New Identifications of the CCH Radical in Planetary Nebulae: A Connection to C₆₀?

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Abstract

New detections of CCH have been made toward nine planetary nebulae (PNe), including K4–47, K3–58, K3–17, M3–28, and M4–14. Measurements of the $N = 1 \rightarrow 0$ and $N = 3 \rightarrow 2$ transitions of this radical near 87 and 262 GHz were carried out using the new 12 m and the Sub-Millimeter Telescope (SMT) of the Arizona Radio Observatory (ARO). The presence of fine and/or hyperfine structure in the spectra aided in the identification. CCH was not observed in two PNe which are sources of C₆₀. The planetary nebulae with positive detections represent a wide range of ages and morphologies, and all had previously been observed in HCN and HNC. Column densities for CCH in the PNe, determined from radiative transfer modeling, were $N_{\text{tot}}(\text{CCH}) \sim 0.2\text{--}3.3 \times 10^{15} \text{ cm}^{-2}$, corresponding to fractional abundances with respect to H₂ of $f \sim 0.2\text{--}47 \times 10^{-7}$. The abundance of CCH was found to not vary significantly with kinematic age across a time span of $\sim 10,000$ years, in contrast to predictions of chemical models. CCH appears to be a fairly common constituent of PNe that are carbon-rich, and its distribution may anti-correlate with that of C₆₀. These results suggest that CCH may be a product of C₆₀ photodestruction, which is known to create C₂ units. The molecule may subsequently survive the PN stage and populate diffuse clouds. The distinct, double-horned line profiles for CCH observed in K3–45 and M3–28 indicate the possible presence of a bipolar flow oriented at least partially toward the line of sight.

Key words: astrochemistry – ISM: molecules – planetary nebulae: general – radio lines: ISM

1. Introduction

Planetary nebulae (PNe) represent the final stage in the evolution of low/intermediate mass ($\sim 0.8\text{--}8 M_{\text{sol}}$) stars after they transition from the asymptotic giant branch (AGB). Throughout the AGB stage, atomic and molecular material is stripped from the surface of the progenitor star in the form of a superwind, leading to the formation of a circumstellar envelope. The end of the AGB phase is marked by the cessation of mass loss, and the vestigial central star, evolving toward a white dwarf, irradiates the shell of gaseous ejecta, ionizing the surrounding material.

Models have suggested that the bulk of the remnant molecular material should be photodissociated within the first few thousand years of the PN stage (e.g., Redman et al. 2003). This concept seemed to be well-substantiated by observations (e.g., Knapp 1985). Although CO has been identified in numerous PNe (e.g., Huggins et al. 1996, 2005), as well as H₂ (e.g., Hora et al. 1999; Bernard-Salas & Tielens 2005; Likkel et al. 2006; Mata et al. 2016), polyatomic molecules were a rarity. Recent measurements, however, are beginning to change this paradigm. The Helix Nebula, for example, has been found to contain an array of molecules, including HCN, HNC, HCO⁺, H₂CO, c-C₃H₂, CCH, and CN (Bachiller et al. 1997; Tenenbaum et al. 2009). Many of these species have been found to be well-distributed throughout the nebula (Zack & Ziurys 2013; Zeigler et al. 2013; Schmidt & Ziurys 2017). Such results are particularly surprising, given that the Helix Nebula is one of the oldest PNe known, with an age of $\sim 10,000$ years. HCN, HNC, HCO⁺, and CN have now been detected toward various planetary nebulae (e.g., Bachiller et al. 1997; Edwards et al. 2014), and observations of the young PNe NGC 7027 and NGC 6537 have revealed a rather surprising molecular inventory, including N₂H⁺, CS, and SO (Zhang et al. 2008; Edwards & Ziurys 2013). Furthermore, in addition to other

species, SiO and SO₂ have been recently identified toward the middle-aged PN M2–48 (Edwards & Ziurys 2014). Perhaps even more remarkable has been the recent discovery of C₆₀ in a few planetary nebulae (e.g., Cami et al. 2010; García-Hernández et al. 2010, 2011, 2012; Otsuka et al. 2013). Clearly, the molecular portfolio of planetary nebulae continues to grow.

Very recent work by Schmidt & Ziurys (2016, 2017) has expanded the number of nebulae detected in HCN, HCO⁺, and HNC by over a factor of 2, suggesting that these molecules are commonly present in PNe. Furthermore, the sample of 11–13 PNe in which these molecules have been found evenly spans a range of kinematic ages (determined from the intrinsic radius and expansion velocity of the nebula), from ~ 900 years to $\sim 11,000$ years, as well as morphologies. Strikingly, the abundances of HCN, HNC, and HCO⁺ did not appear to vary significantly with kinematic age, in complete contradiction to current chemical modeling (e.g., Redman et al. 2003).

It is naturally of interest to investigate the widespread presence of other polyatomic molecules in PNe. One species of interest is CCH, the ethynyl radical. CCH is a common constituent of molecular clouds and C-rich circumstellar envelopes (e.g., Zhang et al. 2009; Nishimura et al. 2016), and has also been identified in a few protoplanetary nebulae and toward diffuse clouds (e.g., Lucas & Liszt 2000; Pardo et al. 2007; Park et al. 2008; Gerin et al. 2011). It has been detected in three PNe to date: NGC 7027, NGC 6537, and the Helix (e.g., Zhang et al. 2008; Tenenbaum et al. 2009; Edwards & Ziurys 2013).

CCH is also significant in another aspect: it may be used as a proxy for C₂, which cannot be observed in the millimeter regime because it does not have a permanent electric dipole moment. In the laboratory, C₂ is thought to be an important building block of C₆₀, which self-assembles through a closed-network mechanism

Table 1
Target List of Planetary Nebulae

Source	α (J2000) (h m s)	δ (J2000) ($^{\circ}$ ' ")	θ_s (")	Age (years)	Morphology	C/O	T_* (10^3 K)
Hb 5	17:47:56.2	−29:59:41.9	31(a)	1500^{+540}_{-540} (b)	bipolar	C-rich(c)	≥ 150 (d)
K3–17	18:56:18.2	+07:07:25.9	8(e)	970^{+300}_{-300} (f)	bipolar	C-rich(c), (g)	...
K3–45	19:46:15.6	+24:11:03.7	7(h)	830^{+300}_{-300} (i)	bipolar	...	...
K3–58	20:21:58.3	+29:59:21.1	17(j)	11070^{+2460}_{-1850} (j)	bipolar	...	...
M1–7	06:37:21.0	+24:00:36.6	11(e)	6000^{+1900}_{-1900} (e)	bipolar	1.1(k)	111(l)
M3–28	18:32:41.3	−10:05:50.0	17(a)	7700^{+2400}_{-2400} (e)	quadrupolar	...	131(m)
M3–55	18:33:14.8	−10:15:19.5	10(j)	5040^{+1960}_{-2240} (j)	bipolar	...	72(n)
M4–14	19:21:00.7	+07:36:52.4	15(j)	5550^{+3700}_{-370} (j)	quadrupolar	...	86(m)
NGC 2440	07:41:54.9	−18:12:29.7	38(a)	~ 3400 (o)	quadrupolar (?)	1.9(p)	200(p)
NGC 6772a(q)	19:14:37.3	−02:42:19.8	76(a)	10900^{+5200}_{-5200} (r)	elliptical	...	135(s)
NGC 6772b(t)	19:14:36.4	−02:42:25.0	...	...	...	...	...
K4–47	04:20:45.2	+56:18:12.1	8(e)	900^{+300}_{-500} (u)	bipolar	C-rich (?)	115–130(v)
M1–12	07:19:21.4	−21:43:55.4	2(e)	~ 1000 (w)	multipolar	1.0(x)	29(n)
M1–20	17:28:57.6	−19:15:53.9	2(a)	< 3900 (w)	elliptical	1.2(y)	40–45(z)

References. (a) Tylenka et al. (2003); (b) López et al. (2012); (c) Hony et al. (2002); (d) Pottasch & Surendiranath (2007); (e) Phillips & Márquez-Lugo (2011); (f) Based on distance from Phillips & Márquez-Lugo (2011); (g) Otsuka (2015); (h) Acker et al. (1992); (i) Giammanco et al. (2011); (j) Dobrinčić et al. (2008); (k) Patriarchi & Perinotto (1994); (l) Stanghellini et al. (2002); (m) Zhang & Kwok (1993); (n) Preite-Martinez et al. (1989); (o) Górný et al. (1997), (note: evolutionary age); (p) Pottasch & Bernard-Salas (2010); Dufour et al. (2015); (q) Milne (1973), converted to J2000.0 coordinates; (r) Ali et al. (2012); (s) Montez et al. (2015); (t) Kerber et al. (2003); (u) Corradi et al. (2000); (v) Gonçalves et al. (2004); (w) Otsuka et al. (2013), (note: evolutionary ages); (x) Otsuka et al. (2014); (y) Delgado-Inglada & Rodríguez (2014); (z) García-Hernández et al. (2012).

involving C and C₂ (e.g., Dunk et al. 2012). In addition, fragmentation of large carbon clusters shows successive loss of C₂ units. Consequently, there may be a correlation or an anti-correlation between C₆₀ and C₂, which could be examined through CCH.

Here we report results of a study of CCH in planetary nebulae. Observations were conducted toward 11 sources from the Schmidt & Ziurys (2016) survey, as well as two known carriers of C₆₀. CCH was newly detected in nine PNe, increasing the number of known CCH-containing nebulae by a factor of 4. From the observations, abundances of this molecule were determined, and correlations with kinematic age and the presence of C₆₀ were examined.

2. Observations

The rotational transitions of CCH, a molecule with a $^2\Sigma$ ground state, exhibit both fine (spin-rotation) and hyperfine splittings, arising from the unpaired electron ($S = 1/2$) and the proton nuclear spin of $I = 1/2$, respectively. Following a Hund’s case $b_{\beta J}$ coupling scheme, the rotational quantum number is N . The electron spin couples to the rotation to generate a doublet fine structure pattern, labeled by J , where $J = N + S$, for every level N except $N = 0$. The nuclear spin I then adds to J to create doublet hyperfine levels, indicated by F , where $F = J + I$. The lines of interest for this work are the two hyperfine components of the $N = 1 \rightarrow 0$, $J = 3/2 \rightarrow 1/2$ spin-rotation component at 87,316.9 MHz ($F = 2 \rightarrow 1$) and 87,328.6 MHz ($F = 1 \rightarrow 0$), as well as the $J = 7/2 \rightarrow 5/2$ and $J = 5/2 \rightarrow 3/2$ fine structure components of the $N = 3 \rightarrow 2$ transition. Each of the fine structure components of the $N = 3 \rightarrow 2$ transition additionally consists of two hyperfine lines: $F = 4 \rightarrow 3$ and $3 \rightarrow 2$ and $F = 3 \rightarrow 2$ and $2 \rightarrow 1$, respectively. The hyperfine doublets are separated by 2.2–2.5 MHz, or 2.5–2.9 km s^{−1}, and are therefore effectively collapsed for the sources studied here. As a consequence, the $N = 3 \rightarrow 2$ transition appears as a doublet with lines at 262,005.3 MHz ($J = 7/2 \rightarrow 5/2$) and 262,066.1 MHz ($J =$

$5/2 \rightarrow 3/2$)—the average frequencies of the collapsed hyperfine doublet. The dipole moment of CCH is ~ 0.77 D (Woon 1995).

Observations of the $N = 1 \rightarrow 0$ and $N = 3 \rightarrow 2$ transitions of CCH were carried out between 2014 November and 2016 June using the facilities of the Arizona Radio Observatory (ARO). The 12 m “European” ALMA prototype antenna at Kitt Peak was used to observe the $N = 1 \rightarrow 0$ transition, while the ARO 10 m Sub-Millimeter Telescope (SMT) on Mt. Graham, AZ was employed to measure the $N = 3 \rightarrow 2$ lines. The beam size and main beam efficiency are $\theta_b \approx 72''$ and $\eta_b \approx 0.88$ at 87 GHz for the 12 m, and $\theta_b \approx 29''$ and $\eta_b \approx 0.75$ at 262 GHz for the SMT.

The observations performed with the 12 m telescope utilized a dual-polarization receiver containing ALMA Band 3 side-band separating (SBS) mixers. The image rejection, intrinsic in the mixer architecture, was typically greater than 15 dB. The temperature scale, T_A^* , was determined by the chopper-wheel method. T_A^* is related to the main beam brightness temperature (T_R) through the equation $T_R = T_A^*/\eta_b$, where η_b is the main beam efficiency. The data were taken using two of three 256-channel filter bank backends with 1 MHz, 250 kHz, and 500 kHz resolutions, depending on the source, and the Millimeter Autocorrelator (MAC) with ~ 781 kHz resolution. All backends were operated in parallel mode to accommodate both receiver channels.

At the SMT, the measurements were conducted with the dual polarization 1.3 mm receiver, which exploits ALMA Band 6 SBS mixers. Image rejection was generally > 15 dB. The temperature scale, T_A^* , was determined by the standard chopper-wheel method, where $T_R = T_A^*/\eta_b$. Two filter banks, with 1 MHz and 250 kHz resolution, respectively, were utilized as backends.

The sources searched for CCH are provided in Table 1, along with their age and size estimates, morphologies, and C/O ratios and central star temperatures, if available. As aforementioned, 11 of these sources were previously detected in HCN by

Schmidt & Ziurys (2016) and HNC by Schmidt & Ziurys (2017). All but two of these sources (K3–45 and NGC 6772) were also detected in at least one transition of HCO^+ . Given the prevalence of carbon-containing molecules in these nebulae, it is likely that they are carbon-rich sources (and indeed some have already been confirmed as such); thus, these PNe were considered to be good candidates for a search for CCH. Depending on the size of the source relative to the beam, observations were conducted in either position-switching or beam-switching mode. For sources for which position-switching was required, an offset of $+30'$ in azimuth was generally used, while a subreflector throw of $\pm 2'$ was used for beam-switching. In order to test for possible image contamination, local oscillator shifts were performed for all measurements. Pointing and focus were checked on an hourly basis using nearby strong continuum sources, such as Jupiter or Mars.

3. Results

CCH was detected in 9 of the 11 survey PNe, principally in the $N = 3 \rightarrow 2$ transition, which exhibits a “fingerprint” doublet structure separated by 61 MHz. In a few sources, the doublet was partially blended together but still discernable. The $N = 1 \rightarrow 0$ line, which consists of two well-separated hyperfine components, was only observed in Hb 5 and M3–28; there was significant Galactic contamination in the latter source. CCH was not detected in NGC 2440 and NGC 6772, as well as either of the two PNe found to contain C_{60} : M1–12 and M1–20 (García-Hernández et al. 2010). Notably, the nebulae in which CCH was detected were exclusively bipolar and quadrupolar; observations of the two elliptical PNe in this work, NGC 6772 and M1–20, resulted in non-detections.

The CCH spectra are presented in Figures 1(a), (b) and 2. The CCH doublet structure is clearly apparent in all spectra, although in some sources it is blended (Hb 5, K3–17). Figure 2 highlights the data from K3–45 and M3–28, and includes the optical images of the two PNe. In these nebulae, the $N = 3 \rightarrow 2$ line profiles show distinct red- and blueshifted velocity components.

Table 2 provides the corresponding line parameters for the transitions measured in each source, including the peak antenna temperature T_A^* , LSR velocity, and FWHM line width. The parameters were determined by a Gaussian fit to the line profile for each hyperfine or spin-rotation component. The blended hyperfine structure within each spin-rotation doublet of the $N = 3 \rightarrow 2$ transition was modeled as a single feature. For K3–45 and M3–28, the red- and blueshifted velocity components of the $N = 3 \rightarrow 2$ spin-rotation doublets were fit individually. As shown in the table, the line intensities fall into the range of ~ 2 –12 mK, while the line widths and LSR velocities are comparable to those seen in HCN, HNC, and HCO^+ (see Schmidt & Ziurys 2016, 2017). The individual nebulae are briefly described below.

Hb 5: Both transitions of CCH were detected in this hot, young nebula. LSR velocities reside in the range of -2 to -8.5 km s^{-1} —consistent with those measured for HCN, HCO^+ , and HNC (Schmidt & Ziurys 2016, 2017). The narrower line widths of ~ 5 –7 km s^{-1} for the 3 mm transitions, as opposed to near 40 km s^{-1} for the $N = 3 \rightarrow 2$ lines at 1 mm, mimic those observed in the HCN and HCO^+ . The difference likely reflects the varying beam sizes coupling to a complex, poly polar source (see López et al. 2012). Note that the prominent bipolar lobes in Hb 5 extend almost an arcminute.

K3–17: Only the $N = 3 \rightarrow 2$ component was detected in this PN. The LSR velocity was observed to be $\sim 28 \text{ km s}^{-1}$, while the line widths were found to be ~ 59 –66 km s^{-1} ; the values are consistent with those measured for HCN, HCO^+ , and HNC (Schmidt & Ziurys 2016, 2017). The CCH line profile, particularly the $J = 7/2 \rightarrow 5/2$ component, may exhibit multiple velocity components. Such velocity features are found in the spectra of HCN, HCO^+ , and HNC, and they likely trace the complex filamentary structure of K3–17.

K3–45: The $N = 3 \rightarrow 2$ transition of CCH detected in this source appears to be double-peaked, particularly in the $J = 7/2 \rightarrow 5/2$ component. The redshifted component lies at a velocity of approximately 45 km s^{-1} , while the blueshifted peak is near 20 km s^{-1} , on average. These velocities are very close in value to those found in the double-peaked profiles of HCN and HNC (Schmidt & Ziurys 2016, 2017). Molecular emission is apparently tracing the bipolar outflow in this source.

K3–58: The $N = 3 \rightarrow 2$ transition of CCH was detected in this small, bipolar nebula. The LSR velocity was observed to be about 21–24 km s^{-1} from the spectrum, with line widths of $\sim 35 \text{ km s}^{-1}$. These values are similar to those seen in the HCN, HNC, and HCO^+ spectra.

M1–7: This PN was detected in the $N = 3 \rightarrow 2$ transition of CCH, with an LSR velocity of about -12 km s^{-1} and line widths of ~ 33 –36 km s^{-1} , equivalent to those found for HCN, HNC, and HCO^+ within the uncertainties. A prominent component near -34 km s^{-1} can be seen, similar to one observed in HNC.

M3–28: This small, quadrupolar nebula was detected in both transitions of CCH. The $N = 1 \rightarrow 0$ transition suffers from Galactic contamination on the redshifted side, obscuring the $F = 2 \rightarrow 1$ hyperfine component. The $N = 3 \rightarrow 2$ spin-rotation components were found to be U-shaped, with the red- and blueshifted peaks at $V_{\text{LSR}} \sim 43$ and 18 km s^{-1} . The redshifted component is about a factor of two broader than its blueshifted counterpart, suggesting some asymmetry in the nebular geometry. Evidence of a U-shape profile was also seen in the $J = 3 \rightarrow 2$ spectra of CO, HCN, and HCO^+ (Schmidt & Ziurys 2016), but appears most prominent in CCH.

M3–55: Only the stronger spin component of the $N = 3 \rightarrow 2$ transition, $J = 7/2 \rightarrow 5/2$, was clearly detected in this small, bipolar nebula. Estimates of the line parameters are therefore less reliable, but the visible $N = 3 \rightarrow 2$ feature indicates $V_{\text{LSR}} \sim 25 \text{ km s}^{-1}$ and $\Delta V_{1/2} \sim 25 \text{ km s}^{-1}$ —parameters consistent with those observed for HCN, HNC, and HCO^+ , though the line appears to be somewhat wider in CCH.

M4–14: CCH was detected in the $N = 3 \rightarrow 2$ transition in this small, quadrupolar nebula. The measured LSR velocity of $\sim 51 \text{ km s}^{-1}$ and $\Delta V_{1/2} \sim 33 \text{ km s}^{-1}$ for CCH are analogous to those observed in HCN, HCO^+ , and HNC.

K4–47: This young, compact, bipolar nebula was detected in the $N = 3 \rightarrow 2$ lines with a velocity of about -24 km s^{-1} and $\Delta V_{1/2}$ of $\sim 38 \text{ km s}^{-1}$. These measurements are consistent with data obtained for HCN, HNC, and HCO^+ . A “central” component and a weaker, broad “plateau” feature that have been seen in other molecules such as HCN and HCO^+ are not apparent in the CCH spectrum (Schmidt & Ziurys 2016).

4. Analysis

CCH column densities were estimated using the non-LTE radiative transfer code RADEX (Van der Tak et al. 2007).

Figure 1. Spectra of the $N = 3 \rightarrow 2$ transitions of CCH near 262 GHz observed toward various planetary nebulae using the ARO SMT at 262 GHz, as well as one $N = 1 \rightarrow 0$ transition measured with the new ARO 12 m at 87 GHz toward Hb 5. Spectral resolution is 2 MHz for all $N = 3 \rightarrow 2$ data, save for M3–55, where it is 4 MHz; the $N = 1 \rightarrow 0$ spectrum of Hb 5 has 1 MHz resolution. The Hb 5 data show the hyperfine pattern for the $N = 1 \rightarrow 0$ transition and the spin-rotation splitting for the $N = 3 \rightarrow 2$ line, both underneath the spectra. The temperature scale is T_A^* . (a) Data obtained toward Hb 5, K3–58, M3–55, and K3–17. (b) Data measured toward M1–7, M4–14, and K4–47.

Briefly, this program predicts line intensities for comparison with those observed by employing the following parameters, which are input by the user: H_2 gas density, temperature, and molecular column density. For further details, see Schmidt & Ziurys (2016). For CCH, both hyperfine and fine structure levels were modeled, based on relative intensities from Ziurys et al. (1982). At most, only two rotational transitions of CCH were observed for a given source such that at least one variable had to be fixed; in this case, the gas kinetic temperature was held constant at $T_K = 20$ K, a standard temperature for

molecular gas in PNe (see Zack & Ziurys 2013; Edwards & Ziurys 2014; Edwards et al. 2014).

For the two sources for which two rotational transitions of CCH were measured, M3–28 and Hb 5, the H_2 density and column density could be adjusted. Specifically, the H_2 density was altered between 1.0×10^4 – 1.0×10^8 cm^{-3} , while the column density was varied between 1.0×10^{11} – 1.0×10^{16} cm^{-2} . The range in H_2 density was based on the critical densities of the relevant transitions and their Einstein A coefficients for an assumed gas kinetic temperature of 20 K. The densities derived from these

Figure 2. Spectra of the $N = 3 \rightarrow 2$ line of CCH observed toward M3-28 and K3-45. The spectral resolution is 2 MHz, and the temperature scale is T_A^* . Optical images of each nebula, obtained from <https://faculty.washington.edu/balick/PNIC/>, are shown below their respective spectrum. The SMT beam size at 262 GHz is overlaid on the images. The U-shaped line profiles are clearly visible in both sets of spectra. The peaks in the K3-45 spectrum are remarkably consistent with those seen in HCN and HNC. These results suggest that both sources contain bipolar outflows oriented partly along the line of sight.

sources fell in the range of $\sim 1\text{--}3 \times 10^5 \text{ cm}^{-3}$, which are consistent with values derived from other molecules in these sources, considering relative dipole moments (e.g., Zack & Ziurys 2013; Schmidt & Ziurys 2017). For the remaining sources, the H_2 density was fixed to the average of the value for M3-28 and Hb 5. The line width for each fit was set to the average line width for the CCH transitions observed in that particular source. Additionally, a source filling factor was applied to all line intensities, based on the size of the given nebula from its optical image (see Table 1). Because the molecular gas has a knotty, non-uniform distribution in PNe, a “clump volume filling factor” (the percent of the volume of the nebula filled with clumped material, in this case taken to be the filling factor in the plane of the sky) was also applied to the data. The clump volume filling factors varied from 0.2 to 0.33, depending on the source (see Schmidt & Ziurys 2016 for more details). Upon applying these corrections, the resultant column densities were found to lie in the range of $N_{\text{tot}}(\text{CCH}) \sim 0.3\text{--}5.8 \times 10^{14} \text{ cm}^{-2}$ when not considering “clumping,” and $N_{\text{tot}}(\text{CCH}) \sim 0.2\text{--}3.3 \times 10^{15} \text{ cm}^{-2}$ when “clumping” was applied. The non-clump and clump calculations were within a factor of $\sim 3\text{--}6$ of each other. The predicted line intensities from the modeling were on average within 20% of the observed values.

Fractional abundances with respect to H_2 were calculated given these column densities. For two sources (K4-47 and K3-58), H_2 column densities were derived from the measured intensities of the $\nu = 1 \rightarrow 0$ S(1) infrared transition at 2.12 microns ($8.81 \times 10^{-13} \text{ erg cm}^{-2} \text{ s}^{-1}$; Lumsden et al. 2001 and $2.27 \times 10^{-12} \text{ erg cm}^{-2} \text{ s}^{-1}$; Guerrero et al. 2000, respectively). The column density expression of O’Dell et al. (2005) was used, scaled by the appropriate excitation temperature. For K4-47, an excitation temperature of 1550 K was assumed (Lumsden et al. 2001). As such information was not available for K3-58, the excitation temperature of the Helix (~ 900 K; Cox et al. 1998) was used, as the ages of the two nebulae are comparable. This method yielded values of $N_{\text{tot}}(H_2) \sim 2.9 \times 10^{20} \text{ cm}^{-2}$ and $\sim 1.1 \times 10^{20} \text{ cm}^{-2}$ for K4-47 and K3-58,

respectively, with corresponding uncertainties of 9% and 30% (see Schmidt & Ziurys 2016). For the other sources, H_2 column densities were scaled from those of CO (from Schmidt & Ziurys 2016), assuming $\text{CO}/H_2 \sim 10^{-4}$. This ratio is consistent with what is seen in other PNe (see, e.g., Healy & Huggins 1990; Huggins et al. 2002; Zack & Ziurys 2013; Edwards et al. 2014). The respective CO column densities are listed in Table 3 in this work. The derived H_2 column densities agree well with those measured in a few PNe based on pure rotational lines of this molecule (Bernard-Salas & Tielens 2005). Fractional abundances thus derived are $f(\text{CCH}/H_2) \sim 0.04\text{--}3.2 \times 10^{-6}$ in the non-clump case and $f \sim 0.02\text{--}4.7 \times 10^{-6}$ with clumping. Overall, M3-28 appears to possess the lowest CCH abundance while Hb 5 has the highest, with K4-47 following closely behind—similar to what was found for HNC and HCN in the same sample of nebulae. Interestingly, M3-28 also exhibits the lowest abundance of HCO^+ .

5. Discussion

5.1. Evolution of CCH Abundances from CSEs to PNe

In circumstellar gas, CCH is believed to be produced through the photodissociation of acetylene near the envelope edge (e.g., Zhang et al. 2008 and references therein):

CCH is subsequently involved in the formation of long carbon chains and higher order hydrocarbons in the outer envelope (e.g., Mookerjee et al. 2012). Observations have shown that CCH is indeed a common molecule in the shells of C-rich AGB stars. Abundances for the species in well-known sources of this type such as IRC+10216, CIT6, IRAS 15194-5115, AFGL 4211, and AFGL 3068 fall in the range of $f(\text{CCH}/H_2) \sim 0.24\text{--}1.6 \times 10^{-5}$ (Nyman et al. 1993; Woods et al. 2003; Zhang et al. 2009). From a survey of 35 evolved stars, Fuente

Table 2
Observations of CCH ($X^2\Sigma^+$) toward Planetary Nebulae^a

Source	Transition	T_A^* (mK)	V_{LSR} (km s ⁻¹)	$\Delta V_{1/2}$ (km s ⁻¹)
Hb 5	$N = 1 \rightarrow 0; J = 3/2 \rightarrow 1/2$			
	$F = 2 \rightarrow 1$	12.0 ± 2.0	-3.2 ± 3.4	7.1 ± 1.7
	$F = 1 \rightarrow 0$	8.0 ± 2.0	-4.1 ± 3.4	4.7 ± 1.7
	$N = 3 \rightarrow 2$			
	$J = 7/2 \rightarrow 5/2^{\text{b,c}}$	7.5 ± 1.0	-8.5 ± 4.6	42.4 ± 4.6
K3-17	$J = 5/2 \rightarrow 3/2^{\text{d,c}}$	5.0 ± 1.0	-2.0 ± 4.6	42.4 ± 4.6
	$N = 1 \rightarrow 0$	<1	...	...
	$N = 3 \rightarrow 2$			
	$J = 7/2 \rightarrow 5/2^{\text{b,c}}$	6.0 ± 3.0	26.1 ± 6.9	58.9 ± 6.9
	$J = 5/2 \rightarrow 3/2^{\text{d,c}}$	4.0 ± 3.9	29.6 ± 6.9	65.9 ± 6.9
K3-45	$N = 1 \rightarrow 0; J = 3/2 \rightarrow 1/2$	<1	...	...
	$N = 3 \rightarrow 2$			
	$J = 7/2 \rightarrow 5/2^{\text{b,c}}$	3.5 ± 1.0	16.5 ± 4.6	13.6 ± 4.6
		2.2 ± 1.0	45.5 ± 4.6	13.6 ± 4.6
	$J = 5/2 \rightarrow 3/2^{\text{d,e}}$	2.0 ± 1.0	24.0 ± 4.6	14.1 ± 4.6
K3-58		2.0 ± 1.0	46.0 ± 4.6	11.8 ± 4.6
	$N = 1 \rightarrow 0; J = 3/2 \rightarrow 1/2$	<2	...	...
	$N = 3 \rightarrow 2$			
	$J = 7/2 \rightarrow 5/2^{\text{b}}$	3.4 ± 1.0	20.5 ± 4.6	35.3 ± 4.6
	$J = 5/2 \rightarrow 3/2^{\text{d}}$	2.8 ± 1.0	24.0 ± 4.6	35.3 ± 4.6
M1-7	$N = 1 \rightarrow 0; J = 3/2 \rightarrow 1/2$	<1	...	...
	$N = 3 \rightarrow 2$			
	$J = 7/2 \rightarrow 5/2^{\text{b}}$	5.5 ± 1.5	-12.5 ± 4.6	36.0 ± 4.6
M3-28	$J = 5/2 \rightarrow 3/2^{\text{d}}$	4.0 ± 1.5	-12.0 ± 4.6	33.0 ± 4.6
	$N = 1 \rightarrow 0; J = 3/2 \rightarrow 1/2$			
	$F = 1 \rightarrow 0^{\text{f}}$	1.8 ± 0.6	$\sim 30^{\text{g}}$	$\sim 30^{\text{g}}$
	$N = 3 \rightarrow 2$			
	$J = 7/2 \rightarrow 5/2^{\text{b,e}}$	8.5 ± 2.5	43.5 ± 4.6	25.9 ± 4.6
M3-55		7.5 ± 2.5	20.5 ± 4.6	14.1 ± 4.6
	$J = 5/2 \rightarrow 3/2^{\text{d,e}}$	6.0 ± 2.0	43.0 ± 4.6	23.5 ± 4.6
		8.0 ± 2.0	16.0 ± 4.6	11.8 ± 4.6
	$N = 1 \rightarrow 0; J = 3/2 \rightarrow 1/2$	<2		
	$N = 3 \rightarrow 2$		...	...
M4-14	$J = 7/2 \rightarrow 5/2^{\text{b,h}}$	1.4 ± 0.4	25.0 ± 4.6	25.2 ± 4.6
	$N = 1 \rightarrow 0; J = 3/2 \rightarrow 1/2$	<2		
	$N = 3 \rightarrow 2$		...	...
K4-47	$J = 7/2 \rightarrow 5/2^{\text{b}}$	2.6 ± 1.0	50.5 ± 4.6	33.0 ± 4.6
	$J = 5/2 \rightarrow 3/2^{\text{d}}$	2.4 ± 1.0	51.0 ± 4.6	33.0 ± 4.6
	$N = 1 \rightarrow 0; J = 3/2 \rightarrow 1/2$	<1		
NGC 2440	$N = 3 \rightarrow 2$			
	$J = 7/2 \rightarrow 5/2^{\text{b}}$	5.0 ± 1.0	-26.9 ± 4.6	37.7 ± 4.6
	$J = 5/2 \rightarrow 3/2^{\text{d}}$	3.4 ± 1.0	-20.4 ± 4.6	37.7 ± 4.6
NGC 6772a ⁱ	$N = 1 \rightarrow 0; J = 3/2 \rightarrow 1/2$	<1	...	...
NGC 6772b ⁱ	$N = 1 \rightarrow 0; J = 3/2 \rightarrow 1/2$	<1	...	...
	$N = 1 \rightarrow 0; J = 3/2 \rightarrow 1/2$	<2	...	...
	$N = 3 \rightarrow 2$	<5		
M1-12	$N = 3 \rightarrow 2$	<4	90.5	
M1-20	$N = 3 \rightarrow 2$	<4	70.9	

Notes.^a Measured with 1 MHz resolution unless noted otherwise.^b Blend of $F = 4 \rightarrow 3$ and $F = 3 \rightarrow 2$ hyperfine components.^c Partially blended spin-rotation components.^d Blend of $F = 3 \rightarrow 2$ and $F = 2 \rightarrow 1$ hyperfine components.^e U-shaped profile; fit with two velocity components.^f Partially obscured by Galactic contamination.^g Blended velocity components.^h Measured with 4 MHz resolution.ⁱ See the text for the source description.

Table 3
Column Densities and Fractional Abundances

Source		$N(\text{H}_2)$ (cm^{-3})	$N_{\text{tot}}(\text{CCH})$ (cm^{-2})	$N_{\text{tot}}(\text{CO})$ (cm^{-2})	f (CCH/ H_2)
Hb 5	Clump	1.4e5	$2.0 \pm 0.4 \times 10^{14}$	$4.3 \pm 1.5 \times 10^{15}$	$4.7 \pm 0.9 \times 10^{-6}$
	Non-clump	1.9e5	$7.9 \pm 2.1 \times 10^{13}$	$2.5 \pm 2.4 \times 10^{15}$	$3.2 \pm 1.6 \times 10^{-6}$
K3–17	Clump	1.8e5	$3.3 \pm 1.9 \times 10^{15}$	$3.9 \pm 2.0 \times 10^{17}$	$8.5 \pm 3.3 \times 10^{-7}$
	Non-clump	2.3e5	$5.8 \pm 3.9 \times 10^{14}$	$6.5 \pm 5.0 \times 10^{16}$	$8.9 \pm 4.5 \times 10^{-7}$
K3–45					
Blue-shifted	Clump	1.8e5	$3.4 \pm 1.9 \times 10^{14}$	$2.9 \pm 1.6 \times 10^{17}$	$1.2 \pm 0.5 \times 10^{-7}$
	Non-clump	2.3e5	$9.5 \pm 6.4 \times 10^{13}$	$6.7 \pm 1.9 \times 10^{16}$	$1.4 \pm 0.5 \times 10^{-7}$
Redshifted	Clump	1.8e5	$2.2 \pm 1.5 \times 10^{14}$	$2.9 \pm 1.6 \times 10^{17}$	$7.6 \pm 3.3 \times 10^{-8}$
	Non-clump	2.3e5	$6.2 \pm 5.0 \times 10^{13}$	$6.7 \pm 1.9 \times 10^{16}$	$9.3 \pm 4.0 \times 10^{-8}$
K3–58	Clump	1.8e5	$2.6 \pm 0.9 \times 10^{14}$	...	$2.4 \pm 0.4 \times 10^{-6}$
	Non-clump	2.3e5	$5.5 \pm 2.5 \times 10^{13}$	...	$5.0 \pm 1.1 \times 10^{-7}$
M1–7	Clump	1.8e5	$5.7 \pm 2.0 \times 10^{14}$	$8.3 \pm 7.4 \times 10^{17}$	$6.9 \pm 3.3 \times 10^{-8}$
	Non-clump	2.3e5	$1.7 \pm 0.7 \times 10^{14}$	$1.1 \pm 0.2 \times 10^{17}$	$1.5 \pm 0.3 \times 10^{-7}$
M3–28					
Blue-shifted	Clump	2.1e5	$2.2 \pm 1.4 \times 10^{14}$	$9.3 \pm 7.5 \times 10^{17}$	$2.4 \pm 1.2 \times 10^{-8}$
	Non-clump	2.7e5	$4.7 \pm 3.1 \times 10^{13}$	$1.3 \pm 0.3 \times 10^{17}$	$3.6 \pm 1.3 \times 10^{-8}$
Redshifted	Clump	1.9e5	$4.3 \pm 2.2 \times 10^{14}$	$9.3 \pm 7.5 \times 10^{17}$	$4.6 \pm 2.2 \times 10^{-8}$
	Non-clump	2.4e5	$9.4 \pm 4.8 \times 10^{13}$	$1.3 \pm 0.3 \times 10^{17}$	$7.2 \pm 2.0 \times 10^{-8}$
M3–55	Clump	1.8e5	$1.9 \pm 0.7 \times 10^{14}$	$1.1 \pm 0.5 \times 10^{17}$	$1.7 \pm 0.5 \times 10^{-7}$
	Non-clump	2.3e5	$3.4 \pm 1.7 \times 10^{13}$	$2.7 \pm 2.1 \times 10^{16}$	$1.3 \pm 0.6 \times 10^{-7}$
M4–14	Clump	1.8e5	$2.4 \pm 1.1 \times 10^{14}$	$3.6 \pm 1.2 \times 10^{16}$	$6.7 \pm 1.9 \times 10^{-7}$
	Non-clump	2.3e5	$4.9 \pm 2.7 \times 10^{13}$	$1.3 \pm 0.8 \times 10^{16}$	$3.8 \pm 1.6 \times 10^{-7}$
K4–47	Clump	1.8e5	$1.0 \pm 0.3 \times 10^{15}$	...	$3.4 \pm 0.5 \times 10^{-6}$
	Non-clump	2.3e5	$3.0 \pm 1.0 \times 10^{14}$	...	$1.0 \pm 0.2 \times 10^{-6}$

et al. (1998) found CCH abundances of f (CCH/ H_2) ~ 0.025 – 1.0×10^{-4} in 17 C-rich stars, with an average value of $\sim 2.7 \times 10^{-5}$.

Studies of CCH in a limited number of protoplanetary nebulae (PPNe) have also been undertaken, including CRL 2688, CRL 618, and SAO 34504, in which abundances of ~ 2.0 – 9.3×10^{-6} were reported (Fuente et al. 1998). As far as PNe are concerned, only a few have been investigated in CCH prior to this work. NGC 7293 (the Helix Nebula), one of the oldest and most well-studied PNe, was found to have a fractional abundance of $f(\text{CCH}/\text{H}_2) \sim 1 \times 10^{-6}$ at one position within the source (Tenenbaum et al. 2009). In the young planetary nebula NGC 6537 (the Red Spider Nebula), which possesses a hot central star ($\sim 340,000$ K; Matsuura et al. 2005), the CCH abundance was estimated to be $f \sim 6.9 \times 10^{-8}$ (Edwards & Ziurys 2013), while another young PN, NGC 7027, was observed to have a value of $f \sim 5.4 \times 10^{-8}$ by Zhang et al. (2008). Our work has expanded the number of PNe detected in CCH to nine additional nebulae, with abundances in the range of $f \sim 0.02$ – 4.7×10^{-6} and an average value of 1.1×10^{-6} .

Overall, there appears to be a small decrease of a factor of ~ 5 in the abundance of CCH from the AGB to PPN phases. Then, the abundance of the molecule does not appear to significantly change between the PPN and PN stages. These results suggest that, as has been found for HNC (Schmidt & Ziurys 2017), CCH undergoes some photodestruction in PPNe, but then the abundance “freezes” at the onset of the planetary nebula stage. Therefore, a large fraction of CCH survives the transition from the AGB stage to the PN stage. This “survival” may result from an even balance between competing production and destruction routes. Based on their models of NGC 7027, Hasegawa & Kwok (2001) and Zhang et al. (2008) suggest that remnant CCH from the AGB phase is destroyed, and that the molecule is resynthesized by the ongoing

photodestruction of HCCH, as per circumstellar chemistry. As will be discussed, CCH could also be a product of C_{60} fragmentation.

5.2. CCH in the Late PNe Stage and Beyond

Few models exist describing the chemistry in PNe. Redman et al. (2003) is one exception, and their model includes CCH. These authors predict a fractional abundance of CCH (with respect to H_2) of 1.9×10^{-5} at 2550 years, 7.6×10^{-8} at 6300 years, and 1.3×10^{-9} at 10,050 years—a decline in abundance of about 10^4 over the expected lifetime of PNe ($\sim 10,000$ years). While the abundance around 4000 years is comparable to the average observed values found here, the prediction at 10,050 years is significantly lower. Moreover, as shown in Figure 3, the CCH abundances of the PNe observed in this work (green circles), as well as those from previous studies (green stars), do not vary significantly with kinematic age. Values span a narrow window of $f \sim 10^{-8}$ – 10^{-6} over a period of $\sim 12,000$ years. Most notable are the CCH abundances for the oldest nebulae, K3–58 ($\sim 11,000$ years) and the Helix ($\sim 12,000$ years), which are comparable (2.4×10^{-6} and 1×10^{-6}) to those of the younger objects. This is consistent with the observed abundances of HCN, HCO^+ , and HNC (also plotted), which are similarly stable over the PN lifetime, though they are lower than those of CCH. Note that some of the ages of the PNe have considerable uncertainties, as listed in Table 1, but the trend nonetheless remains. The estimates of Redman et al. (2003) for CCH are also plotted with green triangles, showing a steady decline to $f \sim 1 \times 10^{-9}$.

Curiously, CCH is among the most abundant molecules in the diffuse ISM. Nyman (1984), for instance, searched for the $N=0 \rightarrow 1$ transition in low-density clouds along the lines of sight, detecting the molecule against W49 with an abundance of $f \sim 5.0 \times 10^{-8}$. More recently, Lucas & Liszt (2000) searched for the $N=0 \rightarrow 1$ line of CCH in absorption toward

Figure 3. Plot of fractional abundances of HCN (red), HCO^+ (blue), HNC (cyan), and CCH (green) relative to H_2 in PNe vs. kinematic age in years. Circles represent data from this work (CCH) and Schmidt & Ziurys (2016, 2017: HCN, HCO^+ , and HNC), while stars indicate measurements for NGC 7027, NGC 6537, M2–48, NGC 7293, NGC 6853, M4–9, NGC 6781, and NGC 6720 from previous studies (Zhang et al. 2008; Tenenbaum et al. 2009; Edwards & Ziurys 2013; ages from Matsuura et al. 2005; Meaburn et al. 2008; Edwards & Ziurys 2014; also see Schmidt & Ziurys 2016, 2017). The red, blue, cyan, and green triangles (with dashed lines) designate the fractional abundances for HCN, HCO^+ , HNC, and CCH, respectively, from the model of Redman et al. (2003). The measured abundances of all molecules appear to stay relatively constant across the $\sim 10,000$ year lifetime of PNe, while the model predicts a significant decrease.

28 background sources in diffuse clouds. These observations revealed fractional abundances with respect to H_2 ranging from $1.6\text{--}4.2 \times 10^{-8}$, with a mean abundance of 2.9×10^{-8} . Additionally, Gerin et al. (2010) observed CCH along the lines of sight toward three massive star-forming regions, finding a mean fractional abundance of 3.2×10^{-8} . Lucas & Liszt (2000) comment that current models do not adequately replicate the abundances reported in their work. Gerin et al. (2011) had more success with their PDR model for CCH, but failed to account for $\text{c-C}_3\text{H}_2$.

The abundances measured for PNe in this work are on the order of 1–2 magnitudes higher than those seen in diffuse clouds, as has been found for HCN, HNC, and HCO^+ (Schmidt & Ziurys 2016, 2017). As argued in these prior works, these results are consistent with the notion that the polyatomic molecules seen in the diffuse ISM originate in planetary nebulae. They are ejected in dense globules, which slowly disperse into the surrounding medium.

5.3. CCH in Bipolar Nebulae

CCH exhibits U-shaped line profiles toward K3–45 and M3–28 in both spin-rotation components (see Figure 2). These profiles suggest the presence of bipolar outflows in these sources oriented at least partially along the line of sight to the observer. Since little kinematic information exists for both of these sources, the CCH data provides a new window on the morphology of the two objects.

For K3–45, these profiles are duplicated in both HCN and HNC, with average peak red- and blueshifted velocities of 46.0 ± 2.2 and $18.5 \pm 2.2 \text{ km s}^{-1}$ (Schmidt & Ziurys 2016, 2017). These values agree well with those for CCH in this source: $45\text{--}46 \pm 4$ and $16\text{--}24 \pm 5 \text{ km s}^{-1}$. Furthermore,

Huggins et al. (2005) noted that the nebula exhibited a double-peaked profile in CO in the $J=2 \rightarrow 1$ line, overlaid with sharp Galactic emission peaks. The optical picture (Figure 2) shows a blurred image that appears to trace a bipolar flow roughly oriented N–S, consistent with the position angle of 18° reported by Corradi et al. (1998), who had first labeled K3–45 as a bipolar nebula from narrowband CCD images. Later, Stanghellini et al. (2002) classified K3–45 as a bipolar nebula based on $\text{H}\alpha$, $[\text{O III}] 5007 \text{ \AA}$, and $[\text{N II}] 6584 \text{ \AA}$ images, taken from Manchado et al. (1996a). Given the classification for this nebula, our spectra suggest a bipolar flow tilted toward the line of sight, though more data are clearly needed to further investigate the orientation of the flow.

In the case of M3–28, the U-shaped spectrum is seen distinctly in CCH, but is not as obvious in HCN or HNC. The optical image shows a clear bipolar flow oriented N–S (Figure 2) in the plane of the sky. From their morphological survey of northern PNe using two filters corresponding to $\text{H}\alpha + [\text{N II}]$ and $[\text{O III}] 5007 \text{ \AA}$, Manchado et al. (1996b) speculated that this source may be quadrupolar. Thus, CCH may be tracing a secondary outflow along the line of sight, or the image is simply misleading. The fact that the HCN, HNC, and HCO^+ spectra are not obviously U-shaped may mean that the bipolar flow has lower density and is better traced in CCH.

5.4. A Connection to C_{60} ?

The formation mechanisms for C_{60} in the ISM remain a puzzle. The “bottom-up” scheme, which entails the creation of C_{60} from smaller compounds such as atomic carbon, C_2 units, or possibly smaller fullerenes, is referred to as “closed-network growth,” or CNG (e.g., Dunk et al. 2012). However, the timescales necessary for such formation are considered to be

too long for low-density settings (Micelotta et al. 2012), though Cherchneff et al. (2000) found that such processes are efficient in the envelopes of evolved stars. The proposed “top-down” routes involve the UV photolysis of hydrogenated amorphous carbon (HACs), or UV dehydrogenation of polycyclic aromatic hydrocarbons (PAHs). In the former scheme, hollow structures containing aromatic clusters connected by aliphatic bridging groups are created, which are subsequently dehydrogenated by UV radiation, leading to large fullerene cages that shrink to C_{60} and C_{70} by releasing C_2 (Micelotta et al. 2012). Indeed, broad 6–9 μm emission, which may be associated with HACs (García-Hernández et al. 2010, 2011, 2012; Otsuka et al. 2014), was seen in many of the fullerene-containing Magellanic Cloud PNe observed by García-Hernández et al. (2011), as well as in the three PNe studied by Bernard-Salas et al. (2012). Model spectra of 3 nm HAC particles produced by Bernard-Salas et al. (2012) show that this broad feature can be reproduced relatively successfully, adding credence to this hypothesis. Furthermore, García-Hernández et al. (2011) argue that the presence of PAH clusters, fullerenes, and planar C_{24} (which they report as having possibly been detected in some of their observed PNe) supports the formation of fullerenes from the vaporization of HACs. A possible detection of C_{24} was also made in the fullerene-containing PN K3–54 (García-Hernández et al. 2012). The latter “top-down” pathway generates graphene, followed by carbon loss and pentagon formation and rearrangement, which then allows the molecule to curl and “stitch” itself up into a closed fullerene (Chuvilin et al. 2010; Berné & Tielens 2012; Berné et al. 2015). Micelotta et al. (2012) noted, however, that under interstellar conditions, it would be impossible to remove the precise number of carbons necessary to close the graphene flake into a fullerene cage.

Both the “bottom-up” and HAC formation mechanisms for C_{60} involve C_2 as either a precursor or a product of cage shrinkage. Therefore, a relationship may exist between C_{60} and C_2 . As discussed, CCH is the millimeter proxy for C_2 . The observations conducted here identified CCH in nine PNe, but failed to detect the molecule in M1–12 and M1–20—two nebulae known to contain C_{60} . While these are small number statistics, the data may suggest an anti-correlation between C_{60} and CCH.

This apparent lack of correlation may be related to the temperature of the central star. García-Hernández et al. (2012) noted that the stellar temperatures for all C_{60} -containing PNe fell within a narrow range of $T_* \sim 30,000$ –45,000 K. All of the PNe in which CCH was detected for which such information was available display significantly higher stellar temperatures than any of the fullerene sources, within the range of 72,200 K and $\sim 131,000$ K (see Table 1). NGC 2440 and NGC 6772 also have high central star temperatures, though CCH was not detected in either object. However, these are more complex sources and may not couple well to the telescope beam (see Schmidt & Ziurys 2016 for optical images and beam sizes at the CCH frequencies). In the case of NGC 6772, the distribution of H_2 is a shell around the central star (Marquez-Lugo et al. 2013); our observations were centered on the hole in this shell, and thus are not optimized. For NGC 2440, H_2 is located in a 10'' region centered on the nebula, and has linear structures extending from this central source (Latter et al. 1995). These structures do not fully fill our 30'' beam, and therefore, beam dilution may be significant. Generally, these data suggest that an increased T_* (and elevated UV flux)

may lead to the photodissociation of C_{60} . The subsequent release of C_2 molecules may then produce CCH through reactions with H_2 . There is a substantial activation energy for ejection of C_2 from C_{60} (e.g., Zettergren et al. 2010; Micelotta et al. 2012), but at sufficiently high stellar temperatures, this energy barrier could be overcome. Clearly H_2 has to be present for CCH to form, however, via the proposed process. In both M1–12 and M1–20, H_2 was only tentatively detected (Lumsden et al. 2001), although the $J = 1 \rightarrow 0$ transition of CO was apparently observed in the former source (Zhang et al. 2000). Additional observations of H_2 and related theoretical work are clearly needed to further examine this prospect.

Alternatively, nondetection of CCH in these nebulae could result from the large distances to these PNe (3.9 kpc and 7.3 kpc, respectively; Otsuka et al. 2014) and the lack of sensitivity rather than the absence of CCH in either source. Using the upper limits for the peak line temperatures of the $N = 3 \rightarrow 2$ transitions and the line width for M1–12 from Zhang et al. (2000), an upper limit column density of $4.4 \times 10^{15} \text{ cm}^{-2}$ (considering clumping) was calculated for both sources. Since neither CO column densities nor H_2 brightnesses were available for either source, the average H_2 column density measured for K4–47 and K3–58 was used to calculate abundances. This average value is consistent with other measured H_2 column densities (Bernard-Salas & Tielens 2005), and is likely a representative number. An upper limit abundance of 2.2×10^{-5} was then obtained, comparable to the abundance prediction of Redman et al. (2003) for 2550 years, the closest point to either nebula’s kinematical age.

6. Conclusions

The detection of CCH in nine new planetary nebulae suggests that yet another polyatomic molecule is a fairly common constituent in these objects. The total number of CCH-bearing PNe is now 12, several of which are quite evolved. CCH abundances with respect to H_2 were seen not to vary with kinematic age, as is also the case for HCN, HNC, and HCO^+ . The molecule therefore maintains a high abundance from the AGB stage to the late PN phase, and may populate the diffuse ISM. Furthermore, CCH is present in those sources that contain HCN, HNC, and HCO^+ —an indicator that these particular nebulae are carbon-rich. The radical may be associated with nebulae containing hot central stars, and be linked to the photodestruction of C_{60} through the intermediate C_2 . More data is needed to support this hypothesis.

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