

## LARGE EXCESS OF HEAVY NITROGEN IN BOTH HYDROGEN CYANIDE AND CYANOGEN FROM COMET 17P/HOLMES

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Received 2008 February 6; accepted 2008 April 4; published 2008 April 23

### ABSTRACT

From millimeter and optical observations of the Jupiter-family comet 17P/Holmes performed soon after its huge outburst of 2007 October 24, we derive  $^{14}\text{N}/^{15}\text{N} = 139 \pm 26$  in HCN and  $^{14}\text{N}/^{15}\text{N} = 165 \pm 40$  in CN, establishing that HCN has the same nonterrestrial isotopic composition as CN. The same conclusion is obtained for the long-period comet C/1995 O1 (Hale-Bopp) after a reanalysis of previously published measurements. These results are compatible with HCN being the prime parent of CN in cometary atmospheres. The  $^{15}\text{N}$  excess relative to the Earth's atmospheric value indicates that N-bearing volatiles in the solar nebula underwent important N isotopic fractionation at some stage of solar system formation. HCN molecules never isotopically equilibrated with the main nitrogen reservoir in the solar nebula before being incorporated in Oort Cloud and Kuiper Belt comets. The  $^{12}\text{C}/^{13}\text{C}$  ratios in HCN and CN are measured to be consistent with the terrestrial value.

*Subject headings:* comets: general — comets: individual (17P/Holmes) — radio lines: solar system

### 1. INTRODUCTION

Comets are made of ices, organics, and minerals that are a record of the chemistry of the outer regions of the primitive solar nebula where they agglomerated 4.6 Gyr ago. Compositional analyses of comets can provide important clues to the chemical and physical processes that occurred in the early phases of solar system formation, and in the natal molecular cloud that predated the formation of the solar nebula (Ehrenfreund et al. 2005). In particular, isotopic ratios in cometary volatiles are important diagnostics of how this matter formed, since isotopic fractionation is very sensitive to chemical and physical conditions. However, such measurements are rare. Strong deuterium enhancements are observed in  $\text{H}_2\text{O}$  and HCN gases of several comet comae that are characteristic of interstellar or protosolar chemistry at low temperature (Ehrenfreund et al. 2005; Bockelée-Morvan et al. 2005). On the other hand, questions arise as to how to explain the nonterrestrial and uniform values of the  $^{14}\text{N}/^{15}\text{N}$  isotopic ratio in CN (Arpigny et al. 2003; Hutsemékers et al. 2005; Manfroid et al. 2005; Jehin et al. 2004), also indicative of interstellar-like chemistry, when this ratio was measured to be terrestrial in HCN (Jewitt et al. 1997; Ziurys et al. 1999), the presumed source of CN radicals in cometary atmospheres. Here we present measurements of the  $\text{HC}^{14}\text{N}/\text{HC}^{15}\text{N}$  and  $\text{H}^{12}\text{CN}/\text{H}^{13}\text{CN}$  isotopic ratios acquired in comet 17P/Holmes by millimeter spectroscopy, together with

$\text{C}^{14}\text{N}/\text{C}^{15}\text{N}$  and  $^{12}\text{CN}/^{13}\text{CN}$  measurements from visible spectroscopy. The brightness of this short-period (6.9 yr) comet of the Jupiter family unexpectedly increased (from a total visual magnitude  $m_v = 17$  to  $m_v = 2.5$ ) on 2007 October 24 while it was at a distance of 1.63 AU from the Earth and 2.44 AU from the Sun (Green 2007). This huge outburst of activity, which is likely related to a sudden fragmentation of the nucleus, followed by the subsequent production of a large quantity of grains, offered us the opportunity to search for weak spectral signatures of rare isotopes using complementary techniques.

### 2. THE $^{14}\text{N}/^{15}\text{N}$ RATIO IN HCN IN 17P/HOLMES

We carried out observations of 17P/Holmes using the 30 m telescope of the Institut de Radioastronomie Millimétrique (IRAM) located in the Sierra Nevada (Spain). Isotopic measurements were performed on October 27–28 UT. The tracking of the comet was done using orbital elements K077/06 from the JPL HORIZONS system. The pointing of the telescope was checked and updated by repeated observations of a nearby quasar. Sky cancellation was performed by wobbling the secondary mirror with a throw of 3' at a rate of 0.5 Hz. Four receivers could be operated at the same time. The  $J = 3-2$  rotational lines of  $\text{H}^{12}\text{C}^{14}\text{N}$  (hereafter referred to as HCN) at 265.9 GHz,  $\text{H}^{13}\text{CN}$  (259.0 GHz) and  $\text{HC}^{15}\text{N}$  (258.2 GHz) were measured (Table 1). The beam diameter (half-power beamwidth) of 9.5'' corresponded to 11,300 km at the distance of the comet. Observations were undertaken in good atmospheric conditions (3–5 mm precipitable water). The lines were observed both at low (1 or 2 MHz) and high (62 kHz) spectral resolutions. Spectra are shown in Figures 1 and 2, and line areas are given in Table 1. Observations of HCN,  $\text{H}^{13}\text{CN}$ , and  $\text{HC}^{15}\text{N}$  were not entirely simultaneous (Table 1). However, several strong lines ( $\text{CS } J = 3-2$ ,  $\text{CH}_3\text{CN } J = 8-7$  [147 GHz], and  $\text{CH}_3\text{OH } J = 3-2$  [145 GHz] lines) were continuously observed, as a way to monitor the comet's activity. Their intensities decreased by 12% during the period (5.5 hr long) when HCN,  $\text{H}^{13}\text{CN}$ , and  $\text{HC}^{15}\text{N}$  data were acquired. This variation was taken into account when deriving the isotopic ratios.

In contrast to the  $\text{HC}^{15}\text{N}$  and  $\text{H}^{13}\text{CN}$  lines,  $\text{HCN } J = 3-2$  is

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TABLE 1  
CHARACTERISTICS OF RADIO LINES AND MOLECULAR PRODUCTION RATES IN COMET 17P/HOLMES

| Molecule           | Line               | Frequency (GHz) | Date UT (2007 October) | Int. Time (minutes) | Line Area (K km s <sup>-1</sup> ) | Opacity | Column Density (10 <sup>12</sup> molecules cm <sup>-2</sup> ) | Production Rate (10 <sup>26</sup> molecules s <sup>-1</sup> ) |
|--------------------|--------------------|-----------------|------------------------|---------------------|-----------------------------------|---------|---|---|
| HCN                | $J = 3-2$          | 265.886434      | 27.96–27.98            | 15                  | 18.23 ± 0.14                      | 0.56    | 20.8 ± 0.17   | 19.85 ± 0.16  |
|                    | $J = 3-2, F = 2-2$ | 265.888516      | 27.96–27.98            | 15                  | 0.958 ± 0.083                     | 0.03    | 20.7 ± 1.8  | 19.74 ± 1.71  |
|                    | $J = 3-2, F = 3-3$ | 265.884883      | 27.96–27.98            | 15                  | 1.097 ± 0.073                     | 0.03    | 23.7 ± 1.6  | 22.60 ± 1.50  |
| H <sup>13</sup> CN | $J = 3-2$          | 259.011798      | 28.08–28.19            | 90                  | 0.220 ± 0.037                     | 0.008   | 1.74 ± 0.30   | 0.164 ± 0.028   |
| HC <sup>15</sup> N | $J = 3-2$          | 258.156996      | 27.96–28.19            | 145                 | 0.191 ± 0.021                     | 0.006   | 1.51 ± 0.16   | 0.140 ± 0.015   |

NOTES.—Total integration time, including time spent off-source; error bars are 1  $\sigma$ ; line areas refer to the main-beam brightness temperature scale; column densities and production rates were determined using the radiative transfer model of Biver et al. (1999), with  $x_{n_c} = 0.5$  and a steady state coma with  $T_{\text{kin}} = 45$  K as described in the text. The production rates determined from the whole HCN line and from the optically thin lines (i.e., the HCN hyperfine components, the H<sup>13</sup>CN and HC<sup>15</sup>N lines) are 6% lower and 6% higher, respectively, using  $T_{\text{kin}} = 65$  K derived by Dello Russo et al. (2008) from HCN infrared observations on 2007 October 27.6.

optically thick (Table 1). Therefore, radiative transfer modeling is required to retrieve the HCN/H<sup>13</sup>CN and HCN/HC<sup>15</sup>N isotopic ratios if the HCN  $J = 3-2$  line is used in the analysis. The coma of comet Holmes was in a nonequilibrium regime following its outburst, with gas-phase species released by icy grains. Unavoidable simplifying model assumptions on the coma structure could introduce systematic opacity-dependent errors in the retrievals and affect the determination of the isotopic ratios. However, the HCN  $J = 3-2$  line is split into six hyperfine components, two of which ( $F = 2-2$  and  $F = 3-3$ ) are well separated from the core of the line and are detected in the HCN spectrum (Fig. 2; Table 1). These hyperfine components have intrinsic line strengths of 3.7% the total strength, according to hyperfine statistical weights, and are optically thin (Table 1). The HCN/H<sup>13</sup>CN and HCN/HC<sup>15</sup>N abundance ratios, determined using the HCN optically thin hyperfine components, do not depend on model assumptions on coma temperature, structure, and temporal variability, because, in this case, emission lines from molecules in the same excitation state and in the same regions of the coma are compared. They are directly given by the line intensity ratios, albeit with minor corrections that account for the slightly different line frequencies. Using the HCN hyperfine components, and correcting for the nonsimultaneity of the HCN, H<sup>13</sup>CN, and HC<sup>15</sup>N measurements, we derive H<sup>12</sup>CN/H<sup>13</sup>CN = 114 ± 26 and HC<sup>14</sup>N/HC<sup>15</sup>N = 139 ± 26.

Column densities and production rates determined with the radiative transfer model of Biver et al. (1999) are given in Table 1. We assumed a steady state isotropic parent molecule distribution, with a gas velocity of 0.56 km s<sup>-1</sup> and a gas kinetic temperature  $T_{\text{kin}}$  of 45 K inferred from IRAM observations of multiple lines of CH<sub>3</sub>OH on October 29.0 UT. Interestingly, isotopic ratios obtained using the HCN production rate deduced from the whole  $J = 3-2$  line are similar to those obtained using the model-independent hyperfine line method. As shown

in Figure 2, when the dayside and nightside HCN velocities are fixed to 0.6 and 0.4 km s<sup>-1</sup>, the model provides a satisfactory fit to the shape of the HCN line. This suggests that our description of the HCN spatial distribution and excitation is correct in first approximation. This conclusion is supported by the good agreement between the HCN production rate measured on October 27.6 in a smaller ( $\sim 1''$ ) aperture (Dello Russo et al. 2008) and those reported in this work.

### 3. THE <sup>14</sup>N/<sup>15</sup>N RATIO IN CN IN 17P/HOLMES

High-resolution optical observations were performed to measure the <sup>14</sup>N/<sup>15</sup>N and <sup>12</sup>C/<sup>13</sup>C ratios in CN. Spectra of the  $B^2\Sigma^+ - X^2\Sigma^+ (0, 0)$  CN band at 388 nm were obtained on October 25.4, 28.3, 29.4, 30.4, and 31.4 and on November 18.4 and 19.3 2007 UT with the 2D coude spectrograph at the 2.7 m Harlan J. Smith telescope of the McDonald Observatory. A series of short exposures, from 30 s to 5 minutes, were also collected on 2007 October 29.6 UT with the High Resolution Echelle Spectrometer of the Keck I telescope installed on Mauna Kea (Hawaii). The observations were carried out under clear weather and low air mass. In both cases, the slit of the spectrograph was  $\sim 1''$  wide and  $\sim 7''$  long, providing a resolving power of about  $\lambda/\Delta\lambda = 60,000$  (0.03 Å pixel<sup>-1</sup>). The slit was centered on the false nucleus in the case of the Keck spectra and displaced in the coma (by up to 20'') for the McDonald exposures (20 minutes), to reduce the contamination by the strong dust-reflected spectrum. The dust-reflected sunlight underlying the spectral lines [among which are rovibrational lines of the <sup>12</sup>C<sup>14</sup>N, <sup>13</sup>C<sup>14</sup>N, and <sup>12</sup>C<sup>15</sup>N (0, 0) band] was removed by subtracting a solar reference spectrum after the appropriate Doppler shift, profile fitting, and normalization were applied (Arpigny et al. 2003; Jehin et al. 2004). The individual CN (0, 0) spectra were then combined with an optimal weighting

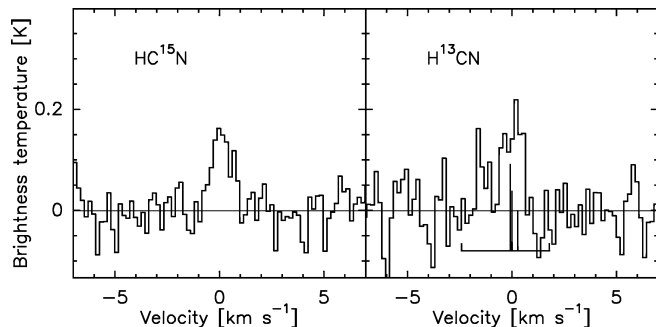


FIG. 1.—Spectra of the  $J = 3-2$  lines of HC<sup>15</sup>N and H<sup>13</sup>CN in comet 17P/Holmes on 2007 October 27–28. The velocity frame is with respect to the comet rest velocity. The positions and relative intensities of the hyperfine components of H<sup>13</sup>CN  $J = 3-2$  are shown.

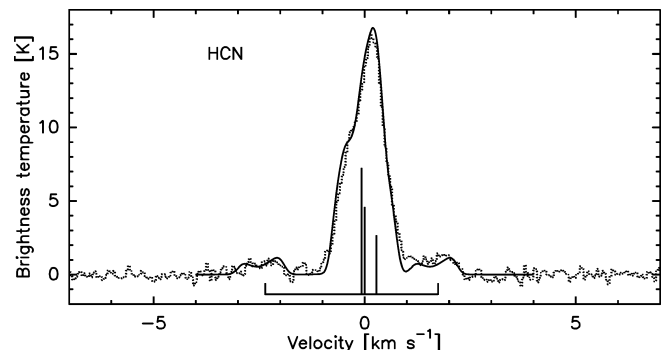


FIG. 2.—Model fit (solid line; see text) to the  $J = 3-2$  HCN line profile observed in comet 17P/Holmes on October 27.97 UT (dotted line). Positions and relative intensities of the hyperfine components are shown.

scheme in order to maximize the overall signal-to-noise ratio. Synthetic spectra of  $^{12}\text{C}^{14}\text{N}$ ,  $^{13}\text{C}^{14}\text{N}$ , and  $^{12}\text{C}^{15}\text{N}$  were computed for each observing circumstance using a fluorescence model (Zucconi & Festou 1985). We took into account slightly different excitation conditions over the period of the observations caused by small variations of the heliocentric distance and velocity. Collisional effects were empirically estimated by fitting the  $^{12}\text{C}^{14}\text{N}$  lines (Manfroid et al. 2005). The synthetic spectra were then co-added in the same way as the data. The isotope mixture was adjusted to best fit the observed continuum-subtracted spectrum. We considered seven *R*-branch lines (*R*3–*R*9), as shown in Figure 3. The isotopic ratios of  $^{12}\text{C}/^{13}\text{C}$  and  $^{14}\text{N}/^{15}\text{N}$  in the final co-added Keck and McDonald spectrum are estimated to be  $90 \pm 20$  and  $165 \pm 40$ , respectively.

#### 4. REANALYSIS OF THE COMET HALE-BOPP DATA

The  $^{14}\text{N}/^{15}\text{N}$  ratios measured in HCN and CN in comet 17P/Holmes are consistent with each other. In contrast, an  $\text{HC}^{14}\text{N}/\text{HC}^{15}\text{N}$  ratio marginally higher than the Earth's atmospheric value (272) was reported for comet C/1995 O1 (Hale-Bopp) (Jewitt et al. 1997; Ziurys et al. 1999), whereas the  $^{14}\text{N}/^{15}\text{N}$  value measured in CN is  $140 \pm 35$  (Arpigny et al. 2003). This led us to reanalyze the measurements made in comet Hale-Bopp.

Our reanalysis of the data of Ziurys et al. (1999) obtained on 1997 March 24 and 25 yields  $^{12}\text{C}/^{13}\text{C} = 65 \pm 13$  and  $^{14}\text{N}/^{15}\text{N} = 152 \pm 30$  (with a 10% calibration uncertainty included), as compared with the  $\text{HC}^{14}\text{N}/\text{HC}^{15}\text{N}$  production rate ratios of  $100 \pm 20$  and  $286 \pm 82$  given by these authors. Ziurys et al. used approximate formulas to analyze the optically thick HCN lines, assuming, in addition, an inappropriate value for the rotational temperature of HCN. Instead, we used full radiative transfer modeling. Our determinations are likely more reliable, as the HCN production rates that we derive from the  $J = 1-0$ ,  $2-1$ , and  $3-2$  HCN lines observed on March 24 are consistent within 5%, whereas the values inferred by Ziurys et al. from the different lines differ by up to a factor of 2. The  $\text{HC}^{15}\text{N}$  and  $\text{H}^{13}\text{CN}$   $J = 3-2$  lines were observed on March 25. As one cannot exclude day-to-day variations in HCN production from March 24 to 25, the  $\text{HC}^{15}\text{N}/\text{H}^{13}\text{CN}$  ratio of  $0.43 \pm 0.10$ , deduced from March 25 data only, could be more secure. In this case, assuming  $^{12}\text{C}/^{13}\text{C}$  to be equal to the terrestrial value of 89, we deduce  $^{14}\text{N}/^{15}\text{N} = 207 \pm 48$ .

The data obtained by Jewitt et al. (1997) at the James Clerk Maxwell Telescope (JCMT) are public and available from the Canadian Astronomy Data Centre. Reanalyzing these data, we found the following: (1) The HCN data were acquired during nighttime near sunrise, whereas  $\text{H}^{13}\text{CN}$  and especially  $\text{HC}^{15}\text{N}$  were observed later during daytime; the beam efficiency may have degraded by 20% according to JCMT specifications. (2) The HCN line was observed with the receiver B3 tuned in double sideband (DSB), whereas the other lines were observed in single sideband; HCN spectra of calibration sources obtained with the same receiver DSB tuning as used for the cometary observations show signals in excess of 15% with respect to reference spectra of the sources. (3) The  $\text{H}^{13}\text{CN}$   $J = 4-3$  line is blended with the  $\text{SO}_2$   $13_{2,12}-12_{1,11}$  line at 345.338538 GHz (Lis et al. 1997); using the  $\text{SO}_2/\text{HCN}$  production rate ratio determined for comet Hale-Bopp (Bockelée-Morvan et al. 2000), we estimate that it affects the  $\text{H}^{13}\text{CN}$  line intensity by 20%. (4) More critically, the  $\text{HC}^{15}\text{N}$  spectra present scan-to-scan intensity variations by a factor of 2 (a factor of 10 above the fluctuations related to the statistical noise) that are likely of instrumental origin. Taking these corrections into account, we infer  $^{12}\text{C}/^{13}\text{C} = 94 \pm 8$  and  $^{14}\text{N}/^{15}\text{N} = 205 \pm 70$ ,

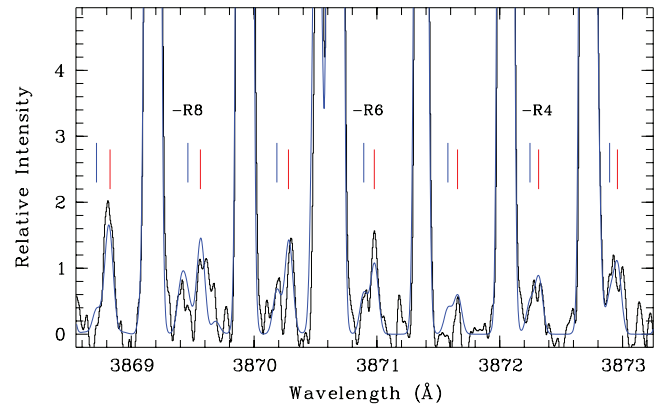


FIG. 3.—Small part of the co-added Keck and McDonald CN (0, 0) band spectra of comet 17P/Holmes showing seven *R*-branch lines (*R*3–*R*9) of CN isotopes (black line). The dust-scattered solar spectrum was removed. The positions of the  $^{13}\text{C}^{14}\text{N}$  (red ticks) and  $^{12}\text{C}^{15}\text{N}$  (blue ticks) lines are indicated; the corresponding lines of the main isotope are on the left. The synthetic spectrum with  $^{12}\text{C}/^{13}\text{C} = 90$  and  $^{14}\text{N}/^{15}\text{N} = 165$  is superimposed (blue line).

whereas the values given in Jewitt et al. (1997) are  $100 \pm 12$  and  $323 \pm 46$ , respectively. The large uncertainty in our  $^{14}\text{N}/^{15}\text{N}$  determination reflects the dispersion of the  $\text{HC}^{15}\text{N}$  measurements.

We conclude that the  $^{14}\text{N}/^{15}\text{N}$  ratio in HCN is rather uncertain for comet Hale-Bopp but is consistent with the value measured in CN.

#### 5. IMPLICATIONS

The  $^{12}\text{C}/^{13}\text{C}$  values in HCN and CN are in agreement with the terrestrial value of 89 and previous measurements in comets (e.g., Bockelée-Morvan et al. 2005).

The  $^{14}\text{N}/^{15}\text{N}$  ratios measured in HCN and CN in comet 17P/Holmes both correspond to a factor of 2  $^{15}\text{N}$  enrichment relative to the Earth's atmospheric value and are consistent with the  $^{14}\text{N}/^{15}\text{N}$  ratios measured in CN in a dozen comets that cluster at  $141 \pm 29$  (Arpigny et al. 2003; Hutsemékers et al. 2005; Manfroid et al. 2005; Jehin et al. 2004). The discrepancy between HCN and CN isotopic ratios previously found for comet Hale-Bopp led to the suggestion of a CN production mechanism other than HCN photolysis in cometary atmospheres, possibly from the thermal degradation of  $^{15}\text{N}$ -rich refractory organics present in dust grains. This interpretation was supported by the presence of CN jets, by the radial distribution of CN, found to be generally less extended than expected from HCN photodissociation, and by the CN/HCN production rate ratio, which exceeds unity in some comets (Fray et al. 2005). However, questions arose as to how to explain the equally low  $\text{C}^{14}\text{N}/\text{C}^{15}\text{N}$  value observed in comet Hale-Bopp at large heliocentric distance, where the CN radicals were expected to be mainly HCN photodissociation products (Manfroid et al. 2005; Rauer et al. 2003). Our reanalysis of the Hale-Bopp data, which shows that the  $^{14}\text{N}/^{15}\text{N}$  ratio in HCN encompasses the CN value, solves this issue. Also, the similar isotopic ratios found in HCN and CN provide a better explanation for the uniform values of the  $\text{C}^{14}\text{N}/\text{C}^{15}\text{N}$  ratio among comets exhibiting large differences in dust-to-gas production rate ratios.

Our isotopic measurements are compatible with HCN being the prime parent of CN in cometary atmospheres. For comet Hale-Bopp, the production rates of the two species were found to be approximately equal (Rauer et al. 2003; Fray et al. 2005). The complex and variable structure of 17P/Holmes's coma after its outburst makes comparisons of the HCN and CN production rates

difficult for this comet. However, Dello Russo et al. (2008) note that the good agreement between the HCN/H<sub>2</sub>O abundance determined from infrared spectra and the OH/CN abundance ratio measured with narrowband photometry (Schleicher 2007) is consistent with CN being mainly produced by HCN photolysis. Yet we cannot exclude that, in other comets, CN has other major progenitors (dust or gas-phase species) sharing the same low <sup>14</sup>N/<sup>15</sup>N isotopic ratio, which would mean that <sup>15</sup>N enrichment is possibly a general property of CN-bearing compounds in comets.

Comets Hale-Bopp and 17P/Holmes are of different dynamical families, the former originating from the Oort Cloud and the latter from the trans-Neptunian scattered disk. An anomalous nitrogen isotopic composition in CN is observed in a number of comets from these two dynamical populations. Hence, comets issued from these two reservoirs likely exhibit similar anomalous N isotopic composition in HCN.

The <sup>15</sup>N excess measured in cometary HCN ( $\delta^{15}\text{N} \sim 1000\%$  relative to the Earth's atmospheric value) and the CN daughter product cannot result from isotopic fractionation in the comet atmosphere. It is comparable to the extreme enrichments measured in interplanetary dust particles (IDPs; Floss et al. 2006) and carbonaceous meteorites (Busemann et al. 2006). High  $\delta^{15}\text{N}$  values are also present at the submicrometer scale in the dust particles collected by the *Stardust* mission from comet 81P/Wild 2 (McKeegan et al. 2006). In IDPs and meteorites, the <sup>15</sup>N-rich nitrogen is carried by nonvolatile macromolecular organic material and is generally believed to be a remnant of interstellar chemistry, although a nucleosynthesis source is often considered as an alternative mechanism given the presence of presolar grains with high <sup>15</sup>N excesses in the matrices of meteorites (e.g., Zinner 1998). These complex organics possibly formed from UV or cosmic radiation processing of simple ices in the presolar cloud or, at later stages, in the cold regions of the solar nebula. The enrichments reported here provide the first evidence for the presence of high <sup>15</sup>N anomalies in the volatiles that composed the icy phase of the outer solar nebula, possibly representing the precursors of the primitive refractory organics.

Cometary HCN and H<sub>2</sub>O ices exhibit strong enrichments in deuterium with respect to the cosmic D/H value (Ehrenfreund et al. 2005; Bockelée-Morvan et al. 2005), and these enrichments are believed to reflect ion-molecule and gas-grain fractionation reactions that took place at low temperature in the

early phases of solar system formation or in the natal molecular cloud. The interpretation of the <sup>15</sup>N enrichment in HCN (by a factor of 3 with respect to the protosolar value in the main nitrogen reservoir; Fouchet et al. 2004; Meibom et al. 2007) is not as compelling as it is for deuterium, because there is still little evidence for N isotopic fractionation in the interstellar medium (Ikeda et al. 2002) and because predicted <sup>15</sup>N enhancements in HCN for exchange reactions involving the main nitrogen reservoir N<sub>2</sub> are modest (Terzieva & Herbst 2000). Rodgers & Charnley (2004, 2008) show that highly fractionated NH<sub>3</sub> ice could have formed in interstellar or protosolar material if N<sub>2</sub> was converted into atomic nitrogen. Whereas this mechanism is attractive for accounting for the high <sup>15</sup>N excesses in primitive refractory organics, if synthesized from NH<sub>3</sub>, the chemical network for explaining the HCN isotopic anomaly in comets still has to be proposed. Alternative mechanisms include a nucleosynthetic origin and photochemical self-shielding in the solar nebula, similar to the mechanism proposed for explaining the oxygen isotope anomalies in meteorites (Clayton 2002a, 2002b). Irrespective of the mechanism, protosolar HCN never isotopically equilibrated with nebular N<sub>2</sub> at the later phases of the evolution of the solar system.

IRAM is supported by INSU/CNRS (France), MPG (Germany), and IGN (Spain). We thank the IRAM staff, and especially P. Cox, for providing us with discretionary director time, and C. Thum, for having scheduled these observations on short notice. Some of the data presented herein were obtained at the W. M. Keck Observatory, which is operated as a scientific partnership among the California Institute of Technology, the University of California, and the National Aeronautics and Space Administration. The Observatory was made possible by the generous financial support of the W. M. Keck Foundation. This Letter includes data taken at the McDonald Observatory of the University of Texas at Austin. We thank G. Punawai, for his invaluable assistance during the observing run at Keck I, and E. Lellouch and D.C. Lis, for helpful comments on the manuscript. J. M. is Research Director, E. J. is Research Associate, and D.H. is Senior Research Associate at FNRS (Belgium). A. L. C. was supported by NASA grant NNG04G162G.

*Facilities:* IRAM:30m, Keck:I, McD:2.7m.

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