

DETECTION OF THE CCP RADICAL ($X^2\Pi_r$) IN IRC +10216: A NEW INTERSTELLAR PHOSPHORUS-CONTAINING SPECIES

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ABSTRACT

The CCP radical ($X^2\Pi_r$) has been detected in the circumstellar gas of IRC +10216, the fifth phosphorus-bearing molecule identified in interstellar space. This identification was made on the basis of new laboratory millimeter/submillimeter direct absorption measurements, conducted in the range 120–413 GHz. Four rotational transitions of this species were observed using the Arizona Radio Observatory (ARO) 12 m telescope on Kitt Peak at 2 and 3 mm in wavelength. Each transition consists of lambda-doublets, which are well-separated in frequency in IRC +10216; five of these eight possible lines of CCP were clearly detected, while the remaining three were contaminated by stronger emission from other species. The column density derived for CCP was $N_{\text{rot}} = 1.2 \times 10^{12} \text{ cm}^{-2}$ and $T_{\text{rot}} = 21 \text{ K}$. Modeling of the line profiles suggests that CCP arises from an extended shell with a maximum radius of $\sim 40''$. The abundance of this radical, relative to H_2 , is $f \sim 1 \times 10^{-9}$ —roughly comparable to that of PN and CP in this source. CCP may be produced from radical-radical reactions of CP, or ion-molecule chemistry involving P^+ and HCCH. The identification of CCP is additional evidence that phosphorus chemistry is active in carbon-rich circumstellar gas.

Subject headings: astrochemistry — circumstellar matter — ISM: abundances — ISM: molecules — radio lines: stars — stars: individual (IRC +10216)

Online material: machine-readable table

1. INTRODUCTION

The astrochemistry of phosphorus, the 18th most cosmically abundant element in the interstellar medium, is an enigma. This element is predicted to condense onto grains in circumstellar envelopes, particularly in the form of schreibersite, $(\text{Fe}, \text{Ni})_3\text{P}$ (Lodders & Fegley 1999). This mineral is a common constituent in certain types of meteorites, supporting the condensation pathway (Pasek & Lauretta 2005). However, phosphorus appears to undergo little, if any, depletion in diffuse clouds (Lebouteiller et al. 2005), suggesting that a large fraction of this element remains in the gas phase. Yet, the only phosphorus-containing molecule observed in dense clouds to date has been PN, with an abundance relative to H_2 of $\sim 2 \times 10^{-10}$ (Ziurys 1987; Turner & Bally 1987).

Despite the predicted condensation, the gas-phase chemistry of phosphorus appears to be active in circumstellar gas (Milam et al. 2008). Recently, PN and PO have been detected in the shell of the oxygen-rich red supergiant VY CMa (Tenenbaum et al. 2007; Ziurys et al. 2007), and PN and HCP have also been observed in the envelope of the carbon-rich proto-planetary nebula CRL 2688 (Milam et al. 2008). In IRC +10216, the well-known carbon-rich star, HCP, CP, and PN have been found (Guélin et al. 1990; Agúndez et al. 2007; Milam et al. 2008). Milam et al. (2008) estimate that only about 11% of the available phosphorus is in known gas-phase molecules toward IRC +10216.

A potential new interstellar species containing this element is CCP. This molecule is predicted to be present in carbon-rich dense clouds (e.g., Charnley & Millar 1994); however, rest frequencies have not been available for CCP for astronomical searches. The only laboratory detection of this free radical was obtained by Sunahori et al. (2007), who measured the $^2\Delta-X^2\Pi_r$ electronic transition with medium resolution ($\pm 0.1 \text{ cm}^{-1}$).

Here we report the first measurement of the pure rotational spectrum of CCP in its $^2\Pi_r$ ground state using millimeter/submillimeter direct absorption techniques. On the basis of this laboratory study, we detected CCP in the circumstellar envelope of IRC +10216. Four transitions of this molecule were observed in the range 108–159 GHz, using the 12 m telescope of the Arizona Radio Observatory (ARO). The fractional abundance found for CCP in the source is $f \sim 10^{-9}$. Here we present both our laboratory and astronomical results and discuss their implications for phosphorus chemistry.

2. EXPERIMENTAL

The rotational spectrum of CCP was measured using one of the millimeter/submillimeter direct absorption systems in the Ziurys laboratory. This instrument consists of a radiation source, a single-pass gas cell, and a detector; see Savage & Ziurys (2005) for additional details. CCP was produced by the reaction of approximately 1–2 mtorr of HCCH with <1 mtorr of gas-phase phosphorus in a 200 W AC discharge in the presence of 40 mtorr of argon carrier gas. The phosphorus was vaporized from its red solid form by heating it to $\sim 300^\circ\text{C}$. The discharge plasma from this mixture glowed faint blue in color.

Initially, a harmonically related doublet was first identified corresponding to a rotational constant of $\sim 6.36 \text{ GHz}$, whose splitting decreased with increasing frequency. Such a pattern is anticipated for the $\Omega = 1/2$ spin component of a molecule with a $^2\Pi_r$ ground state, such as CCP, as a result of lambda-doubling interactions. Chemical tests showed that these doublets arose from both acetylene and phosphorus. The lambda-doublets were measured down to 120 GHz, at which point each line further splits into two features, attributed to hyperfine interactions of the phosphorus nuclear spin of $I = 1/2$. These lines were therefore identified as the $\Omega = 1/2$ spin component of CCP. The spectrum of the doubly substituted ^{13}C isotopologue, $^{13}\text{C}^{13}\text{CP}$, was also observed to confirm the identification; these results will be discussed elsewhere (M. Sun et al., in preparation).

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TABLE 1
OBSERVED TRANSITION FREQUENCIES OF CCP
($X^2\Pi_r$; $\Omega = 1/2$)

$J'' \rightarrow J'$	$F'' \rightarrow F'$	Parity	ν_{obs} (MHz)	$\nu_{\text{obs}} - \nu_{\text{calc}}$ (MHz)
9.5 \rightarrow 10.5	10 \rightarrow 11	<i>e</i>	133577.511	0.044
	9 \rightarrow 10	<i>e</i>	133579.049	0.008
	10 \rightarrow 11	<i>f</i>	133623.741	-0.006
	9 \rightarrow 10	<i>f</i>	133625.600	0.016
20.5 \rightarrow 21.5	^a	<i>e</i>	273489.512	0.010
	^a	<i>f</i>	273519.557	-0.019

NOTE.—Table 1 is published in its entirety in the electronic edition of the *Astrophysical Journal*. A portion is shown here for guidance regarding its form and content.

^a Hyperfine structure collapsed.

Twenty-four rotational transitions of CCP were measured in the range 120–413 GHz (see Table 1), and representative spectra are exhibited in Figure 1. The top panel displays the $J = 20.5 \rightarrow 21.5$ lines near 273 GHz. This transition is split into two lines, labeled by *e* and *f*, due to lambda-doubling. The bottom panel presents the $J = 9.5 \rightarrow 10.5$ transition near 133 GHz. Here each lambda-doublet is additionally split into two hyperfine components.

Because only the $\Omega = 1/2$ spin-orbit component was observed, the spectrum of CCP was analyzed using a Hund's case (c) effective Hamiltonian. The analysis was limited to the lambda-doubling and magnetic hyperfine terms for a $^2\Pi$ state that are diagonal in Ω , namely $p+2q$, h , d , and their centrifugal distortion parameters. The spectroscopic constants determined for CCP are listed in Table 2. The overall rms of the fit is 55 kHz. (The experimental accuracy is ± 50 kHz.)

3. OBSERVATIONS

The data were taken during the period 2007 October–December using the ARO 12 m telescope on Kitt Peak, Arizona.

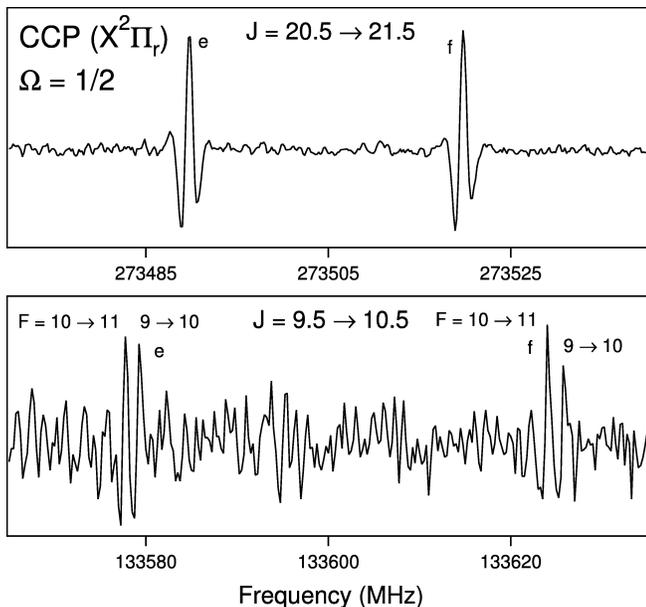


FIG. 1.—Laboratory spectra of the $J = 20.5 \rightarrow 21.5$ (top) and $9.5 \rightarrow 10.5$ (bottom) rotational transitions near 273 and 133 GHz of CCP ($X^2\Pi_r$; $\Omega = 1/2$). Each transition consists of *e* and *f* parity components generated by lambda-doubling interactions. The $J = 9.5 \rightarrow 10.5$ lambda-doublets are each additionally split into two lines because of phosphorus hyperfine coupling, labeled by quantum number F .

TABLE 2
SPECTROSCOPIC CONSTANTS FOR CCP
($X^2\Pi_r$; $\Omega = 1/2$)

Parameter	This Work	Previous Work
<i>A</i>	...	4257000 ^a
<i>B</i>	6362.4080(28)	6390 ^b , 6367 ^b
<i>D</i>	0.0019913(48)	
<i>H</i>	$5.3(2.5) \times 10^{-9}$	
$p+2q$	49.92(54)	
$(p+2q)_D$	-0.01500(48)	
$(p+2q)_H$	$5.6(2.1) \times 10^{-7}$	
<i>h</i>	533(54)	
h_D	1.35(35)	
<i>d</i>	660(210)	
rms	0.055	

NOTE.—Values are in MHz; errors are 3σ in the last quoted decimal places.

^a From Sunahori et al. (2007); *A* originally given in cm^{-1} .

^b Theoretical calculations from Sunahori et al. (2007) and El-Yazal et al. (1997).

The receivers used were dual-channel, SIS mixers in the 2 and 3 mm bands. The mixers were tuned single-sideband with image rejections typically ≥ 20 dB. The back ends employed were 256-channel filter banks with 1 and 2 MHz resolution, respectively, operated in parallel mode (2×128 channels). The temperature scale was determined by the chopper wheel method, corrected for forward spillover losses, and is given as T_R^* . The radiation temperature T_R , assuming the source fills the main beam, is then $T_R = T_R^*/\eta_c$. Here η_c is the corrected beam efficiency, with $\eta_c = 0.84$ – 0.78 for the 12 m at the 2 mm frequencies, and $\eta_c = 0.89$ for the 3 mm measurements. A 10 MHz local oscillator shift was routinely done to identify any image contamination. The measurements were conducted in beam-switching mode with a $\pm 2'$ subreflector throw toward IRC +10216 ($\alpha = 9^{\text{h}}47^{\text{m}}57.4^{\text{s}}$, $\delta = 13^{\circ}16'44''$ [J2000.0]). Rest frequencies and beam sizes are given in Table 3. The pointing accuracy is $\sim \pm 5''$.

TABLE 3
LINE PARAMETERS FOR CCP ($X^2\Pi_r$) IN IRC +10216

Transition	Frequency ^a (MHz)	T_R^* (mK)	$\Delta V_{1/2}$ (km s^{-1})	V_{LSR} (km s^{-1})
<i>J</i> = 8.5 \rightarrow 7.5:				
<i>e</i> : $F = 9 \rightarrow 8$	108,130.5	^b		
<i>e</i> : $F = 8 \rightarrow 7$	108,133.1			
<i>f</i> : $F = 9 \rightarrow 8$	108,179.1	3.0 ± 1.5 ^c	50 ± 6 ^c	-25 ± 6 ^c
<i>f</i> : $F = 8 \rightarrow 7$	108,182.2			
<i>J</i> = 10.5 \rightarrow 9.5:				
<i>e</i> : $F = 11 \rightarrow 10$	133,577.5	^b		
<i>e</i> : $F = 10 \rightarrow 9$	133,579.0			
<i>f</i> : $F = 11 \rightarrow 10$	133,623.7	3.5 ± 2.0	27 ± 4	-29 ± 4
<i>f</i> : $F = 10 \rightarrow 9$	133,625.6			
<i>J</i> = 11.5 \rightarrow 10.5:				
<i>e</i> : $F = 12 \rightarrow 11$	146,300.1	^b		
<i>e</i> : $F = 11 \rightarrow 10$	146,301.4			
<i>f</i> : $F = 12 \rightarrow 11$	146,345.3	2.5 ± 1.5	33 ± 4	-27 ± 4
<i>f</i> : $F = 11 \rightarrow 10$	146,346.7			
<i>J</i> = 12.5 \rightarrow 11.5:				
<i>e</i> : $F = 13 \rightarrow 12$	159,022.2	2.5 ± 1.5	30 ± 4	-27 ± 4
<i>e</i> : $F = 12 \rightarrow 11$	159,023.2			
<i>f</i> : $F = 13 \rightarrow 12$	159,066.1	3.0 ± 1.5	30 ± 4	-25 ± 4
<i>f</i> : $F = 12 \rightarrow 11$	159,067.3			

NOTE.—Line parameters measured for lambda-doubling components *e* and *f*, each consisting of two blended hyperfine lines.

^a Beam sizes at 108, 133, 146, and 159 GHz are $58''$, $47''$, $43''$, and $40''$, respectively.

^b Contaminated by stronger feature of known molecule.

^c Partially resolved hyperfine splitting.

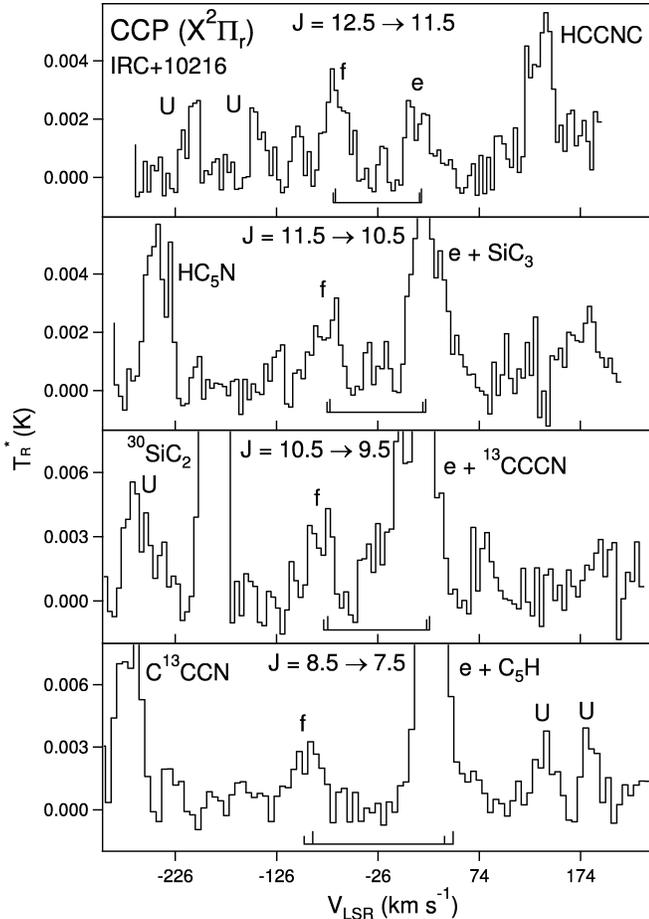


Fig. 2.—Spectra of the $J = 8.5 \rightarrow 7.5$, $10.5 \rightarrow 9.5$, $11.5 \rightarrow 10.5$, and $12.5 \rightarrow 11.5$ transitions of CCP ($X^2\Pi_r$) near 108, 133, 146, and 159 GHz, respectively, observed toward IRC +10216 using the ARO 12 m telescope. The spectral resolution is 2 MHz. Each transition is split into lambda-doublets, labeled by e and f , as well as by smaller hyperfine structure, as indicated underneath the spectra. The lambda-doublet is clearly visible in the $J = 12.5 \rightarrow 11.5$ data, although the e components of the other transitions are contaminated by other species. The $J = 8.5 \rightarrow 7.5$ f line shows evidence of partially resolved hyperfine structure. These spectra were obtained in 25–67 hr of integration time, with typical rms values of 0.5–0.7 mK (1σ).

4. RESULTS AND ANALYSIS

In this study, four rotational transitions were measured toward IRC +10216 at 2 and 3 mm (see Table 3). The lambda-doubling components are split by 44–50 MHz for these transitions, or 83–135 km s^{-1} , and therefore exist as distinct features in IRC +10216, where the typical line width is $\Delta V_{1/2} \sim 30 \text{ km s}^{-1}$. The hyperfine splittings, on the other hand, range in magnitude from 1–3 MHz (2–9 km s^{-1}), and therefore would be partially resolved only for the $J = 8.5 \rightarrow 7.5$ transition near 108.1 GHz.

Of the four transitions searched for CCP, one lambda-doublet was found to be free of contaminating features. For the other three, one component of each doublet was obscured by other lines, such as SiC_3 and C_5H . In total, five clean lines of CCP were detected in IRC +10216, as shown in Figure 2. The frequencies of the hyperfine components for each lambda-doublet are indicated by lines under the spectra. As the figure shows, the lambda-doublet of the $J = 12.5 \rightarrow 11.5$ transition near 159 GHz is clearly visible. The phosphorus hyperfine splitting may be partially resolved for the f component of the $J = 8.5 \rightarrow 7.5$ transition near 108 GHz, as suggested by its larger line width

TABLE 4
ABUNDANCES OF PHOSPHORUS-BEARING MOLECULES
IN IRC +10216

Molecule	θ_s (arcsec)	N_{tot} (cm^{-2})	T_{rot} (K)	f (X/H_2)
PN ^a	36	6.3×10^{12}	11	3×10^{-10}
HCP ^a	22	$(1.0\text{--}1.4) \times 10^{14}$	81–111	3×10^{-8}
CP ^a	44 (shell) ^b	5×10^{12}	50 ^c	5×10^{-9}
CCP	80 (shell) ^d	1.2×10^{12}	21	1×10^{-9}

^a From Milam et al. (2008).

^b Inner radius $r \sim 4''$ and outer radius $r \sim 22''$.

^c Assumed value.

^d Inner radius $r \sim 17''$ and outer radius $r \sim 40''$.

(see Table 3). The line profiles for the features where the hyperfine structure is unresolved are somewhat U-shaped, indicating an outer shell distribution for CCP in IRC +10216.

The line parameters determined for the spectra of CCP are listed in Table 3, determined by a stellar “shell” line fitting program. The measured intensities are consistent among the observed features, and except for the $J = 8.5 \rightarrow 7.5$ transition, the line widths are $\Delta V_{1/2} \sim 29 \text{ km s}^{-1}$, as typical for IRC +10216. The LSR velocities of the lines are also at the canonical value for this source, $V_{\text{LSR}} = -26 \text{ km s}^{-1}$. Furthermore, the line intensities for the uncontaminated lambda-doublets are virtually equal, as expected.

5. DISCUSSION

5.1. Abundance and Distribution of CCP in IRC +10216

To determine the abundance of CCP, a rotational diagram was constructed. Because these features appear somewhat U-shaped, the source is probably resolved by the 12 m beam ($\theta_b \leq 58''$), and thus a uniform filling factor was assumed. This analysis results in a column density of $N_{\text{tot}} = 1.2 \times 10^{12} \text{ cm}^{-2}$ and a rotational temperature of $T_{\text{rot}} = 21 \text{ K}$. The fractional abundance of CCP is therefore $f \sim 10^{-9}$, assuming a mass-loss rate of $3 \times 10^{-5} M_{\odot} \text{ yr}^{-1}$ (Men’shchikov et al. 2002).

The radiative transfer code of Biegging & Tafalla (1993) was also used to estimate the abundance of CCP. For this analysis, the line profiles were modeled assuming a spherical geometry, using a distance of 150 pc, a stellar temperature of 2320 K, and a stellar radius of $R_* = 6.5 \times 10^{13} \text{ cm}$ for IRC +10216. Other input parameters include a mass-loss rate of $3 \times 10^{-5} M_{\odot} \text{ yr}^{-1}$ and an expansion velocity of $V_{\text{exp}} = 14.5 \text{ km s}^{-1}$ (e.g., Agúndez & Cernicharo 2006; Men’shchikov et al. 2002). A $T^{-0.7}$ temperature profile and r^{-2} density law were used (e.g., Kemper et al. 2003). The best fit to the uncontaminated line profiles was a shell with a width of $23''$, a maximum radius of $40''$, and a peak abundance of $f(\text{CCP}/\text{H}_2) = 1 \times 10^{-9}$ at a radius of $28''$ (see Table 4).

5.2. Comparison of CCP and Related Molecules

A comparison of abundances and distributions of phosphorus-containing molecules in IRC +10216 is shown in Figure 3 and Table 4. The parameters for HCP, CP, and PN, based on 12 m observations of Milam et al. (2008), were derived using the same model with identical stellar parameters. As the figure shows, both PN and HCP appear to have spherical distributions in IRC +10216 and are likely synthesized primarily by LTE chemistry in the inner shell. Their abundances start to decrease significantly at $r \sim 2 \times 10^{16} \text{ cm}$, or $r \sim 10''$. CP and CCP, in contrast, have more shell-like distributions with maxima at

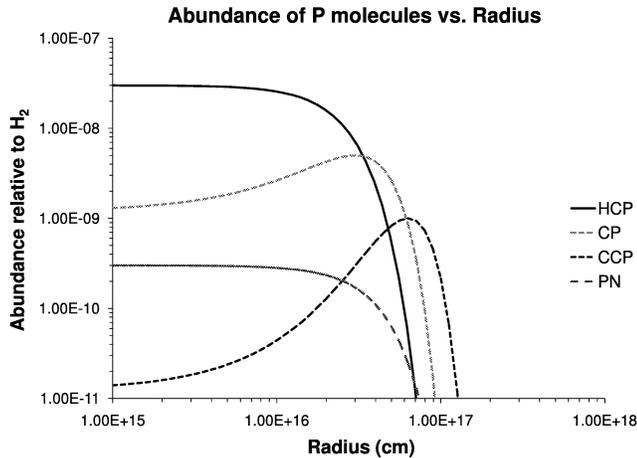


FIG. 3.—Abundances of phosphorus-containing molecules in IRC +10216 as a function of radius from the star. The data for CP, PN, and HCP are from Milam et al. (2008). The plot shows that CCP has a distinct shell distribution that extends farther from the star than that of CP.

$r \sim 4 \times 10^{16}$ cm ($\sim 18''$) and $r \sim 6 \times 10^{16}$ cm ($\sim 28''$), respectively. The abundances of these two radicals begin to increase as those of HCP and PN decrease. The distribution of CP, however, lies within that of CCP.

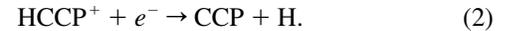
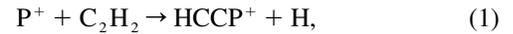
The abundance of CP, relative to H_2 , in IRC +10216 was determined to be $f \sim 5 \times 10^{-9}$ (Milam et al. 2008). Hence, the ratio of CP to CCP is roughly $\sim 5 : 1$. CP is thought to be formed from the photodissociation of HCP, which is quite abundant with $f \sim 3 \times 10^{-8}$ (Agúndez et al. 2007). The relative extent of these two molecules supports this hypothesis. Comparison of their relative spatial distributions suggests that CP may be the parent molecule for CCP (see Fig. 3).

The nitrogen-containing analog of CCP, CCN, has not been detected in IRC +10216 (Fuchs et al. 2004). The upper limit to the column density of CCN is $N_{\text{tot}} < 3.8 \times 10^{12} \text{ cm}^{-2}$ —only a factor of 3 higher than that measured for CCP, $N_{\text{tot}} = 1.2 \times 10^{12} \text{ cm}^{-2}$. The cosmic P/N ratio is ~ 0.003 and the HCP/HCN ratio in IRC +10216 is ~ 0.001 (Milam et al. 2008). The CCP/CCN ratio of >0.3 is therefore inconsistent with these other values, and implies that CCN may be detectable given more sensitive observations.

5.3. Formation of CCP in Circumstellar Gas

Current circumstellar models do not predict an abundance for CCP. However, Millar (1991) modeled the chemistry of

carbon-phosphorus species in dense clouds, including CCP. Based on this model, a plausible formation mechanism for this radical in IRC +10216 is



Here acetylene reacts with ionized phosphorus to produce $HCCP^+$, which then recombines with an electron to form CCP. Smith et al. (1989) measured a rate coefficient of $k \sim 1.3 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ at 300 K for reaction (1), with a branching ratio of 95%. Reaction 2 is thought to have a rate coefficient of $\sim 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ (Woodall et al. 2007). This scheme therefore could occur in the outer shell of circumstellar envelopes. In such regions, P^+ is thought to be present with an abundance near $f \sim 10^{-8}$ (Agúndez et al. 2007). Millar (1991) predicts an abundance of $f(\text{CCP}/H_2) = (1-3) \times 10^{-10}$ for this mechanism in a carbon-rich environment.

On the other hand, there is little evidence for ion-molecule-type chemistry in IRC +10216 (Glassgold 1999). As mentioned previously, the CP radical could be a parent species. Reactions of this diatomic molecule with other C-bearing radicals prevalent in the outer envelope could be responsible for the formation of CCP, for example,



Because the reactants involved are free radicals, the rates for these processes could be relatively high, i.e., $k \sim 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ (Millar & Herbst 1994). Moreover, carbon-chain species such as CCH and C_3H are relatively abundant in the outer shell of IRC +10216 with $f \sim 10^{-5}$ to 10^{-8} (Glassgold 1999). CP would thus function as the rate-limiting reagent. The distribution of CCP should then anticorrelate with CP, as is apparently found (see Fig. 3).

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