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DETECTION OF INTERSTELLAR PN: THE FIRST PHOSPHORUS-BEARING SPECIES OBSERVED IN MOLECULAR CLOUDS

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ABSTRACT

Phosphorus nitride (PN) has been detected in the interstellar medium. The $J = 2\text{–}1$, 3–2, 5–4, and 6–5 rotational lines of this species have been observed toward Orion-KL, and the $J = 2\text{–}1$ transition in Sgr B2 and W51. The PN line profiles in Orion indicate that the molecule's emission arises from the "plateau" or "doughnut" region associated with the outflow from IRc2. The species is thus primarily present in hot, dense gas. Column densities derived for PN toward Orion-KL are $3\text{–}4 \times 10^{13}$ cm^{-2}, but may be as high as 10^{14} cm^{-2}, if the species is located in a 10″ region. These column densities imply a fractional abundance for PN in the Orion "plateau" of $\sim 1\text{–}4 \times 10^{-10}$. Such a large abundance for phosphorus nitride is not predicted by quiescent cloud ion-molecule chemistry and suggests that high-temperature processes are responsible for the synthesis of PN in the KL outflow.

Subject headings: interstellar: abundances — interstellar: molecules

I. INTRODUCTION

The chemistry of interstellar molecules containing elements from the second and third rows of the periodic table has yet to be understood. Part of the difficulty has been that only a few species of this type have actually been detected in the ISM, namely those containing silicon, sulfur, and tentatively, chlorine. Even with this limited sample, observations thus far suggest that the synthesis of these species involves high temperatures, perhaps along with the destruction of dust grains, rather than ion-molecule chemistry (e.g., Johansson *et al.* 1984; Ziurys and Friberg 1987).

It would be useful to observe other interstellar species of this type; an obvious choice are those containing phosphorus. Although phosphorus has a lower cosmic abundance than many other second-row and third-row elements, it is depleted at most by a factor of 3 in diffuse clouds (e.g., Dufton, Keenan, and Hibbert 1986). Also, phosphorus is of interest because little is known about its gas phase chemistry, although it plays a fundamental role in biological systems. Past searches for interstellar phosphorus compounds have been carried out (e.g., Hollis *et al.* 1981), but thus far none have been successful.

In their recent spectral-line survey of Orion-KL, Sutton *et al.* (1985) observed a weak feature near the frequency of the $J = 5\text{–}4$ transition of PN. The line was reported to have an LSR velocity of 8 km s^{-1}, with a linewidth of 4 km s^{-1}, associating the feature with the "spike" component, i.e., the cold quiescent region in Orion (e.g., Johansson *et al.* 1984). In order to verify the existence of interstellar PN and to determine the nature of its chemical environment, we have searched for the $J = 2\text{–}1$, 3–2, 5–4, and 6–5 rotational transitions of this species in molecular sources. We have detected all four lines toward Orion-KL. In this *Letter* we present our results and discuss their chemical implications.

II. OBSERVATIONS

The $J = 2\text{–}1$, 3–2, and 5–4 measurements were made in 1985 November–1986 April, 1987 May, and 1986 January, respectively, using the FCRAO 14 m telescope at 94, 141, and 235 GHz. Telescope parameters for the FCRAO antenna are given in Table 1. The temperature scale was determined by the chopper wheel method and is given in terms of T_A^*. Brightness temperature T_R, assuming the source fills the telescope main beam, is then defined as $T_R = T_A^*/\eta_B$. Three single-channel, cooled mixer receivers were used for the observations. The 3 and 1.2 mm receivers were operated in a single-sideband mode; the 2 mm receiver was used double-sideband. Sideband separation was 2.782 GHz. Two 512 channel filter banks with 1 MHz and 250 kHz resolutions, respectively, were simultaneously employed for most of the measurements. Toward L134N, however, 25 kHz channel resolution was used.

The $J = 6\text{–}5$ observations at 282 GHz were made in 1987 March, using the NRAO 12 m telescope. Telescope parameters for the 12 m are listed in Table 1. The temperature scale for these measurements is given in terms of T_R^*, which is the chopper wheel antenna temperature corrected for forward spillover losses, i.e., $T_R^* = T_A^*/\eta_{\rm fss}$, where $\eta_{\rm fss} = 0.75$. The main beam brightness temperature T_R is defined as $T_R = T_R^*/\eta_c$. The receiver was a single-channel cooled mixer, operated double-sideband with a sideband separation of 3 GHz. Two separate 256 channel filter banks of 1 and 2 MHz resolution were the spectrometers used.

III. RESULTS

PN was searched for toward Orion-KL, W51, Sgr B2, and L134N (NH_3 peak). Figure 1 shows the PN lines detected in Orion. The similar line shapes and LSR velocities of these

TABLE 1

OBSERVED LINE PARAMETERS FOR PN[a]

Source	Transition[b]	ν (MHz)	T_A^* (K)[c]	T_R^* (K)[d]	V_{LSR} (km s^{-1})	$\Delta V_{1/2}$ (km s^{-1})	θ_b	η_B	η_c	T_B (K)[e]	NL^{f}_{tot} (cm^{-2})
Orion-KL[g]	$J = 2$–1	93,979.78	0.019 ± 0.005	...	9 ± 3	19 ± 3	55″	0.56	...	0.29	
	$J = 3$–2	140,967.75	0.057 ± 0.010	...	7.5 ± 2	20 ± 3	34	0.34	...	0.65	4.0–4.2 × 10^{13}
	$J = 5$–4	234,935.69	0.110 ± 0.010	...	9 ± 2	14 ± 3	22	0.20	...	1.43[h]	(1 × 10^{14})
	$J = 6$–5	281,914.13	...	0.220 ± 0.050	9 ± 2	15 ± 4	25	...	0.33	1.71	
Sgr B2[i]	$J = 2$–1	93,979.78	0.052 ± 0.010	...	54 ± 3	13 ± 3	55	0.56	...	0.09	2.5 × 10^{12} [j]
W51[k]	$J = 2$–1	93,979.78	0.022 ± 0.010	...	59 ± 3	27 ± 6	55	0.56	...	0.04	2.0 × 10^{12} [j]
L134N[l]	$J = 2$–1	93,979.78	< 0.1	...	2.5	...	55	0.56	...	< 0.18	≤ 1.5 × 10^{12} [j]

[a] Errors quoted are 2 σ.

[b] Frequencies taken from Wyse, Manson, and Gordy 1972.

[c] Measured with 1 MHz resolution, except for L134N, where 25 kHz resolution was used.

[d] Measured with 2 MHz resolution.

[e] Assumes a source size of $\theta_s = 20''$ and a beam filling factor $f = \theta_s^2/\theta_b^2 + \theta_s^2$ for Orion-KL; for a 10″ source, the T_B values will increase by factors of 3–4. For the other sources, a uniform filling factor was assumed.

[f] Value listed for Orion-KL assumes $\theta_s = 20''$; the value in parentheses assumes $\theta_s = 10''$. For the other sources, the values are beam-averaged column densities.

[g] $\alpha = 5^h32^m47^s.0$; $\delta = 5°24'25''$(1950.0).

[h] Corrected additionally for decrease in efficiency at low elevations.

[i] $\alpha = 17^h44^m11^s.0$; $\delta = -28°22'30''$(1950.0).

[j] Column densities derived assuming $T_K = 50$ K and $n(H_2) = 2 \times 10^5$ cm^{-3} for W51 (Jaffe *et al.* 1984), $T_K = 85$ K and $n(H_2) = 3 \times 10^5$ cm^{-3} for Sgr B2 (Cummins *et al.* 1986; Goldsmith *et al.* 1987), and $T_K = 12$ K and $n(H_2) = 2 \times 10^4$ cm^{-3} for L134N (Swade 1987). See text.

[k] $\alpha = 19^h21^m26^s.2$; $\delta = 14°24'43''$(1950.0).

[l] $\alpha = 15^h51^m32^s.4$; $\delta = -2°40'37''$(1950.0).

features support the case that they all arise from the same molecule. Line parameters for these PN spectra are given in Table 1. The $J = 5$–4 and $J = 6$–5 lines appear to be narrower than the $J = 3$–2 and 2–1 transitions, although such differences are within the errors. Part of this difference may be due to the nitrogen quadrupole splitting in PN, which could introduce a few km s^{-1} line broadening for the lower transitions.

The PN frequencies were checked for possible coincidences with transitions from other molecules. No other known lines exist at the frequencies of the PN $J = 2$–1 and 5–4 transitions. The $J = 3$–2 transition of PN is coincident in frequency with the 32(8, 24)–33(7, 27) line of SO_2, $v_2 = 1$, and is 3 MHz away from the $J = 125$–124 line of HC_7N. Lines due to HC_7N have never been detected in Orion, so it is extremely doubtful that the feature at the $J = 3$–2 PN frequency is attributable to this species. The 6(2, 4)–6(1, 5) transition of SO_2, $v_2 = 1$ lies within our PN $J = 3$–2 bandpass. This line has a comparable line strength to that of the 32(8, 24)–33(7, 27) line, but lies 429 cm^{-1} lower in energy, and may be present in our spectrum at the 20–30 mK level. Since this lower energy line is so weak, it is quite unlikely that a much higher energy transition could account for the feature at the PN $J = 3$–2 frequency, which has an intensity near 60 mK. The $J = 6$–5 line of PN is 2 MHz away in frequency from the 13(0, 13)–12(0, 12) transition of 13-substituted HCOOH, which lies 57 cm^{-1} (82 K) above ground state. Since HCOOH has barely been detected in Orion (Sutton *et al.* 1985), it seems highly unlikely that a rather high-energy line of $H^{13}COOH$ would be present at the 0.2 K level.

Figure 2 shows the $J = 2$–1 spectra of PN observed toward Sgr B2 and W51. As shown in Table 1, both features have LSR velocities and linewidths not unexpected for these sources. The PN spectrum from Sgr B2 may also exhibit a velocity component near 100 km s^{-1}, such as seen for HCO^+ and H_2CO (Turner and Thaddeus 1977). No PN lines were detected, however, toward L134N.

IV. DISCUSSION

a) *Origin of the* PN *Emission*

The rather broad linewidths ($\Delta V_{1/2} \approx 15$–20 km s^{-1}) and LSR velocities near 8–9 km s^{-1} found for the PN lines in Orion indicate that the species' emission arises primarily from the "plateau" or "doughnut" region (Johansson *et al.* 1984; Vogel *et al.* 1984). Except for possibly the $J = 2$–1 transition, there is little evidence in the data that PN has a narrow "spike" component, which characterizes the cool, quiescent gas in Orion. The "doughnut" is thought to be material involved in an outflow from infrared source IRc2 (e.g., Plambeck *et al.* 1982). If PN is located in the "doughnut," it is present in a region of about 20″ in size with a kinetic temperature of 60–100 K and a hydrogen density of $n(H_2) \approx 10^6$–10^7 cm^{-3} (Plambeck *et al.* 1982; Masson *et al.* 1984). Most of the molecules associated with the "doughnut," however, such as SO and SO_2, tend to have broader linewidths ($\Delta V_{1/2} \approx 26$–30 km s^{-1}) than those found for PN. Linewidths on the order of 20 km s^{-1} are more characteristic of SiO, SiS, and "plateau" NH_3, all of which are thought to be present near the inner edges of the doughnut in what is sometimes termed the "18 km s^{-1} flow" (Genzel *et al.* 1982; Wright *et al.* 1983; Ziurys 1987). This region is distinct from the so-called hot core. If present in the "18 km s^{-1} flow," PN would be found in a region with a source size of about 10″,

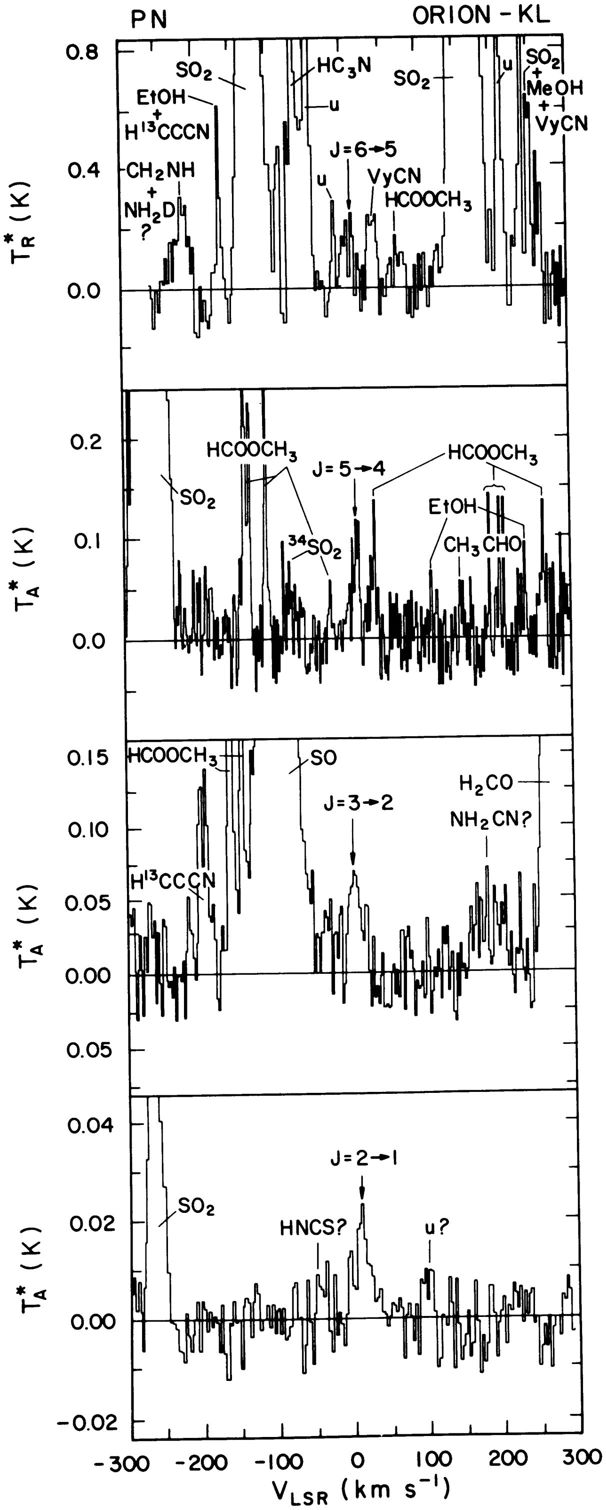

FIG. 1.—Spectra of the $J = 2$–1, 3–2, 5–4, and 6–5 rotational transitions of PN, observed toward Orion-KL. The three lower J transitions were detected in the USB with the FCRAO 14 m telescope, using 1 MHz channel resolution; the $J = 6$–5 line was measured in the LSB with the NRAO 12 m antenna with 2 MHz resolution. (Although not shown here, for observations made with a double-sideband receiver, the PN lines were measured in both lower and upper sidebands for purposes of identification.) The chemical shorthand used in the figure to identify other lines in the bandpasses translates as follows: Me = CH_3, Vy = H_2CCH, and Et = CH_3CH_2. The rather broad PN line shapes, with LSR velocities near 8–9 km s^{-1}, associate the species with the "plateau" or "doughnut" material, i.e., the hot, dense outflow from IRc2.

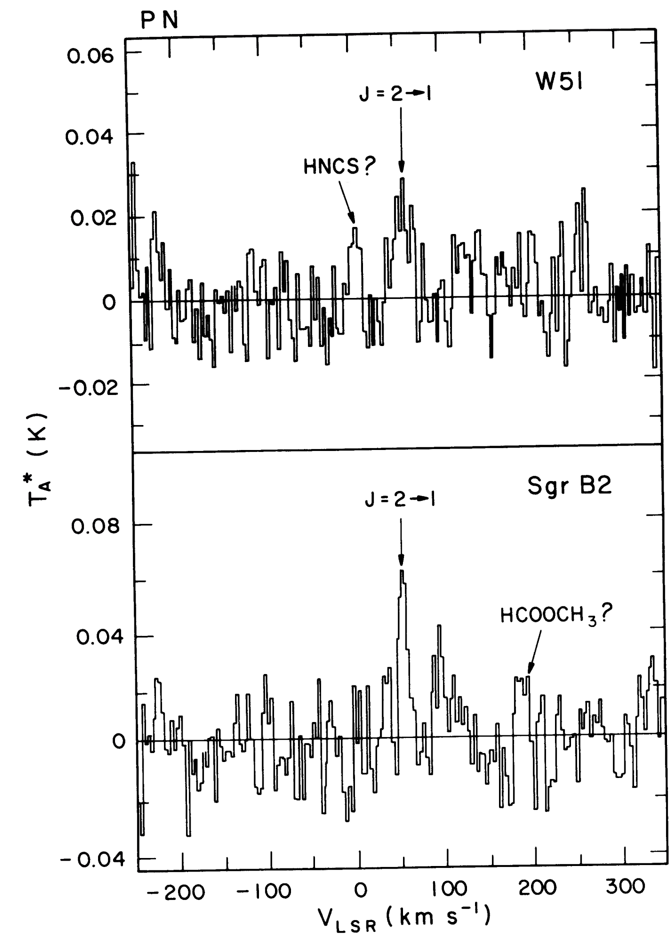

FIG. 2.—Spectra of the $J = 2$–1 transition of PN, observed in the USB toward Sgr B2 and W51 with the 14 m telescope, using 1 MHz resolution. Both lines have widths and velocities typical for these sources. The PN spectrum from Sgr B2 may also show a velocity component near 100 km s^{-1}, as well as one at 54 km s^{-1}.

with $T_K \approx 230$ K and $n(H_2) \approx 10^7$ cm^{-3}. In either case, PN is predominantly present in gas that is both hot and dense.

Like Orion, W51 and Sgr B2 probably contain outflows associated with star formation (e.g., Jaffe, Harris, and Genzel 1987; Vogel, Genzel, and Palmer 1987). PN in W51 and Sgr B2 may primarily be present in such hot, confined regions, but its origin is uncertain on the basis of the present data.

b) *Column Densities and Abundances*

For Orion-KL, column densities were first estimated by a simple analytical calculation, assuming low optical depth. PN has a dipole moment of 2.747D. Therefore, while the $J = 2$–1 and $J = 3$–2 transitions are nearly thermalized at densities typical for the "doughnut" and the "18 km s^{-1} outflow" [i.e., $n(H_2) \approx 3$–7×10^6 cm^{-3}], the $J = 5$–4 and 6–5 clearly are not. A rotational temperature of $T_{rot} = 50$ K was thus assumed. If $\theta_s \approx 20''$, then $NL_{tot} = 3.3$–3.9×10^{13} cm^{-2} for PN, where the range of values reflects the use of the four different transitions. If a 10″ source size is assumed, the column density increases by factors of 3–4.

It is more probable, however, that one single temperature does not accurately depict the population in the PN rotational ladder. Consequently, column densities were also calculated using the large-velocity gradient (LVG) approximation (de Jong, Chu, and Dalgarno 1975). For the LVG modeling, CS–H_2 collisional cross sections from Green and Chapman (1978) were used, and the computations were done considering 13 rotational levels. Three parameters were varied to reproduce the brightness temperatures of the four PN transitions: PN total column density, gas kinetic temperature, and total H_2 gas density. Computations showed that the brightness temperatures could be reproduced for only a narrow range of column densities, while temperature and density had a much broader span of acceptable values. If a 20″ source size is assumed, values of $NL_{tot}(PN) \approx 4.0–4.2 \times 10^{13}$ cm^{-2}, with $T_k \approx 100–160$ K, and $n(H_2) \approx 6 \times 10^6–10^7$ cm^{-3} resulted in reasonable fits to the observed brightness temperatures. These densities and temperatures closely resemble what has been determined for the plateau source from other molecular lines (Plambeck *et al.* 1982; Masson *et al.* 1984). If a 10″ source size is assumed, the PN column density has a somewhat higher value of $NL_{tot} \approx 10^{14}$ cm^{-2}, with $T_K \sim 100–200$ K and $n(H_2) \approx 5 \times 10^6–10^7$ cm^{-3}.

For Sgr B2, W51, and L134N, temperatures and densities were fixed in the LVG modeling and the column density varied to match the observed brightness temperatures. These column densities are listed in Table 1 and were derived assuming the PN source fills the telescope main beam.

To estimate fractional abundances for Orion-KL, interferometric measurements of the dust continuum were used as a source of hydrogen column densities. For the "doughnut" source, Masson *et al.* (1985) derived $NL(H_2) \approx 10^{23}$ cm^{-2}, and also found $NL(H_2) \approx 10^{24}$ cm^{-2} for the 10″ inner region of the doughnut (the "18 km s^{-1} flow"). These values result in fractional abundances of $f \approx 1–4 \times 10^{-10}$ for PN. For W51 and Sgr B2, $NL \approx 10^{24}$ cm^{-2} was assumed (Jaffe, Becklin, and Hildebrand 1984; Goldsmith, Snell, and Lis 1987), yielding $f \approx 2 \times 10^{-12}$ for both sources, if the emission fills the beam. Considering $NL(H_2) \approx 10^{22}$ cm^{-2} (Swade 1987), the upper limit to the PN abundance in L134N is $f \leq 2 \times 10^{-10}$.

c) Implications for Interstellar Phosphorus Chemistry

Thorne *et al.* (1984) have measured or estimated some simple ion-molecule reactions of phosphorus and have constructed a chemical model. Their ion-molecule scheme predicts that PO should be the most abundant phosphorus compound in cool, dense clouds, with $f(PO) \approx 10^{-10}$, while the abundance of PN should be much lower. They also suggest that PN is principally formed through reactions of phosphorus ions with NH_3.

In contrast, our measured PN abundance toward Orion-KL is approximately that predicted for PO. (Although the Sgr B2 and W51 abundances are lower than that for Orion, these values may not be significant because of the uncertainties in source size.) Also, in her study of SiS in Orion, Ziurys (1987) obtained a more sensitive limit to the PO abundance than from previous work (Matthews, Feldman, and Bernath 1987). These new data yield an upper limit to the abundance of PO in the spike component of $f \leq 3.2 \times 10^{-11}$. Alternatively, if PO is located in the doughnut, then PN/PO ≥ 0.6. Perhaps even more significant is the fact that PN appears to be present primarily in the doughnut or 18 km s^{-1} flow. If PN is synthesized through reactions with NH_3, one might expect some correlation between the two species. However, NH_3 is most abundant in Orion-KL in the "hot core" (e.g., Ziurys *et al.* 1981), where PN is not apparently present.

It is not clear, however, that ion-molecule reactions should be invoked for the formation of PN in Orion. This species appears to arise from a region that is both hot and dense. Observations of HCO^+ (Vogel *et al.* 1984) strongly suggest that molecular ions disappear at high densities and temperatures. It may be more likely that PN is formed by neutral-neutral reactions. Although such reactions usually have activation energies and may be endothermic, they will probably take place at the higher temperatures in the doughnut region. Also, PN has only been detected in clouds where elevated temperatures are present, and not in the dark cloud L134N.

PN could also be formed by destruction of or evaporation from grains in the KL outflow. However, phosphorus could be depleted onto grains by a factor of 100, and there still would be enough left in the gas-phase to readily account for the abundance of PN in Orion. It thus seems unnecessary to invoke grains as a source of this molecule.

d) Synthesis of Molecules Containing Second-Row and Third-Row Elements

The high-temperature synthesis of phosphorus, silicon, and sulfur-containing species might be explained in terms of simple chemical bonding. Unlike those of the first row of the periodic table, elements from the second and third rows have a greater number of inner shell nonbonding electrons. Consequently, in a bonding situation, electron-electron repulsion is so great that atoms of these elements cannot come nearly as close to other atoms as those of the first row. Subsequently, bonds to second-row and third-row elements are generally weaker than those to first-row elements. In fact, elements of the second and third rows in general cannot form the usual $p\pi–p\pi$ double and triple bonds, and only manage to form unsaturated bonds at all through back-bonding with empty *d* orbitals.

First-row elements are clearly the most abundant. Therefore, formation of a compound with a second-row or third-row element is likely to involve breaking a bond of a molecule formed of only first-row elements (and H). Such a process will usually entail breaking a strong bond to form a much weaker one, resulting in a reaction that is endothermic. Consequently, high temperatures are necessary. Searches for new species of this type might therefore be better guided by higher temperature thermoequilibrium chemical modeling.

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