

DETECTION OF A NEW INTERSTELLAR MOLECULE: THIOCYANIC ACID HSCN

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Received 2009 June 9; accepted 2009 July 20; published 2009 August 21

ABSTRACT

A new interstellar molecule, HSCN (thiocyanic acid), an energetic isomer of the well-known species HNCS, has been detected toward Sgr B2(N) with the Arizona Radio Observatory 12 m telescope. Eight rotational transitions in the $K_a = 0$ ladder were observed in the 2 mm and 3 mm bands. Five consecutive transitions in the 3 mm band are unblended, but three in the 2 mm band are partially masked by lines of other molecules. The peak intensity of all eight transitions are well described by a rotational temperature that is in very good agreement with that of many other molecules in this source. The line width and radial velocity of HSCN match closely with those of the ground state isomer HNCS (isothiocyanic acid), HNCO (isocyanic acid), and HOCN (cyanic acid); preliminary maps indicate that all four molecules are similarly distributed in Sgr B2. Although HSCN is calculated to lie over 3000 K higher in energy than HNCS, its column density of $1.3 \times 10^{13} \text{ cm}^{-2}$ in Sgr B2(N) is only three times lower than that of HNCS. The fractional abundances of HSCN and HNCS relative to H_2 are 4.5×10^{-12} and 1.1×10^{-11} . By analogy with the isomeric pair HCN and HNC, these two sulfur-bearing isomers are plausibly formed from a common cation precursor.

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

1. INTRODUCTION

Isothiocyanic acid (HNCS), a well-known interstellar molecule with a well-characterized rotational spectrum (e.g., Niedenhoff et al. 1997), was first identified in Sgr B2(OH) 30 years ago (Frerking et al. 1979). A dedicated astronomical search for the next most stable isomer thiocyanic acid (HSCN, calculated to lie only 6 kcal mol⁻¹ or 0.3 eV higher in energy; Wierzejewska & Moc 2003) was not feasible until recently, because it had been observed only trapped in a rare gas matrix (Wierzejewska & Mielke 2001). Recently, Brünken et al. (2009c) measured the rotational spectrum of HSCN in the centimeter wave band with a Fourier transform microwave (FTMW) spectrometer and in the millimeter wave band in a free space discharge cell, providing precise rest frequencies required for an astronomical search. With the laboratory data in hand, HSCN has now been detected in the rich molecular cloud Sgr B2 near the Galactic center with the Arizona Radio Observatory (ARO) 12 m telescope.

It has been known for many years that the chemistry in interstellar gas is far from equilibrium. Striking evidence for this is provided by hydrogen isocyanide (HNC) which is 5600 K higher in energy than HCN, yet is observed at nearly the same abundance in cold molecular clouds where the kinetic temperature is well below 100 K (see Hirota et al. 1998). Similar nonequilibrium effects may also occur in more complicated systems such as the tetratomic molecules considered here, but much less is known about these species. In this Letter, we report the identification of HSCN in Sgr B2, and compare its abundance and angular extent with that of its more stable isomer HNCS and the oxygen analogs HNCO and HOCN.

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2. OBSERVATIONS

The present astronomical observations of HSCN were done between 2002 September and 2009 March with the ARO 12 m telescope⁶ at Kitt Peak, Arizona. Eight transitions were observed in a spectral line survey of Sgr B2(N) in the 2 and 3 millimeter wave bands. Following the initial identification, individual lines were observed over limited bandwidths to confirm that we had definitely detected HSCN. The abundances of HNCS, HNCO, and HOCN were mainly derived from the lines detected in this survey, but some additional observations were done as well.

Several receivers were used for the work here: three dual-polarization SIS mixers, operated in the single-sideband mode with an image rejection of ≥ 16 dB, covering the range from 65 to 180 GHz, and a new 83–116 GHz receiver with dual-polarization ALMA Band 3 sideband-separating mixers with an image rejection of 20 dB. The spectrometers were two 512 channel filter banks with 500 and 1000 kHz resolution, and an autocorrelator (MAC) with either 390 or 781 kHz resolution over a 600 MHz band. All spectrometers were configured in parallel mode to accommodate both receiver channels. Lines present in the image sideband were identified by shifting the local oscillator by 10 MHz, and by direct observation of the image sideband.

The temperature scale T_R^* , corrected for forward spillover losses, was calibrated by the standard chopper wheel method. On the assumption the source fills the main beam, $T_R = T_R^*/\eta_c$, where T_R is the radiation temperature and η_c is the corrected beam efficiency (Kutner & Ulich 1981). All observations were done by position-switching with the OFF position 30' west in azimuth of Sgr B2(N). The pointing accuracy was 10'' or better.

⁶ The 12 m telescope is operated by the Arizona Radio Observatory (ARO), Steward Observatory, University of Arizona, with partial support from the Mt. Cuba Astronomical Foundation.

Table 1
Lines of HSCN and HNCS in Sgr B2(N)

Frequency (MHz)	Transition $J'_{Ka',Kc'} \rightarrow J_{Ka,Kc}$	E_u (K)	η_c	θ_b ($''$)	T_R^* (K)	$\Delta V_{1/2}$ (km s $^{-1}$)	V_{LSR} (km s $^{-1}$)	Comment
HSCN ^a								
68815.15	6 _{0,6} \rightarrow 5 _{0,5}	11.57	0.95	91	0.069 \pm 0.014	23.5 \pm 4.4	69.7 \pm 4.4	Good match
80283.16	7 _{0,7} \rightarrow 6 _{0,6}	15.42	0.94	78	0.073 \pm 0.006	26.1 \pm 3.7	64.8 \pm 3.7	Good match
91750.63	8 _{0,8} \rightarrow 7 _{0,7}	19.83	0.92	68	0.100 \pm 0.005	22.9 \pm 3.3	66.6 \pm 3.3	Good match
103217.47	9 _{0,9} \rightarrow 8 _{0,8}	24.78	0.90	61	0.063 \pm 0.004	26.1 \pm 2.9	66.3 \pm 2.9	Good match
114683.62	10 _{0,10} \rightarrow 9 _{0,9}	30.29	0.88	55	0.074 \pm 0.007	23.5 \pm 2.6	67.2 \pm 2.6	Good match
137613.49	12 _{0,12} \rightarrow 11 _{0,11}	42.96	0.83	46	0.050 \pm 0.004	25.0 ^c	66.0 ^c	Partially resolved
149077.07	13 _{0,13} \rightarrow 12 _{0,12}	50.12	0.80	42	\sim 0.05	25.0 ^c	66.0 ^c	No discernible peak
160539.63	14 _{0,14} \rightarrow 13 _{0,13}	57.83	0.78	39	\sim 0.05	25.0 ^c	66.0 ^c	No discernible peak
HNCS ^b								
82101.82	7 _{0,7} \rightarrow 6 _{0,6}	15.77	0.94	77	\sim 0.08	25.0 ^c	66.0 ^c	Blended with HC ₃ N
93830.05	8 _{0,8} \rightarrow 7 _{0,7}	20.28	0.92	67	0.076 \pm 0.005	25.6 \pm 3.2	68.3 \pm 3.2	Good match
105558.07	9 _{0,9} \rightarrow 8 _{0,8}	25.35	0.90	60	0.089 \pm 0.005	25.6 \pm 2.8	63.8 \pm 2.8	Good match
140740.38	12 _{0,12} \rightarrow 11 _{0,11}	43.93	0.82	45	\sim 0.09	25.0 ^c	66.0 ^c	Edge of 0.10 K line
152467.13	13 _{0,13} \rightarrow 12 _{0,12}	51.25	0.79	41	\sim 0.04	25.0 ^c	66.0 ^c	Edge of 0.13 K line
164193.53	14 _{0,14} \rightarrow 13 _{0,13}	59.14	0.77	38	...	25.0 ^c	66.0 ^c	Contaminated

Notes. Source coordinates (B1950): $\alpha = 17^{\text{h}}44^{\text{m}}09^{\text{s}}.5$, $\delta = -28^{\circ}21'20''$. Spectra were observed with the “Millimeter Auto Correlator” (MAC), and resampled at 1 MHz resolution using a standard cubic spline algorithm. The line strength (S) is approximately equal to J' for the transitions here. Line parameters were derived from a least-squares fit of a Gaussian profile to the spectrum.

^a Frequencies from Brünken et al. (2009c).

^b Frequencies from the CDMS catalog (Müller et al. 2005).

^c Assumed value.

Source coordinates, line frequencies, and telescope beamwidths and efficiencies are given in Table 1.

3. RESULTS

In Sgr B2(N), five consecutive a -type transitions of thiocyanic acid between 68.8 and 114.7 GHz spaced every 11.5 GHz were detected in the 3 mm band, and three consecutive transitions (at 137.6, 149.1, and 160.5 GHz) were detected in the 2 mm band. As shown in Figure 1, all except one in the 3 mm band ($9_{0,9} \rightarrow 8_{0,8}$ at 103.2 GHz) are quite unblended for this crowded source. Although the line at 103.2 GHz has a weak shoulder on the high frequency side, it is otherwise well-resolved and its intensity is fairly close to that of the four other lines in this band. All three lines in the 2 mm band are partially masked by lines from other molecules, but the peak intensities are consistent with those in the 3 mm band. Line parameters of the observed features are summarized in Table 1.

Six transitions of its isomer isothiocyanic acid HNCS were also observed in this source. Two in the 3 mm band, at 93.8 and 105.6 GHz, are unblended, but the third at 82.1 GHz is contaminated by emission and absorption features of HC₃N. In the 2 mm band, the line at 140.7 GHz is obscured by CH₂CN, and those at 152.5 and 164.2 GHz by lines from other molecules. The line parameters of HNCS were derived from the two unblended features in the 3 mm band (Table 1). The transition with the highest peak intensity ($9_{0,9} \rightarrow 8_{0,8}$ at 105.6 GHz) is one higher in J than that in HSCN ($8_{0,8} \rightarrow 7_{0,7}$ at 91.7 GHz). On the assumption that the population of the rotational levels are governed by collisions, the most intense line of HNCS occurs at a slightly higher transition—as expected, because the dipole moment of HNCS is only one half that of HSCN ($\mu_a = 1.7$ versus 3.5 D; Durig et al. 2006).

The evidence that HSCN and only this molecule is the carrier of the lines assigned here in Sgr B2(N) is extremely strong. Unblended lines of five successive transitions are observed in the 3 mm band at about the same intensity. There are no miss-

ing or questionable features in the eight assigned transitions. None of the lines assigned to HSCN are coincident with transitions of other known molecules or recombination lines in Sgr B2(N) with comparable intensities. The LSR velocities (66.9 ± 1.6 km s $^{-1}$) and line widths (24.5 ± 3.5 km s $^{-1}$) are in excellent agreement with those of HNCS, HNCO, and HOCN observed in the same frequency range with the ARO 12 m telescope ($V_{LSR} = 66.6 \pm 1.4$ km s $^{-1}$ and $\Delta V_{1/2} = 24.4 \pm 2.6$ km s $^{-1}$, see Figure 2; D. T. Halfen et al. 2009, in preparation). The rotational temperature (T_{rot}) is the same for HSCN (19 ± 2 K) and HNCS (18 ± 3 K; Figure 3). And finally, preliminary maps in Sgr B2 with the 12 m telescope establish that HSCN and HNCS are not localized to the hot core, but rather are extended by at least $3' \times 6'$ —i.e., both isomers are present in the same regions of Sgr B2, where their distribution is similar to that of the well-studied analogous molecule HNCO (Minh et al. 1998; Jones et al. 2008) and HOCN (D. T. Halfen et al. 2009, in preparation).

Additional strong support for the assignment is provided by the observed line profiles of HNCO, HOCN, HNCS, and HSCN. Shown in Figure 2 are the spectra in Sgr B2(N) for the $5_{0,5} \rightarrow 4_{0,4}$ transition in HNCO and HOCN which originates from rotational levels with upper state energies of 15–16 K. Also shown in this figure is the $8_{0,8} \rightarrow 7_{0,7}$ transition of HNCS and HSCN from levels about 20 K above the rotational ground state. “Hot core” molecules in Sgr B2(N), such as methyl formate, dimethyl ether, and ethyl cyanide, typically have LSR velocities of 63–65 km s $^{-1}$ and much narrower line widths of 8–14 km s $^{-1}$ (Nummelin et al. 2000).

4. DISCUSSION

4.1. Column Densities and Abundances

Column densities for both HSCN and HNCS were derived from standard rotational temperature diagrams (Figure 3), on the assumption that the source fills the telescope beam—as preliminary maps indicate. Although HSCN is predicted to

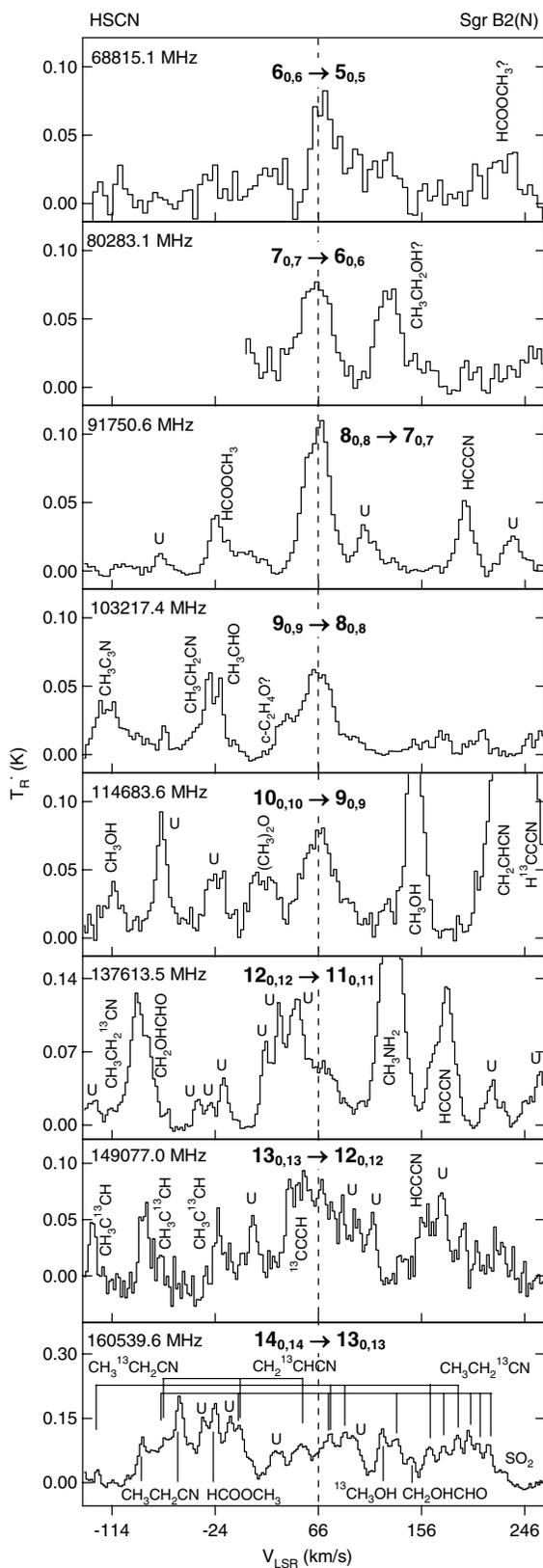


Figure 1. Eight transitions of HSCN observed toward Sgr B2(N) with the ARO 12 m telescope. The dashed line is at 66 km s^{-1} , the assumed source velocity. The spectral resolution is 1 MHz, and the approximate integration time for each spectrum is 4–16 hr.

be about 3000 K higher in energy (Wierzejewska & Moc 2003; Durig et al. 2006), the column density of this molecule ($1.3 \times 10^{13} \text{ cm}^{-2}$) is only three times less than that of its most

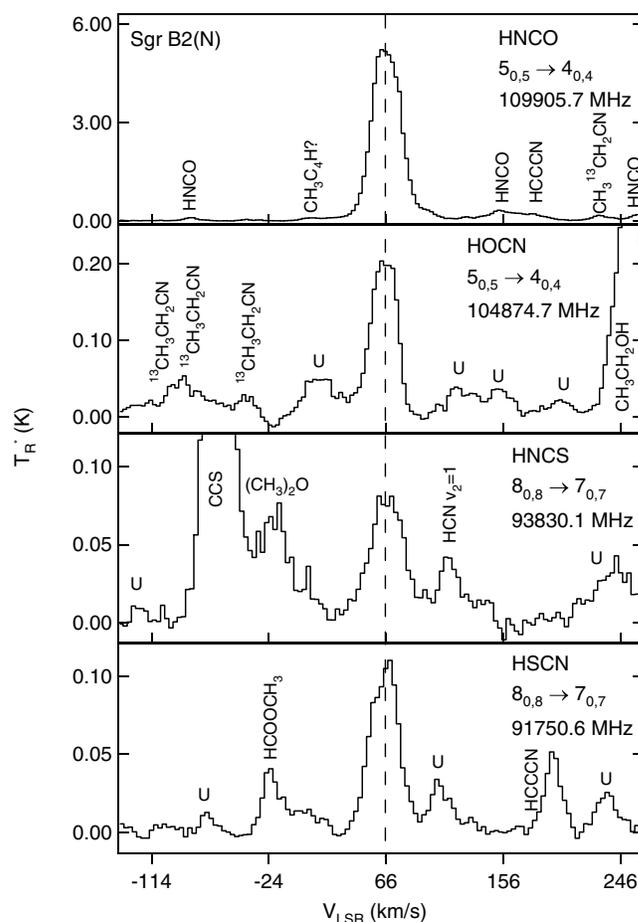


Figure 2. $8_{0,8} - 7_{0,7}$ transition of HNCS and HSCN, and $5_{0,5} - 4_{0,4}$ transition of HNCO and HOCN observed toward Sgr B2(N) with the ARO 12 m telescope. The dashed line is at 66 km s^{-1} , the assumed source velocity. All four spectra have similar line profiles, indicating that the two sets of isomeric pairs arise from the same gas.

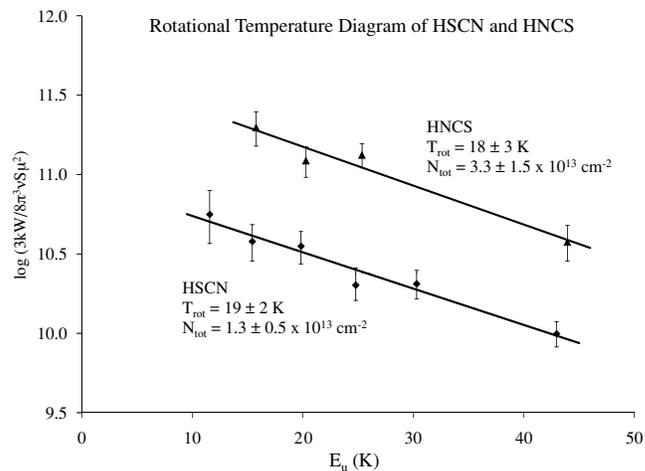


Figure 3. Rotational temperature diagrams of HSCN and HNCS in Sgr B2(N). Column densities and rotational temperatures were derived on the assumption that the source fills the telescope beam, as preliminary maps confirm. Indicated on the plots are the 3σ error bars.

stable isomer HNCS. The fractional abundances of HSCN and HNCS in Sgr B2(N) of 4.5×10^{-12} and 1.1×10^{-11} , respectively, were estimated on the assumption that the column density of H_2 is $3 \times 10^{24} \text{ cm}^{-2}$ (Nummelin et al. 2000).

Because HNC is so abundant relative to HCN, the high abundance of HSCN here is not particularly surprising. HNC and

HCN in space are formed with comparable branching ratios by dissociative electron recombination of the same cation (HCNH^+ ; Ziurys & Turner 1986; Hirota et al. 1998, and references therein). Similarly, the high observed abundance of HSCN relative to HNCS may indicate that both isomers are formed from a common ionic precursor, perhaps HNCSH^+ , which preliminary quantum calculations with a standard *ab initio* program indicate is a stable molecule. Observation of HNCSH^+ in Sgr B2 would provide an important test for this formation scheme, but unfortunately little is known about this ion. A dedicated search for HNCSH^+ in space awaits measurement of its rotational spectrum in the laboratory.

4.2. Comparison with HNCO and HOCN

The abundances of HNCO and HOCN were estimated from spectra in the ARO Sgr B2(N) survey. Fractional abundances of HNCO (5.7×10^{-10}) and HOCN (3.2×10^{-12}), relative to H_2 , imply that the HOCN/HNCO ratio (1/180) is about 60 times smaller than that of HSCN relative to HNCS (Brünken et al. 2009a; D. T. Halfen et al. 2009, in preparation). By analogy, HNCO and HOCN may also have a common precursor, e.g., the HNCOH^+ and H_2NCO^+ cations (Brünken et al. 2009b). Theoretical calculations indicate that HOCN lies about 12,300 K higher in energy than HNCO—i.e., significantly higher than HSCN relative to HNCS (Schuurman et al. 2004). If HNCOH^+ is the precursor for these two oxygen isomers, the branching ratios for the dissociative electron recombination of HNCOH^+ may be much different than that of HNCSH^+ , perhaps accounting for the lower relative abundance of the less stable isomer HOCN. Alternatively, dissociative recombination of H_2NCO^+ may preferentially form HNCO, thus masking the relative yields of HOCN and HNCO produced from HNCOH^+ .

There is evidence for sulfur enhancement in some of the molecules observed in Sgr B2(N). For example, an O/S ratio of 10 inferred from NO/NS, $\text{CH}_3\text{OH}/\text{CH}_3\text{SH}$, and $\text{H}_2\text{CO}/\text{H}_2\text{CS}$ (Nummelin et al. 2000), is three times lower than the cosmic ratio of 30 (Grevesse & Sauval 1998). Our estimate of an O/S ratio of 52 derived from the relative abundances of HNCO and HNCS suggests that this ratio is species dependent, and may reflect different molecular formation mechanisms, not the elemental O/S ratio.

Laboratory kinetic measurements, quantum calculations of the potential energy surface for the dissociative recombination of the cation precursor, and further radio astronomical observations are desirable now that HSCN is known to exist in interstellar gas with comparable abundance to that of the ground state isomer.

Detailed mapping over a wider region in Sgr B2 would allow better determination of the relative abundances of these two related species. Dedicated searches in a representative sample of galactic molecular sources might establish whether HSCN and HNCS are formed from a common precursor. Following the approach adopted in studies of HNC and HCN (see Hirota et al. 1998), the astronomical observations might also yield estimates of the branching ratios in the dissociative recombination of the precursor and activation barriers of the destruction processes, and serve as tests of chemical model predictions of these relatively simple tetratomic molecules.

Note added in manuscript. A search for HNCS and its isomers in Sgr B2 was recently undertaken with the NRAO 100 m Green Bank Telescope (GBT) by A. J. Remijan (2009, private communication). Several lines, possibly from HSCN, were detected. If confirmed, these assignments will be published elsewhere.

We thank the staff of ARO for supporting these observations, and A. J. Remijan for communicating work in progress. The work here was supported in part by the National Science Foundation (NSF) Center for Chemical Innovation (CCI) grant CHE 08-47919. D.T.H. is supported by an NSF Astronomy and Astrophysics Postdoctoral Fellowship under award AST 06-02282.

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