

## LABORATORY DETECTION OF HOCN AND TENTATIVE IDENTIFICATION IN Sgr B2

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Received 2008 December 15; accepted 2009 March 3; published 2009 May 5

### ABSTRACT

The rotational spectrum of cyanic acid, HOCN, has been detected in the centimeter-wave band in a molecular beam by Fourier transform microwave spectroscopy and in the millimeter-wave band by conventional spectroscopy in a low-pressure laboratory discharge. Spectroscopic constants, including the nitrogen hyperfine coupling constant, derived from 31 *a*-type transitions between 21 and 360 GHz with *J* up to 17 and  $K_a \leq 2$  allow the spectrum in the only rotational ladders populated in the interstellar gas to be calculated well into the submillimeter-wave band to 1 km s<sup>-1</sup> or better in equivalent radial velocity. Four consecutive transitions of HOCN between 83.9 and 146.8 GHz were tentatively identified in published spectral line surveys of Sgr B2(OH). An approximate column density in Sgr B2(OH) of  $6 \times 10^{12}$  cm<sup>-2</sup> implies that the HOCN/HNCO ratio is about 0.5%. Because HNCO is widely distributed in the interstellar gas, HOCN may be as well.

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

### 1. INTRODUCTION

Isocyanic acid, HNCO, was one of the first interstellar molecules (Snyder & Buhl 1972) identified in the rapid series of discoveries following the first astronomical observations of ammonia, water, and formaldehyde in the late 1960s. Because of the prior microwave spectroscopy of Kewley et al. (1963), the astronomical identification of HNCO, the most stable of four isomers with this elemental composition (Figure 1), was unchallenged, and this molecule has now been found in over sixty Galactic sources and in nine external galaxies (Martín et al. 2009, 2008; Wang et al. 2004; Zinchenko et al. 2000; Nguyen-Q-Rieu et al. 1991; Jackson et al. 1984). The next most stable isomer, cyanic acid HOCN, 25 kcal/mol (or 1.1 eV) less stable than HNCO (Schuurman et al. 2004, hereafter SMAS), is a plausible astronomical molecule that has received little attention by radio astronomers owing to the lack of laboratory data. It was once a candidate for a harmonic series of rotational lines in Sgr B2 (Thaddeus et al. 1981), but subsequent laboratory detection of this series (Bogey et al. 1984) showed that the carrier is instead the isoelectronic ion HOCO<sup>+</sup>.

HOCN is also of interest from a purely spectroscopic point of view. A comprehensive review of the isomers of isocyanic acid and the important role they and their salts have played in chemistry since the sixteenth century is given by Teles et al. (1989). In the more recent past, work on HNCO and the more energetic isomer fulminic acid, HCNO, focused on their quasi-linearity, resulting from large-amplitude bending vibrations. Both isomers have been extensively studied experimentally by high-resolution spectroscopy from the microwave through the infrared regions (see, e.g., Winnewisser 1985; Niedenhoff et al. 1995a; Albert et al. 1996; Winnewisser et al. 2006, and references therein), and theoretically by high-level quantum calculations (e.g., Koput et al. 1996; SMAS; Mladenović & Lewerenz 2008, hereafter ML) in an attempt to understand their

complex spectra and to determine their molecular structure and dynamics. Cyanic acid, however, has so far only been studied experimentally by low-resolution IR matrix spectroscopy (Jacox & Milligan 1964; Bondybey et al. 1982; Teles et al. 1989). Our laboratory measurements suggest that this isomer may also be quasi-linear.

Here we describe the laboratory gas phase detection of cyanic acid, and evidence for it in the Galactic center source Sgr B2.

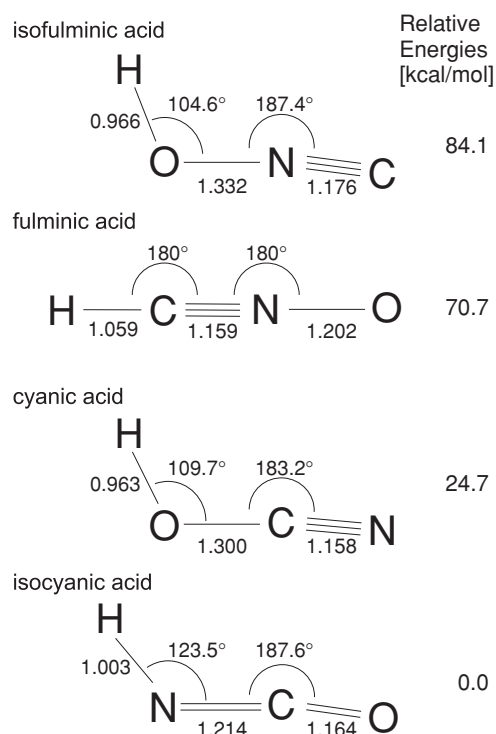
### 2. LABORATORY MEASUREMENTS AND RESULTS

Cyanic acid is a closed-shell asymmetric rotor near the prolate limit ( $\kappa = -0.9995$ ), with a nearly linear heavy-atom backbone closely parallel to the *a* inertial axis (see Figure 1), and a large rotational constant *A*. Both intrastack *a*-type ( $\Delta K_a = 0$ ) and interstack *b*-type ( $\Delta K_a = \Delta K_c = \pm 1$ ) rotational transitions are allowed, and the calculated dipole moments along the two principal axes are fairly large ( $\mu_a = 3.7$  D,  $\mu_b = 1.6$  D; ML). Our laboratory search for HOCN was guided by rotational constants obtained from high-level molecular structure calculations (ML; SMAS).

HOCN was first detected in the centimeter-wave band via its fundamental  $1_{0,1}-0_{0,0}$  transition at 21 GHz in our Fourier transform microwave (FTM) spectrometer (McCarthy et al. 2000). The discharge conditions were optimized on the corresponding transition of HNCO, which was produced in a 900 V DC discharge in the throat of the supersonic nozzle of the spectrometer through a mixture of water (0.035%), and cyanogen (NCCN, 0.03%) or methyl cyanide (CH<sub>3</sub>CN, 0.12%) heavily diluted in neon. Typical gas flow rates were 30 cm<sup>3</sup> min<sup>-1</sup> at standard temperature and pressure at a 6 Hz pulse repetition rate, with pulses 300  $\mu$ s long, and a stagnation pressure of 2.5 kTorr behind the nozzle. Under these conditions, lines of HOCN were only about four times weaker than those of HNCO, which corresponds to a relative abundance of HOCN to HNCO of 12% in the molecular beam (on the assumption that  $\mu_a$  is 1.6 D for HNCO; Hocking et al. 1975).

It is almost certain that HOCN is the carrier of the observed triplet of lines shown in Figure 2. The measured frequency

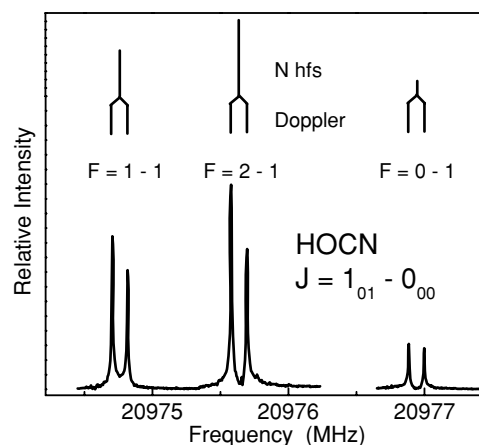
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**Figure 1.** Calculated equilibrium structures and relative energies of the CHNO isomers. Structures for HNCO, HOCN, and HCNO are from CCSD(T)/cc-pCVSZ calculations by ML; the structure of HONC (CCSD(T)/cc-pVQZ) and the relative energies are from SMAS.

is very close to that calculated from two high level *ab initio* equilibrium structure calculations, only 0.02% lower in one case (SMAS), and 0.4% higher in another (ML). In the 1% frequency band covered in our search, it is the only triplet of lines with the expected quadrupole hyperfine structure (hfs; M. Mladenović 2008, private communication), constituting a readily spotted spectral fingerprint. Additional evidence of the identification is provided by the observation of the  $1_{0,1}-0_{0,0}$  and  $2_{0,2}-1_{0,1}$  lines of the deuterated isotopic species DOCN at just the expected isotopic shift (see Table 1). For these measurements, heavy water ( $\text{D}_2\text{O}$ ) was used as a precursor gas together with cyanogen. The additional quadrupole hyperfine structure from the deuterium was resolved for both observed DOCN transitions. The measured deuterium quadrupole coupling constant is in excellent agreement with theory.

On the basis of preliminary rotational constants obtained from the FTM measurements, we then undertook a search for additional *a*-type transitions of HOCN in the millimeter-wave band at 165–360 GHz with our laboratory's free-space absorption spectrometer (Gottlieb et al. 2003). Several lines in the  $K_a = 0$  ladder were readily identified at frequencies close to those predicted. The corresponding closely spaced  $K_a = 2$  doublet transitions were successively found in wide-band scans toward lower frequencies (see Figure 3), and from these the frequencies of the widely spaced  $K_a = 1$  lines were accurately predicted and measured. The strongest lines of HOCN were observed under conditions that yielded the best production of HNCO: a room temperature DC glow discharge (100 mA) through water and cyanogen in an approximately equimolar mixture stabilized with argon at a total pressure of 30 mtorr. Under these conditions, lines of HOCN are about a factor 500 times weaker than the corresponding lines of HNCO, from which an HOCN/HNCO abundance ratio of 0.04% is derived.



**Figure 2.** Calculated (top) and observed (bottom) spectra of the  $1_{0,1}-0_{0,0}$  transition of HOCN, showing the expected nitrogen hyperfine splitting. The spectrum is a synthesis of three settings of the Fabry–Perot cavity, which was tuned to be in resonance with each hyperfine transition. The double-peaked line profile is instrumental, caused by the Doppler shift of the supersonic molecular beam relative to the two traveling waves that compose the confocal mode of the Fabry–Perot cavity. The integration time was less than one minute for each spectrum.

**Table 1**  
Laboratory Frequencies of DOCN

Transition	Frequency <sup>a</sup> (MHz)	$O-C^b$ (kHz)	
$J'_{K'_a, K'_c} - J_{K_a, K_c}$ ( $F'_1, F'_2$ )–( $F_1, F_2$ )			
$1_{0,1}-0_{0,0}$	(1,2)–(1,2)	19883.739	–0.8
	(2,2)–(1,1)	19884.605	0.5
	(2,3)–(1,2)	19884.619	3.4
	(0,1)–(1,0)	19885.918	–3.2
	(0,1)–(1,1)	19885.918	–3.2
$2_{0,2}-1_{0,1}$	(0,1)–(1,2)	19885.918	–3.2
	(2,3)–(2,3)	39767.795	–0.4
	(1,1)–(0,1)	39767.940	0.6
	(1,2)–(0,1)	39767.940	0.6
	(2,3)–(1,2)	39768.667	–4.2
	(3,4)–(2,3)	39768.735	3.8
(1,2)–(1,2)	39770.125	1.5	

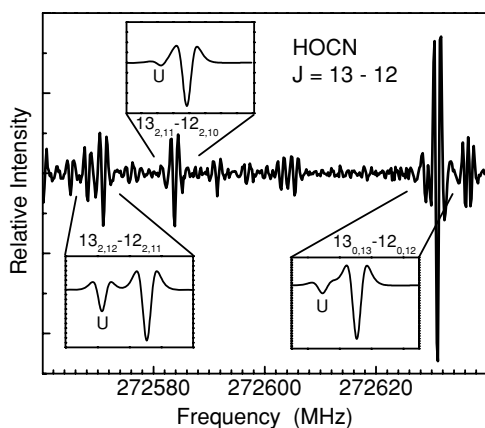
**Notes.**

<sup>a</sup> Estimated  $1\sigma$  measurement uncertainties are 2 kHz.

<sup>b</sup> Calculated from the spectroscopic constants in Table 3.

This ratio is considerably lower than that found in our supersonic jet, perhaps the result of destruction or isomerization reactions of HOCN on the cell walls.

In all, 31 *a*-type transitions of HOCN up to  $J = 17$  in the  $K_a = 0, 1$ , and 2 ladders were measured (Table 2). The data were analyzed with Pickett's program (Pickett 1991) and Watson's *S*-reduced Hamiltonian with five fourth-order and one sixth-order centrifugal distortion terms, and  $D_K$  constrained to the theoretical value. Of the sixth-order terms, only  $H_{KJ}$  was included: it significantly improved the  $\chi^2$  of the fit, and it is the only such term that could be determined to better than 30%. However, since  $H_{KJ}$  is highly correlated with the lower-order parameters, its inclusion changes these by up to three times their calculated uncertainties (with the exception of  $D_{KJ}$  which changes by  $\sim 40$  times its uncertainty). From the hfs-resolved FTM measurements, the nitrogen nuclear quadrupole coupling constant  $\chi_{aa}$  was obtained. With 11 spectroscopic constants (Table 3), the experimental frequencies were reproduced to within the measurement uncertainties. Since the *A* rotational



**Figure 3.** Portion of the  $a$ -type  $J = 13-12$  transition of HOCN observed in a discharge through water and cyanogen with a free-space millimeter-wave absorption spectrometer. Inserts show the  $K_a = 0$  transition and  $K_a = 2$  asymmetry doublet recorded with higher resolution and signal to noise on an expanded frequency scale. Integration times were approximately 5 min for each spectrum. The spectrum also shows the large density of unassigned background lines in our discharge source. The instrumental line shape, approximately the second derivative of a Lorentzian, results from the modulation scheme employed.

constant was not well determined in this analysis, we did not attempt to observe  $b$ -type transitions, although the calculated dipole moment along the  $b$  inertial axis is fairly large. Owing to the large  $A$  rotational constant, the population of successive  $K_a$  levels in our discharge decreases rapidly with increasing  $K_a$ . Because the intensity of lines in the  $K_a = 3$  and 4 ladders was comparable to those from other molecules produced in our discharge, only a limited number of transitions in these ladders could be unambiguously assigned. These higher  $K_a$  transitions are listed in Table 4 to aid future studies, but were omitted from the present analysis (see Section 4).

### 3. IDENTIFICATION OF HOCN IN SGR B2

We examined published spectral line surveys for evidence of HOCN. Of the two galactic sources most extensively surveyed, Orion KL and Sgr B2, the most promising for HOCN is Sgr B2, because the millimeter-wave lines of isocyanic acid are prominent there. The rotational spectrum of HOCN is quite sparse, with only a few transitions accessible in the 2 and 3 mm bands where most surveys have been done in Sgr B2. Transitions in the  $K_a = 0$  rotational ladder are spaced every 21 GHz, while those in the  $K_a = 1$  ladder arise from levels fairly high in energy ( $A \sim 31$  K). In Sgr B2(OH), the  $K_a = 1$  lines of HNC(O) are about 40 times weaker than those in the  $K_a = 0$  rotational ladder (Cummins et al 1986; Turner 1989), and are probably too weak to detect in HOCN if the same ratio applies.

There is tentative evidence for three consecutive  $K_a = 0$  transitions of cyanic acid in Sgr B2 (OH) in the 3 mm band, and a fourth in the 2 mm band. Cummins et al. (1986) detected two lines (carrier unassigned), at 104.9 GHz and 125.8 GHz, with the Bell Laboratories (BTL) 7 m telescope, that we have assigned to the  $5_{0,5}-4_{0,4}$  and  $6_{0,6}-5_{0,5}$  transitions of HOCN at 104874.679 and 125848.270 MHz. Cummins et al. did not detect the third accessible transition at 83.9 GHz ( $4_{0,4}-3_{0,3}$ ) because of signal to noise. In a somewhat more sensitive survey with the NRAO 11 m telescope, Turner (1989) observed the 83.9 GHz and 104.9 GHz lines with similar intensities ( $T_{MB} = 190$  mK) and fairly good signal to noise. Although Turner (1989) tentatively assigned these lines to  $\text{CH}_3\text{OD}$  and  $\text{HCOOH}$ , the present

**Table 2**  
Laboratory Frequencies of HOCN

Transition	Frequency <sup>a</sup> (MHz)	$O-C^b$ (kHz)	
$J'_{K'_a, K'_c} - J_{K_a, K_c}$	$F' - F$		
$1_{0,1} - 0_{0,0}$	1-1 2-1 0-1	20974.760(2) 20975.635(2) 20976.945(2)	0 1 0
$8_{0,8} - 7_{0,7}$		167792.314(50)	-7
$8_{1,7} - 7_{1,6}$		168497.653(30)	-6
$11_{1,11} - 10_{1,10}$		229709.510(30)	11
$11_{2,10} - 10_{2,9}$		230646.618(50)	64
$11_{2,9} - 10_{2,8}$		230654.276(50)	-1
$11_{1,10} - 10_{1,9}$		231672.512(30)	20
$11_{0,11} - 10_{0,10}$		230700.027(50)	14
$12_{1,12} - 11_{1,11}$		250587.149(30)	-3
$12_{2,11} - 11_{2,10}$		251609.435(50)	-38
$12_{2,10} - 11_{2,9}$		251619.513(50)	1
$12_{0,12} - 11_{0,11}$		251666.398(20)	5
$12_{1,11} - 11_{1,10}$		252728.406(50)	-36
$13_{1,13} - 12_{1,12}$		271463.505(20)	11
$13_{2,12} - 12_{2,11}$		272571.095(50)	-6
$13_{2,11} - 12_{2,10}$		272583.871(50)	-6
$13_{0,13} - 12_{0,12}$		272631.095(20)	-22
$15_{2,14} - 14_{2,13}$		314490.078(50)	22
$15_{2,13} - 14_{2,12}$		314509.675(30)	-32
$15_{0,15} - 14_{0,14}$		314555.031(50)	-15
$15_{1,14} - 14_{1,13}$		315887.736(20)	14
$16_{1,16} - 15_{1,15}$		334083.524(20)	-36
$16_{2,15} - 15_{2,14}$		335447.158(30)	-10
$16_{2,14} - 15_{2,13}$		335471.032(30)	5
$16_{0,16} - 15_{0,15}$		335514.014(30)	38
$16_{1,15} - 15_{1,14}$		336937.544(30)	-40
$17_{1,17} - 16_{1,16}$		354953.589(20)	23
$17_{2,16} - 16_{2,15}$		356402.569(50)	10
$17_{2,15} - 16_{2,14}$		356431.206(30)	20
$17_{0,17} - 16_{0,16}$		356470.696(20)	-4
$17_{1,16} - 16_{1,15}$		357985.652(30)	10

#### Notes.

<sup>a</sup> The  $1\sigma$  uncertainties (in parentheses) were estimated on the basis of signal to noise, line profile shape, and degree of blending with background lines.

<sup>b</sup> Calculated from the spectroscopic constants in Table 3.

laboratory measurements show that he was observing instead cyanic acid: First, the astronomical frequency at 83900 MHz is in excellent agreement with that of HOCN (83900.572 MHz), but is 2.7 MHz (or 9.1 km s<sup>-1</sup>) too low for that of  $\text{CH}_3\text{OD}$  (83903.300 ± 0.032 MHz; Anderson et al. 1988). Second, the astronomical frequency at 104874 MHz is also in very good agreement with the laboratory data for HOCN, and, as Turner (1991) notes, a rotational-temperature analysis confirms that this line cannot be  $\text{HCOOH}$  because the intensity is about a factor of 10 too high (see Figure 1 and Section 3.2.17 in Turner 1991). A fourth transition at 146.8 GHz with fairly good signal to noise is present in an unpublished 2 mm survey with the NRAO 12 m telescope that Turner made in 1993–1995 ( $T_{MB} \sim 180$  mK; see Remijan et al. 2008). Again the astronomical frequency (146821.2 MHz) is in excellent agreement with the laboratory data for the  $7_{0,7} - 6_{0,6}$  transition of HOCN at 146820.687 MHz. The next higher transition at 167.8 GHz was also covered in this survey, but owing to poor signal to noise and interfering lines, only a hint of the line was obtained.

The four lines of HOCN were assigned with great confidence, because: (1) the astronomical frequencies are in excellent agreement with the laboratory frequencies which are accurate

**Table 3**  
Spectroscopic Constants of HOCN and DOCN (in MHz)

Constant	HOCN			DOCN		
	Laboratory	Theoretical		Laboratory	Theoretical	
		SMAS <sup>a</sup>	M <sup>b</sup>		SMAS <sup>a</sup>	ML <sup>c</sup>
<i>A</i>	674308(1107)	669157	678504	[360000]	361462	363916
<i>B</i>	10577.0138(22)	10567	10592	10121.43(42)	10079	10118
<i>C</i>	10398.4918(22)	10403	10414	9763.03(43)	9806	9844
$10^3 \times D_J$	4.2504(21)	...	3.87	...	...	...
<i>D<sub>JK</sub></i>	0.6815(11)	...	0.832	...	...	...
<i>D<sub>K</sub></i>	[290]	...	290.0	...	...	...
$10^6 \times d_1$	-70.0(20)	...	...	...	...	...
$10^6 \times d_2$	-18.9(16)	...	...	...	...	...
$10^3 \times H_{KJ}$	-0.81(18)	...	...	...	...	...
$\chi_{aa}(N)$	-2.9133(37)	...	-2.87	-2.9066(24)	...	-2.87
$\chi_{bb}(N)$	[2.08]	...	2.08	[2.08]	...	2.08
$\chi_{aa}(D)$	...	...	...	-0.050(12)	...	-0.05
$\chi_{bb}(D)$	...	...	...	[0.22]	...	0.22
$\sqrt{\chi_v^2}^d$	0.69	...	...	1.3	...	...

**Notes.** Quantities in square brackets were constrained to the theoretical values.

<sup>a</sup> Equilibrium constants from a CCSD(T)/cc-pVQZ calculation.

<sup>b</sup> Ground state rotational constants from a CCSD(T)/cc-pCVTZ calculation; hyperfine coupling constants at the CCSD(T)/cc-pCV5Z level of theory (M. Mladenović 2008, private communication).

<sup>c</sup> Equilibrium constants from a CCSD(T)/cc-pCV5Z calculation.

<sup>d</sup>  $\chi_v^2$  is the reduced  $\chi^2$ , where  $\chi_v^2 = \chi^2/\nu$  and  $\nu$  is the degrees of freedom.

**Table 4**

Laboratory Frequencies of  $K_a = 3$  and 4 Transitions of HOCN

Transition $J'_{K'_a, K'_c} - J_{K_a, K_c}$	Frequency (MHz)
11 <sub>3,9</sub> -10 <sub>3,8</sub>	230571.821(150) <sup>a</sup>
11 <sub>3,8</sub> -10 <sub>3,7</sub>	230571.821(150) <sup>a</sup>
15 <sub>4,12</sub> -14 <sub>4,11</sub>	314237.781(50)
15 <sub>4,11</sub> -14 <sub>4,10</sub>	314237.781(50)
16 <sub>4,13</sub> -15 <sub>4,12</sub>	335179.315(70)
16 <sub>4,12</sub> -15 <sub>4,11</sub>	335179.315(70)
16 <sub>3,14</sub> -15 <sub>3,13</sub>	335342.020(100) <sup>a</sup>
16 <sub>3,13</sub> -15 <sub>3,12</sub>	335342.020(100) <sup>a</sup>
17 <sub>3,15</sub> -16 <sub>3,14</sub>	356291.850(100)
17 <sub>3,14</sub> -16 <sub>3,13</sub>	356291.850(100)

**Note.** Lines in this table were not included in the determination of the spectroscopic constants in Table 3.

<sup>a</sup> Blended with a strong unidentified line.

to 20 kHz (or about 1/300 of the width of the astronomical lines); and (2) the intensities of all four lines are comparable, as expected. Nevertheless, unambiguous identification of a new molecule in a crowded source like Sgr B2 requires considerable caution. In at least two recent cases, mistakes have been made in the identification there of complex organic molecules (Snyder et al. 2005; Apponi et al. 2006). Owing to the difficulty encountered in identifying a new molecule in a rich wide-line source, unusually tight rules of evidence are required to claim a certain detection: specifically, (1) close agreement of astronomical frequencies with laboratory data; (2) detection of more than a few unblended lines with good signal to noise; and (3) observation of the molecule in another source.

The column density of HOCN in Sgr B2(OH) was derived from two lines in the 3 mm survey by Turner (1989). We did not include the line at 146.8 GHz in the derivation because the temperature scale was not corrected for atmospheric opacity in Turner's observations. The column density ( $N = 6 \times 10^{12} \text{ cm}^{-2}$ )

was derived on the assumptions that the rotational temperature ( $T_{\text{rot}}$ ) is comparable to that of HNCO (20 K) and the cloud fills the telescope beam. The latter assumption appears justified, because  $T_{\text{MB}}$  for the 104.9 GHz line observed with the 7 m and 11 m antennas is comparable, and maps of HNCO indicate that the line emission is extended over an area that is several times larger than that of the NRAO telescope beam (see Section 4). The derived column density of HOCN implies that HOCN/HNCO  $\sim 0.4\%$  in Sgr B2(OH) ( $N = 1.3 \times 10^{15} \text{ cm}^{-2}$  for HNCO; Turner 1991).

#### 4. DISCUSSION

Our laboratory study of the rotational spectrum of HOCN closely parallels the initial studies of HNCO. When the rotational spectrum of HNCO was first observed, the large magnitude of the centrifugal distortion constants was an indication that it is quasi-linear (Kewley et al. 1963). Subsequent measurements of transitions from levels with high rotational quantum numbers  $J$  and  $K_a$  showed that a very large number of distortion constants are needed to reproduce the spectrum, confirming that HNCO is quasi-linear (Niedenhoff et al. 1995a). The distortion constants for HOCN (Table 3) are comparable to those for HNCO, so it appears that HOCN may also be quasi linear. The degree of quasi-linearity of a molecule can be expressed in more quantitative terms by referring to the parameter<sup>4</sup>  $\gamma_0$  first introduced by Yamada & Winniewisser (1976). In a well-behaved bent molecule,  $\gamma_0$  departs from +1 by at most a few percent. In HNCO, a prototypical quasi-linear molecule,  $\gamma_0 = +0.84$  (Yamada 1977). Although the calculated barrier to linearity of HOCN is much larger than that of HNCO (9392  $\text{cm}^{-1}$  versus 1899  $\text{cm}^{-1}$ ; ML; Niedenhoff et al. 1995b), HOCN is predicted to be quasi-linear ( $\gamma_0 = +0.93$ , calculated with  $\omega_3 = 1237 \text{ cm}^{-1}$ ;

<sup>4</sup> The quasi-linearity parameter  $\gamma_0 = 1 - 4 \cdot A/\omega_B$ , where  $\omega_B$  is the frequency of the large amplitude bending vibration, with limiting values of -1 for a rigid linear and +1 for a rigid bent molecule.

ML). Therefore, a similarly high number of centrifugal distortion constants as that for HNCO (Niedenhoff et al. 1995a) may be needed to reproduce the rotational spectrum for transitions with high  $J$  and  $K_a$ .

From the spectroscopic constants in Table 3,  $a$ -type rotational transitions of HOCN in the  $K_a = 0, 1$ , and 2 ladders (the only rotational ladders readily populated in the interstellar gas) can now be predicted with formal uncertainties of  $<0.2 \text{ km s}^{-1}$  in equivalent radial velocity up to 800 GHz. Actual uncertainties in the calculated line frequencies above about 350 GHz might be considerably higher, because they lie outside the range of the laboratory measurements and may be subject to systematic errors that are greater than the statistical ones owing to neglect of high-order centrifugal distortion terms. The effect of the missing sixth-order distortion terms on the predicted frequencies was estimated by constraining  $H_{JK}$ ,  $H_K$ , and  $H_J$  to those of HNCO; their contribution to the calculated line frequencies in the  $K_a = 0, 1$ , and 2 ladders of  $1 \text{ km s}^{-1}$  near 800 GHz confirms that the predicted frequencies are adequate for most astronomical searches in the submillimeter-wave band. Calculated frequencies of lines with  $K_a \geq 3$  are considerably more uncertain than those in the lower  $K_a$  ladders, because fewer lines were observed and higher-order terms in the Hamiltonian have not yet been determined. For example, frequencies calculated with the spectroscopic constants in Table 3 differ by 1–5 MHz from the sample measurements in the  $K_a = 3$  and 4 ladders between 230 and 356 GHz (Table 4). Further laboratory studies in the submillimeter and FIR region, including measurements of both  $a$ - and  $b$ -type transitions, would allow improved frequency predictions in the submillimeter-wave band and provide measurements needed to better characterize the bending potential.

The present work demonstrates a simple but efficient method for *in situ* synthesis of the isomers of HNCO in a supersonic molecular beam. Observation of the next higher isomer fulminic acid (HCNO), with an abundance of 3% relative to HNCO under the same discharge conditions that produce HOCN, suggested that it might be feasible with present techniques to detect the highest lying isomer, isofulminic acid (HONC), the only one which had not been characterized in the gas phase. While this manuscript was in preparation, the fundamental rotational transition of isofulminic acid at 22 GHz was observed in the laboratory by FTM spectroscopy (M. McCarthy 2009, in preparation). The experimental determination of the geometrical structures of HOCN and HONC is now well within reach, because isotopically substituted CHNO isomers can be produced readily in our discharge by introducing isotopically enriched precursors. The IR vibrational spectra of HNCO and HCNO are well studied, but it may be feasible to study the vibrational spectra of HOCN and HONC with similar production techniques. Measurement of the low-lying bending vibrations of these new isomers would provide further tests for recent theoretical calculations of the potential energy surface of the CHNO system (ML). It is worth adding that the sulphur analog of cyanic acid, thiocyanic acid (HSCN), has also been detected with our microwave and millimeter-wavelength instruments. These results will be published in a future paper (S. Brünken et al. 2009, in preparation).

In the survey of Sgr B2(OH) by Turner (1989), the compact hot cores Sgr B2(S) and Sgr B2(M) were within the fairly large ( $\sim 80''$ ) beam of the NRAO 11 m telescope; however, in maps of the HNCO emission in Sgr B2, there are no apparent peaks at these hot cores (Buhl et al. 1973; Churchwell et al. 1986; Kuan

& Snyder 1996; Minh et al. 1998; Jones et al. 2008). Although Sgr B2(S) is displaced from the (OH) position by only  $14''$ , only a few molecules containing four heavy atoms or less are observed there (Kuan & Snyder 1996; Jones et al. 2008). The molecule-rich Sgr B2(M), roughly  $30''$  north of Sgr B2(OH), lies near the  $-3 \text{ db}$  point of the NRAO 11 m antenna telescope beam, but owing to its small angular extent of  $\leq 3''$ , we estimate that Sgr B2(M) contributes very little to the observed emission. As a result, spectra in the 3 mm surveys of Sgr B2(OH) are relatively free of blended lines normally associated with hot cores.

Because HNCO is observed in many galactic sources, it should be possible to detect HOCN in sources other than Sgr B2. Recent observations suggest that cold dark clouds may be the most promising regions for future studies of HOCN. We found possible evidence for the strongest hyperfine split component of the fundamental transition at 20975.635 MHz (Table 1) in TMC-1 ( $T_A \sim 15 \text{ mK}$ ) with the 100 m Green Bank Telescope (GBT) on 2007 April 9. If this identification is confirmed, it implies a column density of HOCN of about  $7 \times 10^{10} \text{ cm}^{-2}$  for  $T_{\text{rot}} = 5 \text{ K}$  and an HOCN/HNCO ratio of  $\sim 1\%$ . Recently, Marcelino et al. (2009) observed the next higher isomer HCNO in four dark cloud cores with the IRAM 30 m telescope. The abundance of HCNO with respect to HNCO of  $>1\%$  in those sources is several times higher than that in TMC-1. Marcelino et al. were only able to obtain an upper limit for HCNO in TMC-1 of HCNO/HNCO  $< 0.3\%$ , so the dark clouds where HCNO is observed may be even better sources for HOCN than TMC-1.

Most chemical models of interstellar clouds invoke reactions on interstellar grains for adequate production of HOCN. Garrod et al. (2008) concluded that the principal source of HNCO in the gas phase is by destruction of larger molecules that are produced on grain surfaces by hydrogenation of accreted OCN (e.g., urea  $(\text{NH}_2)_2\text{CO}$ ). Although there is no mention of HOCN in the standard chemical models, it is plausible that it is formed in the same reactions in which HNCO is produced. And there are other possible reactions worth considering. For example, quantum calculations of the reaction pathways of the CHNO system in the free state indicate that HOCN is the major product in two reactions:  $\text{OH} + \text{CN}$  and  $\text{H} + \text{OCN}$  (Mebel et al. 1996). Both of these reactions are predicted to be exothermic and have very low barriers, but radiative association reactions such as these are only important on surfaces since they are normally quite slow in the gas phase (E. Herbst 2009, private communication). The recent observations of HOCN (this work) and HCNO (Marcelino et al. 2009) prompted E. Herbst and co-workers to reinvestigate the chemistry of the CHNO system. A new gas-grain model that combines surface reactions with a complex gas-phase reaction sequence involving the protonated ions  $\text{HNCOH}^+$  and the more stable isomer  $\text{H}_2\text{NCO}^+$ , reproduces the observed HOCN/HNCO ratio fairly well (D. Quan et al. 2009, in preparation). Now that HOCN has been tentatively identified in the interstellar gas, observations toward regions rich in HNCO (such as the Galactic center molecular clouds observed with the IRAM 30 m telescope; S. Brünken et al. 2009, in preparation) may help establish whether HOCN and HNCO are formed by the same process.

Our tentative astronomical detection of the energetic, reactive isomer HOCN is another demonstration of the surprising richness of the chemistry of the interstellar gas. It also suggests the need to include isomers of known interstellar molecules into astrochemical networks. Isomerism is common among complex

interstellar molecules (Hollis 2005), and it is worth investigating how this is related to the isomeric forms of the building blocks that constitute them. HNCO, for example, is thought to be further hydrogenated on grains to larger species such as formamide ( $\text{NH}_2\text{CHO}$ ) and acetamide ( $\text{CH}_3\text{CONH}_2$ ), and at elevated temperatures to more complex molecules such as glycolamide ( $\text{CH}_2(\text{OH})\text{CONH}_2$ ) and urea ( $(\text{NH}_2)_2\text{CO}$ ); Garrod et al. 2008). The relative abundance of isomeric pairs of small molecules, such as HCN and HNC, has proven to be a sensitive probe of the physical and chemical properties of astronomical sources (e.g., Schilke et al. 1992). This is plausibly true as well for the pair HOCN and HNCO.

We wish to thank E. Herbst, R. Garrod, and D. Quan for helpful discussions regarding the formation of HNCO isomers in space; B. Winnewisser and M. Winnewisser for sharing their knowledge about quasi-linear molecules; and M. Mladenović for providing the results of her quantum chemical calculations prior to publication. This work is supported by National Science Foundation grant CHE-0701204 and NASA grant NNX08AE05G. S. B. is grateful to the Harvard College Observatory for the Menzel fellowship.

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