GROUND-BASED MULTIWAVELENGTH OBSERVATIONS OF COMET 103P/HARTLEY 2

A. Gicquel1,2, S. N. Milam2, G. L. Villanueva1,2, A. J. Remjian3, I. M. Coulson4, Y.-L. Chuang5, S. B. Charnley2, M. A. Cordiner1,2, and Y.-J. Kuan6,8

1 Catholic University of America, Physics Department, 620 Michigan Avenue NE, Washington, DC, USA
2 Goddard Center for Astrobiology, NASA Goddard Space Flight Center, 8800 Greenbelt Road, Greenbelt, MD 20771, USA; adeline.gicquel@nasa.gov, stefanie.n.milam@nasa.gov, geronimo.l.villanueva@nasa.gov, steven.b.charnley@nasa.gov, martin.a.cordiner@nasa.gov
3 National Radio Astronomy Observatory, 520 Edgemont Road, Charlottesville, VA 22903, USA; aremjian@nrao.edu
4 Joint Astronomy Centre, 660 North A’ohoku Place University Park, Hilo, HI 96720, USA; icoulson@jach.hawaii.edu
5 National Taiwan Normal University, 88 Sec. 4 Ting-Chou Road, Taipei 116, Taiwan; ylchuang@std.ntnu.edu.tw
6 Academia Sinica Institute of Astronomy & Astrophysics (ASIAA), Taipei 106, Taiwan; kuan@ntnu.edu.tw

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ABSTRACT

The Jupiter-family comet 103P/Hartley 2 (103P) was the target of the NASA EPOXI mission. In support of this mission, we conducted observations from radio to submillimeter wavelengths of comet 103P in the three weeks preceding the spacecraft rendezvous on UT 2010 November 4.58. This time period included the passage at perihelion and the closest approach of the comet to the Earth. Here, we report detections of HCN, H2CO, CS, and OH and upper limits for HNC and DCN toward 103P using the Arizona Radio Observatory Kitt Peak 12 m telescope (ARO 12 m) and submillimeter telecope (SMT), the James Clerk Maxwell Telescope (JCMT), and the Green Bank Telescope (GBT). The water production rate, $Q_{H_2O} = (0.67–1.07) \times 10^{28} \text{ s}^{-1}$, was determined from the GBT OH data. From the average abundance ratios of HCN and H2CO relative to water (0.13 ± 0.03% and 0.14 ± 0.03%, respectively), we conclude that H2CO is depleted and HCN is normal with respect to typically observed cometary mixing ratios. However, the abundance ratio of HCN with water shows a large diversity with time. Using the JCMT data, we measured an upper limit for the DCN/HCN ratio <0.01. Consecutive observations of ortho-H2CO and para-H2CO on November 2 (from data obtained at the JCMT) allowed us to derive an ortho:para ratio (OPR) of $\approx 2.12 \pm 0.59 \ (1\sigma)$, corresponding to $T_{\text{spin}} > 8 \text{ K} (2\sigma)$.

Key words: astrobiology – comets: individual (103P/Hartley2) – radio lines: planetary systems – submillimeter: planetary systems – techniques: spectroscopic

Online-only material: color figures, extended figures

1. INTRODUCTION

Comets are probably the least-altered bodies in the solar system (Festou et al. 2004). As such, they can provide key insights into the physical and chemical processes occurring during its origin and earliest evolutionary epochs, including the origin of long-period and short-period comets (Duncan et al. 2004) and the formation and composition of planets (Dodson-Robinson et al. 2009; Bast et al. 2013). By studying comets from different reservoirs, we can probe the different environments in which they formed and also better understand their role in initiating prebiotic chemistry on the early Earth through the delivery of water and organic matter by cometary delivery.

Comet rendezvous space missions to individual comets present unique scientific opportunities. In situ spacecraft observations of several comets have allowed their nuclei to be imaged and the gas and dust properties of their coma to be studied in great detail. These include 1P/Halley (Newburn et al. 1991), 81P/Wild 2 (Brownlee et al. 2006), 9P/Tempel (A’Hearn et al. 2005), 103P/Hartley 2 (A’Hearn et al. 2011), and the current Rosetta mission to 67P/Churyumov-Gerasimenko (Schulz 2012). Ground-based observing campaigns have also played an important role in support of space missions (Meech et al. 2005, 2011; Knight et al. 2007) and, in the case of 81P/Wild 2, laboratory analyses of the returned Stardust samples have yielded unique insights into the nature of cometary dust (McKeegan et al. 2006; Clemett et al. 2010).

Comet 103P/Hartley 2 (hereafter 103P) is a Jupiter-family comet with a short orbital period (6.5 yr) and a low orbital inclination. This comet was the target of the NASA EPOXI mission (A’Hearn et al. 2011; Meech et al. 2011). The comet...
passed perihelion on 2010 October 28 at $R_\odot = 1.059$ AU and on 2010 October 21 made an exceptionally close approach to Earth at $A = 0.12$ AU. In support of the EPOXI mission, we conducted observations at radio and submillimeter wavelengths of comet 103P in the three weeks preceding the spacecraft rendezvous on UT 2010 November 4.58. Here, we report detections of HCN, H$_2$CO, CS, and OH and upper limits for HNC and DCN, using the 12 m Arizona Radio Observatory Kitt Peak (ARO 12 m) and the 10 m submillimeter telescope (SMT), as well as the 15 m James Clerk Maxwell Telescope (JCMT) and the 100 m Robert C. Byrd Green Bank Telescope (GBT). We present the observational results and determine physical parameters such as column densities and production rates. Finally, the ortho:para ratio has been derived from H$_2$CO, and an upper limit on the D/H ratio was obtained from DCN and HCN measurements.

2. OBSERVATIONS

Comet 103P/Hartley 2 was discovered on 1984 June 4 by Malcolm Hartley at the Siding Spring Observatory (Hartley 1986). 103P has been frequently observed over the 30 yr following its discovery, both by ground-based and space telescopes. Observations provided information about the gas production rate for offset pointing. The GBT beam size at this frequency is $\approx 8\,$s. Pointing of the telescope is achieved by a single “pointing” receptor. Pointing accuracy is estimated at 2$\,$s. Focus is similarly maintained throughout the night by measuring the corrected beam efficiency. Calibration of the ACSIS digital autocorrelation spectrometer. For this work, ACSIS was configured at its highest frequency resolutions (31 MHz). Observations of HCN: $J = 4–3$ (354.5055 GHz), HCN: $J = 3–2$ (265.8864 GHz), $p$-H$_2$CO: $J_{K_a,K_c} = 5_{0,5–4,0,4}$ (362.7360 GHz), $o$-H$_2$CO: $J_{K_a,K_c} = 5_{1,5–4,1,4}$ (351.7686 GHz), DCN: $J = 5–4$ (362.0465 GHz), and HNC: $J = 4–3$ (362.6303 GHz) were measured at the JCMT.

At these frequencies, the JCMT has a Gaussian beam size of $\approx 15\,$s (full width at half power). The HARP receivers are separated by about 30$\,$s, and so the emission from the comet is anticipated to be encompassed by a single receptor—the “pointing” receptor. Zero points were adjusted at the beginning of each observing run by pointing on a nearby quasar. The pointing accuracy of the GBT is 5$\,$s. The latter conditions made observations difficult at these HARP

2.2. Arizona Radio Observatory 12 m (ARO 12 m) and Submillimeter Telescope (SMT)

Observations of HCN: $J = 3–2$ (265.8864 GHz), $o$-H$_2$CO: $J_{K_a,K_c} = 3_{1,2–2,1,1}$ (225.6978 GHz), HCN: $J = 1–0$ (88.6318 GHz), HCN: $J = 2–1$ (177.2612 GHz), and CS: $J = 4–3$ (97.9809 GHz) toward comet 103P were taken between 2010 October 22 and November 4 using the facilities of the Arizona Radio Observatory (ARO): the 12 m telescope on Kitt Peak, Arizona and the SMT on Mount Graham, Arizona. The 1 mm observations were carried out at the SMT with a dual-polarization ALMA Band 6 receiver system, employing sideband-separating mixers with an image rejection of typically 15–20 dB. The back-ends employed were a 2048 channel 1 MHz filter bank used in parallel (2 $\times$ 1024) mode and a 250 kHz filter also in parallel (2 $\times$ 250). The temperature scale at the SMT is $T_A^*$; the radiation temperature is then defined as $T_R = T_A^* / \eta_b$, where $\eta_b$ is the main beam efficiency. The 2 and 3 mm observations were conducted at the ARO 12 m using dual-polarization SIS mixers, operated in single-sideband mode with image rejection $\geq 20$ dB. Filter banks with 512 channels of 100 and 250 KHz resolutions were used simultaneously in parallel mode for the measurements, along with an autocorrelator with 782 kHz resolution. The intensity scale of the 12 m is the chopper-wheel corrected antenna temperature, $T_R^*$, including forward spillover losses, which is converted to radiation temperature by $T_R = T_R^* / \eta_b$, where $\eta_b$ is the corrected beam efficiency. Data at both facilities were taken in position-switching mode with an off position 30$\,$s west in azimuth. The JCMT was used to determine the cometary position using the orbital elements. The pointing accuracy is estimated at 1$\,$s for the SMT and 5$\,$s for the ARO 12 m. Focus and positional accuracy were checked periodically on nearby planets or masers.

2.3. James Clerk Maxwell Telescope (JCMT)

Submillimeter spectroscopic observations of 103P (Programme ID m10bu13) were made from the JCMT, located at the 4000m level on Mauna Kea, Hawaii, on UT 2010 October 21, 22, 23, and 25 and November 02, 03, and 04 using the HARP heterodyne array. HARP is a 4 $\times$ 4 array receiver but was used here in a single-receptor mode. HARP is remotely and quickly tunable to frequencies in the 325–375 GHz ranges and utilizes an image sideband suppressor. The output from the HARP receiver is fed to the “ACSIS” digital autocorrelation spectrometer. For this work, ACSIS was configured at its highest frequency resolutions (31 MHz). Observations of HCN: $J = 4–3$ (354.5055 GHz), HCN: $J = 3–2$ (265.8864 GHz), $p$-H$_2$CO: $J_{K_a,K_c} = 5_{0,5–4,0,4}$ (362.7360 GHz), $o$-H$_2$CO: $J_{K_a,K_c} = 5_{1,5–4,1,4}$ (351.7686 GHz), DCN: $J = 5–4$ (362.0465 GHz), and HNC: $J = 4–3$ (362.6303 GHz) were measured at the JCMT. The opacity of the sky above JCMT was measured by a water vapor meter (WVM) mounted so as to measure along the telescope line of sight. The opacity is expressed as if measured at the zenith at 225 GHz. The opacity (in nepers) on UT October 21, 22, 23, and 25 was, on average, 0.10, 0.05, 0.05, and 0.05 and on November 02, 03, and 04 was 0.09, 0.11, and 0.15. The latter conditions made observations difficult at these HARP
suitable for this program.

(B-band) frequencies, but conditions otherwise were most suitable for this program.

3. RESULTS

Observed line parameters including UT dates, observing frequencies (ν), beam size (Θb), diameter of the projected beam size on the comet (D), beam efficiency (ηc or ηb), temperature (T_R or T_A), FWHM line width (∆V1/2), integrated intensity (∫ T_A ∆V1/2), heliocentric distance (R_h), and comet distance at the times of measurements (Δ) are listed in Table 1. The uncertainties of the line width and the integrated line intensity are determined from a Gaussian fit and are reported at 1σ in the Table 1.

Representative spectra are shown in Figures 1–4 for all facilities. All the spectra are plotted in the cometary velocity frame. The UT date of each observed transition is located in the figure. All data are available in the online journal as supplemental information.

Figure 1 displays the OH detection toward comet 103P/Hartley 2 from the GBT taken on 2010 October 13 and 19. The GBT data were measured in a monitoring sequence every 1, 2, 3, or 5 days. The OH line inversion and gas production rates on these days are reported in Table 2.

Figure 2 displays the J = 4–3 and J = 3–2 transitions of HNC on 2010 October 22 toward comet 103P/Hartley 2 from the JCMT and SMT, respectively. We detected four transitions of HCN with three telescopes (SGT, ARO 12 m, and JCMT). Gas production rates from these transition are reported in Table 3. Figure 2 shows two transitions observed on the same day. Furthermore, the line is mostly resolved with the JCMT and partially resolved with the SMT.

Figure 3 displays the J = 2–1 transitions of CS on 2010 October 22 toward comet 103P/Hartley 2 from the ARO 12 m.
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Figure 1. (a) Detection of OH taken on 2010 October 13 and 19 with the GBT. The spectral resolution is \( \approx 0.274 \) km s\(^{-1}\). Additional spectra for the observing campaign for OH are available in the online journal. (b) Detection and upper limit of OH taken for each day of the observations with the GBT. The spectral resolution is \( \approx 0.274 \) km s\(^{-1}\). Spectra are plotted in a cometocentric velocity frame. The red dashed line denotes the \( J = \frac{3}{2}, \Omega = \frac{3}{2}, F = \frac{1}{2} - \frac{1}{2} \) transition at the comet velocity. Other features present in the spectra are attributed to interstellar features at the time of observations. (An extended and a color version of this figure is available in the online journal.)

Gas production rates from this transition are reported in Table 3. These data were collected with a resolution of \( \approx 0.310 \) km s\(^{-1}\) and show a narrow line width. The line profile is not resolved here and only provides details on abundance and not molecular origin within the coma.

Figure 4 displays, respectively, the \( J_{K_a,K_c} = \frac{5}{2}, \frac{5}{2}, \Omega = \frac{3}{2}, F = \frac{3}{2} \) transitions of \( p\)-H\(_2\)CO and \( o\)-H\(_2\)CO on 2010 November 2 toward comet 103P/Hartley 2 from the JCMT. We observed \( p\)-H\(_2\)CO and \( o\)-H\(_2\)CO on the same day only with JCMT. A detailed discussion on the ortho:para ratio can be found in Section 4.4.

4. ANALYSIS

4.1. Column Densities, Production Rates, and Abundances

The production rate for water was indirectly measured from the observation of its photodissociation product OH with the GBT. We used the equation of Tacconi-Garman et al. (1990) to determine the total OH production rate \( \dot{Q}_{\text{OH}} \) for each observation:

\[
\dot{Q}_{\text{OH}} = \left( \frac{7.06 \times 10^{25}}{i} \right) \left( \frac{3.3}{T_{\text{BG}}} \right) \left( \frac{10^5}{\tau_{\text{OH}}} \right) \left( \frac{\Delta}{1} \right)^2 \left( \frac{I_{\text{OH}}}{1} \right),
\]

where \( i \) is the inversion of the ground state, \( T_{\text{BG}} \) (K) is the background temperature, \( \tau_{\text{OH}} \) (s) is the lifetime of the OH molecule, \( \Delta \) (AU) is the Earth-comet distance, and \( I_{\text{OH}} \) (mJy km s\(^{-1}\)) is the integrated flux. The dominant source of error in this formalism comes from the accuracy of the integrated flux observation.
measurement, as well as the inversion parameter $i$, although the latter is negligible for these data.

Given that the values of the heliocentric velocity ($\dot{R}$) of the comet ranged from $-5$ to $+2$ (Table 2), a polynomial function was fit to the data presented in Table 5 of Schleicher & A'Hearn (1988) between these values in order to find the inversion at the comet’s heliocentric velocity on the date and UT time of the observations. This inversion value is given in Table 2. The OH photodissociation lifetime ($\tau_{\text{OH}}$) is $1.2 \times 10^5 R_2^5$ s (taken from Tacconi-Garman et al. 1990) and is used in the final production rate calculation; we assume $T_\text{BC}=2.7$ K. The measured intensity and line width of each transition is given in Table 1. The $Q_{\text{OH}}$
OH. The photodissociation of the H$_2$O molecule into H and OH was observed with the JCMT. The spectral resolutions were ≈0.909 km s$^{-1}$ and ≈0.468 km s$^{-1}$ for p-H$_2$CO and o-H$_2$CO, respectively. The detection of H$_2$CO for all facilities and dates are available in the online journal. (b) Detection of H$_2$CO taken on 2010 October 29 with the SMT. The spectral resolution is ≈0.332 km s$^{-1}$. Spectra are plotted in a cometary velocity frame. (c) Detection of H$_2$CO taken for each day of observations with the JCMT. The spectral resolutions were ≈0.984 km s$^{-1}$, ≈0.252 km s$^{-1}$, and ≈0.468 km s$^{-1}$ on 21 October, 23 October, 2.69 November, and 2.58 November, respectively. Spectra are plotted in a cometary velocity frame.

(An extended and a color version of this figure is available in the online journal.)

d value is then corrected by a factor $P$, which is defined as the fraction of molecules in the coma that are contained within the GBT beam. We computed $P$ using a Monte-Carlo Hase model (Hase 1957) for daughter molecules, assuming $\tau_{\text{H}_2\text{O}} = 8.0 \times 10^4 \tau_0$ (s) (Huebner et al. 1992), $v_{\text{OH}} = 0.95$ km s$^{-1}$, and $v_{\text{H}_2\text{O}} = 0.80$ km s$^{-1}$ (Crovisier et al. 2013). The final production rates for OH on each date are given in Table 2. $Q_{\text{OH}}$ shows large diversity with time. The average measured production rate of OH over this monitoring campaign is $Q_{\text{OH}} = (7.03 \pm 0.44) \times 10^{27}$ s$^{-1}$. The conversion to $Q_{\text{H}_2\text{O}}$ is made by dividing $Q_{\text{OH}}$ by the branching ratio of water dissociation to OH. The photodissociation of the H$_2$O molecule into H and OH is the most important process, accounting for 85.5% of all water molecules that are dissociated (Harris et al. 2002). The mean water production rate was therefore $Q_{\text{H}_2\text{O}} = (8.22 \pm 0.51) \times 10^{27}$ s$^{-1}$.

Water production was directly measured in this comet from submillimeter rotational transitions from space with Odin (Biver et al. 2011), using the three instruments of Herschel (Lis et al. 2010; Hartogh et al. 2011; Meech et al. 2011), and from rovibrational lines in the infrared from the ground (Dello Russo et al. 2011; Mumma et al. 2011). It was indirectly measured from the observation of its photodissociation products: OH in the near-UV (Knight & Schleicher 2012), H from the Ly--α line observed by SOHO/SWAN (Combi et al. 2011), and OH at 18 cm (here and Crovisier et al. 2013). Published water production rates from concurrent observations within ±50 days of perihelion (labeled as J) ranged from 0.1 to $1.9 \times 10^{28}$ s$^{-1}$ and are summarized in Figure 5. The values from this work are consistent with the value derived by Mumma et al. (2011) and Combi et al. (2011). The observed variation in $Q_{\text{H}_2\text{O}}$ has been attributed to the rotation of the nucleus (Mumma et al. 2011; Biver et al. 2011).

Beam-averaged column densities were derived for HCN, H$_2$CO, CS, DCN, and HNC assuming that the cometary coma filled the beams of the respective telescopes. In the case of the upper limits, a 3σ rms was assumed to derive the integrated intensity of DCN and HNC, set at a linewidth of ≈1 km s$^{-1}$. The column density for the observations was calculated from

$$N_{\text{tot}} = \frac{8\pi k v_\text{ul}^2 \int T_R \Delta v_\text{ul} / 2 \xi_{\text{rot}} \varepsilon E_\text{up} / kT_\text{up}}{h c^3 A_{\text{ul}} \sigma_p},$$

where $k$ is the Boltzmann constant, $\xi_{\text{rot}}$ is the partition function, $h$ is the Planck constant, $c$ is the speed of the light, $A_{\text{ul}}$ [s$^{-1}$] is the Einstein coefficient, $\varepsilon_{\text{up}}$ is the statistical weight, $T_\text{rot}$ [K] is the rotational excitation temperature, $E_\text{up}$ [cm$^{-1}$] is the upper state energy, and $N_{\text{tot}}$ [cm$^{-2}$] is the total number of molecules observed in the beam. Drahus et al. (2012) concluded that the rotational temperature from CH$_3$OH (157.225 GHz; IRAM 30 m telescope) varied strongly due to the nucleus rotation, with the average value being 47 K (between 19 and 179 K). Additionally, Boissier et al. (2014) derived $T_\text{rot}$ from CH$_3$OH (157.225 GHz; IRAM 30 m telescope and the Plateau de Bure) as a function of the radii of the projected beam sizes on the coma. They concluded that the increase of $T_\text{rot}$ from ≈35 K to ≈46 K is due to the increase of the beam radii from ≈150 km to ≈1500 km. In this analysis, we assumed $T_\text{rot} = 50$ K, which is the average from CH$_3$OH observations conducted at the same facilities during our observations (Y.-L. Chuang et al., in preparation). This is consistent with other results considering a diameter of the projected beam sizes on the coma between ≈1200 km and ≈46,400 km (Table 1). The column densities derived for HCN, H$_2$CO, CS, DCN, and HNC are listed in Table 3. The minimum ($T_\text{rot} = 19$ K) and maximum rotational ($T_\text{rot} = 179$ K) temperatures obtained by Drahus et al. (2012) provide $N_{\text{tot}} = (6.29 \pm 0.34) \times 10^{11}$ cm$^{-2}$ and $N_{\text{tot}} = (2.32 \pm 0.12) \times 10^{11}$ cm$^{-2}$, respectively, on 2010 October 22 for HCN: $J = 3–2$. The D/H and ortho:para ratio are discussed in Sections 4.3 and 4.4, respectively.

Most of the molecular species measured are considered to be parent species, thus production rates were determined from a Monte Carlo model (Milam et al. 2004, 2006) tracing the trajectories of molecules within the telescope beam ejected from the comet nucleus. The observed column density is then matched for an output molecular production rate, $Q$. H$_2$CO is considered as both a parent and extended source species, so production rates were derived for both cases by employing the models of Milam et al. (2006). Table 3 summarizes the production rates of the molecules observed toward comet 103P, the production rate of water and the ratio $Q/Q_{\text{H}_2\text{O}}$ with the SMT, ARO 12 m, and JCMT. This model assumes isotropic outgassing, which is reasonable for the analysis of these data since the model
simulates the observed column densities within a large beam (with respect to the comet). The uncertainties introduced into the modeled production rates are dominated by the errors on the measured column densities.

4.2. 103P/Hartley 2 Previous Measurements

Crovisier et al. (2013) observed the short-term variation of the OH production rate at Nancay in 2010 October. The production rate increased steeply and progressively before perihelion, reaching a maximum just before the EPOXI flyby. The water production rate preceding perihelion measured by SOHO/SWAN also shows an increase by a similar amount (Combi et al. 2011). By using the GBT data, one can also see that $Q_{\text{OH}}$ increased as the comet was approaching the Sun. The time step of the GBT data cannot be used to correlate the temporal evolution of the water production rate with the rotational period of the comet, as studied with some other data (Meech et al. 2011) and Crovisier et al. (2013) derived $Q_{\text{H}_2\text{O}} = 1.2 \times 10^{28} \text{ s}^{-1}$ and $Q_{\text{H}_2\text{O}} = (1.9 \pm 0.3) \times 10^{28} \text{ s}^{-1}$, respectively.

They also concluded that the molecules are produced from the sublimation of icy grains but that there might be two distinct phases of ice in 103P; one enriched in H$_2$O and CH$_3$OH, and another enriched in more volatile species (HCN, C$_2$H$_2$, and C$_2$H$_6$). This asymmetry in the line profile mentioned by Kawakita et al. (2013) can be observed for HCN with the JCMT. In Table 3, we can see that the abundance ratio of HCN with water shows large variation with time, and so the average is more representative of the global chemistry. This range can be explained by the asymmetric spatial profiles of the molecules (Kawakita et al. 2013) because the molecules are from different parts of the nucleus, or because of the sublimation of icy grains. The significant contribution of grain sublimation to the production of volatiles is supported by numerousmeasurements (A'Hearn et al. 2011; Mumma et al. 2011; Dello Russo et al. 2011; Drahus et al. 2012; Knight & Schleicher 2012). By averaging the abundance ratio of HCN and $\alpha$-H$_2$CO with water, we obtain $Q(\text{HCN})/Q(\text{H}_2\text{O}) = 0.13 \pm 0.03\%$ and $Q(\text{H}_2\text{CO})/Q(\text{H}_2\text{O}) = 0.14 \pm 0.03\%$. Boissier et al. (2014) derived an average abundance of HCN relative to water from millimeter observations consistent with our results. They detected HCN on 2010 October 23 and November 4 and 5 with the IRAM interferometer located at the Plateau de Bure and obtained $Q(\text{HCN})/Q(\text{H}_2\text{O}) = 0.16\%$. The HCN abundances from millimeter observations were lower than the values from infrared data ($Q(\text{HCN})/Q(\text{H}_2\text{O}) \approx 0.3\%$ Dello Russo et al. 2011, 2013; Mumma et al. 2011; Kawakita et al. 2013) by a typical factor of $\approx 2$ (Villanueva et al. 2013). We deduced an average abundance of H$_2$CO relative to water in good agreement with Dello Russo et al. (2013) and Kawakita et al. (2013) $\approx 0.11\%$, but the value from this work is lower than that from Mumma et al. (2011). The discrepancy between radio and IR results is not surprising given the strong temporal variability of the coma and differences in the field of view. However, by comparison with other comets, we find the same approximate relationships between species in

![Figure 5. Water production rates measured in comet 103P/Harley 2 as a function of the time from perihelion on 2010 October 28.26 (defined as $J_r$). Between $J_r+1$ and $J_r+3$ days, the observations are essentially from Biver et al. (2011), who studied the short-term variability of water. Lis et al. (2010) and Knight & Schleicher (2012) derived $Q_{\text{H}_2\text{O}} = (1.0 \pm 0.2) \times 10^{28} \text{ s}^{-1}$ at $J_r$ and $Q_{\text{H}_2\text{O}} = 1.15 \times 10^{28} \text{ s}^{-1}$ at $J_r+2$ days, respectively. At $J_r+7$ days, the observations are essentially from Dello Russo et al. (2011), Meech et al. (2011) and Crovisier et al. (2013) derived $Q_{\text{H}_2\text{O}} = 1.2 \times 10^{28} \text{ s}^{-1}$ and $Q_{\text{H}_2\text{O}} = (1.9 \pm 0.3) \times 10^{28} \text{ s}^{-1}$, respectively.](image-url)
normal, CH3OH normal, CH4 depleted, and CO depleted. Spectral resolutions are the upper limit of DCN taken on 2010 October 22–23 with the JCMT. The Detection of HCN taken on 2010 October 22 and average for Figure 6.

The D/H ratio obtained here is <0.01. Our value is consistent with previous measurements (e.g., D/H = 0.002 in comet Hale–Bopp; Meier et al. (1998), and 1.6 × 10^−4 in comet 103P; Hartogh et al. (2011)), although it does not place any new constraints. In comparison, a range of (0.4–7.0) × 10^−2 for the DCN/HCN ratio was determined in the interstellar medium (Roberts et al. 2002; Jørgensen et al. 2004).

4.4. OPR Ratio from H2CO

Molecules that contain multiple H atoms can be spectroscopically distinguished based on the orientation of the spins of their H nuclei, either aligned in parallel or anti-parallel states (e.g., H2, H2CO, and H2O), giving rise to ortho and para forms. Quantum-mechanically, transitions between the different forms are strictly forbidden, giving rise to two distinct spectra and ortho:para ratios (OPRs) which define the spin temperature (Tspin) of that species. This means that the relative abundances of nuclear spin isomers are expected to remain invariant over time, and the OPR has therefore been long thought to reveal information about the temperature of formation of cometary ices. However, some processes are hypothesized to change the OPR without breaking molecular bonds (e.g., Limbach et al. 2006), and phase transitions are effective in bringing the molecules into an equilibrated OPR (e.g., Hama & Watanabe 2013). In their study of water molecules trapped in low-temperature (∼4 K), solid Ar matrices, Sliter et al. (2011) found that upon desorption at T > 260 K, fast ortho—para conversion occurred. In addition, theoretical investigations (Anderson & van Dishoeck 2008) showed that photosorption of water ice at 10 K would typically lead to bond breaking (with the subsequent loss of OPR information). Of the processes investigated by Anderson & van Dishoeck (2008), only the “kick-out” mechanism would preserve the OPR during desorption at low temperatures. On the other hand, it is not straightforward to extrapolate the high-temperature desorption and Ar matrix—ice studies by Sliter et al. (2011) to the release of volatiles from cometary ices and which process dominates the desorption of ices at low temperatures. The cosmogenic significance of OPR and spin temperature in comets is therefore not clear and the lack of OPR measurements for molecules with smaller ortho—para energy deficiencies (e.g., H2CO and CH3OH) has further limited our understanding of this indicator in comets.

### Table 4

| UT Date      | QHCN (s⁻¹) | UT Date      | QDCN (s⁻¹) | D/H     |
|--------------|------------|--------------|------------|---------|
| 2010 Oct 22.43 | 6.80 × 10²⁴ | 2010 Oct 22.58–23.57 | <1.37 × 10²³ | <2.01 × 10⁻² |
| 2010 Oct 22.78 | 1.23 × 10²⁵ |             | <1.37 × 10²³ | <1.11 × 10⁻² |
| 2010 Oct 23.41 | 5.81 × 10²⁴ |             | <1.37 × 10²³ | <2.36 × 10⁻² |
| 2010 Oct 23.77 | 9.02 × 10²⁴ |             | <1.37 × 10²³ | <1.52 × 10⁻² |
| 2010 Nov 2.77  | 6.79 × 10²⁴ | 2010 Nov 2.69 | <3.77 × 10²³ | <3.46 × 10⁻² |
| 2010 Nov 4.44  | 8.07 × 10²⁴ | 2010 Nov 4.67 | <5.27 × 10²³ | <6.63 × 10⁻² |

Note. We average QDCN on UT 2010 October 22.58–23.57.

Figure 6. Detection of HCN taken on 2010 October 22 and average for the upper limit of DCN taken on 2010 October 22–23 with the JCMT. The spectral resolutions are ≈0.232 km s⁻¹ and ≈0.025 km s⁻¹ for HCN and DCN, respectively. Spectra are plotted in a cometocentric velocity frame. The D/H ratio in HCN and DCN, both species were sampled on the same day. We average the gas production rate of DCN on UT 2010 October 22.58 and UT 2010 October 23.57 (Figure 6). The D/H ratio in HCN is given in Table 4. As discussed in Section 4.2, we note the variability of the HCN with time, and this short-term variability has been studied in detail by Boissier et al. (2014) and Drahus et al. (2012). We measured only upper limits for DCN, for which we assumed a constant HCN production rate over the period between the HCN and DCN observations on a given day.

Relevant deuterium fractionation ratios have been measured for both comets and the interstellar medium. Crovisier et al. (2004), Kawakita et al. (2005), Kawakita & Kobayashi (2009), Gibb et al. (2012), and Bonev et al. (2009) have presented upper limits for the production rates of several cometary molecules. D/H isotope ratios have been measured for two cometary molecules in 103P: water and hydrogen cyanide. Compared to models of interstellar chemistry, both the measured HDO/H2O and DCN/HCN ratios are compatible with ion–molecule chemistry in gas at about 30–35 K. With this work we measured an upper limit for the DCN/HCN ratio of <0.01. Our value is consistent with previous measurements (e.g., D/H = 0.002 in comet Hale–Bopp; Meier et al. (1998), and 1.6 × 10⁻⁴ in comet 103P; Hartogh et al. (2011)), although it does not place any new constraints. In comparison, a range of (0.4–7.0) × 10⁻² for the DCN/HCN ratio was determined in the interstellar medium (Roberts et al. 2002; Jørgensen et al. 2004).
The OPR of H$_2$CO for Hartley 2 was obtained from consecutive observations of the ortho-H$_2$CO (5$_0$,$_5$–4$_0$,$_4$) and para-H$_2$CO (5$_1$,$_1$–4$_1$,$_1$) lines on November 2 from data obtained at the JCMT (see Table 1). The periodicity of the comet presents some uncertainty in abundances, though these two observations were in close enough proximity (<3 hr). Therefore, the variation in rotation temperature is likely not a major factor. Other observational uncertainties are factored out in the ratio. For these data, we obtain an OPR of ≈2.12 ± 0.59 (1σ), or $T_{\text{spin}}$ of ≈13.5–7.5 K (1σ), although at only 1.5σ our OPR measurement cannot distinguish from equilibrium ($T_{\text{spin}} >$ 9 K at 1.5σ). Similarly, Villanueva et al. (2012a) have measured $T_{\text{spin}}$ > 18 K for CH$_3$OH in comet C/2001 A2 (LINEAR), which is consistent with that in Hale–Bopp $T_{\text{spin}} >$ 15 K (Pardanaud et al. 2007). Our results are also consistent (within 1σ) with those obtained for water by Bonev et al. (2013) for OPR of ≈2.79 ± 0.13 (mean of five measurements).

The complexity of obtaining simultaneous observations of ortho and para-H$_2$CO, and the difficulty in obtaining a good signal-to-noise ratio for these data, enforces the future need for sensitive, broadband telescope receivers where these can be readily measured toward any comet. Such measurements will provide the necessary context to better understand the cosmogetic significance (or lack of) of our OPR measurement of ≈2.12 ± 0.59 (1σ).

5. COMPARISON AMONG VARIOUS COMETS

Knowledge of the volatile chemistry of Jupiter-Family comets (Kuiper Belt) is very limited from both infrared and radio observations because Jupiter-Family comets typically have lower activity.

Crovisier et al. (2009) show the compositional diversity among Jupiter-Family comets from radio observations. Before the observation of 103P, about a dozen Jupiter-Family comets had been observed using radio techniques. By comparing the relative abundance of HCN among Jupiter-Family comets, Crovisier et al. (2009) reported that 2P/Encke, 9P/Temple 1, and 22P/Kopff are organics-normal, like 103P, while 19P/Borrelly, 21P/Giacobini-Zinner, and 73P/Schwassmann-Wachmann 3 are organics-depleted. This suggests distinct processing histories for organics-depleted, organics-normal, and organics-enriched comets. Dello Russo et al. (2011) and Kawakita et al. (2013) compared the abundances ratios among the Jupiter-family sampled from infrared observations. The limited sample of few Jupiter-Family comets shows again that diversity is notable. For example, Dello Russo et al. (2011) concluded that 73P/Schwassmann-Wachmann 3 and 103P are extremely different in their chemical composition.

Correlations between short-term temporal variations in the production rates of primary volatiles with nucleus rotation have been suggested only for two Oort cloud comets. Biver et al. (2009) reported a periodic variation of 40% in the water production rate in C/2001 Q4 (NEAT) with a period of 19.58 ± 0.1 hr. Anderson (2010) observed a variation in production rates for H$_2$O, CO, H$_2$CO, and CH$_3$OH in comet C/2002 T7 (LINEAR) with a period of 2.32 days. Comet 103P is the third comet for which periodic variation in the production of primary volatiles has been demonstrated, and the first one for which unambiguous association with nucleus rotation can be made through imaging (A’Hearn et al. 2011; Harmon et al. 2010, 2011).

To date, OPRs have been measured in a few species, namely, NH$_3$, H$_2$O, and CH$_4$, for several comets by ground-based observations (see Bockelée-Morvan et al. 2004; Dello Russo et al. 2005; Kawakita & Watanabe 2002; Dello Russo et al. 2001; Mumma et al. 2011). Dello Russo et al. (2005) reported from H$_2$O, $T_{\text{spin}} >$ 30 K, $T_{\text{spin}} = 30^{+15}_{-7}$ K, and $T_{\text{spin}} = 23^{+4}_{-3}$ K, respectively, in comets C/1999 H1 (Lee), C/1999 S4 (LINEAR), and C/2001 A2 (LINEAR). Kawakita et al. (2001) and Kawakita & Watanabe (2002) derived an OPR of ammonia equal to 1.17 ± 0.04 and 1.12 ± 0.03 (or $T_{\text{spin}} = 30^{+3}_{-2}$ K), respectively, in C/1999 S4 (LINEAR) and C/2001 A2 (LINEAR). Some of the OPR ratios imply formation temperatures for comet ice species of 25–35 K, similar to the formation temperature implied by the D/H ratios in H$_2$O and HCN, but a growing sample of comets also show equilibrated OPR ($T_{\text{spin}} >$ 35 K, e.g., Villanueva et al. 2012b; Mumma et al. 1993). For example, Mumma et al. (1993) reported a water OPR of 3.2 ± 0.2 for C/1986 P1 (Wilson) ($T_{\text{spin}} >$ 50 K).

6. CONCLUSIONS

We conducted observations of comet 103P/Hartley 2 at both perihelion and at the time of the EPOXI flyby. We report detections of HCN, H$_2$CO, CS, and OH and upper limits of HNC and DCN using the ARO Kitt Peak 12 m and SMT, JCMT, and the GBT toward comet 103P. We derived column densities, production rates, and relative abundances toward comet 103P. We concluded that 103P is normal in HCN and depleted in H$_2$CO, which is in good agreement with other studies. We obtained an upper limit for the (D/H)$_{\text{HCN}}$ ratio of <0.01 and an ortho/para ratio of 2.2 ± 0.59 (1σ) has been derived from H$_2$CO.

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