INTERSTELLAR CARBODIIMIDE (HNCNH): A NEW ASTRONOMICAL DETECTION FROM THE GBT PRIMOS SURVEY VIA MASER EMISSION FEATURES

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ABSTRACT

In this work, we identify carbodiimide (HNCNH), which is an isomer of the well-known interstellar species cyanamide (NH2CN), in weak maser emission, using data from the Green Bank Telescope PRIMOS survey toward Sgr B2(N). All spectral lines observed are in emission and have energy levels in excess of 170 K, indicating that the molecule likely resides in relatively hot gas that characterizes the denser regions of this star-forming region. The anticipated abundance of this molecule from ice mantle experiments is ~10% of the abundance of NH2CN, which in Sgr B2(N) corresponds to ~2 × 1013 cm−2. Such an abundance results in transition intensities well below the detection limit of any current astronomical facility and, as such, HNCNH could only be detected by those transitions which are amplified by masing.

Key words: astrochemistry – ISM: clouds – ISM: individual objects (Sagittarius B2(N)) – ISM: molecules

Online-only material: color figures

1. INTRODUCTION

Historically, searches for new astronomical molecules resulted in the detection of favorable, high line strength transitions based on a thermal approximation to the excitation of these species in interstellar environments. At the temperatures of hot molecular cores inside molecular clouds, these transitions often reside at (sub)millimeter wavelengths. However, line confusion near the Boltzmann peak can lead to ambiguous identifications, and the peak intensities of low abundance, large organic molecules may never rise above the noise floor or the confusion limit. The success of molecule searches at centimeter wavelengths has shown that unique excitation conditions can lead to the unambiguous identification of very low abundance species with high accuracy.

Carbodiimide (HNCNH) is the second most stable isomer of cyanamide (NH2CN), with cyanamide being more stable by ~4.0 kcal mol−1 (Duvernay et al. 2004; Tordini et al. 2003). Since the detection of NH2CN by Turner et al. (1975) toward the high-mass star-forming region Sgr B2(N), HNCNH has been recognized as a candidate interstellar molecule. HNCNH is also a tautomer of NH2CN and can be formed via an isomerization reaction whereby an H atom can migrate along the molecular backbone from the amine group. At room temperature, HNCNH is in thermally induced equilibrium with NH2CN at a fraction of ~1%. Given typical abundances of NH2CN and temperatures in many astrophysical environments of ≲300 K, gas-phase tautomerization of NH2CN is unlikely to produce HNCNH in appreciable abundance. Yet, HNCNH may exist in detectable abundance out of thermal equilibrium with NH2CN as in the case of interstellar hydrogen cyanide (HCN) and interstellar hydrogen isocyanide (HNC)—in which HNC is in greater abundance in some clouds (see Allen et al. 1980, and references therein).

Although tautomerization is likely inefficient in the gas phase under interstellar conditions, experimental studies have shown that NH2CN → HNCNH conversion in water ices and matrices is far more efficient (Duvernay et al. 2005, and references therein). In the solid phase, the association of up to five water molecules with NH2CN on an ice surface has been shown to significantly lower the activation barrier to tautomerization and promote the formation of HNCNH (Duvernay et al. 2005). In fact, HNCNH formation on a water–ice surface is shown to occur at temperatures as low as 70 K. The relative abundance of HNCNH formed from this process has been measured to range from 4% of NH2CN at 80 K to as much as 13% at 140 K (Duvernay et al. 2005). In the laboratory, HNCNH sublimation occurs between 80 K and 170 K, with no additional desorption observed above 170 K (Duvernay et al. 2004). In the interstellar medium (ISM), non-thermal desorption via shocks is also a likely liberation mechanism. Assuming that tautomerization of NH2CN on dust grain ice mantles is the dominant formation pathway for HNCNH, and that subsequent desorption occurs for both species, the gas phase abundance of HNCNH may be capp ed at ~10% of NH2CN.

NH2CN has an estimated column density of ~2 × 1014 cm−2 toward Sgr B2(N) (Nummelin et al. 2000); we therefore anticipate an HNCNH column density on the order of ~1013 cm−2. If thermal emission at hot core temperatures dominates the spectrum of HNCNH, the most favorable high line strength transitions are at millimeter and submillimeter wavelengths. Nevertheless, we have previously used the Robert C. Byrd Green Bank Telescope (GBT) to detect new molecular species including trans-methyl formate (Neill et al. 2012) and cyanoformaldehyde (Remijan et al. 2008) which only had measurable astronomical line intensities detected at centimeter wavelengths. Encouraged by these results, we searched for centimeter wave transitions of HNCNH. All data were taken as part of the
Table 1
HNCNH Rotation–Torsion Doublets, Spectroscopic, and Observed Astronomical Parameters

| Transition        | Frequency* (MHz) | log10(Aij) | E_u (cm⁻¹) | Intensityb (mK) | FWHMb (km s⁻¹) | Intensityb (mK) | FWHMb (km s⁻¹) |
|-------------------|------------------|------------|------------|----------------|---------------|----------------|---------------|
| A₁₁ 18(0,18)–A₁₁ 17(1,17) | 4344.009         | −9.10      | 1182475    | 85(5)          | 16(1)         | 13(6)          | 8(5)          |
| A₁₁d 16(1,16)–A₁₁ 17(0,17) | 16395.527        | −7.35      | 1063485    | ...            | ...           | ...            | ...           |
| A₁₁ 19(0,19)–A₁₁ 18(1,18) | 25083.265        | −6.81      | 1313845    | 27(4)          | 14.0(0.5)     | 28(1)          | 22(2)         |
| A₁₁d 15(1,15)–A₁₁ 16(0,16) | 37135.395        | −6.28      | 952855     | ≤12            | ...           | ≤12            | ...           |
| A₁₁d 20(2,20)–A₁₁ 19(1,19) | 45822.046        | −6.03      | 1452126    | 25(1)          | 13(2)         | 23(2)          | 12(1)         |
| A₁₂ 18(0,18)–A₁₂ 17(1,17) | 4802.956         | −8.97      | 1182542    | 89(2)          | 15.9(0.4)     | 23(2)          | 12(1)         |
| A₁₂d 16(1,16)–A₁₂ 17(0,17) | 15936.094        | −7.38      | 1063399    | ...            | ...           | ...            | ...           |
| A₁₂ 19(0,19)–A₁₂ 18(1,18) | 25541.620        | −6.79      | 1313912    | ...            | ...           | ...            | ...           |
| A₁₂ 15(1,15)–A₁₂ 16(0,16) | 36675.469        | −6.30      | 952770     | ≤11            | ...           | ≤11            | ...           |
| A₁₂d 20(2,20)–A₁₂ 19(1,19) | 46279.903        | −6.01      | 1452193    | ...            | ...           | ...            | ...           |

Notes.

* All lines except those at 4 GHz have been experimentally measured with (Obs – Calc) frequency uncertainties ≤30 kHz. Uncertainties on the 4 GHz lines are calculated to be ≤30 kHz, type A, k = 2 (σ) (Taylor & Kuyatt 1994).

b The uncertainties for the intensities and linewidths are type B, k = 1 (σ) (Taylor & Kuyatt 1994).

c No data.

d Transition contaminated by CH₃OH emission.

e Estimated based on a Gaussian fit to the low-frequency shoulder of the CH₃OH emission at +82 km s⁻¹.

Figure 2 shows the spectra for the observed passbands. The red and blue vertical lines indicate the location of the emission feature at LSR velocities of +64 km s⁻¹ and +82 km s⁻¹, respectively. We find four unblended lines of HNCNH in this region (panels (a)–(c) and (g)). One frequency range was unobservable by the GBT (16 GHz) while two spectral feature were contaminated by transitions of CH₃OH (panels (d) and (g)). Finally, one transition was not observed due to lack of frequency coverage (46.2 GHz). Of the observable transitions, we show clear detections of both the +64 km s⁻¹ and +82 km s⁻¹ components at 4.3, 4.8, and 25.8 GHz, and the +64 km s⁻¹ component at 45.8 GHz (Figure 1). The four line detections and two non-detections are consistent with only masing lines being detectable, as discussed in Section 3.

3. DISCUSSION

The initial identification of HNCNH was based on only the two lines at 4.3 and 4.8 GHz. In order to quantify the probability of coincidental overlap of features at these frequencies which could lead to a possible misassignment, we used the method outlined in Neill et al. (2012). We find 37 observed transitions within a representative window of 200 MHz of PRIMOS at C-band (4–4 GHz), 14 of which are within ±50% of the intensity of the detected features. This line density is typical of the PRIMOS survey in this frequency range. Of these 14 features, 4 were in emission. If we then assume a conservative FWHM line width of 25 km s⁻¹ (almost twice our measured FWHM), we calculate the probability of a single line falling coincidentally within one FWHM of our line to be 0.75%. For two detected lines that probability drops to 0.002%. We find this is both compelling evidence for a clear detection and an excellent example of the power of the GBT in new molecule detections at centimeter wavelengths, where line confusion is drastically reduced relative to the millimeter and submillimeter regimes.

Initially, the large beamwidths and high-energy nature of the observed lines pointed to emission arising from the hot, extended source that surrounds the cold LMH and couples well to the beam at these frequencies. A local thermodynamic...
Figure 1. Carbodiimide (HNCNH) spectral passbands toward Sgr B2(N) recorded from the GBT PRIMOS Survey. Rotation–torsion doublet transition quantum numbers are shown in each panel. The passband width displayed is 500 km s$^{-1}$ in each case. The spectra are plotted as a function of frequency (MHz), corrected for an LSR source velocity of +64 km s$^{-1}$. The blue and red vertical lines indicate the location of the transition rest frequency (see Table 1) at an assumed LSR source velocity of +64 km s$^{-1}$ and +82 km s$^{-1}$, respectively. Data in all panels were Hanning smoothed for display purposes.

(A color version of this figure is available in the online journal.)
transition out of this level is very slow, with an Einstein
millimeter and submillimeter transitions; the only downward
coefficient of $\sim 10^{-9}$ s$^{-1}$. Downward and upward transitions
out of the lower level ($A_{2d}^{17}(1,17)$), labeled “A–D,” how-
ever, occur rapidly with Einstein A values between $0.2-2 \times 10^{-2}$ s$^{-1}$. This creates a population inversion between the
$A_{2d}^{18}(0,18)$ and $A_{2d}^{17}(1,17)$ levels, leading to the observed
maser transition at 4.8 GHz. An analogous process occurs for the torsion
doublets, leading to masing in these transitions as well.

For the 36.7 GHz line (labeled “X,” Figure 2(b)), the upper
state ($A_{2d}^{15}(1,15)$) is again coupled to higher energy levels
via fast transitions, with the 36.7 GHz transition being the
slow emission path to $A_{2c}^{16}(0,16)$. In this case, however, a
fast downward transition is allowed to the $A_{2a}^{14}(0,14)$ state
(transition labeled “N”). Population inversion is not achieved
because of the presence of this drain, and the 36.7 GHz transition
does not mase. A similar scenario holds for the 15.9 GHz
transitions, as well as their torsion doublets. In summary,
an analysis of the energy levels of HNCNH predicts a population
inversion resulting in masing for the torsion doublets at 4, 25,
and 46 GHz, with no masing by the doublets at 15 and 36 GHz.
Furthermore, the 4 GHz doublets should show a greater degree
of inversion due to the longer lifetime of the transitions (Table 1)
than the 25 or 46 GHz transitions, resulting in more intense lines,
which is in excellent agreement with our observations.

The observed maser emission is relatively weak and displays
no line narrowing, suggesting that these are unsaturated maser
lines. As collisional and radiative pumping rates for HNCNH are
unknown, a full pumping model was not possible and is beyond
the scope of this work. A zeroth-order calculation of the critical
density for the fast transitions connecting the maser transitions
was, however, performed. Using collisional coefficients for
similar transitions in HNCO, we find critical densities required to
thermalize these transitions on the order of $10^{9-10^{10}}$ cm$^{-3}$,
far higher than those typically associated with the region.

Given this, and that the Sgr B2(N) region is known to contain
a broad range of favorable radiative excitation conditions, a
radiative excitation mechanism for these transitions is possible.
The current observations, however, do not provide a definitive
answer to the excitation question, and further investigation is
warranted. A mapping study of the 4 GHz lines in Sgr B2(N)
would be extremely beneficial to elucidating the environment
these signals are arising from, including their spatial correlation
with other known maser such as CH$_3$OH, and therefore the most
likely excitation mechanisms.

We have also carried out an analysis of the expected intensity
of HNCNH lines in this frequency region based on a thermal
population of HNCNH. Assuming LTE conditions, we calculate
a column density of HNCNH giving rise to the 4 GHz maser
lines of $\sim 2 \times 10^{16}$ cm$^{-2}$ at 150 K, although this value is largely
invariant over temperatures from 80 to 500 K. Given this column
density, the expected intensity of the 36.7 GHz transition would
be $\sim 740$ mK. Further, at a column density of $\sim 2 \times 10^{13}$ cm$^{-2}$
Figure 2. Energy level structure of the relevant transitions for the 4.8 GHz maser (top) and 36.6 GHz line (bottom). Energy levels are ordered by increasing energy, but are not drawn to scale. Allowed transitions are indicated by arrows.

(∼10% of NH$_2$CN in this source; Nummelin et al. 2000), we would expect the most intense lines in this region to be less than 1 mK for rotational temperatures above 80 K. Given this, and the lack of any detection at 36.7 GHz with an rms noise level of ∼10 mK, we conclude these transitions are not arising from a thermal population.

This is consistent with our non-detection of transitions which are not masing. In gas above 80 K, the most intense lines of HNCNH at LTE would fall at millimeter and submillimeter wavelengths. Numerous high-resolution, high-sensitivity spectral line surveys of this region have been carried out (see Wang et al. 2011; Tercero et al. 2010; Nummelin et al. 2000, and references therein) covering these transitions up to ∼1.8 THz. With an abundance of 10% NH$_2$CN, the strongest transitions under LTE emission at 80 K would be on the order of the rms noise level of the survey observations. With increasing temperature, the expected line strengths decrease rapidly. Thus, at these column densities, a thermal population of HNCNH would likely not be detectable in even the most sensitive line surveys to date.

This is in itself remarkable. A heroic effort has been performed in recent years on compiling molecular inventories and facilitating new molecule detections using state-of-the-art millimeter and submillimeter observatories and molecular line surveys. These surveys have provided invaluable information on the physical and chemical conditions present in the ISM and their high scientific value is unquestionable. They suffer,
however, from extremely high line densities and long integration times, relative to lower-frequency telescopes. Because of this, identifications of new molecular species, especially those in low abundance, can be difficult due to the line confusion at the noise floor and the degree of coincidental overlap of target lines with other molecular transitions.

In this work, we have shown that a molecule which would be undetectable via transitions arising from a thermal population can be identified via maser transitions at centimeter wavelengths. This detection was possible only through low frequency surveys of a chemically rich region by the GBT through a dedicated project (PRIMOS). The number of transitions which display significant maser activity in any given molecule is likely to be small, but weak masing behavior has been observed in a number of molecules such as H$_2$CO and NH$_3$ (Forster et al. 1980; Gaume et al. 1991). In addition, at centimeter wavelengths the lack of line confusion makes definitive identification of a species possible with only a small number of observed transitions. This may represent a new strategy for searches for key molecules of interest to the astrochemistry and astrobiology communities which have not yet been detected due to their low abundances.

In summary, we have detected four transitions of carbodiimide (HNCNH) toward Sgr B2(N) with very high confidence. All four signals have been found to be the result of maser activity. We also report two transitions that were not detected, consistent with HNCNH only being detectable toward Sgr B2(N) through maser lines. This detection presents a new methodology for searches for interstellar molecular candidates which may be too low in abundance to be detected in thermal emission by modern radio observatories.

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