Absorption Spectra of the PO₂ and PO₃ Radicals in Solid Argon

Robert Withnall, Matthew McCluskey, and Lester Andrews*

Chemistry Department, University of Virginia, Charlottesville, Virginia 22901 (Received: April 4, 1988; In Final Form: July 6, 1988)

Codeposition of PH₃ with ¹⁶O and ¹⁸O atoms from a microwave discharge and YAG laser ablation products from solid P_4O_{10} with excess argon at 12 K produced three common structured electronic band systems, which are due to binary phosphorus-oxygen species. The 240-290-nm progression is due to PO based on isotopic shifts and agreement with earlier workers. The sharp 300-nm band system is assigned to PO₂ owing to agreement with gas-phase absorption and excitation bands, vibronic intervals, and isotopic shifts. A new 695-nm progression is assigned to the PO₃ radical on the basis of isotopic shifts and on general agreement with NO₃ spectra and a photoelectron band difference for SO₃.

Introduction

Luminescence from phosphorus-oxygen reactions has been of interest to scientists for three centuries.¹ Several species have been postulated to explain the strong green emission, and the PO₂ radical is preferred by several authors.²⁻⁴ The PO₂ radical has been examined in the gas phase by absorption, microwave, and laser-induced fluorescence spectroscopies, 5-7 and the antisymmetric P–O stretching fundamental for PO_2 has been observed in solid argon following O atom matrix reactions with PH₃ and P₄.^{8,9} The PO_3 radical and molecular P_2O_5 were also identified in the matrix infrared work;⁸ however, no electronic spectroscopy has been performed on PO₃, although ab initio calculations have been done on the low-lying electronic states.⁹ It was desired to obtain supplementary electronic spectra for these species and to seek alternate but complementary methods of production to support identification of these transient radicals in matrix isolation experiments.

Experimental Section

The cryogenic refrigeration system, vacuum vessel, and technique for microwave discharge of argon/oxygen streams have been described previously.^{8,10,11} PH_3 (Matheson) was used directly, and PD_3 was prepared from D_2O and calcium phosphide. For a different series of experiments, anhydrous P₄O₁₀ was pressed into a disk (1-cm diameter \times 5 mm thick) and mounted on an adjustable rod 1 cm in front and to the side of the cold window. Argon was deposited on the cold window at 2-3 mmol/h while P_4O_{10} and its decomposition products were ablated by focused 1064-nm radiation from a DCR-11 YAG laser (Quanta Ray) operating at 5 Hz in Q-switched mode at 20-40% of maximum power.

In ultraviolet-visible absorption experiments $Ar/PH_3 = 200:1$ samples were codeposited onto a 12 K sapphire plate with O atoms produced by the extended discharge of an $Ar/O_2 = 50:1$ mixture for periods of 4-5 h. Spectra were recorded on a Cary 17 recording spectrophotometer after deposition, photolysis, and annealing to characterize the product band systems. YAG laser evaporation of P_4O_{10} into an argon matrix was done for 15-min periods, and spectra were recorded on the Cary 17. Several expanded scale scans (1.5 nm/in.) were recorded (0.1 nm/s) in

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TABLE I: Red Absorption Bands Attributed to the PO₃ Radical Produced by Reaction of Oxygen Atoms with Phosphine during Condensation with Excess Argon at 12 K

¹⁶ O			¹⁸ O			
$\lambda,^a$ nm	ν, cm ⁻¹	$\Delta \nu$, cm ⁻¹	$\lambda,^a$ nm	ν , cm ⁻¹	$\Delta \nu$, cm ⁻¹	
695.5	14 378		695.5	14378		
671.3	14903	525	671.8	14885	507	
654.0	15 291	913	655.9	15246	868	
632.5	15810	526	634.7	15755	509	
617.3	16 200	909	620.7	16111	865	
584.8	17100	900	589.2	15892	861	

^a Wavelength accuracy of band center near peak is ± 0.2 nm (± 5 cm⁻¹).

TABLE II: Visible Absorption Band Zero-Phonon Line Positions for PH₂ Radical in Solid Argon at 12 K

assignt	$\lambda,^a$ nm	ν, cm ⁻¹	$\Delta \nu$, cm ⁻¹	
0-0	549.0	18 21 5	,	
1-0	521.8	19164	949	
2-0	497.3	20109	945	
3-0	475.1 ^b	21 048	939	
4-0	455.0	21978	930	
5-0	436.5	22910	932	
6-0	419.5	23838	928	
7-0	405.0	24 691	910	

^a Wavelength accuracy of sharp peak is ± 0.1 nm. ^b Resolved fine structure at 475.1, 473.6, and 472.1 nm with $66 \pm 4 \text{ cm}^{-1}$ spacing; similar fine structure observed on adjacent bands.

each experiment to make accurate measurements on the new absorption bands.

Results

Absorption spectra of new species produced by the reaction of PH₃ with O atoms from a microwave discharge and by YAG laser ablation from P_4O_{10} will be presented.

Microwave Discharge. The reaction of O atoms with PH_3 in the presence of vacuum-ultraviolet radiation from the extended microwave discharge produced several strong electronic absorption systems. A new red absorption band system beginning at 695 nm is illustrated in Figure 1a, and the band positions are given in Table I. The spectrum was recorded on expanded wavelengths scale in four different experiments; the strong vibronic bands (160 cm⁻¹ fwhm) were measured to within $\pm 5 \text{ cm}^{-1}$. Unfiltered mercury (full) arc photolysis had no effect on the band intensities. Two experiments were done with ${}^{18}O_2$; the bands shifted and their expanded scale positions are given in Table I, and a spectrum is shown in Figure 1b. Two similar experiments employed ^{16,18}O₂, the band positions were intermediate between the pure ${}^{16}O_2$ and ¹⁸O₂ positions, and no isotopic structure could be resolved.

The strong, structured 549-405-nm band system illustrated in Figure 2 showed no dependence on isotopic oxygen. This band is in general agreement with a previous assignment¹² to the PH_2

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Figure 1. Absorption spectra in the 550–750-nm region for $Ar/PH_3 =$ 200:1 samples codeposited at 12 K with Ar/oxygen samples passed through an extended discharge: (a) ${}^{16}O_2$ and (b) ${}^{18}O_2$.



Figure 2. Absorption spectra in the 375-575-nm region for sample prepared by discharge oxygen matrix reaction with PH₃.

radical in solid argon; measured positions are listed in Table II. It is of interest to note that the band origin is red-shifted 62 cm⁻¹ and the ν_2' fundamental is red-shifted 2 cm⁻¹ by the matrix.¹³ Strong bands at 342.0 and 321.5 nm with 344.0- and 323.5-nm shoulders are in agreement with PH bands in solid argon.¹²

Figure 3 illustrates a band at 310.8 nm due to OH radical produced in the $PH_3 + O$ reaction based on proximity to the gas-phase band origin¹⁴ at 32682 cm⁻¹ and agreement with the matrix excitation spectrum of OH in solid argon;¹⁵ the 285.0-nm feature is likewise due to OH. In addition, sharp, new bands were observed at 300.66, 295.80, and 292.38 nm (fwhm = 50 cm^{-1}); expanded scale spectra in several experiments provide measurement of the sharp bands to ± 0.02 nm (± 2 cm⁻¹). A progression of vibronic bands (fwhm = 300 cm^{-1}) was found at 242-291 nm, in agreement with bands previously assigned to PO radical.¹² The first six bands in the PO progression reported earlier average 40 cm⁻¹ lower than the present bands perhaps due to the presence of N_2 from the N_2O source of oxygen in the studies of Larzilliere and Jacox.¹² Table III lists the band positions with ¹⁶O₂ and ¹⁸O₂ in the discharge. Again, ^{16,18}O₂ gave intermediate positions and no resolved structure. Full arc photolysis had no effect on the



Figure 3. Absorption spectra in the 240-320-nm region for (a) Ar/PH₃ = 200:1 samples codeposited with ^{16}O atoms and (b) with ^{18}O atoms and for (c) P₄O₁₀ ablated by YAG laser and codeposited with excess argon at 12 K.

TABLE III: Ultraviolet Absorptions for the OH, PO2, and PO Radicals Produced by Reaction of Oxygen Atoms with PH₃ during Condensation with Excess Argon at 12 K

¹⁶ O			¹⁸ O				
λ, nm	$\nu, {\rm cm}^{-1}$	$\Delta \nu$, cm ⁻¹	λ, nm	ν, cm ⁻¹	$\Delta \nu$, cm ⁻¹		
ОН							
310.8ª	32175		310.9	32166			
285.0ª	35 088	2913	285.2	35 063	2897		
PO							
300.66	33 260	_		33 247			
295.80 ^b	33 807	547	296.10	33 772	525		
292.38 ^b	34 202	942	292.80 ^b	34153	906		
287.85°	34 740	538					
284.77°	35120	918					
PO							
291.0 ^d	34 364		291.0	34 364			
282.6	35 386	1022	282.8	35 361	997		
274.8	36 390	1004	275.1	36 227	976		
267.5	37 383	993	268.1	37 300	963		
260.7	38 359	975	261.5	38 241	941		
254.3	39 324	966	255.3	39170	929		
248.3	40 274	950	249.5	40 080	910		
242.7	41 203	929	244.1	40 967	887		

^a Wavelength accuracy of OH vibronic bands is ± 0.1 nm; substructure 310.2, 310.8, and 311.5 nm observed on origin and 285.0 and 285.7 nm on first component. The major OD counterparts were 310.4 and 290.5 nm. ^b Wavelength accuracy of sharp bands is ± 0.02 nm (± 2 cm⁻¹). ^cProduced by YAG evaporation of P_4O_{10} . ^dWavelength accuracy ± 0.1 nm.

visible band progression, the PH absorptions were halved, the OH band was not changed, the sharp 300.65- and 292.38-nm bands increased by 50%, as did the PO band system, and the sample became slightly more transparent in the ultraviolet region. This may arise from photodissociation of ozone produced and trapped in these extended discharge experiments,8 which absorbs strongly in the 250-nm region.

Warming the matrix samples to 20 ± 1 K resulted in a 20% increase in the 695- and 300-nm band systems, no change in the 549-405-nm absorption, major reductions in PH, OH, and PO bands, and appearance of a blue chemiluminescence. Further warming to 30-32 K in two different experiments halved the 695-nm band system intensity, almost destroyed PH₂ and PH bands, increased light scattering below 330 nm such that bands could not be observed, and produced a very strong blue chemiluminescence. Although identification of the luminescent species cannot be made here with certainty, Hamilton and Murrells² propose HOPO for a similar blue emission, and this species was observed in parallel infrared studies.8

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Finally, one experiment was done with PD_3 and ${}^{16}O_2$. The structured absorption band systems in Figures 1 and 3 were unchanged, and considerable additional structure was observed on the 549-405-nm progression for deuteriated and partially deuteriated species supporting its assignment of PH₂.

Laser Evaporation. Five experiments were performed trapping the species ablated from solid P_4O_{10} by a pulsed YAG laser beam. Spectra of the ablated species were simpler: PH₂ and PH were not observed, and very little OH was detected, as can be seen in Figure 3c. The structured PO band system was weaker, relative to the sharp 300.66-nm band, with laser ablation; the band maxima were approximately 60 cm⁻¹ blue-shifted from their positions in the discharge experiments. The first three sharp bands in the 300.66-nm system were measured by precisely the same (± 0.02) nm) position in laser ablation and O atom reaction experiments. Owing to lack of OH interference, additional sharp, weak bands were observed at 287.85 and 284.77 nm. In the red region, the same spectrum was observed as is shown in Figure 1a with two differences: the band system was weaker (60%) relative to the sharp 300.66-nm band system, and the major peaks were 3 nm to the blue of the Table I values with shoulders at the Table I values

A similar ablation experiment was done with solid red phosphorus. An $Ar/O_2 = 10:1$ stream was passed over the surface during laser ablation, and excess argon was deposited separately. The absorption spectrum was 20% as strong as observed with P_4O_{10} ; however, the same major bands were observed in the red and ultraviolet regions with the same relative intensities.

Discussion

The new absorption band systems will be assigned to phosphorus-oxygen species. Observation of the same band systems from the $O + PH_3$ reaction and laser ablation of P_4O_{10} verify the binary nature of the product species.

 PO_3 . The PO₃ radical has been observed in infrared studies of samples prepared by the O atom-PH₃ reaction.⁸ A strong 479.5-cm⁻¹ band was observed for the out-of-plane bending mode. This band was split into a 1:3:3:1 quartet with mixed oxygen isotopes, which provided evidence for three equivalent oxygen atoms in the ground state of PO₃. The ν_3 fundamental of PO₃ was also observed at 1273 cm⁻¹.

The structured red absorption spectrum (Figure 1, Table I) is assigned to the PO_3 radical for the following reasons: (1) the 695-nm origin falls just below the 662-nm origin for the ${}^{2}E' \leftarrow$ ${}^{2}A_{2}'$ transition of the isoelectronic D_{3h} nitrate radical, 16,17 (2) the vibronic intervals are appropriate for the v_1' (a_1' , symmetric stretching) and ν_4' (e', antisymmetric bending) modes by analogy with the NO₃ excitation spectrum where $v_1'(a_1')$ dominated but $\nu_4(e')$ was observed,¹⁶ and (3) the photoelectron spectrum of SO₃¹⁸ predicts an allowed transition for the isoelectronic SO_3^+ species at 2.04 eV (608 nm), which is in the region of the PO_3 origin at 695 nm. The SO₃⁺ upper state exhibits a resolved progression in ν_1' (890 ± 50 cm⁻¹), which is also in agreement with ν_1' of PO₃ $(913 \pm 10 \text{ cm}^{-1})$ in solid argon. The ²E' state of PO₃ observed here is substantially higher in energy than calculated⁹ for the ${}^{2}E''$ state, which is the same relationship proposed for NO_3 .

The isotopic data support the assignments of the major vibronic interval to the ν_1' mode. The ν_1' vibration for P¹⁶O₃ at 913 ± 10 cm⁻¹ is expected to shift to 861 cm⁻¹ with ¹⁸O₃ substitution, which is in agreement with the ν_1' band observed for P¹⁸O₃ at 868 ± 10 cm⁻¹. Unfortunately, the isotopic shift is not accurate enough to rule out a phosphorus contribution to the reduced mass and confirm the D_{3h} symmetry of the upper state. The 525-cm⁻¹ interval shows the appropriate ¹⁸O shift (18 cm⁻¹) for the ν_4 deformation mode. Although the ν_1' mode (913 cm⁻¹) is probably lower than the ground-state value (unknown), the ν_4 mode (525 cm⁻¹) is above the ground-state value (435 cm⁻¹).⁸ A similar relationship has been found for these modes of ground- and excited-state NO₃.19

 PO_2 . The PO₂ radical has been identified in parallel infrared studies of $O + PH_3$ samples⁸ from a sharp band at 1319.1 cm⁻¹. This band shifted to 1280.2 cm^{-1} with ${}^{18}\text{O}_2$ and exhibited a 1:2:1triplet with mixed isotopes, which are in accord with the C_{2V} species characterized by the microwave spectrum.⁶ A similar sharp 1319-cm⁻¹ band has been observed in preliminary matrix infrared studies of laser ablation products from solid P₄O₁₀ and from red phosphorus with an overflow of oxygen.²⁰ In fact, the 1319-cm⁻¹ infrared ν_3 band for PO₂ was severalfold stronger than the 1273-cm⁻¹ ν_3 band for PO₃ in the P₄O₁₀ ablation experiments, demonstrating that PO_2 is favored over PO_3 by the ablation method. Reactive laser vaporization from red phosphorus has been used to prepare PO₂ for matrix ESR studies.²¹

The sharp 300.66-nm band system was not observed by Larzilliere and Jacox¹² after photolysis of N_2O and PH_3 , which gave strong PO absorptions. In addition, the 300.66-nm and PO band systems showed different relative intensities in the present O + PH_3 and P_4O_{10} or $P + O_2$ ablation experiments (Figure 3, a vs c). The sharp band system is clearly not due to PO. Furthermore, the sharp UV band system was stronger relative to the red band system in P_4O_{10} laser ablation studies compared to $O + PH_3$ reaction experiments, which shows that the sharp system is not due to PO₃ and suggests that the carrier of the sharp band system has less oxygen than PO₃ and is in fact PO₂. Finally, the PO₂⁻¹ anion can be ruled out owing to absence of O_3^- in the blue visible¹¹ and infrared regions in similar extended discharge⁸ and laser ablation²⁰ experiments where O_3 was observed.

The very sharp ultraviolet matrix absorptions between 300.66 and 284.77 nm (Figure 3, Table III) as assigned to the $B^2B_2 \leftarrow$ X^2A_1 absorption for the PO₂ radical for the following reasons: (1) these bands are in the region of absorption and excitation bands^{5,7} observed for gaseous PO_2 , (2) the major matrix vibronic interval $(930 \pm 12 \text{ cm}^{-1})$ is near $910 \pm 13 \text{ cm}^{-1}$ spacings in the gas-phase absorption and excitation spectra, and (3) the matrix interval has essentially the same ¹⁸O shift ($36 \pm 8 \text{ cm}^{-1}$) as the gaseous species $(40 \pm 3 \text{ cm}^{-1})$.⁵ Both matrix and gas-phase ¹⁸O shifts are less than required for the v_1' mode of a linear molecule (54 cm⁻¹) or predicted (45 cm⁻¹ by approximate vibrational analysis) for the v_1' mode of 135° bent PO₂, which rule out a linear or near-linear upper state for PO_2 in this absorption. If, as predicted by Lohr,⁴ the PO₂ chemiluminescence arises from a near-linear or linear upper state, it is clearly not the same upper state observed here and in the gas-phase absorption studies.^{5,7} The ${}^{2}B_{1}$ Lohr state may be longer lived and slightly lower in energy than the bent ${}^{2}B_{2}$ upper state observed in absorption. This lower ${}^{2}B_{1}$ state could be populated by nonradiative processes from the ${}^{2}B_{2}$ state and thus contribute to the green chemiluminescence.⁷ The ${}^{2}B_{1}$ state is not observed in absorption presumably owing to low absorption cross section from the bent ground-state $(^{2}A_{1})$ PO₂ species to a linear or near-linear excited $({}^{2}B_{1})$ state.

Additional comparisons can be made between the gaseous and matrix electronic spectra of PO2. First, it must be realized that matrix-isolated PO₂ at 12 K is completely vibrationally relaxed, but the gaseous species produced by O atom reaction with PX₃ species under discharge conditions is known to be highly excited. Under these circumstances it is reasonable to expect slightly different Franck-Condon absorption profiles for the hot gaseous and cold matrix-isolated molecules. Second, the relatively long fluorescence lifetime for the PO₂ emission⁷ demonstrates extensive perturbations in the upper PO_2 state. The electronic states of PO_2 may be compared to those of NO2, which has a longer than expected fluorescence lifetime, highly perturbed energy levels, and correspondingly complex spectra, which may involve interelectronic level mixing and mixing of vibrational levels.²² These severe

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Figure 4. Plot of vibrational spacing against vibrational quantum number for (a) $P^{16}O$ in gas phase (ref 24), (b) $P^{16}O$ in solid argon, and (c) $P^{18}O$ in solid argon.

perturbations are not removed in matrix-isolated NO₂, where the visible bands experience blue shifts of 55–70 cm⁻¹.²³ Accordingly, vibrational assignment of the matrix bands is not a straightforward matter.

If the strong first band observed at 33 260 cm⁻¹ in solid argon were assigned to the electronic origin, the resulting blue matrix shift of approximately 2900 cm⁻¹ from the gas-phase origin would be excessive and cast doubt on this vibronic assignment. The next possibility is that severe perturbation has reduced intensity in bands below 33 260 cm⁻¹ in energy, and this strong first observed band is considerably above the electronic origin. As mentioned above, the major vibronic intervals, 942 and 918 cm⁻¹, are in agreement with gas-phase spacings, and the three bands thus separated could be assigned to $v_100 \leftarrow 000$ absorptions with $v_1 = 3, 4, \text{ and } 5,$ respectively; this vibronic assignment would result in a blue matrix shift of 108 cm⁻¹ (based on Verma and McCarthy assignments).⁵ Such an assignment requires $v_1 10 \leftarrow 000$ assignments for the weak bands at 33 807 and 34 740 cm⁻¹ and suggests a ν_2' interval near 547 cm⁻¹, which is much larger than the 396-cm⁻¹ gas-phase value. An alternate assignment of the major sharp progression is to v_1v_20 \leftarrow 000 absorptions with $v_2 = 2$ and $v_1 = 2$, 3, and 4; this assignment results in a blue matrix shift of 238 cm⁻¹ for the strong first band. The remaining two weak bands at 33807 and 34740 cm⁻¹ are then assigned as $310 \leftarrow 000$ and $410 \leftarrow 000$ absorptions, respectively. A very attractive feature about the latter assignment is that two gas-phase vibrational spacings, 936 and 396 \pm 1 cm⁻¹, are nicely reproduced by the matrix spectrum, namely, 942 and $942 - 547 = 395 \pm 4 \text{ cm}^{-1}$, and the oxygen-18 counterpart gasphase spacings, 896 and $383 \pm 2 \text{ cm}^{-1}$, are also observed in the matrix spectrum as 906 and 906 - 525 = $381 \pm 4 \text{ cm}^{-1}$. In the latter scheme, if v_2 were 1 and the strong first band 210 \leftarrow 000, a blue matrix shift of 625 cm⁻¹ would result, which is also an acceptable possibility, and assignments of the other bands follow. In summary, it is possible that severe perturbations known to exist for PO₂ and complete vibrational relaxation in the 12 K matrix diminish intensity of low vibronic levels and make $2v_20 \leftarrow 000$ $(v_2 = 1 \text{ or } 2)$ the first and strongest observed vibronic absorption in the matrix; this assignment nicely reproduces the two symmetric fundamentals of the gaseous species in the matrix band system.



PO. Since PO has been studied extensively in the gas phase, the PO electronic band system in solid argon is of value primarily to establish matrix shifts for excited-state phosphorus-oxygen species. The major PO absorption in Figure 1a is in agreement with that of Larzilliere and Jacox¹² except for the weak 295.4-nm band tentatively assigned to the B' \leftarrow X absorption, which was not detected here. The PO band system was also observed from ablation of P₄O₁₀, and the infrared fundamental of PO was detected at 1218 cm⁻¹ in similar infrared experiments²⁰ only 2 cm⁻¹ red-shifted from the gas phase.²⁴ In addition, the p¹⁸O absorption data observed in the present experiments provide support for the PO assignment.

A plot of vibronic separation against quantum number is shown in Figure 4 for gas-phase²⁴ P¹⁶O and matrix-isolated P¹⁶O and P¹⁸O using the quantum number assignment suggested by Larzilliere and Jacox.¹² The argon matrix has perturbed the PO excited state as the slope and intercept of the gas and matrix P¹⁶O data are clearly different. For this vibrational numbering, $T_e =$ $31250 \pm 20 \text{ cm}^{-1}$, $\omega_e = 1076 \pm 10 \text{ cm}^{-1}$, and $\omega_e X_e = 8.6 \pm 1 \text{ cm}^{-1}$ in solid argon compared to $T_e = 30731 \text{ cm}^{-1}$, $\omega_e = 1164.9 \text{ cm}^{-1}$, and $\omega_e X_e = 13.7 \text{ cm}^{-1}$ in the gas phase.²⁴ Increasing the vibrational numbering by 1 predicts $T_e = 30110 \pm 20 \text{ cm}^{-1}$, $\omega_e = 1093 \pm$ 10 cm⁻¹, and $\omega_e X_e = 8.6 \pm 1$ cm⁻¹ in solid argon. It is readily seen that further increases in vibrational numbering bring ω_e closer to the gas-phase value but red shift the origin more. Unfortunately, the matrix data are not accurate enough to determine the origin from the oxygen isotopic shifts. In the case of the PO absorption spectrum, the origin could be red- or blue-shifted by the matrix on the order of 500 cm^{-1} (compare OH which is red-shifted 460 cm⁻¹) or perhaps even more, and ω_e could be red-shifted 70-100 cm⁻¹. We suggest that a higher vibrational numbering of the matrix system is more likely correct. Unfortunately, this so-called $B^2\Sigma^+$ state of PO is not a good comparison for other phosphorus-oxygen species owing to partial Rydberg character,^{12,25} which can sustain an unusually large matrix interaction, as is also suggested by the large vibronic bandwidths.

Conclusions

New electronic band systems observed in solid argon at 695 and 300 nm produced by the matrix reaction of O atoms with PH₃, by YAG laser dissociative evaporation of P_4O_{10} , and by reactive laser ablation of red phosphorus in a stream of oxygen are characterized as simple new transient binary phosphorus-oxygen species. The red band is identified as PO₃ on the basis of comparisons with isoelectronic NO₃ and SO_3^+ and proper oxygen-18 isotopic shifts for the 913 \pm 10 and 525 \pm 10 cm⁻¹ vibronic intervals. The sharp ultraviolet band system is assigned to PO₂ on the basis of observation of PO_2 in similar infrared²⁰ and ESR^{21} experiments and agreement with gaseous absorption and excitation band positions, vibrational intervals, and isotopic shifts.^{5,7} The PO_2 and PO_3 radicals are reactive intermediate species, but they can be trapped in solid argon for ultraviolet and visible spectroscopic study. Their further reaction to give P_2O_5 , characterized in parallel infrared studies,8 could not be monitored owing to the short wavelength limit of the present experiments.

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