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DETECTION OF INTERSTELLAR PN: THE FIRST IDENTIFIED PHOSPHORUS COMPOUND IN THE INTERSTELLAR MEDIUM

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ABSTRACT

We have identified interstellar PN in Ori (KL), W51M, and Sgr B2, by observations of its $J = 2$–1, 3–2, and 5–4 rotational transitions. PN appears to occur in regions of relatively high excitation, with fractional abundances of 1(-11) to 1(-10). Ion-molecule gas phase reactions involving phosphorus at low temperatures cannot account for the observed PN abundances, especially when combined with upper limits for interstellar PO. Other processes, such as high-temperature gas phase reactions (unlikely) or grain disruption seem necessary to explain interstellar PN.

Subject headings: interstellar: abundances — interstellar: molecules

I. INTRODUCTION

Although interstellar chemistry of the abundant first-row elements C, N, and O owes its richness in part to the large abundance of these elements, and in part to their volatility, the chemistry of the second-row elements (Na, Mg, Si, P, S, Cl) is much less understood. Among second-row elements, only Si, S, and possibly Cl have been identified so far in interstellar molecules, and the abundances of these species bear essentially no relationship to the elemental abundances. For example, [Mg] ≈ [Si] cosmically, yet [MgO]/[SiO] < 1(-3); similarly, [Na]/[Cl] ≈ 6.6, yet HCl has apparently been detected and NaH has not. In general, if molecules containing second-row elements formed with efficiencies comparable to those containing first-row elements, then second-row molecular species would be easily detectable in the ISM. The scarcity of second-row compounds presumably stems from either a large depletion within dense molecular clouds, or from peculiarities of the gas-phase chemistry of these elements which do not favor molecule formation at low interstellar temperatures.

Because of the fairly high cosmic abundance of P ([P] > [Cl]), the availability of accurate spectroscopic constants for several P compounds, and recently some detailed laboratory studies of gas-phase P chemistry (Thorne, Anicich, and Huntress 1983; Thorne *et al.* 1984), several searches (all unsuccessful) have been made for P compounds including PN itself (Morris *et al.* 1973; Hollis *et al.* 1980), PH_3 (Hollis *et al.* 1980), HCP (Hollis *et al.* 1981; Thaddeus 1982), NCCP (Avery 1982), and PO (Matthews, Feldman, and Bernath 1981). All of these searches were made at 3 mm; if P compounds are preferentially formed in energetic, highly compact regions, much greater sensitivity would be gained by searching at shorter wavelengths. In their spectral survey of the 215–247 GHz region in the Ori (KL) core, Sutton *et al.* (1985) detected a single line at 234.936 GHz which they recognized as consistent with the $J = 5$–4 transition of PN as deduced from spectroscopic constants measured by Wyse, Manson, and Gordy (1972). In this *Letter* we report the detections of the $J = 2$–1 (93.97978 GHz), $J = 3$–2 (140.96775 GHz), and $J = 5$–4 (234.93569 GHz) transitions of PN in Ori (KL), W51M, and Sgr B2, and thus the identification of the first interstellar P-containing molecule.

II. OBSERVATIONS

The $J = 2$–1 observations were made 1986 July with the NRAO 12 m telescope equipped with a dual-channel SIS junction receiver tuned for single-sideband operation, whose SSB noise temperature was 135 K at 93 GHz. Orthogonal linear polarizations were accepted by the two channels. The beamwidth was 69″, forward spillover efficiency $\eta_{fss} \approx 0.75$, and main-beam fractional efficiency $\eta_c \approx 0.79$. The $J = 3$–2 observations at 140 GHz were made 1987 January–March with the BTL 7 m telescope, whose beamwidth was 90″, $\eta_{fss} \approx 0.95$, and $\eta_c \approx 0.68$. A single-channel SIS receiver operated in single-sideband mode and accepted linear polarization. The $J = 5$–4 observations at 234 GHz were made 1987 January with the NRAO 12 m telescope, equipped with a dual-channel cooled Schottky mixer receiver operating double-sideband and accepting orthogonal linear polarization. At 234 GHz the beamwidth was 33″, $\eta_{fss} \approx 0.75$, and $\eta_c \approx 0.47$. At the 12 m telescope the measured intensity is T_R^*, the chopper-wheel antenna temperature corrected for forward spillover losses, i.e., $T_R^* = T_A^*/\eta_{fss}$. At the BTL telescope, T_A^* is measured. The brightness temperature (not including the source beam-filling factor) is $T_R = T_R^*/\eta_c$. These various

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quantities are given for the three PN transitions in Table 1. All data were taken position-switching the telescopes, and with spectral resolution 1 MHz (plus 500 kHz at 93 GHz).

III. RESULTS

Figure 1 shows the spectra of the $J = 2$–1, 3–2, and 5–4 rotational transitions of PN toward Ori (KL). Directly measured frequencies for these lines (Wyse, Manson, and Gordy 1972) are indicated in the figure for V_{lsr} taken as 9.0 km s^{-1} for each line. No other known molecular transitions coincide with the $J = 2$–1 or 5–4 frequencies (Lovas 1984). The 32(8,24)–33(7,29) transition of SO_2, $v_2 = 1$ at an excitation energy of 444 cm^{-1} lies within 0.1 MHz of the $J = 3$–2 transition. SO_2, $v_2 = 1$ is, however, unable to explain our observed emission at 140.96775 MHz for the following three reasons:

1. Although two other tentative emission lines in Ori (KL) coincide with SO_2, $v_2 = 1$ transitions (Sutton *et al.* 1985; Blake *et al.* 1986), we calculate from their observed intensities, energies, and line strengths that T_R^* for the 32(8,24)–33(7,29) transition should be only 0.4–1.1 mK for the BTL 7 m telescope, or 35–90 times weaker than our observed PN line. These estimates utilize a rotational temperature of 175 K (Blake *et al.* 1986), although T_{rot} might be even lower (e.g., 150 K as suggested by Schloerb *et al.* 1983 for the highest energy SO_2, $v_2 = 0$ lines) in which case the predicted intensity of the SO_2, $v_2 = 1$ line at 140.967 MHz is even lower.
2. The velocities and widths of the other SO_2, $v_2 = 1$ lines are 6.0 and ~ 6 km s^{-1}, respectively, differing significantly from our PN parameters given in Table 1. Furthermore, a width as narrow as ~ 6 km s^{-1} may argue against identifying these other lines as SO_2, $v_2 = 1$ because such a species would be expected to arise in the hot core or plateau component of Ori (KL) whose linewidths are 10–15 km s^{-1}.
3. Our feature at 140967.75 MHz in Sgr B2 and W51M cannot be explained by SO_2, $v_2 = 1$ because many other lower energy transitions of this species have been sought without success in both sources.

Ambiguous results were obtained for IRC +10216, with a possible detection at $T_R^* \approx 0.015$ K at $J = 2$–1 and ~ 0.01 K at $J = 3$–2, but no detection ($T_R^* < 0.03$ K) at $J = 5$–4.

IV. DISCUSSION

a) *Line Profiles*

The spectra of Ori (KL) in many molecular species reveal the existence of at least three well-defined kinematic components: the narrow ambient-cloud feature at $V_{lsr} \approx 9$ km s^{-1} ($\Delta v < 5$ km s^{-1}); the broad "plateau" feature, also at $V_{lsr} \approx 9$ km s^{-1}, but with $\Delta v > 30$ km s^{-1} for most species, and arising from the disk, doughnut, extended outflow, and high-velocity outflow components as defined by Plambeck *et al.* (1985); and the "hot core" component, at $V_{lsr} \approx 3$–5 km s^{-1}, $\Delta v < 10$–15 km s^{-1} (cf. Johansson *et al.* 1984). Our $J = 2$–1 and 3–2 transitions seem to indicate both the spike and plateau components, especially in the blue wing, but the $J = 5$–4 transition may not. Consistent with our limited signal-to-noise ratio, we analyze each transition as a single component; the resultant V_{lsr} and Δv are each consistent with the plateau kinematic component (Table 1).

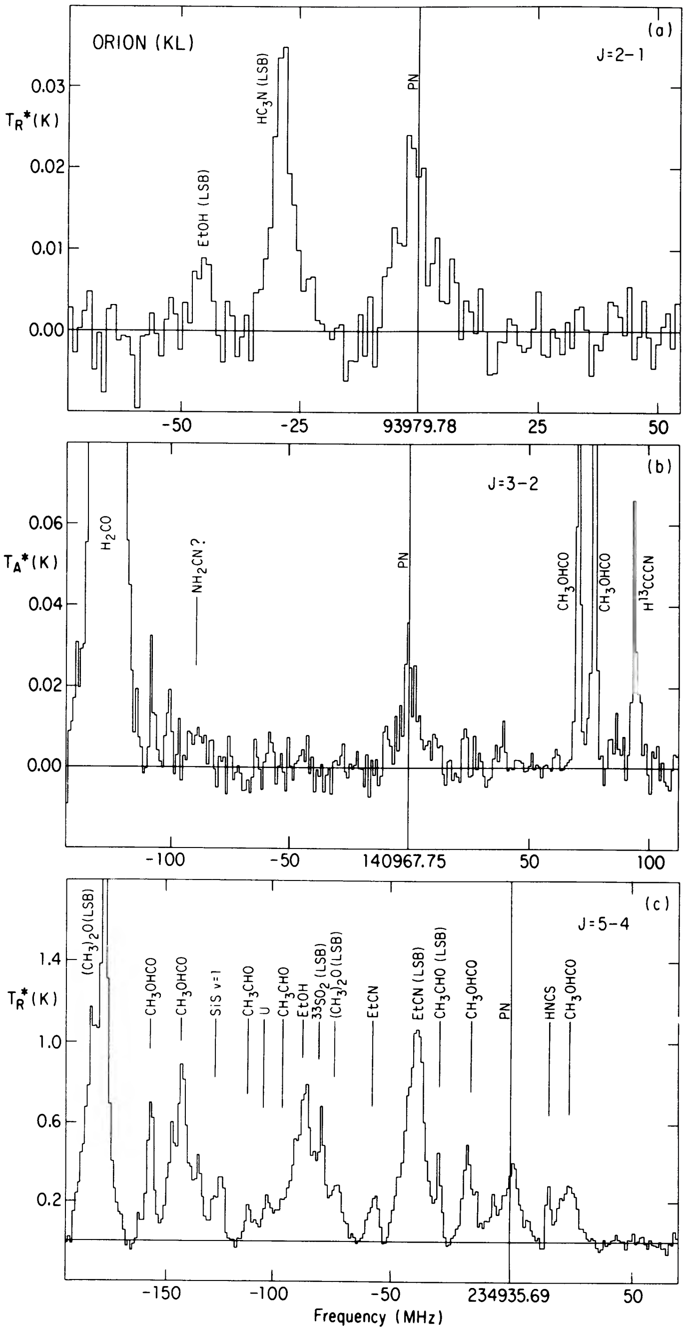

FIG. 1.—The three rotational transitions of PN observed toward Ori (KL), at $\alpha(1950) = 05^h32^m47^s0$, $\delta(1950) = -05°24'21''$. The vertical lines represent the measured frequencies of Wyse *et al.* (1972), shown below, when $v_{lsr} = 9.0$ km s^{-1} is assumed.

In W51M, all three transitions are at $V_{lsr} = 57$ km s^{-1}, $\Delta v \approx 10$ km s^{-1}, characteristic of the warm, dense cloud in the region of W51M (Jaffe, Becklin, and Hildebrand 1984). No emission is apparent from the cooler, lower density, W51 cloud at 67 km s^{-1} often seen in lower excitation species, along the same line of sight.

In Sgr B2 our two observed transitions occur at the unusual velocity of ~ 54 km s^{-1}, noticeably different from the 58–64

TABLE 1

PN OBSERVATIONS

Source	Transition (J = n–n)	V_{lsr} (km s^{-1})	Δv (km s^{-1})	T_A^* (mK)	T_R^* (mK)	T_R (mK)	θ_B	θ_S	T_B (K)
Ori (KL).......	2–1	8.8 ± 1.6	12.7 ± 1.6	...	23 ± 3	29.1	69″	20″	0.50
	3–2	8.0 ± 1.1	12.8 ± 2.2	31.5 ± 5	...	48.8	90	20	1.42
	5–4	7.7 ± 0.6	10.8 ± 2.0	...	400 ± 25	851.	33	20	2.84
W51M	2–1	57.1 ± 1.6	10.5 ± 1.6	...	20 ± 3	25.3	69	20	0.435
	3–2	59.2 ± 2.1	10.6 ± 2.1	22 ± 5	...	31.0	90	20	0.906
	5–4	58.7 ± 1.3	7.7 ± 1.3	...	88 ± 12	187.2	33	20	0.624
Sgr B2	2–1	54 ± 1.6	14.4 ± 1.6	...	44 ± 5	55.7	69	> 90	0.056
	3–2	55 ± 3.2	21 ± 4.3	40 ± 5	...	61.9	90	> 90	0.062
	5–4	...	...	...	< 50	< 106.	33	> 90	< 0.106

TABLE 2

LVG DETERMINATION OF PN COLUMN DENSITIES

Source	n (cm^{-3})	T_K (K)	X'	N (cm^{-2})	dv/dR (km s^{-1} pc^{-1})	X	N(PN)/N(H_2)
Ori (KL).......	1(6)	140	1.2(−12)	4.3(13)	258	3.1(−10)	1.7(−10)
W51M	5(5)	35	8.0(−13)	1.1(13)	13.7	1.1(−11)	1.1(−11)
Sgr B2	4(5)	13.5	8.0(−14)	1.7(12)	1.55	1.2(−13)	1.7(−12)

km s^{-1} range characteristic of most other molecules at the "OH" position (Cummins, Linke, and Thaddeus 1986). Velocities of ~ 54 km s^{-1} describe a few species (e.g., SiO, CH_3OH) 1′ south of Sgr B2OH.

Rotational transitions of PN are hyperfine-split because of the electric quadrupole moment of the N atom ($I = 1$). The electric quadrupole coupling constant is measured at 5.1416 MHz (Lovas and Tiemann 1974). The hyperfine splitting is too small to be observed in our sources; we calculate that 72% of the line intensity is at line center (±0.1 MHz) for J = 2–1, 92.4% for J = 3–2, and 97% for J = 5–4.

b) Column Densities and Fractional Abundances

Table 1 lists the brightness temperatures $T_B \equiv T_R/\eta_f$, where $\eta_f \equiv (\theta_s/\theta_B)^2 \ln 2/ \{1 - \exp[-(\theta_B/\theta_s)^2 \ln 2]\}$, appropriate for a disklike source of angular size θ_s convolved with a Gaussian beam of size θ_B at half-power. For an optically thin source with the same excitation temperature for each transition, we expect $T_B(2\text{–}1)/T_B(3\text{–}2)/T_B(5\text{–}4) = 1/1.5/2.5$. Smaller observed ratios would indicate optical thickness, while larger ratios can occur under conditions of subthermal excitation and certain ranges of kinetic temperatures T_K.

For Ori (KL) we adopt a source size of 20″ appropriate for the "plateau" source. The resulting ratios of T_B indicate high excitation temperatures as expected for the "plateau" component.

For W51M the source size of ~ 20″ is suggested by studies of rotationally excited CH (Ziurys and Turner 1985) and far-IR continuum (Jaffe, Becklin, and Hildebrand 1984). For $\theta_s = 20''$ the ratios of T_B indicate much lower excitation temperature than for Ori (KL) and subthermal excitation, or less likely, significant opacity.

There is essentially no information on θ_s for Sgr B2. Most molecular species with modest excitation seem to fill a region of size > 2′ (e.g., Brown and Cragg 1985), while higher excitation species [CH_3CN; $HC_3N(\nu_7, 2\nu_7)$; SO_2; CH_3OH] presumably fill a considerably smaller region (cf. Cummins, Linke, and Thaddeus 1986). Our three values of T_R are self-consistent if we assume 90″ for PN, i.e., no beam dilution for any of the transitions; then $T_B(3\text{–}2)/T_B(2\text{–}1) = 1.11$, consistent with small opacity, or more likely, with subthermal conditions at low excitation temperature. If $\theta_s < 74''$, then $T_B(3\text{–}2)/T_B(2\text{–}1)$ exceeds the optically thin, LTE limit.

Because nonnegligible opacity or subthermal excitation is likely, we use large velocity gradient (LVG) radiative transfer analysis to calculate PN column densities. An isothermal, homogeneous, spherical cloud is assumed. Eighteen rotational levels of PN are included, as well as HC_3N–H_2 collisional cross sections, taken from Green and Chapman (1978). Input parameters for the LVG analysis are total gas density n, gas kinetic temperature T_K, and the quantity $X' = X/(dv/dR)$, where X is the fractional abundance and dv/dR is the velocity gradient (in units of km s^{-1} pc^{-1}), assumed constant throughout the cloud. The column density is then given by $N = X' * n * 2R * (dv/dR) = \Delta v_{1/2} * X' * n$, independent of cloud radius R; dv is set equal to the observed linewidth $\Delta v_{1/2}$.

Table 2 presents the results of the LVG analysis.

The solution for Ori (KL) yields values for n and T_K typical of the plateau region. For Sgr B2 we find a value of T_K rather lower than the ~ 20 K found for many other molecular species (HC_3N, HC_5N, HNCO, OCS, NH_2CHO; Brown and Cragg 1985). Our derived density is ~ 4 times higher than is typical. If PN is more localized than these other species (all of whose angular sizes are ≳ 2′), then we would derive higher values of T_K because the ratio of $T_B(3\text{–}2)/T_B(2\text{–}1)$ would be higher than we have used. For W51M our derived values of (n, T_K) seem entirely consistent with other studies (Ziurys and Turner 1985; Jaffe, Becklin, and Hildebrand 1984).

To derive fractional abundances $X = X'(dv/dR)$, the sizes of the PN clouds must be known. We adopt 4′ or 11.6 pc at a distance of 10 kpc for Sgr B2 (McGee *et al.* 1973); 20″ or 0.68

pc at a distance of 7 kpc for W51M (Ziurys and Turner 1985); and 20″ or 0.0465 pc at a distance of 480 pc for Ori (KL) (Johansson *et al.* 1984). The corresponding values of dv/dR and of X are given in Table 2. Alternatively, fractional abundances may be estimated from independent information for $N(H_2)$, which yields the values 1(24) cm^{-2} for both W51M (Jaffe, Becklin, and Hildebrand 1984) and for Sgr B2 (Scoville, Soloman, and Penzias 1975). $N(H_2)$ is uncertain for the "plateau" region of Ori (KL) because the particular kinematic component is not well defined. We adopt $N(H_2) \approx$ 2.5(23) cm^{-2}, intermediate between the value 5(22) cm^{-2} found for the "outflow" component (Vogel *et al.* 1984) and 1.5(24) cm^{-2} for the "doughnut" (Plambeck *et al.* 1982). The resulting values of $N(PN)/N(H_2)$ are given in Table 2.

The two estimates for fractional abundance are quite disparate for Sgr B2, but are consistent for Ori (KL) and W51M. X is likely underestimated for Sgr B2 because the PN region is possibly much smaller in extent than 4′. A not unreasonable assumption is that dv/dR is similar for all three sources, since all contain known outflows. Thus we consider $N(PN)/N(H_2)$ to be the more reliable estimate of fractional abundance and adopt it in what follows. We also consider $N(PN)$ to be underestimated in Sgr B2, because we assumed no beam dilution for want of information. Thus a fractional abundance for PN of $1(-11)$ to $1(-10)$ is a reasonable estimate in general.

c) *Chemistry of Phosphorus and of PN*

Phosphorus has not previously been detected in any form in dense interstellar clouds. In diffuse clouds its abundance is quite uniform and is depleted by no more than a factor of 3 below the solar value of $3(-7)$. If a similar depletion factor holds for dense clouds, then our results show that $[PN]/[P] \approx$ $3(-5)$ to $5(-4)$ so that PN is only a trace repository of interstellar phosphorus.

The central question is whether interstellar phosphorus compounds in general, and PN in particular, arise from ion-molecule processes, or from other processes ("shock" chemistry: either high T_K gas phase reactions, or grain disruption).

Based on ion-cyclotron-resonance techniques, Thorne *et al.* (1984) have shown that the ion-molecule chemistry of P is significantly different from that of the closely related N atom under interstellar conditions. Unlike NH_n^+ ions, PH_n^+ ions react endothermically with H_2 so that PH_n compounds ($n =$ 1–3) are very unlikely. Species containing the P—O bond are predicted to dominate, because P^+ and PH^+ react readily with H_2O, which is highly abundant. $H_3O^+ + P$ also contributes. PO is predicted to be the most abundant P species, with $[PO]/[H_2] = 1.4(-10)$ for $n = 1(5)$ cm^{-3}. Other P-compounds predicted by Thorne *et al.* (1984) with abundances above $1(-14)$ are PO^+, HPO^+, PH^+, and H_2PO^+. Conversely, species containing P—N and P—C bonds are predicted to be rare because they require reaction of P^+ or PH^+ with NH_3 and CH_4, which are much less abundant than H_2. The predicted abundance of PN is $< 1(-14)$.

Present observational information is inconsistent with these predictions. Not only is our PN abundance 1(3) to 1(4) times higher than predicted, but the fractional abundance of PO, based on an unsuccessful search by Matthews, Feldman, and Bernath (1987) is less than $1.4(-11)$ in Ori (KL), and $\leq$ $1.6(-11)$ in Sgr B2, 10 times less than predicted. Thus the observed ratio [PO]/[PN] is $\leq 1(-4)$ to $\leq 1(-5)$ of the predicted ratio.

The ion-molecule predictions can be reconciled with observations if (1) P is depleted by more than a factor of 10 in dense clouds (explaining the failure to observe PO); and (2) PN is created by other processes which do not produce PO, HCP, or PH_3, none of which are observed. Regarding point (2), high-temperature gas-phase reactions ("shock" chemistry) appear unpromising, because the endothermicity of PH_n^+ reactions with H_2 would be overcome, and significant abundances of PH_n compounds would be expected. Could PN be a product of grain disruption? As a *direct* product, PN might be favored over other P compounds if its bond strength were greater than that of other P species. Bond energies for simple P compounds are essentially unknown, although Thorne *et al.* (1984) estimate bond energies decrease in the order PC, PH, P_2, PH_2, PN, PH_3, PO. PN does not seem favored on this argument, although searches for PC, PH, PH_2 would be interesting. As an *indirect* product of grain disruption, PN might be formed efficiently by gas-phase reactions between species released from the grain mantles. Large abundances of NH_3, H_2O (much greater than can be produced by ion-molecule reactions) are known to be released by grain breakup (Walmsley *et al.* 1986; Henkel *et al.* 1987). Major uncertainties under such conditions are (1) whether any molecular ions, needed to initiate the P chemistry, are present; and (2) whether NH_3 is more abundant than H_2O, as required by the observed [PN]/[PO] ratio.

Phosphorus is now the fourth second-row element (after S, Si, Cl?) to be discovered in interstellar molecules. In each case, ion-molecule chemistry fails to predict the sizable abundances of these species. Although the known molecular species are only tracers of these elements, their fractions, which differ widely in the energetic Ori (KL) core, may be a clue to the chemistry. Thus, $[SiO]/[Si] \approx 3.4(-4)$, $[\Sigma\text{S-molecules}]/[S] \approx$ $1.8(-2)$, and $[PN]/[P] \approx 5.0(-4)$ relative to the cosmic abundances. Here, the sum over S-molecules includes SO, SO_2, CS, OCS (Johansson *et al.* 1984). The similarity of the [SiO]/[Si] and [PN]/[P] fractions, and the much larger [ΣS-molecules]/[S], may point to two distinct mechanisms, e.g., high-temperature gas-phase chemistry for S, grain disruption for Si, P.

Note added in manuscript.—The $J = 6$–5 transition of PN at 281914.13 MHz was detected 1987 March 20–21 at the 12 m telescope. T_R^* is 0.10 K and 0.33 K for W51M and Ori (KL) respectively, which for $\eta_c \approx 0.3$ yields values of T_R and T_B in satisfactory agreement with our model of the PN excitation.

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