the 1σ uncertainties in units of the last digits.

^a Gruebele et al. (1987).

^b Calculated with the ACES2 suite of programs of Stanton et al. (2005; see the text).

^c Pak et al. (1997).

^d Includes zero-point vibrational corrections from Pak et al. (1997).

H_2CCC^- , and NCO^- . The most promising of these is NCO^- . Prior to the astronomical detection of the first molecular anion C_6H^- (McCarthy et al. 2006), an unsuccessful search was made for NCO^- in three galactic sources (the cold dark cloud L134, a translucent cloud CB 228, and Sgr B2; Morisawa et al. 2005), but this failure is hardly surprising because no anion has yet been observed in these sources. Of the two other anions, H_2CCN^- benefits from the collapse of the resolved spin doublets and hfs in the cyanomethyl radical in narrow line sources, but the anion has a small dipole moment (1.1 D; H. Gupta 2007, private communication) and the binding energy is small (1.543 eV; Lykke et al. 1987). H_2CCC^- has a large dipole moment (4.5 D; Blanksby et al. 2001), but it is an open shell anion with fine and hyperfine structure, and the binding energy is fairly small (1.794 eV; Yokoyama et al. 1996).

Because NCO^- shares the same heavy-atom backbone as NCO and HNCO, astronomical detection of this anion might provide useful information about the formation of this family of molecules. The NCO radical is not observed in galactic molecular sources, and apparently no dedicated searches have been done. This radical is predicted to have a large abundance in dark clouds, but so far it remains undetected, probably owing to its small dipole moment and the presence of fine and hyperfine structure in the $^2\Pi_{3/2}$ ground state that will be resolved in these narrow line sources (Marcelino et al. 2009). Nondetection of the radical does not preclude detection of the anion. For the same concentration, lines of the anion in sources with widths $< 10 \text{ km s}^{-1}$ will be up to 18 times more intense than those of the radical at frequencies of 300 GHz and lower, owing to the smaller partition function and the higher dipole moment of the anion (1.5 D versus 0.6 D).

The formation of NCO and HNCO in the interstellar gas may be closely related. It has long been proposed that NCO may be formed by $\text{CN} + \text{O}_2 \rightarrow \text{NCO} + \text{O}$ (Iglesias 1977; Prasad & Huntress 1978), an exothermic reaction with no activation barrier (Boden & Thrush 1968). If NCO is indeed produced in this way, it may be most readily observed in sources where the abundance of CN is high (Prasad & Huntress 1978). In recent gas-grain chemical model calculations representing a wide range of conditions D. Quan & E. Herbst (2010, private communication) find that the NCO and H_2NCO^+ abundances may be quite high in warm sources, particularly after the passage of time. Recently, the positive ions H_2NCO^+ and HNCOH^+ were detected in our laboratory in the same molecular beam in which NCO^- was observed (McCarthy 2010; Lattanzi et al. 2010). Observation of all three ions in the same laboratory source may

stimulate future laboratory studies and astronomical searches to clarify the astronomical formation of NCO, and HNCO and its isomers.

There is an increased interest in the analogous sulfur containing anion thiocyanate (NCS^-), owing to the recent detection of HSCN (metastable isomer of HNCS) in the laboratory and in space (Brünken et al. 2009b; Halfen et al. 2009). The rotationally resolved spectrum of the analogous sulfur containing anion thiocyanate (NCS^-) has also been studied in the IR (Polak et al. 1987). The electron affinity (Bradforth et al. 1993) and dipole moment (Pak et al. 1995) of NCS^- are similar to that of NCO^- , and the rotational constant was determined to comparable precision in the IR. By analogy with the work here on NCO^- , the rotational spectrum of NCS^- may be detectable in the same discharge sources in which HSCN was observed. Thiocyanate may also be a good candidate for astronomical detection when precise frequencies are in hand.

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