

HCNH⁺: A NEW INTERSTELLAR MOLECULAR ION

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ABSTRACT

A new molecular ion, HCNH⁺, or protonated HCN, has been detected in the interstellar medium. The $J = 1-0$, $2-1$, and $3-2$ rotational transitions of this species have been observed toward Sgr B2. Using a large velocity gradient model calculation, the column density of HCNH⁺ is found to be $\sim 4 \times 10^{14} \text{ cm}^{-2}$, about one order of magnitude less than that estimated for HCO⁺ and HCN in this source. Such a column density implies a fractional abundance for HCNH⁺ in Sgr B2 of $\sim 3 \times 10^{-10}$, one to several orders of magnitude greater than the values predicted by ion-molecule models of interstellar chemistry. The high observed abundance of this species, relative to theoretical calculations, suggests that the destruction of HCNH⁺ by dissociative recombination is slower than expected, or that the formation rate of the ion has been underestimated.

Subject headings: interstellar: abundances — interstellar: molecules — molecular processes

I. INTRODUCTION

The linear molecular ion HCNH⁺ is one of the key species in the ion-molecule scheme of interstellar chemistry. It is postulated to be the main precursor to both HCN and HNC, which are formed through the rapid dissociative recombination of HCNH⁺ (e.g., Herbst 1978). Virtually equal amounts of HCN and HNC are thought to be produced via this reaction and therefore should result in an interstellar [HNC]/[HCN] ratio of approximately 1. Observations thus far, however, have found this ratio to vary from values as large as 4.4, as in the dark cloud L134, to as small as 0.014, as seen toward Orion-KL (e.g. Goldsmith *et al.* 1981). This apparent discrepancy has led to the postulation that certain high-temperature reactions may in some sources be preferentially synthesizing HCN and/or converting HNC to HCN (e.g., Watson and Walmsley 1982); under other conditions, the formation of the formaldehyde-type isomer of HCNH⁺, H₂NC⁺, leads to the favored production of HNC (e.g., Allen, Goddard, and Schaefer 1980). However, little is accurately known about such processes and their actual role in the synthesis of HCN and HNC (Herbst 1985). Nonetheless, if HCNH⁺ is the major pathway to both HCN and HNC, it should be present at some concentration in molecular clouds where ion-molecule chemistry dominates. Thus, observation of this species constitutes an important test for ion-molecule theory and should give valuable insight into the varying [HNC]/[HCN] ratio.

In this *Letter* we report the first interstellar detection of HCNH⁺. The $J = 1-0$, $2-1$, and $3-2$ rotational transitions of this molecule at 74, 148, and 222 GHz have been observed toward Sgr B2. The initial search for HCNH⁺ was carried out using frequencies estimated from the work of Altman, Crofton, and Oka (1984); the recent measurement of the laboratory microwave spectrum of this ion by Bogey, Demuynck, and Destombes (1985) has substantiated our detection.

II. OBSERVATIONS

The $J = 1-0$ observations were carried out on 1984 October 28–31, using the NRAO 12 m dish. At the observing frequency of 74 GHz, the half-power beamwidth was 85'' and the aperture efficiency was $\eta_a = 0.5$. The temperature scale is given in terms of T_R^* , which is the chopper wheel antenna temperature corrected by forward spillover losses, i.e., $T_R^* = T_A^*/\eta_{\text{fss}}$, where $\eta_{\text{fss}} = 0.75$. The brightness temperature T_R (not considering the source beam filling factor) is $T_R = T_R^*/\eta_c$, where $\eta_c = 0.9$ (P.R. Jewell, private communication). The receiver was a dual-channel, double-sideband cooled mixer, operating with opposite linear polarization and a sideband separation of 9.5 GHz. Both polarizations were observed simultaneously in each of two separate 256 channel filterbanks of 1 MHz and 500 kHz resolution.

The $J = 2-1$ and $J = 3-2$ data were taken with the Texas Millimeter Wave Observatory (MWO) 4.9 m dish on 1984 November 20–27 and 1985 April 8–16, respectively. At the two observing frequencies of 148 and 222 GHz, the half-power beamwidths were 105'' and 75'' with $\eta_a = 0.4$ and 0.27. The temperature scale for these measurements is in terms of T_A^* , the chopper wheel-corrected antenna temperature. $T_R = T_A^*/\eta_c\eta_{\text{fss}}$, with $\eta_c\eta_{\text{fss}} \approx 0.6$ at 148 GHz and 0.55 at 222 GHz. Different receivers were used for the $J = 2-1$ and $3-2$ ob-

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servations, both being single-channel, double-sideband cooled mixers with a sideband separation of 2.8 GHz. In both cases a 256 channel filter bank with 1 MHz resolution was used. Data for all three lines were taken position switching.

III. RESULTS

Figure 1 shows the spectra of the $J = 1-0$, $2-1$, and $3-2$ rotational transitions of HCNH^+ toward Sgr B2. Measured rest frequencies for these lines are given in the figure. $V_{\text{LSR}} = 62.0 \text{ km s}^{-1}$ is assumed for each line. These frequencies were carefully checked for coincidences with other molecular transitions. No other known lines occur at the frequencies of the $J = 1-0$ and $J = 3-2$ HCNH^+ transitions, although there may be an unidentified feature close to the $J = 3-2$ line. A methyl formate (HCOOCH_3) transition [37(9,29)–36(10,26)] lies 10 MHz above the $J = 3-2$ line. The possibility that it is responsible for the emission observed at the HCNH^+ ($J = 3-2$) frequency can be dismissed for the following reasons: (1) it would imply an LSR velocity 13 km s^{-1} higher than is observed for all other HCOOCH_3 lines (Cummins, Linke, and Thaddeus 1985); (2) it lies 463 K above the ground state and thus cannot be excited at the low rotational temperature of 23 K found by Cummins *et al.* to fit all 29 lines of this species observed in their survey.

The $J = 2-1$ transition of HCNH^+ , on the other hand, is 2 MHz lower in frequency than the $7(2,6)$ – $6(2,5)$ line of formamide (NH_2CHO) at 148,223.14 MHz, which lies 33 K in energy above ground state with a line strength of 6.4 (Lovas 1985). In the Cummins *et al.* survey, 18 lines of formamide were observed in Sgr B2, arising from states as high in energy as 48 K and having comparable line strengths to the $7(2,6)$ – $6(2,5)$ transition. It is therefore quite likely that the $J = 2-1$ HCNH^+ line is contaminated by this formamide transition.

In order to evaluate the degree of this contamination, we observed other formamide lines which lie close in frequency to the $7(2,6)$ – $6(2,5)$ transition and which bracket it in energy above ground state. These lines were the $7(1,7)$ – $6(1,6)$ and $7(3,5)$ – $6(3,4)$ transitions at 142,701.33 and 148,667.30 MHz, which lie 24 K and 48 K above the ground state, with corresponding line strengths of 6.9 and 5.7, respectively. The results of our observations are shown in Figure 2. We detected the $7(1,7)$ – $6(1,6)$ formamide transition at an intensity of $T_A^* = 0.1 \text{ K}$; the $7(3,5)$ – $6(3,4)$ line, however, was not observed above a peak-to-peak noise level of about $T_A^* = 0.075 \text{ K}$. For comparison, the original spectrum taken at the HCNH^+

$J = 2-1$ frequency is also shown in Figure 2. A line with an intensity of $T_A^* = 0.14 \text{ K}$ is present at the $\text{HCNH}^+/\text{NH}_2\text{CHO}$ frequency.

This 0.14 K feature clearly is a blend of the $7(2,6)$ – $6(2,5)$ transition of formamide and the HCNH^+ ($J = 2-1$) transition; it is too strong to be due to NH_2CHO alone. From a fit to their 18 detected lines of NH_2CHO ranging from 10 to 48 K above ground state, Cummins *et al.* find $T_{\text{rot}} = 12.8 \pm 0.9 \text{ K}$. Thus the $7(2,6)$ – $6(2,5)$ transition should have an intensity only 0.45 of that of the $7(1,7)$ – $6(1,6)$ line, i.e., $T_A^* \approx 0.04 \text{ K}$, in contrast to the observed antenna temperature of 0.14 K. Under the same assumptions, the $7(3,5)$ – $6(3,4)$ line of formamide should exhibit $T_A^* \approx 0.01 \text{ K}$, consistent with our upper limits for this transition. If we take the $7(1,7)$ – $6(1,6)$ line profile, scale it by the estimated $7(2,6)$ – $6(2,5)/7(1,7)$ – $6(1,6)$ ratio of 0.45, and subtract from the blended line, the resultant is the feature shown in Figure 1, which is exactly at the rest frequency of $J = 2-1$ HCNH^+ , and therefore is attributable to this species.

IV. DISCUSSION

a) Line Profiles

Table 1 lists the line parameters derived from the data shown in Figure 1. As the table illustrates, the LSR velocity of HCNH^+ is consistently about 62 km s^{-1} . The HCNH^+ linewidths, however, appear to be somewhat discrepant, the $J = 1-0$ width being somewhat narrower than the other two transitions, although none of the quoted linewidths are atypical for this source (Cummins *et al.*). This apparent discrepancy could result from the presence of several separate gas components in HCNH^+ . Indeed, such a variation in linewidth has been found for HC_3N in Sgr B2, whose $J = 1-0$, $2-1$, and $3-2$ transitions have widths of 11.6, 16.2, and 20.6 km s^{-1} , respectively, while the $J = 8-7$ line has $\Delta V_{1/2} = 23.5 \text{ km s}^{-1}$ (Avery *et al.* 1979). Avery *et al.* (1979) explain this variation as due to a complicated source structure consisting of three components and also as arising from a weak maser effect in the lowest rotational transitions, which may narrow the $J = 1-0$ line. The $J = 1-0$ transition of HCNH^+ may also be anomalously excited, as discussed in the next section.

b) Column Densities

The HCNH^+ column density for Sgr B2 was derived by two methods. First, a simple analytical calculation was performed in the optically thin limit, assuming a rotational temperature

TABLE 1
HCNH⁺ OBSERVATIONS TOWARD SAGITTARIUS B2^a

Transition	ν (MHz)	Telescope	θ_b (")	T_A^* (K)	T_R^* (K)	V_{LSR} (km s ⁻¹)	$\Delta V_{1/2}$ (km s ⁻¹)	T_R (K)
$J = 1 \rightarrow 0$	$74,111.3 \pm 0.3^b$	NRAO 12 m	85	...	0.10 ± 0.03	62 ± 4	9 ± 5	0.11
$J = 2 \rightarrow 1$	$148,221.42 \pm 0.12^c$	MWO 4.9 m	105	0.09 ± 0.02	...	63 ± 2	18 ± 5	0.15
$J = 3 \rightarrow 2$	$222,329.40 \pm 0.18^c$	MWO 4.9 m	75	0.11 ± 0.04	...	62 ± 4	22 ± 4	0.20

^a Taken toward $\alpha = 17^{\text{h}}44^{\text{m}}11^{\text{s}}.0$; $\delta = -28^{\circ}22'30''$ (1950.0); given errors are 3σ .

^b Calculated from rotational constants determined by Bogey *et al.* 1985.

^c Measured by Bogey *et al.* 1985.

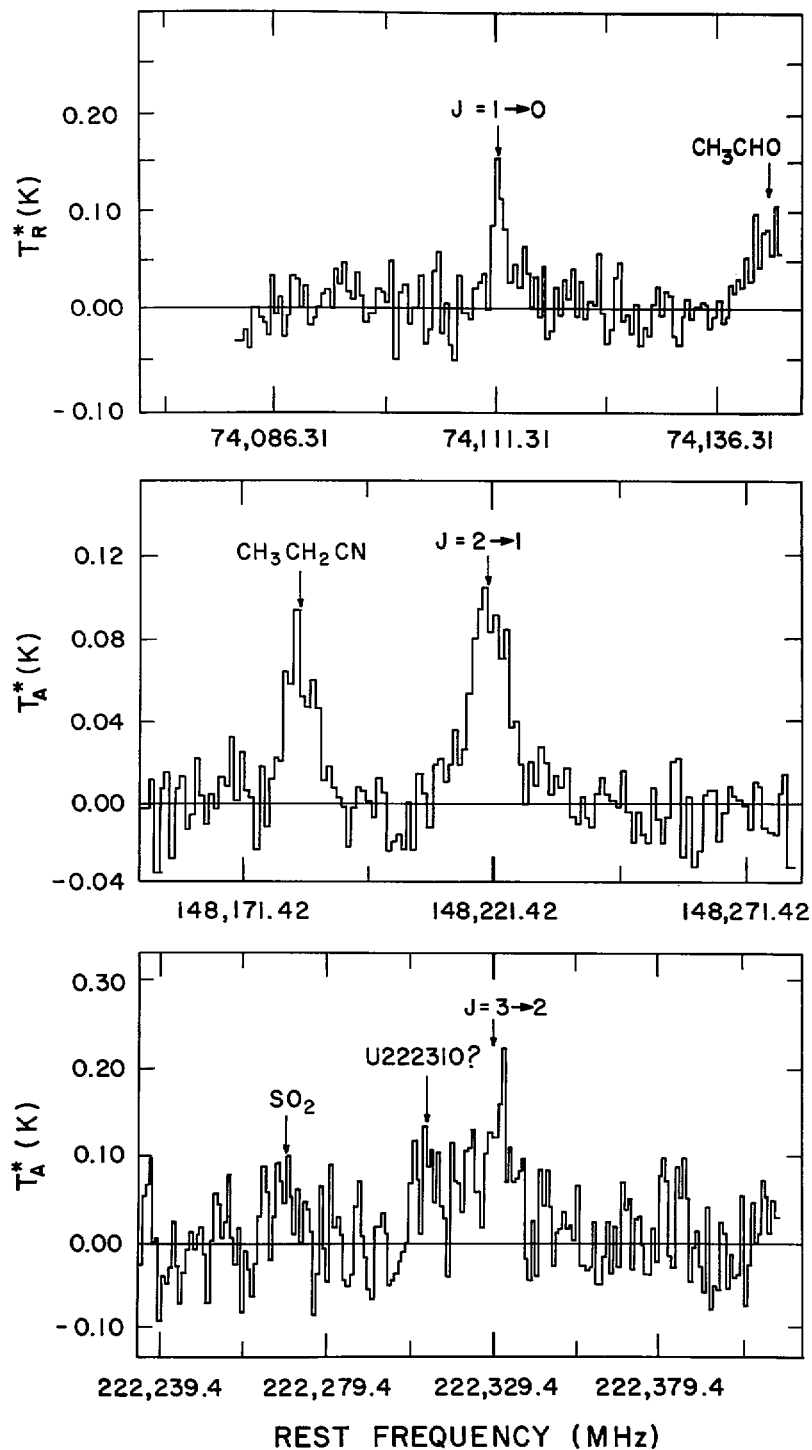


FIG. 1.—Spectra of the $J = 1-0$, $2-1$, and $3-2$ rotational transitions of HCNH^+ , observed toward Sgr B2 ($\alpha = 17^{\text{h}}44^{\text{m}}11^{\text{s}}.0$; $\delta = -28^{\circ}22'30''$ [1950.0]). The $J = 1-0$ line, measured in the LSB, was observed using the NRAO 12 m antenna, with a 500 kHz channel resolution. The $J = 2-1$ and $J = 3-2$ transitions were observed at the Texas MWO, the $2-1$ line measured in the USB and the $3-2$ in the LSB, both with 1 MHz resolution. HCNH^+ rest frequencies, taken from Bogey *et al.* (1985), are shown for each spectrum. Other features in these spectra are the $2(1,2)-1(0,1)$ E transition of acetaldehyde at 83,582 MHz, observed in the USB; the $16(1,15)-15(1,14)$ transition of $\text{CH}_3\text{CH}_2\text{CN}$ at 145,418 MHz, measured in the LSB; and the $13(2,12)-13(1,13)$ line of SO_2 (USB). The tentative feature U222310 in the $J = 3-2$ spectrum could be the $5(2,4)-5(0,5)$ line of HCOOD . Both ethyl cyanide and SO_2 appear at different frequencies than expected due to a velocity shift in the other sideband.

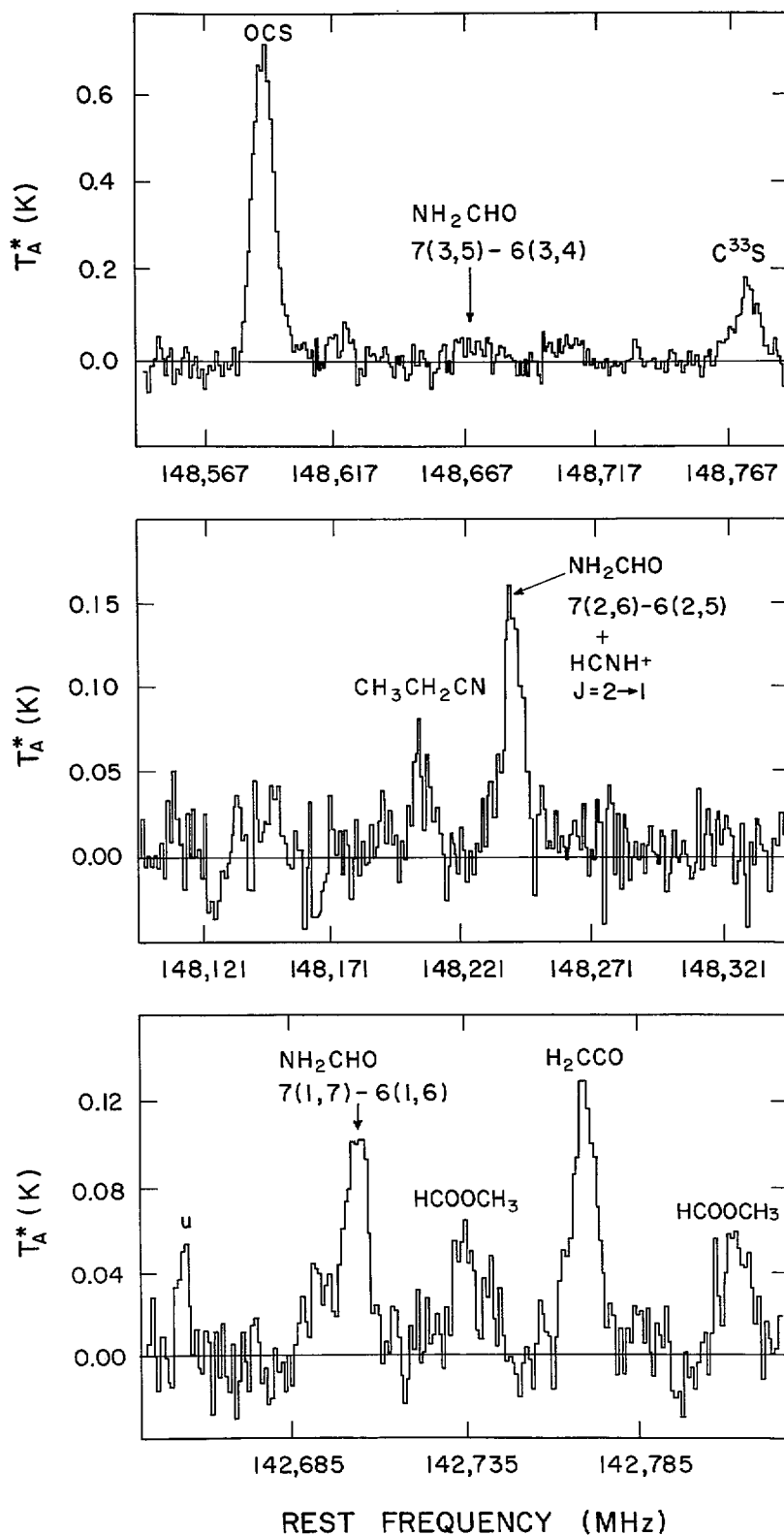


FIG. 2.—Spectra of NH₂CHO and HCNH⁺ observed in Sgr B2 with the MWO telescope. Filter resolution is 1 MHz. The top spectrum is data taken at the frequency of the 7(3,5)–6(3,4) transition of NH₂CHO, which was not detected. Also in the bandpass is the $J = 12-11$ line of OCS at 145,947 MHz (LSB), and the $J = 3-2$ line of C³³S at 145,756 MHz (LSB). The middle spectrum shows the blend of the NH₂CHO 7(2,6)–6(2,5) and HCNH⁺ $J = 2-1$ lines, as well as the CH₃CH₂CN feature described in Fig. 1. The HCNH⁺ transition contributes $T_A^* = 0.09$ K to the total intensity of this blend, and NH₂CHO accounts for the rest, i.e., $T_A^* \approx 0.04$ K, which is 0.45 of the intensity of the NH₂CHO transition shown in the lower spectrum (see text). This line is the 7(1,7)–6(1,6) transition of NH₂CHO. Also present in the lower spectrum is the 7(1,6)–6(1,5) line of ketene at 142,769 MHz, the 13(0,13)–12(0,12) and 13(1,13)–12(1,12) lines of methyl formate at 142,817, and 142,735 MHz, and a U line near 142,647 MHz.

of 20 K, and an HCNH⁺ dipole moment of 0.3 *D*, taken from ab initio calculations (Dardi and Dykstra 1980). We estimate a HCNH⁺ column density $NL_{\text{tot}} = (2-3) \times 10^{14} \text{ cm}^{-2}$, where the range of values reflects the use of the three rotational lines independently.

It is probably not the case that one temperature describes the population in the HCNH⁺ rotational ladder. Consequently, the HCNH⁺ column density was also calculated using a large velocity gradient (LVG) model. For this calculation a simple, isothermal homogeneous cloud with spherical geometry was assumed. Twelve rotational levels of HCNH⁺ were included in the computation, as well as HCO⁺-H₂ collisional cross sections, taken from Flowers (1985).

The LVG model calculates brightness temperatures for rotational transitions based on several input parameters, which include the total gas density *n*, the gas kinetic temperature *T_K*, and the quantity $X' = X/(dv/dR)$, where *X* is the fractional abundance and *dv/dR* is the velocity gradient (in units of km s⁻¹ pc⁻¹), assumed to be constant throughout the cloud. The column density is then given by $NL = X'n2R(dv/dR) = \Delta V_{1/2} X'n$, independent of cloud radius *R*; *dv* is set equal to the observed linewidth.

These input parameters were varied in order to reproduce the HCNH⁺ brightness temperatures *T_R*. It is thus assumed that all three lines originate in the same gas. No one set of input parameters fits the HCNH⁺ intensities exactly; the best fit reproduces the *J* = 2-1 and 3-2 temperatures, but *T_R* for the *J* = 1-0 transition is calculated to be too low by about 40%. The computation also predicts enhanced or even negative excitation temperatures for the *J* = 1-0 line. These results suggest that the *J* = 1-0 transition may act as a weak maser, whose effect would be important mainly in small clumps, whose velocity widths are small. Anomalously strong *J* = 1-0 lines have been observed for other molecules in Sgr B2, including HC₃N (Morris *et al.* 1976) and HC₅N. Such enhanced excitation implies that the HCNH⁺ distribution may be clumped in Sgr B2. Alternatively, the 40% difference between observed and calculated intensities may result from multiple gas components with different filling factors and physical conditions.

The best fit to the HCNH⁺ data yields $n = 5 \times 10^4 \text{ cm}^{-3}$, *T_K* = 20 K, and $X' = X/(dv/dR) = 1.5 \times 10^{-10}$. These values for *n* and *T_K* agree well with those derived from LVG modeling of other molecules (e.g., Brown and Cragg 1985). The column density of HCNH⁺ thus derived from these computations is $4 \times 10^{14} \text{ cm}^{-2}$, using $\Delta V_{1/2} = 18 \text{ km s}^{-1}$. This column density is about one order of magnitude less than that of HCO⁺ ($2.3 \times 10^{15} \text{ cm}^{-2}$; Woods *et al.* 1983), but is over 10 times that estimated for N₂H⁺ ($1 \times 10^{13} \text{ cm}^{-2}$; Turner and Thaddeus 1977) for Sgr B2. However, all three ions have differing velocity components in Sgr B2, and HCO⁺ and N₂H⁺ may be suffering the effects of self-reversal; simple comparison of column densities may not be particularly valid.

c) Fractional Abundance

In order to derive the fractional abundance, the size of the HCNH⁺ Sgr B2 cloud is assumed to be the same as for

HC₃N, i.e., 4' or 11.6 pc at a distance of 10 kpc (McGee *et al.* 1973). Then *dv/dR* is 1.55 km s⁻¹ pc⁻¹, if the HCNH⁺ linewidth is 18 km s⁻¹, yielding $X = 2.3 \times 10^{-10}$ from the LVG calculation. Alternatively, if the column depth of H₂ is taken to be 10²⁴ cm⁻², as derived from CO observations (Scoville, Solomon, and Penzias 1975), then the HCNH⁺ fractional abundance is 4×10^{-10} . These abundances are considerably higher than those predicted by ion-molecule chemistry. For example, Prasad and Huntress (1980) predict $X(\text{HCNH}^+) = 3.9 \times 10^{-14}$ for $n \approx 10^4 \text{ cm}^{-3}$ and $X = 2.12 \times 10^{-15}$ for $n \approx 10^5 \text{ cm}^{-3}$ at *T_K* = 50 K. Mitchell, Ginsberg, and Kuntz (1978) predict $X(\text{HCNH}^+)$ to be 6.5×10^{-13} at $n = 10^4 \text{ cm}^{-3}$ and 5.6×10^{-14} at $n = 10^5 \text{ cm}^{-3}$. Leung, Herbst, and Huebner (1984) calculate $X(\text{HCNH}^+) = (0.63-7.2) \times 10^{-12}$ for the density range 10⁴-10⁵ cm⁻³ for their low metal abundance model; their high metal abundance model yields $X = 7.8 \times 10^{-14}$ to 3.0×10^{-13} , over the same density range; both cases are steady state solutions. However, Leung *et al.* estimate $X(\text{HCNH}^+) = (1.6-2.8) \times 10^{-10}$ in their low-metal model, but only when the cloud was in its early chemical phases. Unless such early phases characterize Sgr B2, HCNH⁺ appears to be from 30 to many orders of magnitude more abundant than ion-molecule models estimate.

d) Chemical Implications

The apparent high abundance of HCNH⁺ in Sgr B2 could have important implications for the HNC/HCN ratio. This ratio is difficult to derive directly for Sgr B2, because both species may be self-absorbed near *V_{LSR}* = 62 km s⁻¹ (e.g., Cummins *et al.*). Nevertheless, an upper limit to the HNC/HCN ratio can be estimated from the *J* = 1-0 HC¹⁵N line, which shows little evidence of self-reversal, and the upper limit to the H¹⁵NC *J* = 1-0 transition, both measured by Cummins *et al.* and by the NRAO spectral survey (Turner and Ziurys 1986). Using the more sensitive NRAO results, the ratio is found to be $[\text{HNC}]/[\text{HCN}] \leq 0.13$, significantly less than the predicted value of 1. The HCNH⁺/HCN ratio is also important. An estimate of the HCN column depth, based on the HC¹⁵N *J* = 1-0 line is $NL = 4 \times 10^{15} \text{ cm}^{-2}$, if *T_{rot}* = 20 K, ¹⁴N/¹⁵N = 300 (Wannier, Linke, and Penzias 1981), and if $\tau \ll 1$ for the HC¹⁵N transition. The LSR velocity of HC¹⁵N is $51 \pm 7 \text{ km s}^{-1}$ (Turner and Ziurys 1986), however, so that HCN may not be entirely coextensive with HCNH⁺. Nevertheless, HCN appears to be only one order of magnitude more abundant than HCNH⁺, contrary to the predictions of chemical models that use HCNH⁺ as the major source of HCN. Even in the early cloud phase/low metal calculations of Leung *et al.*, where $X(\text{HCNH}^+)$ does match the observations, HCN/HCNH⁺ is predicted to be $\geq 10^3$.

It is not possible to estimate the HCNH⁺/HNC ratio. Still, the above results for Sgr B2 do imply one or more of the following: (1) the destruction of HCNH⁺, and thus the production of both HCN and HNC via this pathway, is slower than expected; (2) the formation rate of HCNH⁺, perhaps involving proton transfer to HCN and HNC (e.g., Millar *et al.* 1985), has been underestimated; (3) HCN and HNC destruction rates are not properly accounted for in the models.

V. CONCLUSIONS

HCNH⁺ has been predicted to play a central role in the ion-molecule scheme of interstellar chemistry as the main source of HCN and HNC. Thus, its observation and study could prove valuable in understanding the interstellar HNC/HCN ratio, as well as in providing additional evidence for ion-molecule chemistry. This first initial detection of interstellar HCNH⁺ in Sgr B2 already suggests it may be an important chemical probe. Its estimated fractional abundance is at least one to several orders of magnitude larger than predicted by

numerous ion-molecule models; coupled with a relatively low abundance of HCN and a small HNC/HCN ratio, this suggests that HCNH⁺ is not channeled into HCN or HNC as rapidly as thought. Additional observations of this species are clearly needed in order to evaluate its significance for ion-molecule chemistry.

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Note added in proof.—Additional observations of the $J = 1-0$ line of HCNH⁺ toward Sgr B2 have shown it to exhibit an intensity approximately 30% less than initially measured, consistent with the predictions of the LVG model and confirming the high column density of this species toward this source.

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