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LETTER TO THE EDITOR

## Tentative detection of phosphine in IRC +10216<sup>★</sup>

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### ABSTRACT

**Aims.** The  $J_K = 1_0-0_0$  rotational transition of phosphine ( $\text{PH}_3$ ) at 267 GHz has been tentatively identified with a  $T_{\text{MB}} \sim 40$  mK spectral line observed with the IRAM 30-m telescope in the C-star envelope IRC +10216.

**Methods.** A radiative transfer model was used to fit the observed line profile.

**Results.** The derived  $\text{PH}_3$  abundance relative to  $\text{H}_2$  is  $6 \times 10^{-9}$ , although it may have a large uncertainty due to the lack of knowledge about the spatial distribution of this species. If our identification is correct, it implies that  $\text{PH}_3$  has a similar abundance to what is reported for HCP in this source and that these two molecules (HCP and  $\text{PH}_3$ ) together take up about 5% of phosphorus in IRC +10216. The abundance of  $\text{PH}_3$ , like that of other hydrides in this source, is not well explained by conventional gas-phase LTE and non-LTE chemical models, and may imply formation on grain surfaces.

**Key words.** stars: individual: IRC +10216 – stars: carbon – radio lines: stars – astrochemistry – line: identification – stars: AGB and post-AGB

## 1. Introduction

Of the nearly 150 molecules detected so far in interstellar and circumstellar media, around 3/4 can be formed from just four elements (H, C, N, and O). The remaining 1/4 contain metals (Na, K, Al, Mg, and Fe), halogens (F and Cl), and to a large extent the second-row elements Si, P, and S. The scarcity of molecules containing the second-row elements Si, P, and S, compared to their first-row analogs C, N, and O, on one hand, reflects a lower cosmic abundance (Si/C  $\sim$  1/8, P/N  $\sim$  1/300, and S/O  $\sim$  1/30; Asplund et al. 2005) and, on the other, important chemical differences. Second-row elements have generally a larger refractory character; i.e., they tend to form solid condensates and deplete from the gas phase (Field 1974; Turner 1991; Lodders & Fegley 1999). Also, chemical bonds formed by first-row elements are generally stronger and the resulting molecules are stabler than the corresponding second-row analogs. For example, the high stability of C-C bonds allows a wide variety of organic molecules to form, while an Si-based chemistry is much more limited.

The very limited number of interstellar and circumstellar P-bearing molecules known for a long time, just PN and CP (Turner & Bally 1987; Ziurys 1987; Guélin et al. 1990) in contrast to the nearly 50 N-bearing molecules found, may have been related to a sort of mixing of all the factors mentioned

above: first, the more than hundred-fold decrease in the cosmic abundance of P compared to that of N; second, the likely strong depletion of phosphorus suggested by observations of some P-bearing species (Turner et al. 1990); and lastly, some important differences between the chemistry of P and that of N, which are indicated by, for example, the non reactivity of  $\text{PH}_n^+$  ( $n = 0, 3$ ) ions with  $\text{H}_2$  as opposed to the case of  $\text{NH}_n^+$  (Thorne et al. 1984; Adams et al. 1990).

In recent years, however, we have seen the discoveries, mostly in circumstellar media, of new phosphorus compounds such as HCP, PO, and  $\text{C}_2\text{P}$  (Agúndez et al. 2007; Milam et al. 2008; Tenenbaum et al. 2007; Halfen et al. 2008), which permit us to discuss the chemistry of phosphorus on a wider observational basis. In this letter we present the tentative detection of  $\text{PH}_3$ , the phosphorus analog of  $\text{NH}_3$ , in the carbon-rich circumstellar envelope IRC +10216. This species, known to be abundant in the atmospheres of the giant gaseous planets Jupiter and Saturn (Weisstein & Serabyn 1996), has never been observed outside the Solar System.

## 2. Observations and results

The phosphine molecule,  $\text{PH}_3$ , is an oblate symmetric top, thus its rotational levels are given by two quantum numbers ( $J$ ,  $K$ ), and radiative transitions are only allowed within levels of the same  $K$  ladder ( $\Delta J = 1$ ,  $\Delta K = 0$ ). The  $K$  ladders are grouped into two distinct forms: ortho ( $K = 3n$ ,  $n$  an integer) and para ( $K \neq 3n$ ), between which both radiative and collisional transitions are severely forbidden. Its rotational spectrum has been extensively investigated in the laboratory, allowing for the very weak

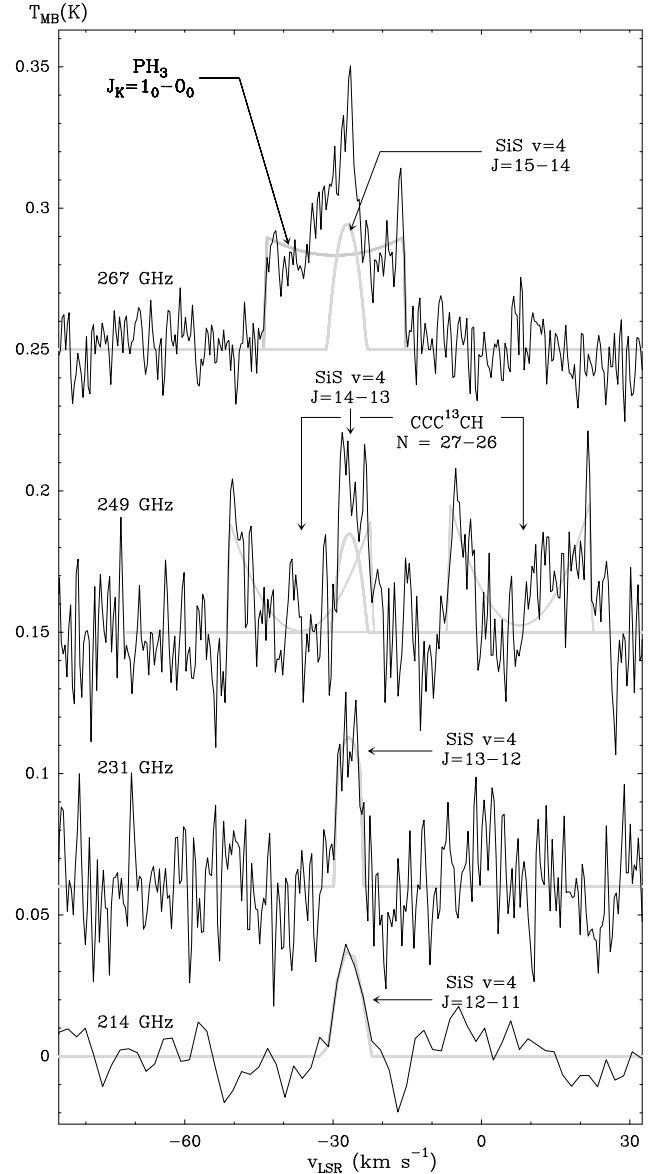
<sup>★</sup> Based on observations carried out with the IRAM 30-m telescope and the Caltech Submillimeter Observatory (CSO). IRAM is supported by INSU/CNRS (France), MPG (Germany), and IGN (Spain). The CSO is operated by the California Institute of Technology under funding from the National Science Foundation, Grant No. AST-0540882.

“forbidden” transitions ( $\Delta J = 0$ ,  $\Delta K = \pm 3$ ) to be measured and for the hyperfine structure due to the <sup>1</sup>H and the <sup>31</sup>P nuclear spins to be resolved (see Cazzoli & Puzzarini 2006, and references therein). In contrast to NH<sub>3</sub>, no evidence of inversion doubling has been found in the case of PH<sub>3</sub>. The electric dipole moment has been measured as  $0.57395 \pm 0.0003$  D (Davies et al. 1971).

Following the recent detection of HCP in IRC +10216 (Agúndez et al. 2007), it was speculated that PH<sub>3</sub> might be detectable in this source if the PH<sub>3</sub>/HCP abundance ratio is similar to the NH<sub>3</sub>/HCN one. Prompted by this hypothesis we searched for the fundamental ortho-PH<sub>3</sub>  $1_0-0_0$  line, at 267 GHz, with the IRAM 30-m telescope. Preliminary observations with a low spectral resolution, 1.25 MHz, were done in 2007 May and we found significant emission at the frequency of the PH<sub>3</sub>  $1_0-0_0$  line and with the expected linewidth ( $v_{\text{exp}} = 14.5$  km s<sup>-1</sup> for most of the molecular lines in IRC +10216; Cernicharo et al. 2000). The line, however, showed a profile unusual for IRC +10216: neither really U-shaped nor flat-topped. Encouraged by this result we returned to the 30-m telescope in 2008 February and April to observe this transition again with 4 times higher spectral resolution (320 kHz). Two SIS receivers operating at 1 mm were used simultaneously with upper sideband rejections of  $\sim 10$  dB. The local oscillator was shifted by 80 MHz to identify any contribution from the image sideband. An autocorrelator was used as backend to provide the required spectral resolution of 320 kHz. The secondary mirror was wobbed by  $\pm 90''$  at a rate of 0.5 Hz. The pointing and focus of the telescope were checked every 1–2 h on Saturn, which was closer than  $10^\circ$  to IRC +10216. Here we express the intensity scale in units of main beam brightness temperature  $T_{\text{MB}}$ . The parameter  $B_{\text{eff}}/F_{\text{eff}}$ , used to convert  $T_{\text{A}}^*$  into  $T_{\text{MB}}$ , is 0.51 and the beam size is  $9''$  at 267 GHz for the 30-m.

The resulting spectrum at 267 GHz is shown at the top of Fig. 1. The line profile indicates the blend of a normal cusped line of width  $\sim 29$  km s<sup>-1</sup>, characteristic of optically thin lines arising in the outer envelope (e.g. C<sub>2</sub>H), with a narrower ( $\sim 6$  km s<sup>-1</sup>) sharply peaked line, characteristic of vibrationally excited lines arising close to the star. This latter line was soon identified as the  $J = 15-14$  transition of SiS in its  $v = 4$  vibrational state, based on SiS laboratory spectroscopic data (Sanz et al. 2003; Müller et al. 2007). Emission of SiS in vibrationally excited states up to  $v = 3$  has been reported toward IRC +10216 (Turner 1987; Fonfría et al. 2006; Cernicharo et al. 2000). The linewidths of vibrationally excited SiS are unusually narrow implying that the emission arises from the innermost envelope where the gas has not yet reached the terminal expansion velocity of 14.5 km s<sup>-1</sup>. To constrain the possible contribution of the  $J = 15-14$  line of SiS  $v = 4$  to the 267 GHz line, we observed the immediate previous  $J$  transitions. In Fig. 1 we show the  $J = 14-13$  and  $J = 13-12$  lines of SiS in the  $v = 4$  state (both observed with a spectral resolution of 320 kHz at the time of the 267 GHz observations) and the  $J = 12-11$  line (observed in a previous run in 2005 January with a spectral resolution of 1.25 MHz).

Except for the  $J = 14-13$  line of SiS  $v = 4$ , which is partially blended with a fine structure component of the  $N = 27-26$  transition of CCC<sup>13</sup>CH, the observations clearly show that SiS  $v = 4$  lines are narrow, with expansion velocities of about 3 km s<sup>-1</sup> (see Table 1). With this in mind, the observed emission feature at 267 GHz has been fitted by two line components, a narrow one corresponding to the  $J = 15-14$  transition of SiS  $v = 4$  and a wider line whose width,  $v_{\text{exp}} = 14.1 \pm 0.3$  km s<sup>-1</sup>, agrees with the expansion velocity of 14.5 km s<sup>-1</sup> in IRC +10216, and whose center rest frequency,  $266944.5 \pm 0.3$  MHz, is in very good agreement with the laboratory frequency of the  $1_0-0_0$  line



**Fig. 1.** Spectra of IRC +10216 observed with the IRAM 30-m telescope showing on top the  $J_K = 1_0-0_0$  line of PH<sub>3</sub> blended with a narrower line assigned to the  $J = 15-14$  line of SiS  $v = 4$ . Shown below are the immediate lower rotational transitions of SiS  $v = 4$ . Fits to the line profiles using the CLASS *shell* method are shown as thick grey lines.

of PH<sub>3</sub> (see Table 1). The hyperfine structure is not resolved as the components are separated by less than 0.2 km s<sup>-1</sup> in velocity (Cazzoli & Puzzarini 2006), which is lower than the spectral resolution. The good agreement between the observed and laboratory frequencies is the strongest evidence of PH<sub>3</sub> detection in IRC +10216.

Besides the SiS  $v = 4$  line, there are some other lines with frequencies close to that of PH<sub>3</sub>  $1_0-0_0$ . Most of them, such as SO<sub>2</sub>  $30_{9,21}-31_{8,24}$  at 266943.344 MHz or CH<sub>3</sub>CH<sub>2</sub>CN  $15_{4,12}-15_{2,13}$  at 266951.639 MHz, are ruled out as likely contributors since many other lines of these species should have been detected. A more plausible species is HC<sub>3</sub>N in the  $v_7 = 4$  vibrational state, whose transition  $J = 29-28$   $\ell = 0_e$  lies at 266943.313 MHz (Mbosei et al. 2000). Although several lines of HC<sub>3</sub>N in the vibrational excited state  $v_7 = 1$  have been observed in IRC +10216 (Cernicharo et al. 2000), we rule out that HC<sub>3</sub>N  $v_7 = 4$  is the main contributor to the 267 GHz emission based on the

**Table 1.** Observed line parameters in IRC +10216.

Transition	Cal. Freq. (MHz)	Obs. Freq. (MHz)	$v_{\text{exp}}^a$ (km s <sup>-1</sup> )	$\int T_{\text{MB}} dv$ (K km s <sup>-1</sup> )
PH <sub>3</sub>				
$J_K = 1_0-0_0$	266944.514	266944.5(3)	14.1(3)	1.002(40)
SiS $v = 4$				
$J = 15-14$	266941.754	266942.4(7)	4.0(7)	0.237(40)
$J = 14-13$	249155.372	249155.6(4)	3.5(4)	0.172(40)
$J = 13-12$	231366.976	231367.2(3)	2.7(3)	0.256(30)
$J = 12-11$	213576.710	213576.9(5)	3.5(5)	0.207(40)

NOTE. Number in parentheses are  $1\sigma$  uncertainties in units of the last digits. Observed frequencies are given in the rest frame of IRC +10216 assuming a systemic velocity of  $v_{\text{LSR}} = -26.5$  km s<sup>-1</sup>.

<sup>a</sup>  $v_{\text{exp}}$  is the half width at zero level.

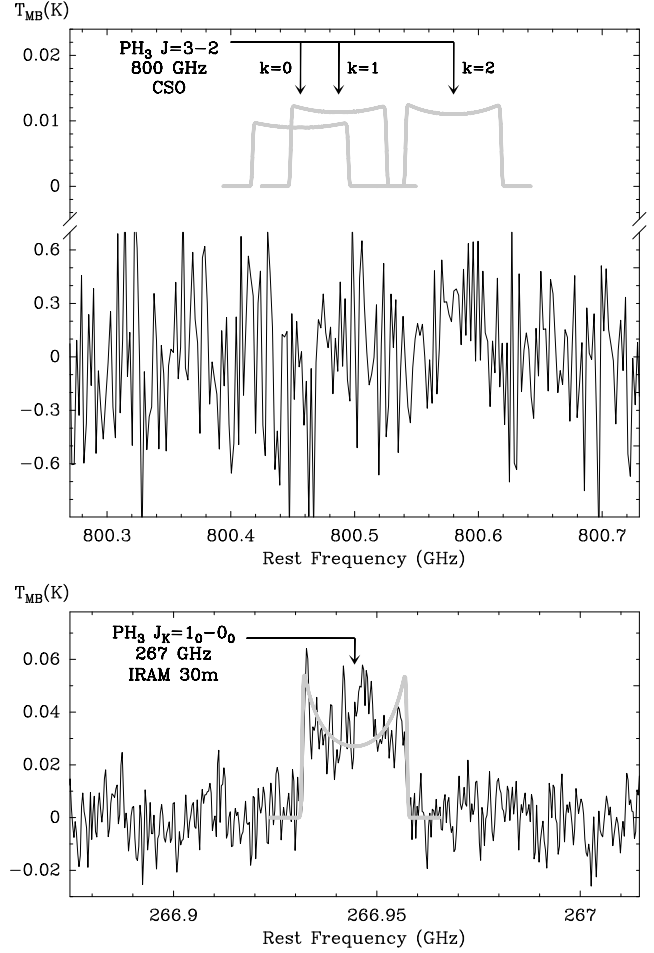
upper limit of  $T_{\text{MB}} < 0.01$  K that we have from our 30-m data archive for the lower- $J$  transition  $J = 26-25 \ell = 0e$  transition at 239370.171 MHz.

We tried to confirm the identification of PH<sub>3</sub> by observing other transitions. The  $J = 2-1$  line at 534 GHz is not reachable from the ground due to severe atmospheric absorption. We, thus, searched for the  $J = 3-2$  transition at 800 GHz with the Caltech Submillimeter Observatory (CSO). The observations were carried out in 2008 January using the chopping secondary mode with a throw of  $\pm 90''$  at a rate of 1.2 Hz. The SIS receiver was tuned in double sideband and a Fast Fourier Transform Spectrometer was used as backend to provide a spectral resolution of 0.12 MHz. The pointing of the telescope was checked on Saturn. The beam size of the CSO at 800 GHz is  $11.5''$  and the beam efficiency is 0.28. In spite of the good atmospheric conditions (zenith sky opacity at 225 GHz was 0.04–0.08), the high opacity of the atmosphere at 800 GHz ( $T_{\text{sys}}$  ranged from 3000 K to 8000 K) did not allow us to reach a low enough noise level to confirm or discard the presence of PH<sub>3</sub> (see top panel in Fig. 2).

### 3. Analysis and discussion

To interpret the observations, we computed line profiles by means of excitation and radiative transfer calculations based in the large velocity gradient (LVG) formalism (Castor 1970), coupled to the spectral catalog of J. Cernicharo (Cernicharo et al. 2000). We consider separately both the ortho (o-PH<sub>3</sub>) and para (p-PH<sub>3</sub>) species of phosphine (the ortho-to-para ratio was assumed to be 1, the statistical value). The energy levels and transition frequencies were computed from the rotational constants reported by Cazzoli & Puzzarini (2006). We included rotational levels in the ground vibrational state up to  $J_K = 7_6$  for o-PH<sub>3</sub> and up to  $J_K = 5_5$  for p-PH<sub>3</sub>. As rate coefficients for collisional de-excitation of o-PH<sub>3</sub>(p-PH<sub>3</sub>) with H<sub>2</sub> and He, we adopted those computed for collisions of o-NH<sub>3</sub>(p-NH<sub>3</sub>) with p-H<sub>2</sub> (Danby et al. 1988) and He (Machin & Roueff 2005) respectively, properly corrected to the case in which inversion doubling is not resolved.

We assumed a distance to IRC +10216 of 150 pc and simulated the circumstellar envelope as a spherically distributed gas expanding at a constant velocity of 14.5 km s<sup>-1</sup>. The gas density and temperature profiles were taken from Agúndez & Cernicharo (2006). Phosphine was assumed to be distributed between an inner radius  $R_{\text{in}}$  and an outer radius  $R_{\text{out}}$ , with a constant abundance,  $x(\text{PH}_3)$ , relative to H<sub>2</sub>. We took  $R_{\text{in}} = 1.3 \times 10^{15}$  cm (about 20 stellar radii), the value adopted by Hasegawa et al. (2006) for NH<sub>3</sub>. The values of  $R_{\text{out}}$  and  $x(\text{PH}_3)$  were varied



**Fig. 2.** The lower panel shows the PH<sub>3</sub>  $J_K = 1_0-0_0$  line at 267 GHz as observed with the IRAM 30-m telescope, in which the fit to the SiS  $v = 4$   $J = 15-14$  line has been subtracted. The upper panel shows the observation at 800 GHz with the CSO smoothed to a spectral resolution of 2 MHz. The thick grey lines in both panels correspond to the line profiles given by the LVG model.

until obtaining the best fit to the observed PH<sub>3</sub>  $1_0-0_0$  line profile. Since both gas density and temperature vary greatly with radius, we divided the envelope into various shells and solved for the level populations in each shell independently of the others. We then computed the emergent intensity and weighted it with the main beam of the selected telescope.

In the bottom panel of Fig. 2 we plot the observed  $1_0-0_0$  PH<sub>3</sub> line profile, obtained by subtracting the fit to the SiS  $v = 4$  blended line. Also shown is the profile resulting from our best LVG model, whose parameters are  $R_{\text{out}} = 2 \times 10^{16}$  cm and  $x(\text{PH}_3) = 6 \times 10^{-9}$ . The model indicates that the upper level involved in the  $1_0-0_0$  PH<sub>3</sub> line is mostly populated by collisions in the inner  $4 \times 10^{15}$  cm, which corresponds to an angular diameter of about  $4''$  and is thus spatially diluted in the  $9''$  beam of the 30-m telescope. The top panel of Fig. 2 shows the corresponding prediction for the PH<sub>3</sub>  $J = 3-2$  line profiles as observed with the CSO. It is seen that the expected intensity is well below the noise of the observed spectrum and is thus consistent with the IRAM 30-m result for the  $J = 1-0$  line. The spatial dilution is also important for the CSO observations and plays against our efforts to detect the  $J = 3-2$  lines.

It should be noted that the derived abundance and distribution of PH<sub>3</sub> are very uncertain. Since we observed just one

single PH<sub>3</sub> line, a considerable degeneracy exists between models with different values of  $R_{\text{in}}$ ,  $R_{\text{out}}$ , and  $x(\text{PH}_3)$ . Moreover, infrared pumping to excited vibrational states, not considered in our model, may play an important role in the excitation of the rotational levels in the ground vibrational state. Phosphine has indeed many vibrational bands in the spectral region around 10  $\mu\text{m}$ , a wavelength at which the central source has its maximum flux (Cernicharo et al. 1999).

Confirmation of our tentative detection may rely on further observations of other PH<sub>3</sub> transitions. The  $J = 2-1$  and  $J = 3-2$  lines at 534 GHz and 800 GHz, respectively, are observable with the Herschel Space Observatory (HSO), although our LVG model predicts somewhat weaker intensities than with the CSO due to the stronger dilution effect. In the case of the Atacama Large Millimeter Array (ALMA), the high angular resolution that it will provide, better than 3'' at 800 GHz, will perfectly fit with the expected size of the  $J = 3-2$  emission. The predictions indicate main beam brightness temperatures of about 1 K, which provide a good opportunity for detecting it in spite of the high atmospheric opacity at this frequency. We note that these predictions are based on our best LVG model, but the  $J = 2-1$  and  $J = 3-2$  lines could be more intense than expected if infrared pumping is playing an important role, or if PH<sub>3</sub> is present in hot regions closer to the star than the inner cutoff of  $1.3 \times 10^{15}$  cm assumed here.

The derived abundance of PH<sub>3</sub>,  $x(\text{PH}_3) = 6 \times 10^{-9}$ , implies that it takes up about 1.3% of the available phosphorus. The PH<sub>3</sub>/HCP ratio is then found to be 1/2.3 (Agúndez et al. 2007), noticeably higher than the NH<sub>3</sub>/HCN ratio, which is about 1/50 in IRC +10216 (Hasegawa et al. 2006; Fonfría et al. 2007). The formation of PH<sub>3</sub> in the gas phase is difficult to explain. Its LTE abundance in the inner envelope is rather low,  $<10^{-12}$ , and gas phase reactions yield no net formation in the outer envelope (Agúndez et al. 2007). Besides PH<sub>3</sub>, other hydrides such as NH<sub>3</sub>, CH<sub>4</sub>, H<sub>2</sub>O, SiH<sub>4</sub>, and H<sub>2</sub>S are observed in IRC +10216 with relatively high abundances (Keady & Ridgway 1993; Hasegawa et al. 2006; Agúndez & Cernicharo 2006). Many of them are usually assumed as parent molecules, i.e. formed in the inner envelope, in most chemical models of IRC +10216 (e.g. MacKay & Charnley 2001; Agúndez & Cernicharo 2006). However, chemical equilibrium calculations, similar to those reported in Agúndez et al. (2007), indicate much lower abundances than observed, except perhaps for CH<sub>4</sub>. A widely invoked explanation, when gas phase chemistry fails to explain an observed abundance, is that of grain surface reactions. In the case of hydrides such as PH<sub>3</sub>, a likely formation process is the direct hydrogenation of the heavy atom taking place on grain surfaces.

#### 4. Conclusions

We have tentatively detected PH<sub>3</sub> in IRC +10216 through its  $J_K = 1_0-0_0$  transition at 267 GHz. The derived abundance relative to H<sub>2</sub> is  $6 \times 10^{-9}$ . Despite considerable uncertainty, this value is similar to the HCP abundance found in this source (Agúndez et al. 2007). These two species, HCP and PH<sub>3</sub>, would then take up about 5% of the phosphorus in IRC +10216. The formation of PH<sub>3</sub>, unlike that of HCP, is difficult to explain in

the gas phase and could occur on grain surfaces. It remains a target for the future to confirm this tentative detection by observing the  $J = 3-2$  transition, at 800 GHz, with the ALMA facility. Also, further observations at 267 GHz in other sources such as CRL 2688, where HCP has been also detected (Milam et al. 2008), will be of great interest to support this tentative detection and to understand the chemistry behind it.

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*Note added in proof.* We have very recently been aware that E. D. Tenenbaum and L. M. Ziurys (ApJL, in press) have observed with the Arizona Radio Observatory (ARO) Submillimeter Telescope (SMT) the same emission line at 267 GHz, which they also interpret as the  $J_K = 1_0-0_0$  transition of PH<sub>3</sub>, in IRC +10216 and also in CRL 2688.

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