Detection of the Phosphorus-bearing Molecules PO and PN in the Outer Galaxy

Lilia Koelemay  
University of Arizona  
https://orcid.org/0000-0001-9334-3149

Katherine Gold  
University of Arizona

Lucy Ziurys  
(✉️ lziurys@arizona.edu)  
University of Arizona

Physical Sciences - Article

Keywords:

Posted Date: May 26th, 2023

DOI: https://doi.org/10.21203/rs.3.rs-2978405/v1

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Abstract

Phosphorus is a key element in biology\textsuperscript{1} and plays a role in the formation of Earth-like planets\textsuperscript{2}. Despite its importance, phosphorus has been identified only in a small section of the Milky Way, and its general Galactic distribution is not known. The lack of information about this element is partly due to unfavorable atomic transitions, but phosphorus-containing molecules offer another avenue for investigation. Here we present the detection of gas-phase phosphorus in the Outer Galaxy through spectra of PO and PN. The rotational lines in the 2 and 3 mm regions of these molecules were observed in the dense cloud WB89-621, located 22.6 kpc from the Galactic Center. The abundances of PO and PN in WB89-621 are comparable to values near the Solar System within the measurement uncertainties\textsuperscript{3}. Phosphorus is created in supernovae, which are not typically present in the Outer Galaxy\textsuperscript{4}. The detection of PO and PN at such large Galactic distances is surprising, but could be a consequence of a “Galactic Fountain”, where elemental enrichment occurs from redistribution of supernovae material ejected into the halo and circumgalactic medium\textsuperscript{5}. The identification of phosphorus at this galactocentric distance therefore provides new insight into the chemical evolution of the Galaxy.

Full Text

Although the cosmic abundance of phosphorus is not particularly high (P/H $\sim$ 2.6 $\times$ 10\textsuperscript{-7})\textsuperscript{[3]}, this element is one of the six most crucial for biological systems, along with carbon, oxygen, nitrogen, sulfur and hydrogen\textsuperscript{6}. Phosphorus also plays a role in the Solar System. It is routinely found in mineral form in planetary bodies such as meteorites and moon rocks, either as phosphates (e.g., apatite (Ca$_5$(PO$_4$)$_3$(OH,F,Cl)), merrillite (Ca$_9$NaMg(PO$_4$)$_7$), or in phosphides, in particular schreibersite ((Fe, Ni)$_3$P)\textsuperscript{[7]}. Phosphorus has been identified in the gas-phase in the atmospheres of Jupiter and Saturn as phosphine PH$_3$, as well\textsuperscript{8}, and additionally in various forms in comet volatiles. Furthermore, it is speculated that phosphorus in schreibersite may be an important component of the cores of rocky planets\textsuperscript{1}.

Investigating phosphorus outside the Solar System has been problematic. The common method to study elements in the interstellar medium (ISM) is to observe atomic transitions, typically with ground-based telescopes. The lines of neutral phosphorus (PI) lie at 10500-10600 Å, in the near infrared region of the spectrum, but they are often obscured by atmospheric telluric features\textsuperscript{9}. Furthermore, these transitions are considerably weaker as compared to atomic lines of other elements because of oscillator strengths. PI, along with PII (P$^+$), can also be studied at ultraviolet (UV) wavelengths near 2100-2600 Å, but are typically obscured by atmospheric molecular lines such as ozone\textsuperscript{10}. Space-based measurements for phosphorus with satellites such as FUSE and Copernicus in the UV range have been carried out as an alternative\textsuperscript{11}, but many of the accessible transitions are blended with iron or chromium lines\textsuperscript{10}.

Despite observational challenges, investigations of phosphorus have been pursued. PII lines have been detected in several diffuse clouds within 5 kpc of Earth, based on line of sight observations towards stars\textsuperscript{12-14}. These data suggest that phosphorus is only slightly depleted in the diffuse ISM\textsuperscript{15}. Atomic
phosphorus has also been observed in ~20 planetary nebulae between $R_{GC} = 6$-11 kpc$^{11,16-25}$. Measurements of this element in stellar photospheres have been conducted, including those of host stars of planetary systems$^9$. However, due to the observational constraints, the phosphorus abundance has been measured only in ~1% of all such host stars$^1$. Moreover, the objects where such measurements have been possible are typically within a few kpc of the solar neighborhood, although one detection is ~ 15 kpc from the Galactic Center. As illustrated in Figure 1, our understanding of the general Galactic distribution of this element is therefore limited.

The origin of phosphorus as an element is thought to be in neutron capture processes during hydrostatic burning in massive stars, and subsequent release to the ISM in Type II supernovae (SNe)$^9$. Observations of PI towards the SN remnant Cassiopeia A support this scenario$^{26}$. However, modeling of the SN production of phosphorus generates abundances that disagree with those established from the current stellar disk sample. To match the observed data, models of Galactic Chemical Evolution (GCE) must arbitrarily increase the stellar production of this element by a factor of ~3$^{[27]}$.

Molecular line observations offer an alternative method by which to study the phosphorus distribution in the Galaxy. To date, seven P-bearing molecules have been identified in the ISM through millimeter-wave measurements: PN, PO, CP, CCP, HCP, PH$_3$, and SiP (see ref. 28, and references therein). Although all of these species were detected in circumstellar envelopes of evolved stars, PN and PO are also found in molecular clouds, including Orion-KL, AFGL 5142, and W51$^{29-32}$. The first phosphorus-bearing molecule to be detected in the ISM, PN, was identified in Orion-KL$^{33}$. The molecular detections of phosphorus thus far have also been limited to within 5 kpc of the solar neighborhood; see Figure 1.

The Outer Galaxy, roughly defined as >16 kpc from the Galactic Center, has not been a region targeted for measurements of phosphorus. At such distances, molecular clouds are typically small and sparse, as traced by CO$^{34,35}$, resulting in a significantly lower star formation rate$^{34}$. Supernovae in this part of the Milky Way are also extremely rare$^4$, as few as 1 in 215. However, recent observations of so-called Galactic Edge Clouds have demonstrated that dense gas at large galactocentric distances (~ 15-24 kpc) may be fairly rich in metals such as carbon and oxygen. A slew of more complex molecules has been detected towards these objects, including CH$_3$OH, CH$_3$CCH, and NH$_2$D$^{36,37}$. CH$_3$OH is of particular significance, as the abundance of this species appears to remain constant with respect to galactocentric distance over the range 8-24 kpc, despite predictions of a major metallicity gradient$^{37}$.

Given the chemical complexity found in the Galactic Edge Clouds, we conducted a search for phosphorus-bearing molecules in one of these objects, WB89-621. Our goal was to examine the presence of phosphorus at large galactocentric distances. WB89-621 is located at a galactocentric radius of 22.6 kpc$^{34}$, has a gas kinetic temperature of ~ 25 K, and contains several organic molecules, including H$_2$CO and CH$_3$OH$^{34,36,37}$. Millimeter-wave observations of WB89-621 were conducted with the Arizona Radio Observatory (ARO) 12-m and the Institut de Radioastronomie Millimétrique (IRAM) 30-m telescopes. A tentative detection of PN via the J = 3→2 transition at 2 mm was initially made at the ARO 12-m during
March 2022. This identification was confirmed by the observation of a second line of PN (J = 2→1 transition) at 3 mm at IRAM in July 2022. In addition, PO was also identified in this source through the observation of four hyperfine/lambda-doubling components of the J = 2→1.5 transition (see Table 1).

The measured spectra of PN and PO in WB89-621 are shown in the top six panels in Figure 2. As shown in the figure, the spectral profiles have intensities near 6-10 mK, exhibit narrow linewidths typically ~ 1.5 km s⁻¹, and have an LSR velocity near -25.5 km s⁻¹. Such line profiles are characteristic of molecular material in WB89-621, as illustrated in the lower four panels of Figure 2. Here spectra of the J = 1→0 transition of HCN and N₂H⁺ are shown, as well as the Jₜ = 8₀→ 7₁ A and the J_{κₐ,κₖ} = 10₁₉→ 10₀₁₀ of CH₃OH and SO₂, respectively. These data were also obtained at the IRAM 30-m. In the HCN and N₂H⁺ features, nitrogen quadrupole hyperfine components are resolved. All four profiles exhibit equally narrow line widths and are at V_{LSR} ~ -25.5 km s⁻¹, in agreement with the PO and PN spectra. Line parameters for all species, determined from Gaussian fits to the line profiles, are summarized in Table 1. The linewidths and LSR velocities are consistent between the phosphorus-bearing species and the other four molecules. Therefore, it is clear that phosphorus is present in molecular form in WB89-621.

From the measured rotational transitions, abundances of PN and PO were derived using RADEX®⁵⁸, a non-LTE radiative transfer code (see Methods). In these calculations, the gas kinetic temperature was assumed to be ~ 25 K, as derived from previous molecular observations. Based on the two transitions of PN that were measured, a gas density of n(H₂) ~ 1.5 × 10⁵ cm⁻³ was also determined, which was subsequently used to model the single rotational line observed for PO. The abundances, relative to H₂, derived for PN and PO were 3.0 ± 1.6 × 10⁻¹² and 2.0 ± 1.1 × 10⁻¹¹, respectively. These values are no more than a factor of 10 lower than those measured for PN and PO in molecular clouds near the solar neighborhood, as summarized in Figure 3. In some cases, they are comparable. There may be a decrease in the abundance of these two P-bearing molecules from R_{GC} ~ 5-10 kpc to ~23 kpc. However, the dearth of PO and PN detections between 10-22 kpc suggests more observations are needed to establish such a trend.

The abundances of the elements are thought to decrease with distance from the Galactic Center, with the decline of the star formation rate⁵⁹. Few studies, however, characterize the metallicity of the Galaxy beyond 16 kpc⁶⁰, and there are no measurements of phosphorus in any form in this region, prior to this work. Furthermore, studies in other spiral galaxies suggest that the metallicity gradient flattens at large galactocentric distances⁶⁰. One metallicity gradient⁶¹ has been established over the range of 12-20 kpc for iron, with [Fe/H] = -0.027 ± 0.007 dex kpc⁻¹. Assuming phosphorus behaves like iron, it is estimated that the abundance of the element would decrease by roughly a factor of five from the solar neighborhood to ~ 23 kpc. However, this extrapolation is based on numerous assumptions.

Refractory elements such as phosphorus are typically depleted in the ISM compared to stellar values because of condensation into dust grains, which principally occurs in circumstellar ejecta. Phosphorus in circumstellar gas is predicted to condense primarily into the mineral schreibersite, according to
thermodynamical calculations\textsuperscript{42}. About \(~ 50\%\) of the available phosphorus is thought to be contained in such dust grains\textsuperscript{[15]}. It is speculated that at least in certain molecular clouds, phosphorus is first liberated from dust grains due to shock waves, and then forms gas-phase molecules such as PN and PO\textsuperscript{29,43}. Such a scenario is supported by the broad linewidths (\(~ 10-25 \text{ km s}^{-1}\) ) displayed in PN and PO spectra in star-forming clouds; in the Orion-KL region, the line profiles clearly associate these two molecules with the “plateau,” an outflow containing hot, shocked gas, including vibrationally-excited H\textsubscript{2}, a known shock tracer\textsuperscript{29}. Furthermore, a survey of PN in massive star-forming molecular clouds showed that the spectra of this molecule displayed high velocity wings indicative of shocks\textsuperscript{44} in at least 9 objects where it was detected. These sources were not cold, with \(T_K \sim 20-90 \text{ K}\).

However, there are unique instances in which PN appears to arise from cooler, more quiescent gas. In three star-forming cores with \(T_K \sim 20-40 \text{ K}\), PN was detected with narrow (1.5-3 km s\textsuperscript{-1}) spectral linewidths\textsuperscript{43,45}. Although these cores have shocks, as evidenced by the broader linewidths (5-10 km s\textsuperscript{-1}) of SiO, the narrowness of the PN line profiles indicate that they are not currently present in shocked gas. PO has not been observed in these objects\textsuperscript{43,45}. However, decade-long searches for phosphorus-bearing molecules in dark molecular clouds, where \(T \sim 10 \text{ K}\), have been unsuccessful\textsuperscript{46}. The formation of PN may involve chemical pathways that can occur in cooler, but not the coldest, material, rather than in shocks. On the other hand, PN may remain in the gas phase after the shocked material has cooled to \(~ 25 \text{ K}\) as “fossil” material.

The molecules in WB89-621 typically display narrow linewidths (1.2-3 km s\textsuperscript{-1}; see Table 1), indicating reasonably quiescent gas. Furthermore, the gas kinetic temperature has been estimated to be \(T_K \sim 25 \text{ K}\). Note that the evaporation of phosphorus molecules from grain surfaces occurs \(> 35 \text{ K}\)\textsuperscript{[43]}. Unlike the other cool clouds where PN has been observed, in WB89-621, PO is present as well. Formations in hot, shocked gas do not seem likely in this object.

Alternatively, the existence of phosphorus-bearing molecules in the Outer Galaxy may be the result of a Galactic fountain. In the fountain model, stellar activity, such as SN explosions, ejects gas into the halo/disk-halo interface where it travels considerable distances, cools, and preferentially “rains” down onto the outer regions of the disk\textsuperscript{5}. Although this ejected gas mixes with mainly hydrogen in the halo/interface, the suspected fountain material is found to have enhanced metallicities\textsuperscript{47}. Because phosphorus is thought to be produced by SNe\textsuperscript{26}, the fountain model provides a path for phosphorus to be selectively deposited in the Outer Galaxy. As the gas settles back into the disk, atomic phosphorus could react to form PN and PO, which remain as the material further cools to the observed temperatures seen in WB89-621.

The infall from a fountain may actually create distinct clouds in the Outer Galaxy\textsuperscript{48}. Such clouds have “forbidden velocities,” indicating that they do not follow the galactic rotation curve\textsuperscript{5}. Given the location of WB89-621, the rotation curve\textsuperscript{5,48} would indicate \(V_{\text{LSR}} \sim 0 \text{ km s}^{-1}\). The cloud has an actual LSR velocity
of -25.4 km s\(^{-1}\), which is suggestive. Most fountain clouds have velocities in the range 40 - 90 km s\(^{-1}\) and > 90 km s\(^{-1}\) and are termed intermediate-velocity (IVC) and high velocity (HVC) clouds, respectively\(^{48}\). A third group of objects has been more recently identified with \(V_{\text{LSR}}\) of -20 to -40 km s\(^{-1}\), which are classified as low-velocity clouds (LVCs)\(^5\) of which WB89-621 might be a candidate. On the other hand, WB89-621 resides roughly 300 pc \((b = 0.8197^\circ)\) above the Galactic midplane near the “top” of the thin disk. Most objects characterized as LVCs have galactic latitudes > 3° such that they are clearly separated from the disk\(^5\). Moreover, velocities < 30 km s\(^{-1}\) in clouds can be accounted for by turbulence due to Galactic rotation\(^{48}\).

WB89-621 may simply be a cloud that has been “polluted” by infall from the halo/circumgalactic medium, increasing the availability of metals for molecular formation. Notably, WB89-621 exhibits a higher temperature \((T \sim 25 \text{ K})\) than expected for a molecular cloud without star formation \((T < 10 \text{ K})\). The elevated gas kinetic temperature could be attributed to the mixing of warm fountain material with the cold, pre-existing gas in the cloud. On the other hand, metal enrichment could result from other mixing processes, such as outward radial flows, angular momentum redistribution, and turbulence\(^{40}\). They would probably achieve a similar enrichment and could elevate gas temperatures.

Whether phosphorus in WB89-621 comes from a Galactic fountain or is the product of other mixing, the element is clearly present at the edge of the Galaxy. Moreover, it has been identified in molecular carriers. This discovery should encourage new searches for this element at large galactocentric distances in both elemental and molecular form. Such new data would better define the contribution of phosphorus in GCE and constrain the evolution of the Outer Galaxy.

**Declarations**

**Data availability**

All data is available within the paper which supports the findings of this study. Any additional information may be obtained from the corresponding author upon reasonable request.

**Acknowledgements**

This research is supported by NSF Grant AST-1907910 and NASA grant 80NSSC18K0584 (Emerging Worlds).

**Author Contributions**

L.A.K. and K.R.G. conducted observations of the astronomical object. L.A.K. led the data reduction and analysis with input from L.M.Z and K.R.G. All authors discussed the results and wrote the manuscript.

**Competing Interest Statement**

The authors declare no competing interests.
Additional Information

Correspondence should be addressed to L.M.Z (lziurys@arizona.edu)

References


**Methods**

**Observations.** All molecular spectra were obtained using the ARO 12-m telescope and the IRAM 30-m telescope, located on Kitt Peak, Arizona and Pico Veleta, Spain, respectively. Observations at the ARO 12-m were taken with a dual-polarization receiver with sideband-separating mixers. Image rejection was typically >18 dB. The temperature scale ($T_A^*$) for both the ARO 12-m and IRAM 30-m, determined by the chopper wheel method, is related to the main-beam brightness temperature, $T_R$, by $T_R = T_A^*/\eta_B$, where $\eta_B$ is the main-beam efficiency (0.82 and 0.81, respectively). The ARO 12-m observations were conducted at 2 mm with the ARO Wideband Spectrometer (AROWS) as the backend, configured to a frequency resolution of 156 kHz and 1 GHz bandwidth, per polarization. The IRAM measurements were taken with the Eight Mixer Receiver (EMIR) at 3 mm in dual-polarization mode, with the FTS 200 (fast Fourier transform spectrometer with a resolution of 200 kHz). The line parameters are provided in Table 1. Total integrations times required for the new identifications were 28.6 hours at the ARO 12-m and 17.4 hours at the IRAM 30-m, respectively.

**Analysis.** The column densities were calculated using the non-LTE radiative transfer code RADEX$^{38}$. The program employs the Sobolev approximation to produce line profiles to compare with measured spectra. RADEX varies the molecular column density ($N_{\text{tot}}$), gas kinetic temperature ($T_k$), and the H$_2$ gas density ($n(\text{H}_2)$). The data files, which consist of the energy levels, transitions, and collisional rate information for each molecule, were obtained from the Leiden Atomic and Molecular Database (LAMDA)$^{49}$. Because only two rotational transitions of PN were measured, only two parameters could be varied at a time. The gas kinetic temperature was set to 25 K, a value determined by other molecules that had multiple transitions, such as CH$_3$OH and CH$_3$CN. The H$_2$ density was varied between $1 \times 10^5 - 1 \times 10^7$ cm$^{-3}$ and the column density was varied from $1 \times 10^9 - 1 \times 10^{14}$ cm$^{-2}$. The “best fit” was determined through a reduced $\chi^2$ program.

**Methods References**

**Tables**

**Table 1**: Observations of PN ($X^1\Sigma^+$), PO ($X^2\Pi_r$) and Other Molecules Towards WB89-621
<table>
<thead>
<tr>
<th>Molecule</th>
<th>Transition (^a)</th>
<th>Frequency (MHz)</th>
<th>(T_A^*) (mK)</th>
<th>(\Delta V_{1/2}) (km/s)</th>
<th>(V_{\text{LSR}}) (km/s)</th>
<th>(f(X/H_2)^c)</th>
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<td>PN</td>
<td>J=2→1</td>
<td>93979.77</td>
<td>10 ± 2</td>
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<td>88630.42</td>
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<td>(\text{CH}_3\text{OH})</td>
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<td>95169.39</td>
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<td>(SO_2)</td>
<td>(J_{Ka,Kc}=10_{1,9}→10_{0,10})</td>
<td>104239.3</td>
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a. Measured with the IRAM 30-m unless indicated otherwise.
b. Measured with the ARO 12-m.
c. Abundance relative to H$_2^{34}$.
d. From Bernal et al. $^{37}$. 

Figures
**Figure 1**

**Currently known Galactic distribution of phosphorous.** A graphic illustrating the Galactic distribution of phosphorus to 25 kpc from the Galactic Center, as identified from stellar and interstellar observations. Detections by atomic transitions in stellar photospheres are denoted by green stars (from ref 9. and references therein), in diffuse clouds by purple circles (refs. 12 and those therein, 13, 14), and in planetary nebulae by blue triangles$^{11,16-25}$, while magenta circles and cyan diamonds mark the identifications in molecular clouds and circumstellar envelopes (from molecular lines)$^{28,29,32}$. The red square shows the position of WB89-621. The orange X indicates the solar system. The APOGEE survey detections are not shown per possible contamination. WB89-621 is the only known source of phosphorus beyond 15 kpc.
Figure 2

Spectra of molecular rotational transitions of PO, PN, and related species in molecular cloud WB89-621. Spectra are plotted as intensity ($T_A^*$), in mK, versus velocity with respect to the local standard of rest ($V_{\text{LSR}}$), in kilometers per second. The top two panels show the PN $J = 2 \rightarrow 1$ and $J = 3 \rightarrow 2$ transitions, followed by the four hyperfine components of the PO $J = 2.5 \rightarrow 1.5$ transition. The bottom four panels display other molecules containing the “NCHOPS” elements, including HCN $J = 1 \rightarrow 0$, N$_2$H$^+$ $J = 1 \rightarrow 0$, CH$_3$OH $J = 8_0 \rightarrow 7_1$ A and the SO$_2$ $J_{K_a,K_c} = 10_{1,9} \rightarrow 10_{0,10}$ transitions. Each panel includes the molecular species and quantum numbers corresponding to the rotational transition shown. The $J = 2 \rightarrow 1$ of PN (156 kHz spectral resolution) was measured with the 12-m antenna of the Arizona Radio Observatory (ARO), while all others were observed using the IRAM 30-m telescope (200 kHz spectral resolution).

Figure 3

Abundances of PN and PO as a function of distance from the Galactic Center. Molecular abundances, relative to H$_2$, are plotted with respect to R$_{\text{GC}}$ (kpc) for AFGL 5142, G+0.693-0.03, W3(OH), W51, L1157,
Orion-KL$^{29}$, B1-a, NGC 1333-IRAS 3, Ser SMM1, L723$^{32}$ and WB89-621. Abundances of PO and PN are shown in red and black, respectively, with estimated uncertainties.