

UPPER LIMITS TO INTERSTELLAR PO

H. E. MATTHEWS AND P. A. FELDMAN
 Herzberg Institute of Astrophysics

AND

P. F. BERNATH
 Department of Chemistry, University of Arizona
 Received 1985 July 5; accepted 1986 June 25

ABSTRACT

Laboratory work has established that PO is likely to be the most abundant molecule containing phosphorus in dense interstellar clouds. Using recently measured microwave frequencies, we have searched for the $J = 5/2 \rightarrow 3/2$ transition of PO at 109 GHz in four galactic sources. Our limit in DR 21(OH), in particular, suggests that phosphorus may be severely depleted in dense molecular clouds.

Subject headings: interstellar: abundances — interstellar: molecules

I. INTRODUCTION

Phosphorus-bearing molecules are expected, *a priori*, to be present in fair degree in dense interstellar molecular clouds since phosphorus is reasonably abundant cosmically (e.g., $[P]/[S] \approx 1/60$, $[P]/[N] \approx 1/400$). Extraterrestrial phosphine, PH_3 , has been found in the Jovian atmosphere (Ridgway, Wallace, and Smith 1976), and ionized atomic phosphorus has been detected in several diffuse clouds by its UV absorption spectrum (Jura and York 1978). At radio wavelengths attempts have been made to find a few simple phosphorus-bearing molecules for which accurate spectroscopic constants are known. However, all those earlier searches, for PN and PH_3 (Hollis *et al.* 1980), for HCP (Thaddeus 1982; Hollis *et al.* 1981), and for NCCP (Avery 1982), have been unsuccessful.

Recently, Thorne, Anicich, and Huntress (1983) have studied the reactions of PH_n^+ ions ($n = 0-4$) with a number of simple neutral molecules using ion-cyclotron-resonance techniques. Their laboratory experiments indicate that the ion-molecule chemistry of phosphorus is significantly different from that of nitrogen under conditions obtaining in dense interstellar clouds. Namely, the results show that, unlike NH_n^+ ions, none of the PH_n^+ ions reacts with H_2 . However, PO^+ and HPO^+ ions are readily formed in a number of reactions between P^+ and PH^+ ions and such oxygen-bearing neutrals as H_2O , O_2 , and CO_2 (but not CO). In consequence, Thorne *et al.* (1983) were led to conclude that "a molecule containing a P-O bond, and originating from PO^+ or HPO^+ , may be the most likely candidate for an interstellar molecule containing phosphorus." More recently, Thorne *et al.* (1984) employed a simple kinetic model to calculate the relative abundances of phosphorus species in dense interstellar clouds. The key finding is that at chemical steady state the most abundant P-bearing molecule is PO. Molecules such as PH_3 are difficult to synthesize by gas-phase ion-molecule reactions in interstellar clouds; molecules such as PN and HCP are expected to have abundances much lower than PO because of lower abundances of the necessary reactants. These findings may provide an explanation to why previous searches for P-bearing molecules have been unsuccessful.

Our search for PO has been facilitated by the recent laboratory determination of the microwave rotational spectrum of this radical in the gas phase by Kawaguchi, Saito, and Hirota

(1983). Since the ground $X^2\Pi$ state of PO has a spin-orbit coupling constant ($A_0 = 224 \text{ cm}^{-1}$; Verma and Singhal 1975) which is considerably larger than the rotational constant ($B_0 = 0.7305 \text{ cm}^{-1}$; Kawaguchi *et al.*), the spectrum of PO exhibits Hund's case (a) coupling for all reasonable values of J . The large positive spin-orbit constant also means that only energy levels of the lower $^2\Pi_{1/2}$ spin component are likely to be populated in interstellar conditions. Like the CH and OH molecules, there are two nearly degenerate energy levels for each J -value which is split by Λ -doubling. Each Λ -doublet is further split into two levels by the nuclear hyperfine interaction of ^{31}P ($I = \frac{1}{2}$).

In the present work we observed at the 109 GHz frequencies of the $J = 5/2 \rightarrow 3/2$ transitions, as measured by Kawaguchi *et al.* Our source list was chosen to include objects known to contain regions of high molecular density and excitation.

II. OBSERVATIONS

The observations were made in 1983 June using the recently resurfaced 12 m telescope of the NRAO¹ at Kitt Peak. Position-switching by 10', 15', and 20' in azimuth was applied, and the oscillating corner reflector was used to minimize standing-wave baseline ripple. At 109 GHz the telescope beamwidth is approximately 1.0 (FWHM), and the aperture and beam efficiencies are approximately 0.40 and 0.50, respectively.

No attempt could be made to calibrate the observations accurately because of variable cloudy conditions throughout the observing session, although a rough calibration was obtained once per hour by the insertion of a vane into the optical path. Comparison of our results with those of other observers for the HC_3N ($J = 12 \rightarrow 11$) transition, after allowing for the recent improvement in the antenna, suggests that our calibration is unlikely to be inaccurate by more than 20%, however.

A dual-channel receiver was employed, accepting both senses of circular polarization. After correction for atmospheric absorption and emission, and for telescope losses, the typical effective system temperatures ranged upward from 1300 K. The PO lines were placed in the upper sideband which was

¹ The National Radio Astronomy Observatory is operated by Associated Universities, Inc., under contract with the National Science Foundation.

centered at 109,102 MHz. Since there are no strong molecular lines expected to occur within the frequency range of the lower sideband ($99,602 \pm 128$ MHz), and since the insertion of an image-rejection filter results in additional noise in the system, none was employed. An attempt was made to distinguish between weak features in the upper and lower sidebands by applying a frequency offset of 10 MHz to part of the data.

The filter spectrometer was operated in a series configuration, each bank consisting of 256 1 MHz channels (equivalent to 2.75 km s^{-1} at 109,102 MHz and 3.01 km s^{-1} at 99,602 MHz). The data from each bank were subsequently combined during the reduction. With this arrangement it was possible to include both of the strongest hyperfine components ($F = 3 \rightarrow 2$), e at 108,998.445(8) MHz and f at 109,206.200(17) MHz, at opposite ends of the spectrum, along with the weaker $F = 2 \rightarrow 1$ (e) component at 109,045.396(13) MHz.

III. RESULTS

The sources observed in this program are listed in Table 1, with their positions and assumed velocities with respect to the local standard of rest. Our results are shown in Figure 1, where the spectra of all four sources are plotted on a common frequency scale, and the expected positions of the PO transitions in this frequency range are indicated.

The spectrum of each of the sources is quite distinct in character. In the cases of Orion KL and Sgr B2(OH) it is rich in line emission, while for DR 21(OH) only one feature appears. In all cases, however, it seems that the spectral regions where the two most intense PO features should occur are fairly clean. Hence upper limits may be assigned to PO emission in these lines with some confidence. In Sgr B2(OH), and to a certain extent in Orion KL, it appears we are approaching the line confusion limit discussed by Turner (1983) and Sutton *et al.* (1984), and the upper limit is no longer determined solely by the rms noise on the spectrum.

Our upper limits (3σ) to PO emission in the ${}^2\Pi_{1/2}$, $J = 5/2 \rightarrow 3/2$ transition, $F = 3 \rightarrow 2$ (e and f) and $F = 2 \rightarrow 1$ (e) lines, are given also in Table 1. In each case, the limits are derived from the hanning-smoothed spectra in Figure 1. The $F = 2 \rightarrow 1$ (e) line is confused with the HCC^{13}CN and HC^{13}CCN ($J = 11 \rightarrow 10$) transitions arising in the lower sideband (see below and Table 2). In only one case (Sgr B2) does a possible feature appear at the position of one of the PO lines ($F = 3 \rightarrow 2$, f), but it is of marginal significance. In view of the number of spectral features in the Sgr B2 spectrum, the detection of at least the two strongest PO lines would be required before a detection could be claimed.

In Table 2, we summarize the other lines detected in the spectra of Figure 1. In each case, the spectrum is dominated by

the $J = 12 \rightarrow 11$ rotational lines of HC_3N and the $J = 11 \rightarrow 10$ lines of its isotopes HC^{13}CCN and HCC^{13}CN , and we are confident of their identification. In some of the other cases we have been able to determine in which sideband the lines arise, and hence their frequencies. In the remaining instances the features are too weak for us to have been able to assign a frequency. In at least one instance lines arising in both sidebands overlap in our observed spectra (at 99,684 and 109,019 MHz); the ambiguity was resolved by observations at an offset frequency for Orion KL. We have attempted to provide identifications for the weaker lines listed in Table 2, and some suggestions are included in the "Notes" column.

Observations of IRC +10°216 and Orion KL have been made over a frequency range similar to that covered here by Goldsmith *et al.* (1982), during their observations of vibrationally excited HC_3N . Upper limits to the PO $J = 5/2 \rightarrow 3/2$, $F = 3 \rightarrow 2$ (f) transition estimated from their spectra are comparable to those reported in the present work. The relatively strong pair of lines at 109,139 and 109,152 MHz in Orion KL were attributed by Goldsmith *et al.* to CH_3OH without specific assignments. The former is $J_K = 14_5 \rightarrow 15_4$, E_1 , $v_t = 0$ at 109,138.71 MHz (Lees and Baker 1968); the latter was also reported by Lees and Baker at 109,153.19 MHz but was only recently assigned as the Q -branch line $J_K = 16_{-2} \rightarrow 16_1$, E_1 , $v_t = 0$ by Sastry, Lees, and DeLucia (1984). These transitions require high excitation, arising from $\sim 254.7 \text{ cm}^{-1}$ and $\sim 228.5 \text{ cm}^{-1}$, respectively, above the lowest levels of their symmetry species. We note that these lines may also be present in our spectrum of Sgr B2.

Finally, in Figure 2 we include profiles of the HC_3N ($J = 12 \rightarrow 11$) transition for each of our sources which exhibit some of the different shapes observable in molecular sources (e.g., parabolic for IRC +10°216, core-pedestal for Orion KL). Such high signal-to-noise ratio profiles are rarely obtained and published, but they are of value in establishing an accurate calibration for the new 12 m telescope. Hence they are included here.

IV. DISCUSSION

We can use our upper limits to the PO line intensities to obtain upper limits to the column densities in the four sources studied. To do this, we have made a number of simplifying assumptions:

- 1) The level populations are in thermal equilibrium with rotational excitation temperatures of 15 to 75 K (typical of these regions, but essentially unknown for the putative case of PO);
- 2) The clouds observed fill the beam in each case;

TABLE 1
OBJECTS SEARCHED FOR PO

Object	$\alpha(1950)$	$\delta(1950)$	v_{LSR} (km s^{-1})	Line Width ^a Δv (km s^{-1})	Line Strength ^b T_A^* (mK)	Column Density $N(\text{PO})$ (cm^{-2})
Orion KL	05 ^h 32 ^m 47 ^s .0	-05°24'20"	9	8 ³	<65	<2.1 × 10 ^{13 c}
IRC +10°216	09 45 14.8	13 30 39	-26	25	<20	<0.7 × 10 ¹³
Sgr B2(OH)	17 44 11.0	-28 22 30	62	21	<50	<1.6 × 10 ¹³
DR 21(OH)	20 37 13.9	42 12 00	-3	7	<15	<1.8 × 10 ¹²

^a Corrected for spectral resolution.

^b 3σ upper limit, corrected for atmospheric absorption; velocity resolution 2.75 km s^{-1} .

^c If the line width is taken to be $\sim 4 \text{ km s}^{-1}$, characteristic of the N-S extended Orion ridge, $N(\text{PO}) < 1.1 \times 10^{13} \text{ cm}^{-2}$.

1987ApJ...312...358M

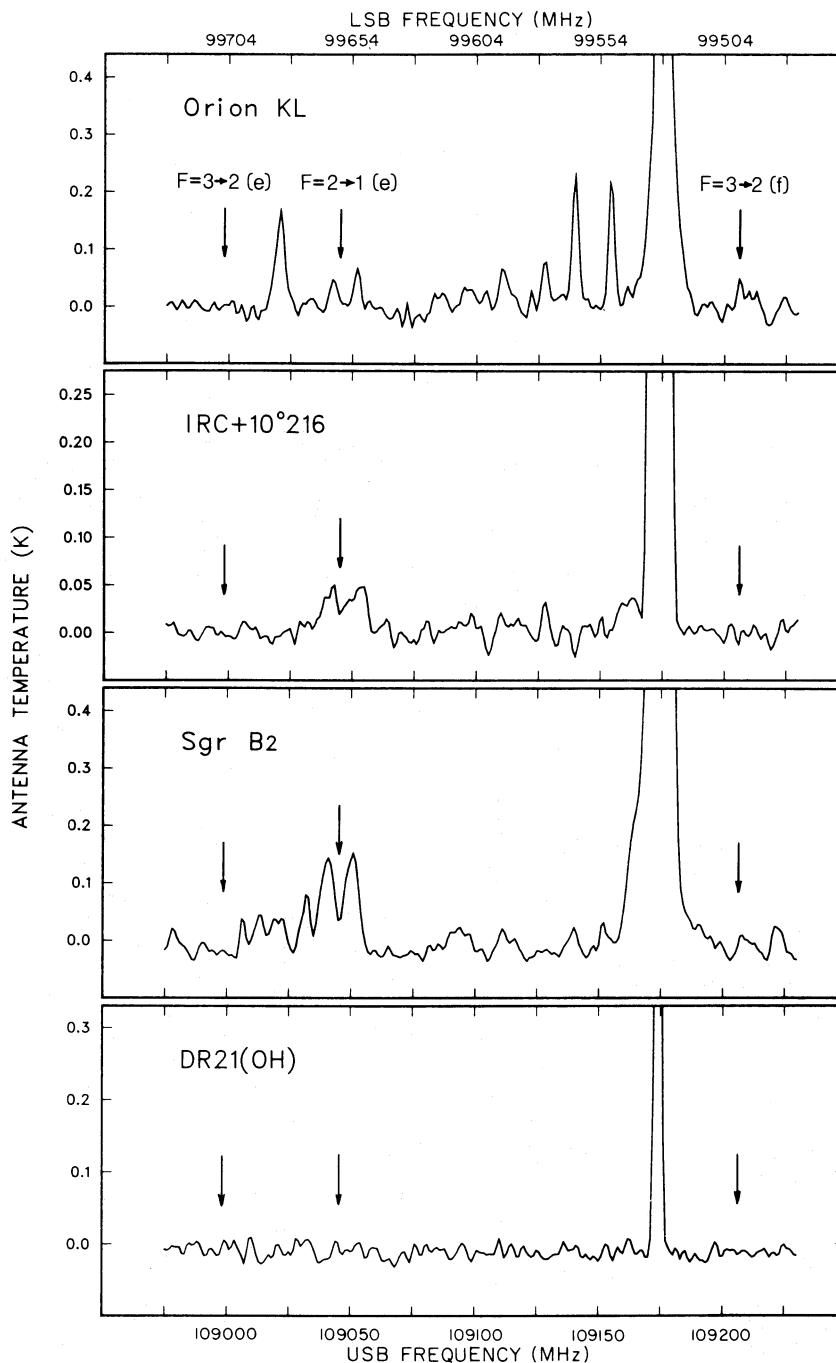


FIG. 1.—Spectra of four sources searched for PO. Expected positions of PO features are indicated, and the HC₃N ($J = 12 \rightarrow 11$) profiles are clipped to show other weak spectral lines. Lower frequency scale refers to the receiver upper sideband (USB), while upper frequency scale refers to the receiver lower sideband (LSB); the latter is accurate only to a few MHz because of the differential Doppler shift between the upper and lower sidebands. Spectra are smoothed to a resolution equivalent to 3.3 km s⁻¹. The relatively strong pair of lines at 109,139 and 109,152 MHz in Ori KL are due to CH₃OH. The $F = 2 \rightarrow 1(e)$ line of PO (${}^2\Pi_{1/2}$, $J = 5/2 \rightarrow 3/2$) is confused with the $J = 11 \rightarrow 10$ HCC¹³CN and HC¹³CCN transitions at 99,661.5 and 99,651.9 MHz, respectively, arising in the lower sideband.

3) The line widths are the same as those measured for HC₃N ($J = 12 \rightarrow 11$);

4) The dipole moment of PO is ~ 2.13 Debye.

While the dipole moment of PO has not yet been measured in the laboratory, it has been calculated by Grein (1984) for the equilibrium internuclear separation by ab initio methods using extensive configuration interaction (CI). The value obtained, 2.13 D, is somewhat smaller than the corresponding value at

the self-consistent field (SCF) level of theory (2.78 D). Lohr's (1984) SCF value is 2.76 D. However, it is considerably larger than the value (0.70 D) calculated by Boyd and Lipscomb (1967) using a minimal basis set. It is worth noting that Grein's value for the dipole moment of PO is ~ 13 times larger than that of the related molecule NO. The latter was detected in Sgr B2 in its ${}^2\Pi_{1/2}$ $J = 3/2 \rightarrow 1/2$ transition by Liszt and Turner (1978).

TABLE 2
LINES DETECTED IN SPECTRA OF FIGURE 1

Orion KL	LINE STRENGTH T_A^* (K)			FREQUENCY (MHz)		NOTES
	IRC +10°216	Sgr B2(OH)	DR 21(OH)	LSB ^a	USB ^b	
0.11 ^b	99732	...	Possibly CH ₃ OH ($J_K = 6_1 \rightarrow 5_0, E_1, v_t = 1$) at 99,730.90 MHz ^c
...	...	0.05	...	99726	108977	Possibly ¹³ CH ₃ CCH ($J, K = 6, 4 \rightarrow 5, 4$) at 99,726.79 ± 0.06 MHz ^d in LSB
...	0.015(?)	0.09	...	99698	109005	Doubtful in IRC +10°216
...	...	0.06	...	99691	109012	
0.13}	...	0.07	...	99684	{ ... }	Confused due to overlap
0.08}	{ 109019 }	
...	...	0.11	...	99671	109032	Doubtful; possibly CH ₃ CCD ($J, K = 7, 0 \rightarrow 6, 0$) at 109,031.25 ± 0.16 MHz ^d in USB
0.06	0.05	0.15	...	99663	...	HCC ¹³ CN ($J = 11 \rightarrow 10$) at 99,661.471 ± 0.006 MHz ^d
0.08	0.05	0.17	...	99653	...	HC ¹³ CCN ($J = 11 \rightarrow 10$) at 99,651.864 ± 0.012 MHz ^d
...	0.02	0.05	...	99611	109092	
0.08	0.02	0.04	...	99592	109110	Possibly O ¹³ CS ($J = 9 \rightarrow 8$) at 109,110.848 ± 0.003 MHz ^d in USB
0.08	0.03	99577	109126	Probably LSB
0.30	...	0.05	109139	CH ₃ OH ($J_K = 14_5 \rightarrow 15_4, E_1, v_t = 0$) at 109,138.71 MHz ^c
0.29	...	0.06	109152	CH ₃ OH ($J_K = 16_{-2} \rightarrow 16_1, E_1, v_t = 0$) at 109,153.19 MHz ^{c,e}
...	0.03	99542	109161	Possibly HC ₅ N ($J = 41 \rightarrow 40$) at 109,161.46 ± 0.34 MHz in USB
3.3	1.2	3.8	1.5	...	109174	HC ₃ N ($J = 12 \rightarrow 11$) at 109,173.64 MHz
...	...	0.04	...	99496	109207	See § III
...	...	0.06	...	99482	109221	

^a LSB = lower sideband, USB = upper sideband. There is a differential Doppler shift between the USB and LSB which introduces an error of not more than ~3 MHz in the rest frequencies of the LSB lines. The correction is dependent on date and source and has not been applied here.

^b Line appears when LSB offset to higher frequencies than indicated in Fig. 1.

^c Lees and Baker 1968.

^d Poynter and Pickett 1981.

^e Sastry, Lees, and DeLucia 1984.

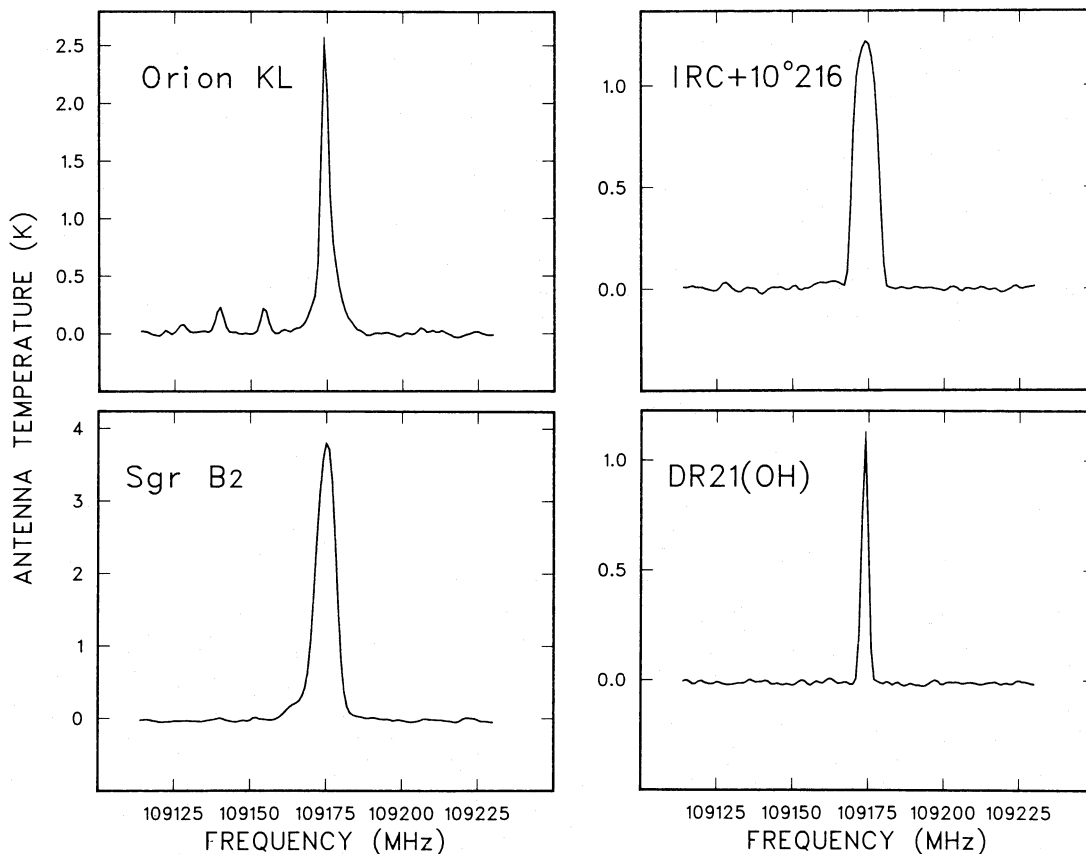


FIG. 2.—Profiles of the HC₃N ($J = 12 \rightarrow 11$) line. Details as for Fig. 1, except that the ordinate has been compressed to show the full profile, and only a limited frequency range has been plotted.

Upper limits to the column density of PO are then given for either of the strongest $F = 3 \rightarrow 2$ components of the $J = 5/2 \rightarrow 3/2$ transition by

$$N(\text{PO}) = 4.70 \times 10^8 T_{\text{ex}} e^{9.20/T_{\text{ex}}} \left[\frac{2.13 D}{\mu(D)} \right]^2 \times [T_{\text{ex}}^*(\text{mK}) \Delta V (\text{km s}^{-1})] \text{ cm}^{-2},$$

where each $F = 3 \rightarrow 2$ line is assumed to contribute 29.2% (in LTE) of the total intensity of the six lines comprising the $J = 5/2 \rightarrow 3/2$ transition. We adopt typical rotational excitation temperatures as follows: Orion KL (ridge), 75 K; IRC +10°216, 15 K; Sgr B2(OH), 20 K; and DR 21(OH), 25 K. Upper limits to $N(\text{PO})$ in these sources are then computed from the observed upper limits to the line strengths T_{ex}^* and from the estimated line widths tabulated in Table 1. These values, which fall in the approximate range $10^{12.3} - 10^{13.4} \text{ cm}^{-2}$, are also given in Table 1. We note that this simple approach may underestimate the (unobserved) PO column densities in the less dense clouds by up to a factor of 3. However, this would not affect our conclusions below, particularly those for DR 21(OH).

We note that the relative abundance of PO compared to NO in Sgr B2(OH) is less than 10^{-3} , where we have taken $N(\text{NO}) \approx 2 \times 10^{16} \text{ cm}^{-2}$ from the work of Liszt and Turner (1978). This is somewhat less than the $\sim 1/400$ cosmic abundance ratio of $[\text{P}]/[\text{N}]$. However, our upper limit is not yet significant since the P^+ abundance in diffuse clouds is already known to be depleted by up to a factor of 3 below the solar

value (Jura and York 1978). Furthermore, there are likely to be systematic errors of ~ 2 in estimation of molecular column densities.

A more meaningful comparison can perhaps be made with the prediction of the simple kinetic model of phosphorus ion chemistry constructed by Thorne *et al.* (1984). This model finds that at chemical steady state for a dense molecular cloud with hydrogen number density $n(\text{H}_2) = 10^5 \text{ cm}^{-3}$ the fractional abundance of PO is $f_{\text{PO}} = 1.4 \times 10^{-10}$, which is greater than any other P-bearing molecular species. Our upper limits for three sources, Orion KL, IRC +10°216, and Sgr B2(OH), are consistent with this expectation. (Of course, in the instance of the extreme carbon star IRC +10°216 the O-bearing molecule PO is not expected to be formed in any case.) However, the excellent upper limit obtained for DR 21(OH) can be used to estimate a PO fractional abundance in the range $3.6 \times 10^{-13} - 1.2 \times 10^{-11}$, depending on the tracer molecule used to determine $n(\text{H}_2)$ (see Wooten, Shell, and Evans 1980; Evans 1980) and hence $N(\text{H}_2)$. This range corresponds to (0.003–0.09) of f_{PO} calculated by Thorne *et al.* (1984), which suggests that phosphorus may be much more severely depleted in dense molecular clouds than it is in diffuse clouds.

We are indebted to S. Saito and F. Grein for providing us with results in advance of publication. We thank J. Petersen for help with the methanol line identifications, J. H. Black for his comments on the manuscript, and Rick Foster for valuable assistance with the operation of the equipment at Kitt Peak.

REFERENCES

- Avery, L. W. 1982, private communication.
 Boyd, D. B., and Lipscomb, W. N. 1967, *J. Chem. Phys.*, **46**, 910.
 Evans, N. J., II. 1980, in *IAU Symposium 87, Interstellar Molecules*, ed. B. H. Andrew (Dordrecht: Reidel), pp. 1–19.
 Goldsmith, P. F., Snell, R. L., Deguchi, S., Krotkov, R., and Linke, R. A. 1982, *Ap. J.*, **260**, 147.
 Grein, F. 1984, private communication.
 Hollis, J. M., Snyder, L. E., Blake, D. H., Lovas, F. J., Suenram, R. D., and Ulich, B. L. 1981, *Ap. J.*, **251**, 541.
 Hollis, J. M., Snyder, L. E., Lovas, F. J., and Ulich, B. L. 1980, *Ap. J.*, **241**, 158.
 Jura, M., and York, D. B. 1978, *Ap. J.*, **219**, 861.
 Kawaguchi, K., Saito, S., and Hirota, E. 1983, *J. Chem. Phys.*, **79**, 629.
 Lees, R. M., and Baker, J. G. 1968, *J. Chem. Phys.*, **48**, 5299.
 Lees, R. M., Lovas, F. J., Kirchoff, W. H., and Johnson, D. R. 1973, *J. Phys. Chem. Ref. Data*, **2**, 205.
 Liszt, H. E., and Turner, B. E. 1978, *Ap. J. (Letters)*, **224**, L73.
 Lohr, L. L. 1984, *J. Phys. Chem.*, **88**, 5569.
 Poynter, R. L., and Pickett, H. M. 1981, JPL Publ. No. 80–23, Rev. 1.
 Ridgway, S. T., Wallace, L., and Smith, G. R. 1976, *Ap. J.*, **207**, 1002.
 Sastry, K. V. L. N., Lees, R. M., and DeLucia, F. C. 1984, *J. Molec. Spectrosc.*, **103**, 486.
 Sutton, E. C., Blake, G. A., Masson, C. R., and Phillips, T. G. 1984, *Ap. J. (Letters)*, **283**, L41.
 Thaddeus, P. 1982, private communication.
 Thorne, L. R., Anicich, V. G., and Huntress, W. T. 1983, *Chem. Phys. Letters*, **98**, 162.
 Thorne, L. R., Anicich, V. G., Prasad, S.S., and Huntress, W. T. 1984, *Ap. J.*, **280**, 139.
 Turner, B. E. 1983, *Ap. Letters*, **23**, 217.
 Verma, R. D., and Singhal, S. R. 1975, *Canadian J. Phys.*, **53**, 411.
 Wooten, A., Snell, R., and Evans, N. J. 1980, *Ap. J.*, **240**, 532.

P. F. BERNATH: Department of Chemistry, University of Arizona, Tucson, AZ 85721

P. A. FELDMAN and H. E. MATTHEWS: Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa K1A 0R6, Canada