The Astrophysical Journal, 675:931–936, 2008 March 1

HYDROGEN ISOCYANIDE IN COMET 73P/SCHWASSMANN-WACHMANN (FRAGMENT B)

D. C. Lis,[1,2] D. Bockelée-Morvan,[3] J. Boissier,[3] J. Crovisier,[3] N. Biver,[3] and S. B. Charnley[4]
Received 2007 May 4; accepted 2007 November 28

ABSTRACT

We present a sensitive 3 σ upper limit of 1.1% for the HNC/HCN abundance ratio in comet 73P/Schwassmann-Wachmann (fragment B), obtained on 2006 May 10–11, using Caltech Submillimeter Observatory (CSO). This limit is a factor of ∼7 lower than the values measured previously in moderately active comets at 1 AU from the Sun. Comet 73P/Schwassmann-Wachmann was depleted in most volatile species, except of HCN. The low HNC/HCN ratio thus argues against HNC production from polymers produced from HCN. However, thermal degradation of macromolecules, or polymers, produced from ammonia and carbon compounds, such as acetylene, methane, or ethane appears a plausible explanation for the observed variations of the HNC/HCN ratio in moderately active comets, including the very low ratio in comet 73P/Schwassmann-Wachmann reported here. Similar polymers have been invoked previously to explain anomalous $^{14}N/^{15}N$ ratios measured in cometary CN.

Subject headings: comets: individual (73P/Schwassmann-Wachmann) — molecular processes — radio lines: solar system

1. INTRODUCTION

Hydrogen isocyanide, HNC, a metastable isomer of HCN, was first detected in the interstellar medium (ISM) over a third of a century ago as the unidentified line U90.7 (Snyder & Buhl 1972; Zuckerman et al. 1972; the identification subsequently confirmed in the laboratory by Blackman et al. 1976). The interstellar HNC/HCN abundance ratio has been shown to be strongly temperature dependent (e.g., Schilke et al. 1992; Hirota et al. 1998 and references therein). The current understanding of the HNC chemistry in molecular hot cores is that in warm, dense gas HCN is first produced efficiently by ion-molecule chemistry from ammonia and C^+. HNC is subsequently produced by proton transfer to HCN to form $HCNH^+$, followed by dissociative recombination or proton transfer to ammonia (e.g., Rodgers & Charnley 2001a; Charnley et al. 2002). The temperature dependence of the HNC/HCN abundance ratio is explained primarily by proton transfer reactions cycling between the two isomers via the $HCNH^+$ ion. However, additional HNC formation routes may be required in dark clouds where the HNC/HCN ratio exceeds unity. These are presumably neutral-neutral reactions (e.g., $C + NH_2 = HNC + H$; Herbst et al. 2000) and consequently are probably too slow to efficiently form HNC in expanding cometary atmospheres.

The initial detection of HNC in a cometary atmosphere was by Irvine et al. (1996) in comet C/1996 B2 (Hyakutake). The measured HNC/HCN abundance ratio, ∼6%, was similar to that in interstellar clouds with a temperature of order 50 K, suggesting that cometary HNC may be unprocessed interstellar material incorporated into the comet's nucleus. However, Irvine et al. (1996) argued that a number of alternative processes may also explain the observed HNC/HCN ratio in comet Hyakutake, including irradiation of icy matrix containing HCN, nonequilibrium chemical processes in the solar nebula, gas-phase processes in the coma itself, infrared relaxation of HCN from excited vibrational levels of the ground electronic state, or photodissociation of a heavier parent molecule.

A strong variation of the HNC/HCN abundance ratio in comet C/1995 O1 (Hale-Bopp) with heliocentric distance (from ≲2% at 2.9 AU to ∼20% near 1 AU; Biver et al. 1997; Irvine et al. 1998) questioned the interstellar origin of cometary HNC and suggested a production mechanism in the coma itself as a more likely explanation. Rodgers & Charnley (1998) presented a comprehensive model of the cometary coma chemistry and suggested that in very active comets, such as comet Hale-Bopp, the observed variation of the HNC abundance with the heliocentric distance, as observed with single-dish telescopes, can be explained by isomerization of HCN driven by the impact of fast hydrogen atoms produced in photodissociation of parent molecules. However, their model overproduced the HNC abundance at ∼3 AU by about a factor of 2. In a subsequent paper Rodgers & Charnley (2001b) showed that the same mechanism cannot reproduce observed HNC/HCN abundance ratios in moderately active comets at ∼1 AU, such as comet C/1999 H1 (Lee). The applicability of the model to very active comets has also been questioned by interferometric observations of HNC and HCN in comet Hale-Bopp (Bockelée-Morvan et al. 2005; Bockelée-Morvan 2008), which show that the HNC/HCN visibility ratio is almost flat as a function of baseline, and equal to the single-dish flux ratio. This suggests that, contrary to model predictions, HNC in comet Hale-Bopp was produced efficiently in the inner coma (parent scale-length ≪2000 km).

Comet 73P/Schwassmann-Wachmann is a short-period (5.34 yr) comet of the Jupiter family that likely originated from the trans-Neptunian population in the outer solar system. Narrowband photometry and spectroscopic observations during the 1990 apparition showed that this comet is strongly depleted in C_2 and NH_2 relative to CN and OH, placing it in the 21P/Giacobini-Zinner class of odd comets with extreme depletions (A'Hearn et al. 1995; Fink & Hicks 1996). During its 1995 perihelion passage, comet 73P split into several fragments (Boehnhardt et al. 2002). Its 2006 apparition thus offered an exceptional opportunity to measure the HNC/HCN ratio in fragments of a Jupiter-family comet of deviant composition. Indeed, comet 73P made a very close approach to Earth in 2006 May (at 0.067 and 0.079 AU for fragments B and C,

[1] California Institute of Technology, Downs Laboratory of Physics 320-47, Pasadena, CA 91125; dcl@caltech.edu.
[2] Visiting Scientist, LESIA, Observatoire de Paris.
[3] LESIA and UMR 8109 du CNRS, Observatoire de Paris, 5 place Jules Janssen, 92195 Meudon, France; Dominique.Bockelee@obspm.fr, Jeremie.Boissier@obspm.fr, Jacques.Crovisier@obspm.fr; Nicolas.Biver@obspm.fr.
[4] Space Science and Astrobiology Division, MS 245-3, NASA Ames Research Center, Moffet Field, CA 94035; charnley@dusty.arc.nasa.gov.

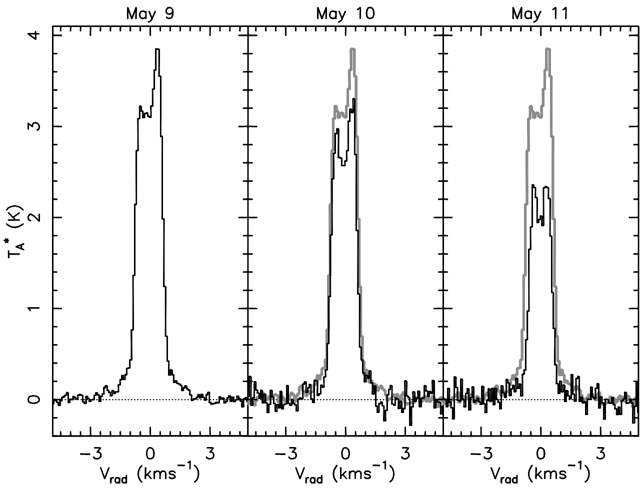

FIG. 1.— HCN $J = 4$–3 spectra in comet 73P/Schwassmann-Wachmann (fragment B) obtained on May 9–11 (*left to right, respectively*). Gray curves in the two right panels show the May 9 spectrum.

respectively), that compensated for its moderate activity (water production rate of a few $\times 10^{28}$ s^{-1} at perihelion) and allowing sensitive investigations.

In the present paper we compile the existing measurements of the HNC/HCN ratio in moderately active comets, including our sensitive upper limit obtained in comet 73P/Schwassmann-Wachmann and discuss possible implications for the origin of HNC in cometary atmospheres.

2. OBSERVATIONS

Observations of Comet 73P/Schwassmann-Wachmann (fragment B) presented here were carried out on 2006 May 9–11, UT using the 10.4 m Leighton Telescope of Caltech Submillimeter Observatory (CSO) on Mauna Kea in Hawaii. The heliocentric and geocentric distances of the comet at the time of the CSO observations were 1.02 and 0.072 AU, respectively. We used the 345 GHz facility SIS receiver and acoustooptical spectrometers with total bandwidths of 50 MHz and 1 GHz. The frequency scale of the spectrometers (the reference channel and the channel width) was established by injecting calibration signals from 10 and 100 MHz frequency comb generators, for the 50 MHz and 1 GHz AOS, respectively. The effective frequency resolution of the high-resolution (50 MHz bandwidth) spectrometer was 95 kHz (2 channels), corresponding to $\sim$0.08 km s^{-1}. Pointing of the telescope, checked by performing five-point continuum scans of Jupiter in the south, was determined to drift by $\lesssim 5''$ on timescales of $\sim$3 hr at the time of the observations (one-fifth of the $\sim 25''$ FWHM CSO beam at 360 GHz). The accuracy of the cometary ephemeris, checked by performing five-point scans of the HCN $J = 4$–3 transition in the comet, was determined to be $\sim 7''$–$9''$. The main-beam efficiency, determined from total-power observations of Jupiter, Saturn, and Mars, was measured to be $\sim$74%. The absolute calibration uncertainty of the individual measurements is $\sim$20%. However, since the HCN and HNC lines were observed almost simultaneously, with the same receiver, we estimate the calibration uncertainty of the HNC/HCN line ratio to be smaller, of order 15%.

HCN $J = 4$–3 spectra (rest frequency 354.50547 GHz) taken on May 9–11 UT are shown in Figure 1 and the line intensities are listed in Table 1, along with the corresponding statistical uncertainties, as determined from the noise level measured in the spectra. A significant decrease in the HCN intensity (by a factor of 1.8) is seen over the period of our observations, following an earlier outburst. The low-level pedestal, seen most clearly in the May 9 spectrum, is due to the HCN hyperfine structure (e.g., Lis et al. 1997). HNC $J = 4$–3 spectra (rest frequency 362.63031 GHz) taken on May 10–11 UT are shown in Figure 2. The HNC and HCN observations on these two nights were interleaved in time to account for the time variability of the outgassing. No HNC emission is detected (Table 1).

TABLE 1

HCN AND HNC LINE INTENSITIES

UT Date (2006)	I(HCN)	I(HNC)
May 9	5.35 ± 0.04	. . .
May 10	4.21 ± 0.08	0.073 ± 0.025
May 11	3.01 ± 0.06	−0.021 ± 0.018
May 10–11	3.62 ± 0.05	0.026 ± 0.015

NOTES.—Integrated line intensities, $T_A^*\,dv$ (K km s^{-1}), computed over the velocity range of −2 to 2 km s^{-1} (HCN; includes all hyperfine components) and −1 to 1 km s^{-1} (HNC). The uncertainties listed are 1 σ statistical uncertainties, as determined from the noise level measured in the spectra. The May 10–11 entry is a uniformly weighted average of the two corresponding spectra.

Fragment B of comet 73P underwent several outbursts during the 2006 April–May apparition, shedding tens of fragments, as imaged for example by the *Hubble Space Telescope* around 18 April (e.g., Weaver et al. 2006). On 8.0 May UT fragment B entered a new outburst phase, beginning as a strong brightness increase of its central condensation. Visual magnitudes reported in International Comet Quarterly (2006a, 2006b, 2006c, 2006d, 2006e) showed a fivefold increase in total brightness the following day and a 5–10 times increase in the water outgassing rate was seen in the Nançay and Odin data between May 7 and 10 (Crovisier et al. 2006; Colom et al. 2006).

Molecular production rates of HCN and HNC (3 σ upper limits) on May 10–11 are listed in Table 2. The resulting 3 σ upper limit for the HNC/HCN abundance ratio, based on the average of the May 10 and May 11 data is 1.1%. IRAM 30 m observations impose upper limits of 2.9 and 3.8% for the HNC/HCN

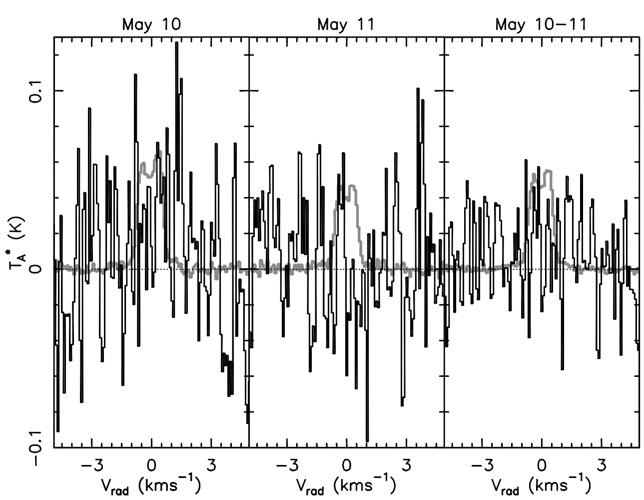

FIG. 2.—HNC $J = 4$–3 spectra in comet 73P/Schwassmann-Wachmann obtained on May 10–11 (*left and middle panels, respectively*). The right panel shows an uniformly weighted average of the two data sets. Gray curves show HCN $J = 4$–3 spectra on the corresponding days, scaled down by a factor of 50.

TABLE 2
HCN and HNC Production Rates

UT Date (2006)	Q(HCN)	Q(HNC)	Q(HCN)/Q(HNC) (%)
May 10	$(4.85 \pm 0.09) \times 10^{25}$	$<0.7 \times 10^{24}$	<1.4
May 11	$(3.05 \pm 0.06) \times 10^{25}$	$<0.5 \times 10^{24}$	<1.7
May 10–11	$(3.90 \pm 0.05) \times 10^{25}$	$<0.4 \times 10^{24}$	<1.1

Notes.—Productions rates (mol s^{-1}) computed assuming a gas temperature of 65 K and expansion velocities of 0.62 and 0.58 km s^{-1}, on May 10 and 11, respectively. Average pointing offsets of 3″ and 4″ for HCN and HNC, respectively, have been assumed. Since the HCN and HNC transitions studied here have similar rest frequencies and line strengths, the derived Q(HNC)/Q(HCN) ratio is insensitive to the detailed model assumptions.

ratio on May 14 and 18, respectively (Biver et al. 2006a), consistent with the low value presented here.

3. HNC/HCN RATIO IN COMETS

HNC has now been detected in 11 comets with water production rates in the range 3×10^{28}–4×10^{30} mol s^{-1} (e.g., Irvine et al. 1996; Crovisier et al. 2005; Biver et al. 2006b, 2006c), not counting the very active comets Hale-Bopp and C/2006 P1 (McNaught), where different chemical processes may be at work. The observed HNC/HCN abundance ratio is plotted in Figure 3 as a function of the water production rate. The plot appears to show a distinction between comets with water production rates above and below $\sim 4 \times 10^{29}$ mol s^{-1}. More productive comets seem to display a relatively high HNC/HCN ratio, ~0.2, with little scatter. The scatter increases significantly in weaker comets and no clear dependence of the observed abundance ratio on the water production rate is seen. Since water production rates in comets vary with the heliocentric distance and the measurements included in our sample span a wide range in r_h, we have outlined with gray circles in Figure 3 the measurements with r_h limited to a narrow range of 0.5–0.8 AU. This subsample includes four comets, which cover a wide range of water production rates. No dependence of the HNC/HCN ratio on the water production rate is seen. Therefore we conclude that, as explained below, the apparent distinction between the more productive and weak comets in Figure 3 is simply caused by selection effects, as all active comets in our sample happened to be observed at small heliocentric distances.

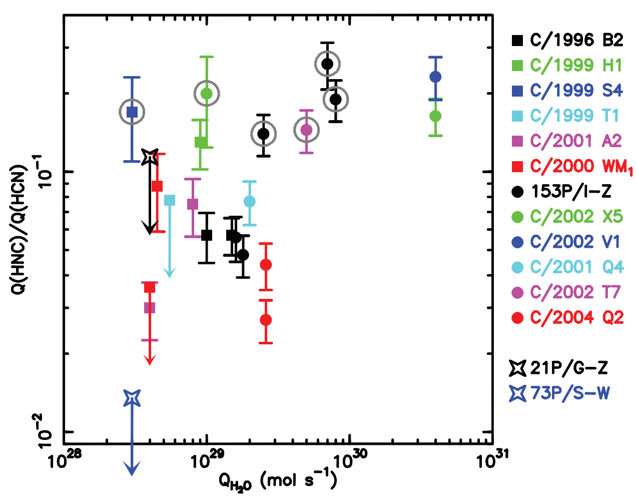

Fig. 3.—Observed HNC/HCN abundance ratio in comets as a function of the water production rate, Q_{H_2O}. Measurements at the heliocentric distances between 0.5 and 0.8 AU are surrounded by gray circles. References: C/1996 B2 (Hyakutake): Irvine et al. 1996; C/1999 H1 (Lee): Biver et al. 2000; C/1999 S4 (LINEAR): Bockelée-Morvan et al. 2001; C/1999 T1 (McNaught-Hartley): Biver et al. 2006b; C/2000 WM$_1$ (LINEAR): Biver et al. 2006b, Irvine et al. 2003; C/2001 A2 (LINEAR): Biver et al. 2006b; 153P/Ikeya-Zhang: Biver et al. 2006b, Irvine et al. 2003; C/2001 Q4 (NEAT), C/2002 T7 (LINEAR), C/2002 V1 (NEAT), C/2002 X5 (Kudo-Fujikawa), and C/2004 Q2 (Machholz): Biver et al. (2005) Crovisier et al. 2005; 21P/Giacobini-Zinner: Biver et al. 1999; 73P/Schwassmann-Wachmann: this work. The combined uncertainties of the individual measurements in the figure are assumed to be equal to the statistical uncertainties, as measured from the individual spectra, plus a 15% calibration uncertainty, added in quadrature.

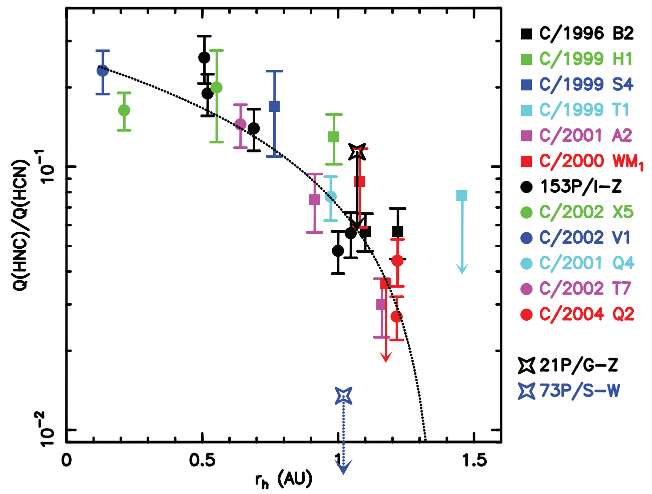

Fig. 4.—Observed HNC/HCN abundance ratio in comets as a function of the heliocentric distance, r_h. The dotted line shows a linear fit to the data for r_h between ~0.5 and 1.2 AU. The fitted slope is 0.192 ± 0.021; the observed variation of the HNC/HCN abundance ratio with r_h is thus statistically significant.

Figure 4 shows the dependence of the HNC/HCN ratio on the heliocentric distance of the comet. A clear variation is seen and, for r_h between ~0.5 and 1.2 AU, the ratio is well described by the linear relation

$$Q_{\rm HNC}/Q_{\rm HCN} = 0.26 - 0.19 r_h({\rm AU}), \quad (1)$$

shown as the dotted line in Figure 4. The formal 1 σ uncertainties of the intercept and the slope are 0.024 and 0.021, respectively. The two measurements at the smallest heliocentric distances, $r_h \sim 0.1$–0.2 AU (comets C/2002 X5 and C/2002 V1, both with relatively high water production rates of $\sim 4 \times 10^{30}$ mol s^{-1}), do fall slightly below the best-fit line. This may indicate that the dependence of the HNC/HCN abundance ratio on the heliocentric distance flattens for $r_h \lesssim 0.5$ AU. The least-squares fit given above is based on all measurements in the 0.5–1.2 AU heliocentric distance range. However, a similar r_h dependence is obtained from measurements of comets with the water production rates below 4×10^{29} mol s^{-1}, which restricts the r_h range to 0.75–1.2 AU (the slope given by the least-squares fit is 0.144 ± 0.031 vs. 0.191 ± 0.021 above; a ~1.3 σ difference). The more productive comets in our sample thus follow essentially the same HNC/HCN dependence on the heliocentric distance, as derived for weak comets. The apparent distinction between the two groups in Figure 3 is caused by the fact that all more productive comets in our sample happened to be observed preferentially close to the Sun.[5] The observed variation in the HNC/HCN abundance ratio

[5] Another way to separate the dependence of the HNC/HCN abundance ratio on r_h and Q_{H_2O} is by fitting the data with a combined power-law in the form $R = a r_h^b Q^c$, with a, b, and c being free parameters. The power-law fit diverges at small heliocentric distances, but in the range of r_h considered here, 0.5–1.2 AU, is a good representation of the measurements. For r_h in AU, and Q in the units of 10^{29} s^{-1}, the best-fit parameters are $a = 0.059 \pm 0.004$, $b = -2.30 \pm 0.21$, and $c = -0.09 \pm 0.08$. This confirms the presence of a strong dependence of the HNC/HCN ratio on the heliocentric distance and no statistically significant trend with the water production rate.

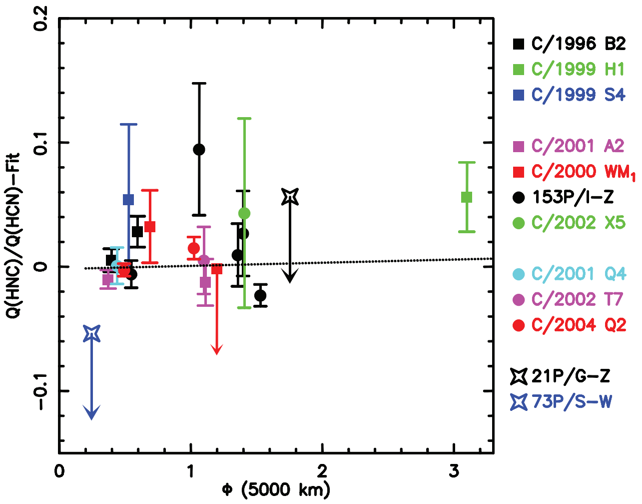

FIG. 5.—Deviation of the HNC/HCN abundance ratio from the best-fit line described in Fig. 4, in comets with r_h between 0.5 and 1.2 AU, plotted as a function of the telescope field of view (in the units of 5000 km). The dotted line shows a formal least-squares fit to the data. The fitted slope is 0.0025 ± 0.0063; no statistically significant trend is seen.

with the heliocentric distance is likely related to the change in the temperature of the grains in the coma, as the comet approaches the Sun.

The 3 σ upper limit of 1.1% for the HNC/HCN ratio in comet 73P/Schwassmann-Wachmann based on our observations is ~7 times lower than the typical value at 1 AU given by the least-squares fit to the measurements in other comets (Fig. 4, *dotted line*). Given the small geocentric distance of comet 73P at the time of our observations (0.072 AU), the HNC production rate could be significantly underestimated if the emission originates from an extended source in the coma. The production rates given above are computed assuming a parent density distribution for both molecules (direct release from the nucleus). The HNC production rate would increase by a factor of 7 if a daughter density distribution with a parent scale-length of ~5000 km is assumed. The resulting HNC/HCN abundance ratio in comet 73P would then be consistent with other measurements in moderately active long-period comets at 1 AU. Observations of comet Hale-Bopp with the Plateau de Bure Interferometer imply an HNC parent scale-length ≪2000 km (Bockelée-Morvan et al. 2005; Bockelée-Morvan 2008). The HNC parent scale-length has never been constrained directly by interferometric observations in moderately productive comets. However, observations of comet 153P/Ikeya-Zhang presented by Biver et al. (2006b) suggest that the HNC parent scale-length in this comet was less than 2500 km (equivalent to less then 7500 km when scaled to 1 AU), with the best-fit $L_p = 0$. To further investigate the effects of a possible extended source of HNC on the measured HNC/HCN abundance ratios, we plot in Figure 5 the HNC/HCN ratio in the long-period comets observed to date as a function of the telescope field of view (the linear trend with the heliocentric distance given by equation (1) has been subtracted out). The formal linear fit is shown as a dotted line; no statistically significant trend is seen. A combined power-law fit to the HNC/HCN abundance ratio, as a function of the heliocentric distance and the field of view, Φ (in the units of 5000 km), in the form $R = ar_h^b\Phi^c$, gives $a = 0.058 \pm 0.004$, $b = -2.03 \pm 0.21$, and $c = 0.10 \pm 0.12$. This confirms that no trend with the field of view is apparent in the data. We note that other comets in our sample, including comet Hyakutake, were observed with a telescope field of view ~2000 km. If the HNC parent scale-length at 1 AU is indeed of order 5000 km, the HNC production rates and the resulting HNC/HCN abundance ratios in these objects would scale up accordingly. While only future sensitive interferometric observations will be able to unequivocally constrain the HNC parent scale-length, a possible extended source of HNC cannot explain the discrepancy between the HNC/HCN ratio in comet 73P and the values measured in other moderately active comets at 1 AU.

Comet 73P/Schwassmann-Wachmann is the first short-period (Jupiter-family) comet in which a sensitive upper limit for the HNC/HCN ratio has been obtained. Our observations might thus indicate that HNC is depleted in Jupiter family comets, for example due to evolutionary effects in the ices in the outer layers of the nucleus. However, comet 73P was in the process of break-up and fragmentation, with fresh unprocessed material exposed for the first time to solar radiation. Infrared and radio observations (Dello Russo et al. 2008; Biver et al. 2006a) show remarkable similarity in the composition of fragments B and C. All measured volatiles, except HCN, were depleted with respect to water in both fragments, compared to other comets. Furthermore, no evidence of temporal variations in the compositions of the fragments during and between outbursts was seen. The explanation of the low HNC/HCN ratio in comet 73P/Schwassmann-Wachmann as due to evolutionary effects in the surface layers of the nucleus thus appears unlikely.

A comparison of the HNC abundance in comet 73P/Schwassmann-Wachmann with that measured in comet C/1999 S4 (LINEAR) is particularly interesting, as both comets were in the process of break-up, with fresh material exposed to the solar radiation. Based on their IR measurements, Dello Russo et al. (2008) argue that relative abundances of parent volatiles in comet 73P/Schwassmann-Wachmann (with the exception of HCN) resemble those in C/1999 S4 and are in the depleted range with respect to the majority of comets characterized to date (see also Villanueva et al. 2006). HNC was detected in C/1999 S4 with an abundance of ~17% with respect to HCN at a heliocentric distance of 0.77 AU in a small field of view of 2600 km (Bockelée-Morvan et al. 2001). Correcting for the difference in the heliocentric distance, as given by equation (1), this is a factor of ~11 higher than the 3 σ upper limit in 73P/Schwassmann-Wachmann. The HNC abundance relative to water is also higher in C/1999 S4, by a factor of ~8–9; 1.7×10^{-4} (Bockelée-Morvan et al. 2001) versus $\lesssim 2 \times 10^{-5}$ (N. Biver et al., in preparation) We next consider coma chemistry versus gas-grain processes as means of producing HNC.

4. ORIGIN OF COMETARY HNC

Rodgers & Charnley (2001b) considered a wide range of possible explanations for the origin of HNC in moderately active comets. They ruled out the production by ion-molecule chemistry or by reactions of energetic hydrogen atoms with HCN. They also ruled out photodissociation of small organic molecules, such as CH_2NH, HNCO, and other N-bearing compounds. This left large organic molecules or polymers as possible parents of HNC. One possible candidate was hexamethylenetetramine (HMT; $C_6H_{12}N_4$), produced by UV irradiation of simple ices containing ammonia, water, formaldehyde, and methanol. However, this compound was shown to be stable to thermal degradation (Fray 2004) and therefore an unlikely parent of HNC. Rodgers & Charnley (2001b) also suggested HCN polymers (or oligomers), produced from irradiated HCN molecules in the nuclear or precometary ices, as a possible parent of HNC (once HCN tetrameters are formed, they can easily polymerize to polyaminocyanomethylene (PACM; [-(NH_2)C(CN)-]$_n$), which can then undergo ring closure to form ladder polymers). If such polymers are present in cometary nuclei, one would expect their abundance in the coma to be correlated with that of HCN. The abundance of HCN in comet 73P/Schwassmann-Wachmann implied by IR and radio observations (Biver et al. 2006a; Villanueva et al. 2006; Dello Russo et al. 2007) is near the high end of measurements in $\sim$30 comets observed at radio wavelengths (Biver et al. 2002, 2006b). PACM polymers should thus be quite abundant in this particular comet and the low HNC abundance implied by our measurements appears to argue against PACM as a source of cometary HNC.

A different class of HCN polymers, formed not from HCN molecules, but instead from ammonia and acetylene, has been invoked to explain the low $^{14}N/^{15}N$ ratio observed in CN in several comets, a factor of 2 below that measured in HCN in comet Hale-Bopp (e.g., Jehin et al. 2004). In this scenario, some CN is produced from photodissociation of HCN, however a secondary, presumably polymeric, source of CN is needed. In cold, dense interstellar material, large ^{15}N enhancements may be present in ammonia ices (Charnley & Rodgers 2002). These ices could be precursors of cometary material. Further energetic processing is required to incorporate this nitrogen reservoir into organic material (e.g., addition of NH_2 side-groups to PAH molecules; Charnley 2002). The secondary source of CN in cometary comae may thus be a polymer produced from ammonia, since only interstellar ammonia can obtain sufficiently low $^{14}N/^{15}N$ ratios, and from carbon compounds, such as acetylene, methane, or ethane.

The initial analysis of the *Stardust* organic data (Sandford et al. 2006) indicates that a significant fraction of organic nitrogen is in a form of aliphatic carbon, with methylamine (CH_3NH_2) and ethylamine ($CH_3CH_2NH_2$) being the two major carriers identified, with similar abundances. These species are very volatile, and Sandford et al. (2006) argue that they are likely present in the cometary material in a form of an amine-rich organic polymer rather than as a free primary amine. One may speculate that energetic processing of ices containing ammonia, methane, and ethane could produce these molecules, as well as perhaps some organic polymers. Laboratory studies are urgently needed to test this idea. If such polymers are also a source of cometary HNC, the low HNC abundance in comet 73P/Schwassmann-Wachmann appears consistent with the observed depletion of ammonia and acetylene implied by IR observations (Dello Russo et al. 2007).

We note that the rotational spectrum of methylamine in the 49–326 GHz frequency range has now been measured in the laboratory (Ilyushin et al. 2005). It is thus feasible to search for this species in relatively active comets.

A comparison of the HNC/HCN ratio in comet 73P/Schwassmann-Wachmann with measurements in other members of the 21P/Giacobini-Zinner compositional class is of great interest. This class includes objects with extreme C_2 and NH_2 depletions that are related to C_2H_2 and NH_3 depletions in nuclear ices. We would expect a low HNC/HCN ratio in these objects as well. So far, very few members of this class have been identified (Fink & Hicks 1996). The upper limit for the HNC/HCN ratio in Giacobini-Zinner obtained during its 1998 apparition (<11%, Biver et al. 1999; Fig. 3) is not sensitive enough to draw definitive conclusions. Comet 21P/Giacobini-Zinner will make a favorable apparition in 2018 (at 0.4 AU from the Earth), during which sensitive measurements will be possible using the Atacama Large Millimeter/Submillimeter Array (ALMA).

5. SUMMARY

Observations of hydrogen isocyanide in cometary atmospheres carried out to date indicate that the HNC production has to be efficient in the inner coma, just as the material leaves the nucleus. The process has to be temperature dependent to explain the observed variation in the HNC/HCN ratio with the heliocentric distance. Thermal degradation of macromolecules or polymers produced from ammonia and carbon compounds, such as acetylene, methane, or ethane appears consistent with all existing data, including the very low HNC/HCN ratio in comet 73P/Schwassmann-Wachmann reported here. Such polymers have been invoked previously to explain anomalous $^{14}N/^{15}N$ ratios measured in cometary CN.

Additional interferometric observations of HNC in comets are needed to provide constraints on the spatial distribution of this molecule in the cometary comae. Such observations will soon be possible in moderately productive comets with (sub)millimeter interferometers (e.g., e-SMA). Measurements of the $H^{15}NC/H^{14}NC$ isotopic ratio would be instrumental in determining whether the HCN polymers similar to those invoked to explain the enhanced ^{15}N abundance in CN may also be a source of cometary HNC. However, such measurements will have to await the commissioning of ALMA.

This research has been supported by NSF grant AST 05-40882 to the Caltech Submillimeter Observatory. D. C. L. acknowledges support from the Observatoire de Paris during his stay in Meudon. S. B. C. acknowledges support from NASA's Planetary Atmospheres Program. We thank N. Fray for useful discussions and the referee, M. DiSanti, for a thorough and helpful review of the manuscript.

REFERENCES

A'Hearn, M. F., Millis, R. L., Schleicher, D. G., Osip, D. J., & Birch, P. V. 1995, Icarus, 118, 223
Biver, N., Bockelée-Morvan, D., Crovisier, J., Colom, P., Henry, F., Moreno, R., Paubert, G., Despois, D., & Lis, D. C. 2002, Earth Moon Planets, 90, 323
Biver, N., et al. 1997, Science, 275, 1915
———. 1999, in Asteroids, Comets, and Meteors, Book of Abstracts (Ithaca: Cornell Univ.), 50
———. 2000, AJ, 120, 1554
———. 2006a, BAAS, 38, 484
———. 2006b, A&A, 449, 1255
———. 2006c, in IAU Symp. 229, Asteroids, Comets, and Meteors, ed. D. Lazzaro, S. Ferraz-Mello & J.A. Fernández (Cambridge: Cambridge Univ. Press), 43
Blackman, G. L., Brown, R. D., Godfrey, P. D., & Gunn, H. I. 1976, Nature, 261, 395
Bockelée-Morvan, D., Gunnarsson, M., Biver, N., Charnley, S., Crovisier, J., Lis, D. C., & Rodgers, S. 2005, in Asteroids, Comets, and Meteors, Book of Abstracts (Ithaca: Cornell Univ.), 111
Bockelée-Morvan, D. 2008, Ap&SS, in press
Bockelée-Morvan, D., et al. 2001, Science, 292, 1339
Boehnhardt, et al. 2002, Earth Moon Planets, 90, 131
Charnley, S. B. 2002, in Proc. Second European Workshop on Exo/Astrobiology, ed. H. Locoste (ESA SP-518; Noordwijk: EAS), 33
Charnley, S. B., & Rodgers, S. D. 2002, ApJ, 596, L113
Charnley, S. B., Rodgers, S. D., Kuan, Y.-J., & Huang, H.-C. 2002, Adv. Space Res., 30, 1419
Colom, P., Crovisier, J., Biver, N., Bockelée-Morvan, D., Boissier, J., & Lecacheux, A. 2006, in SF2A-2006: Semaine de l'Astrophysique Française, ed. D. Barret et al. (Paris: French Astron. Soc. Astrophys.), 389
Crovisier, J., et al. 2005, BAAS, 37, 646
———. 2006, BAAS, 38, 485
Dello Russo, N., et al. 2007, Nature, 448, 172
Fink, U., & Hicks, M. D. 1996, ApJ, 459, 729
Fray, N. 2004, Ph.D. thesis, Univ. Paris XII
Herbst, E., Terzieva, R., & Talbi, D. 2000, MNRAS, 311, 869
Hirota, T., Yamamoto, S., Mikami, H., & Ohishi, M. 1998, ApJ, 503, 717

Ilyushin, V. V., Alekseev, E. A., Dyubko, S. F., Motiyenko, R. A., & Hougen, J. T. 2005, J. Mol. Spectrosc., 229, 170
International Comet Quarterly. 2006a, 139, 100
———. 2006b, 139, 116
———. 2006c, 140, 137
———. 2006d, 140, 151
———. 2006e, 140, 174
Irvine, W. M., Bergin, E. A., Dickens, J. E., Jewitt, D., et al. 1998, Nature, 393, 547
Irvine, W. M., Bockelée-Morvan, D., Lis, D. C., Matthews, H. E., Biver, N., et al. 1996, Nature, 383, 418
Irvine, W. M., et al. 2003, Origin of Life Evol. Biosphere, 33, 609
Jehin, E., Manfroid, J. Cochran, A. L., Arpigny, C., et al. 2004, ApJ, 613, L161
Lis, D. C., et al. 1997, Icarus, 130, 355
Rodgers, S. D., & Charnley, S. B. 1998, ApJ, 501, L227
———. 2001a, ApJ, 546, 324
———. 2001b, MNRAS, 323, 84
Sandford, S. A., et al. 2006, Science, 314, 1720
Schilke, P., Walmsley, C. M., Pineau des Forêts, Roueff, E., Flower, D. R., & Guilloteau, S. 1992, A&A, 256, 595
Snyder, L. E., & Buhl, D. 1972, in Ann. NY Acad. Sci. 194, Natl. Radio Astron. Obs., Rep. Ser. B, No. 317, 17
Weaver, H. A., et al. 2006, BAAS, 38, 490
Villanueva, G. L., et al. 2006, ApJ, 650, L87
Zuckerman, B., Morris, M. P., Palmer, P., & Turner, B. E. 1972, ApJ, 173, L125