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TECHNICAL REPORT BRL-TR-2627

MEASUREMENT OF FRANCK-CONDON FACTORS
FOR THE $V'=0$ PROGRESSION IN
THE B-X SYSTEM OF PO

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December 1984

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) gkl Laser Fluorescence of PO produced in a microwave discharge through organophosphonate esters has been studied. The fluorescence was pumped in the B doublet sigma plus - X doublet pi 3250 Angstrom system. Relative intensities of fluorescence for the v' prime equals zero progression were measured. These intensities were used to derive Franck-Condon factors for the v' prime equals zero progression.		

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I. INTRODUCTION

Electronic spectra of the PO radical have been known and studied for over 50 years.¹ Studies of the transition between the two lowest-lying electronic states, the $B^2\Sigma^+ + X^2\Pi$ 3250Å system, have concerned rotational²⁻⁵ and vibrational^{3,4} analyses and B state perturbations.^{3,5} More recent investigations have reported the laser excited fluorescence (LEF)⁶ and multiphoton ionization spectra.^{7,8} Our interest in this radical results from its involvement in several possible fragmentation detection schemes for nerve agents since their chemical structure is centered around a PO double bond. In the present work, LEF of the B-X system was further studied. A more detailed account of the procedures and results is given than has previously appeared.⁹ The PO was produced in a microwave discharge through two chemicals

¹References to earliest work may be found in Spectroscopic Data, Heteronuclear Diatomic Molecules, Vol. I, ed. S.N. Suchard, IFI/Plenum Data Company, NY, 1975. A compilation of papers from 1955 to 1979 is available in K.P. Huber and G. Herzberg, Molecular Spectra and Molecular Structure, IV. Constants of Diatomic Molecules, Van Nostrand Reinhold, Co., NY, 1979.

²N.L. Singh, "Rotational Analysis of the β Bands of Phosphorus Monoxide," Can. J. Phys., Vol. 37, p. 136, 1959.

^{3a}R.D. Verma and S.R. Singhal, "New Results on the $B^2\Sigma^+$, $b^4\Sigma^-$ and $X^2\Pi$ States of PO," Can. J. Phys., Vol. 53, p.411, 1975.

^bS.R. Singhal, "High Resolution Study of the Spectral Region 3000Å - 3900Å of the PO Molecule," Ph. D. Thesis, University of New Brunswick, Fredericton, New Brunswick, Canada, 1973.

⁴C. Couet, N. Tuan Anh, B. Coquart and H. Guenebaut, "Contribution A L'Etude Des Systemes Electroniques du Radical PO. 3^e Partie: Le Systeme β (transition $B^2\Sigma^+ - X^2\Pi$), J. Chim. Phys., Vol. 65, p. 217, 1968.

^{5a}S.B. Rai, D.K. Rai, and K.N. Upadhyya, "Analysis of Some Bands of the β System of PO," J. Phys. B: Atom. Molec. Phys., Vol. 5, p. 1038, 1972.

^bS.B. Rai, B.R. Yadav, and D.K. Rai, "Perturbations in the $B^2\Sigma^+$ State of PO," J. Chim. Phys., Vol. 73, p. 905, 1976.

⁶M.A.A. Clyne and M.C. Heaven, "Laser-Induced Fluorescence of the PO Radical," Chem. Phys., Vol. 58, p. 145, 1981.

⁷K.C. Smyth and W.G. Mallard, "Two-Photon Ionization Processes of PO in a C_2H_2 /Air Flame," J. Chem. Phys., Vol. 77, p. 1779, 1982.

⁸J.S. Chou, D. Sumida, and C. Wittig, "2-Frequency 2-Photon Ionization of Nascent PO ($X^2\Pi$) from the Collision Free IR Photolysis of Dimethyl-Methylphosphonate," Chem. Phys. Lett., Vol. 100, p. 397, 1983.

⁹W.R. Anderson, S.W. Bunte, and A.J. Kotlar, "Laser-Excited Fluorescence of PO from Organophosphonate Esters," Conference on Lasers and Electro-Optics 83, Paper THD4, Baltimore, MD, May 1983.

structurally similar to nerve agents, either dimethyl-methylphosphonate [DMMP, $(\text{CH}_3\text{O})_2(\text{P}=\text{O})\text{CH}_3$] or its ethyl substituted analog, diethyl-ethylphosphonate (DEEP) which yielded comparable results. Excitation scans of the (0,0) band of the B-X system were obtained, similar to previous results.⁶ In addition, relative fluorescence intensity measurements were made for the vibrational progression emitted from the $v'=0$ excited level. Franck-Condon factors (FCFs) derived from these measurements are compared with values calculated from the RKR potentials. Though the nerve agents are violently poisonous, the simulants are only mildly toxic.* In fact, it is suggested that the simulants are safer and much more easily handled than the poisonous PO precursors used in previous studies.²⁻⁶

II. EXPERIMENTAL

PO was produced by flowing about 7×10^{-2} torr of DMMP or DEEP in about 1 torr of argon diluent through a 2450 MHz microwave discharge. The PO was excited downstream from the discharge in a stainless steel cell using radiation in the 3250Å region from a flashlamp pumped, tunable dye laser (Chromatix CMX-4). The laser linewidth was 0.3 cm^{-1} FWHM. Typical pulse energies were $\sim 0.2 \text{ mJ}$ with pulse duration $\sim 1 \text{ usec}$. Fluorescence was detected using either a monochromator with photomultiplier tube or a photomultiplier tube with a visible cutoff filter. A small portion of the laser radiation was sampled by a reference photodiode prior to its entry into the fluorescence cell. Signals from the photomultiplier and power reference photodiode were processed, and their ratio was taken in a boxcar averager. Hard copy was obtained using a chart recorder or computer.

All of the figures and quantitative measurements presented herein involved DMMP as the precursor. However, as previously stated, qualitatively similar spectra were obtained using DEEP. Though careful quantitative studies were not performed using DEEP, the intensities of PO fluorescence from the two precursors were comparable indicating similar yields of PO for each.

III. RESULTS AND DISCUSSION

(0,0) Band Excitation Scans

The spectrum of PO was first identified by running excitation scans through the $(v', v'') = (0,0)$ region of the B-X system and comparing results to the previously measured emission^{2,3a} and LEF⁶ spectra. Since the spin-orbit constant of the X state is quite large (224 cm^{-1}),²⁻⁴ a large spectral splitting of the subbands from the $^2\Pi$ ground state is observed. Scans of both the $\text{B}^2\Sigma^+ + \text{X}^2\Pi_{1/2}$ and $\text{B}^2\Sigma^+ + \text{X}^2\Pi_{3/2}$ subbands are shown in Figure 1. The spectrum was obtained by scanning the laser wavelength while the monochromator remained fixed at 3250Å with a bandpass of 33Å FWHM. This bandpass encompassed nearly the entire (0,0) region so that results using the monochromator-photomultiplier vs filter-photomultiplier combinations were almost identical.

*Of course, one should not go out of one's way to ingest or breathe the simulants.

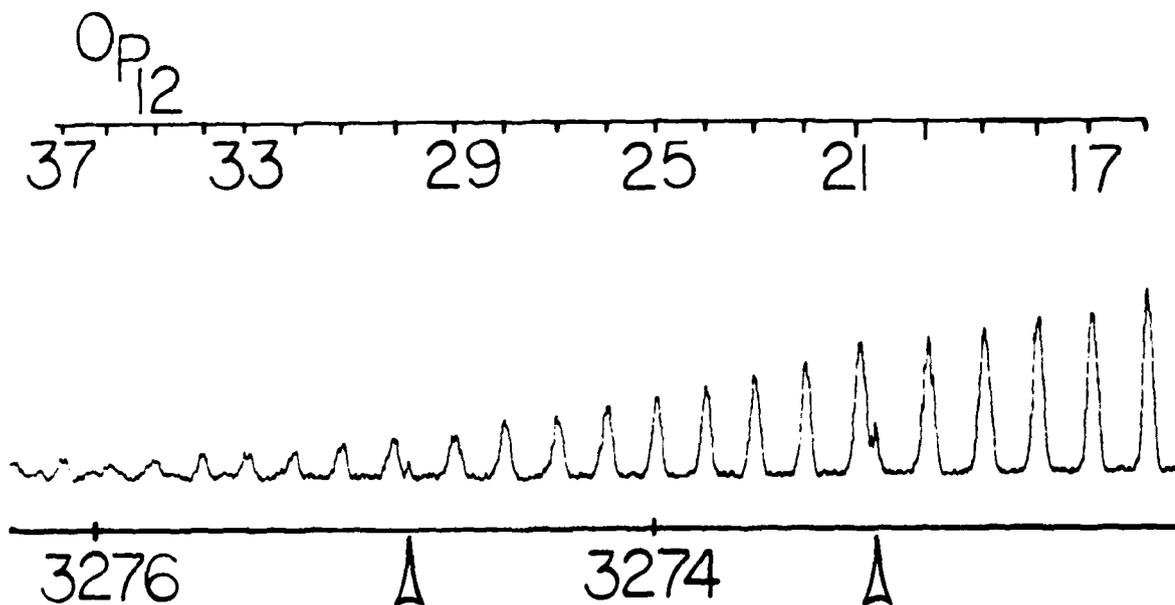


Figure 1a. A Laser Excitation Scan Through The (0,0) Band Of The $B^2\Sigma^+ + X^2\Pi$ System Of PO. Triangles On The Wavelength Scale Indicate Laser Etalon Reset Positions, An Artifact Of The Tuning Mechanism. A. The $B^2\Sigma^+ + X^2\Pi_{3/2}$ Subband. Wavelengths In Angstroms. (Continued)

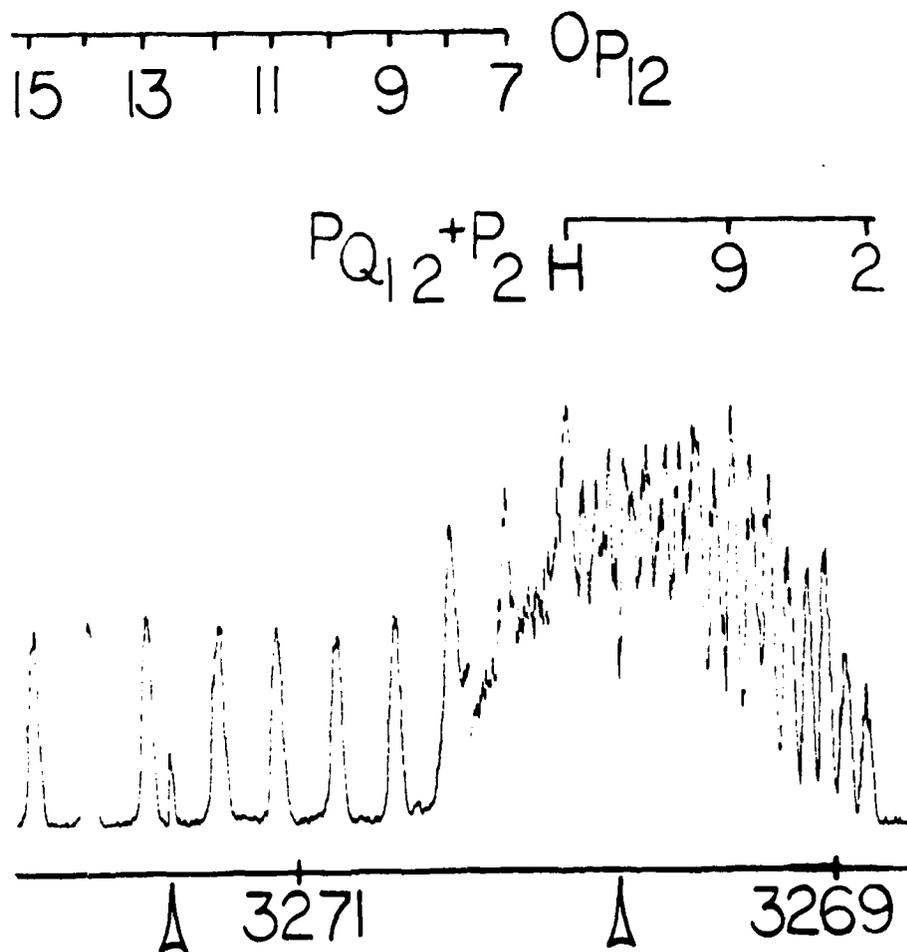


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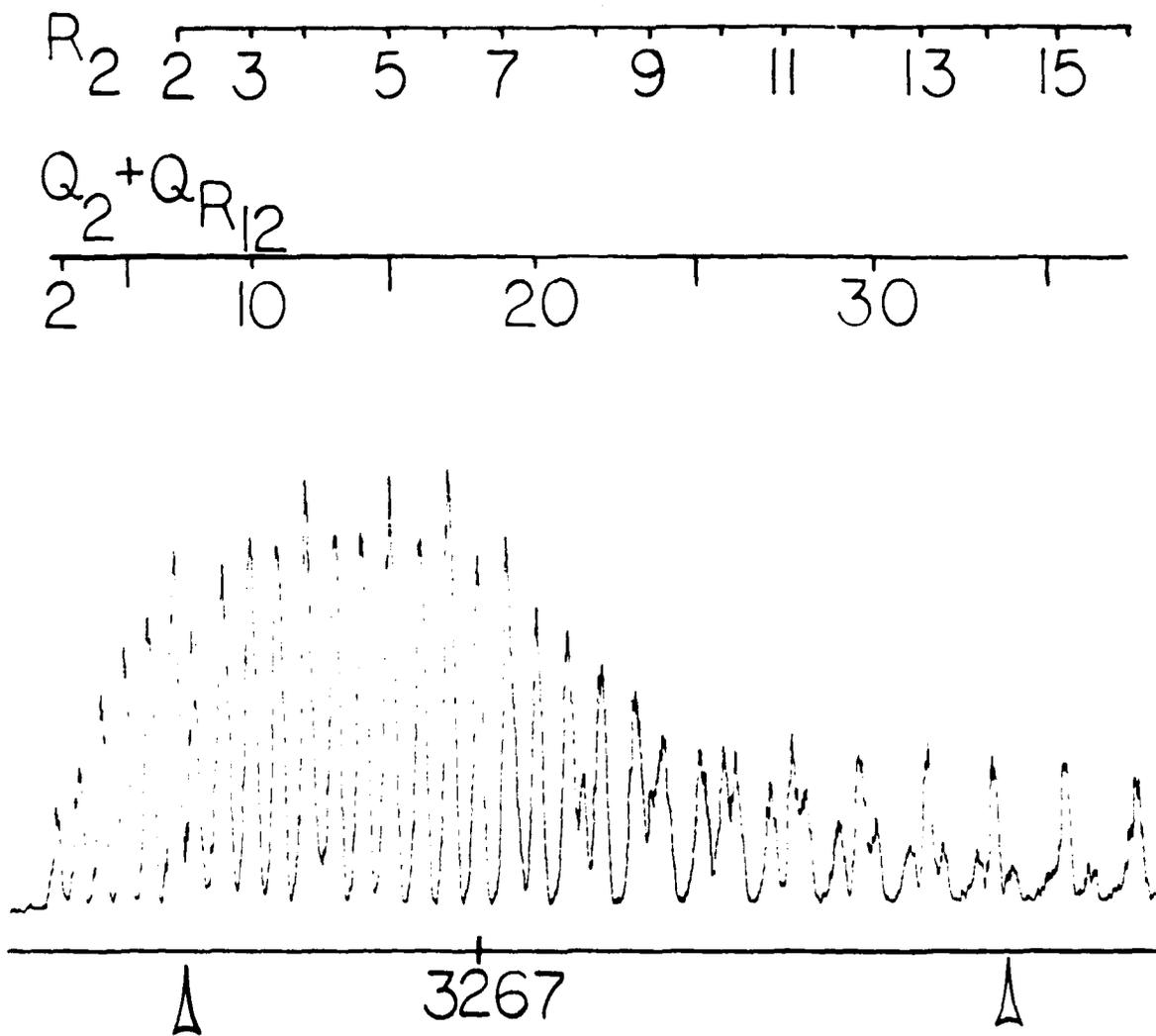


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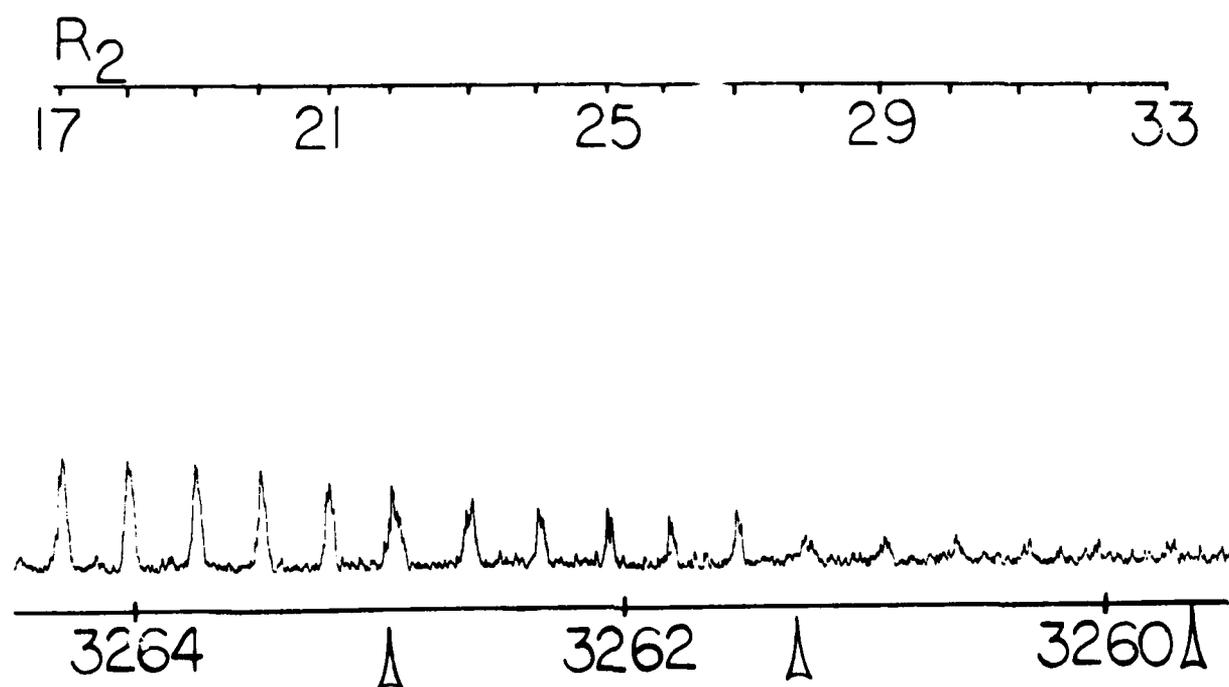


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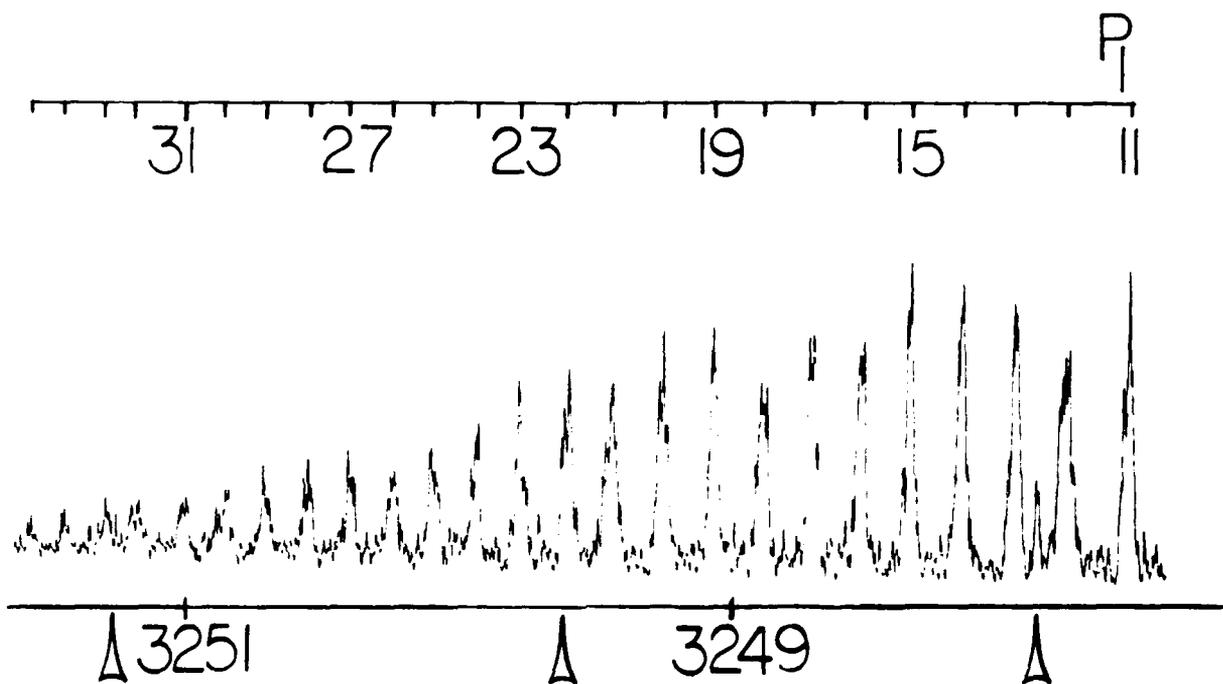


Figure 1b. A Laser Excitation Scan Through The (0,0) Band Of The $B^2\Sigma^+ + X^2\Pi$ System Of PO. Triangles On The Wavelength Scale Indicate Laser Etalon Reset Positions, An Artifact Of The Tuning Mechanism. B. The $B^2\Sigma^+ + X^2\Pi_{1/2}$ Subband. Wavelengths In Angstroms. The Q_1 Branch, From $N''=6$ To The Head, Was Recorded At A Sensitivity About Two Times Lower Than The Rest Of The Subband. (Continued)

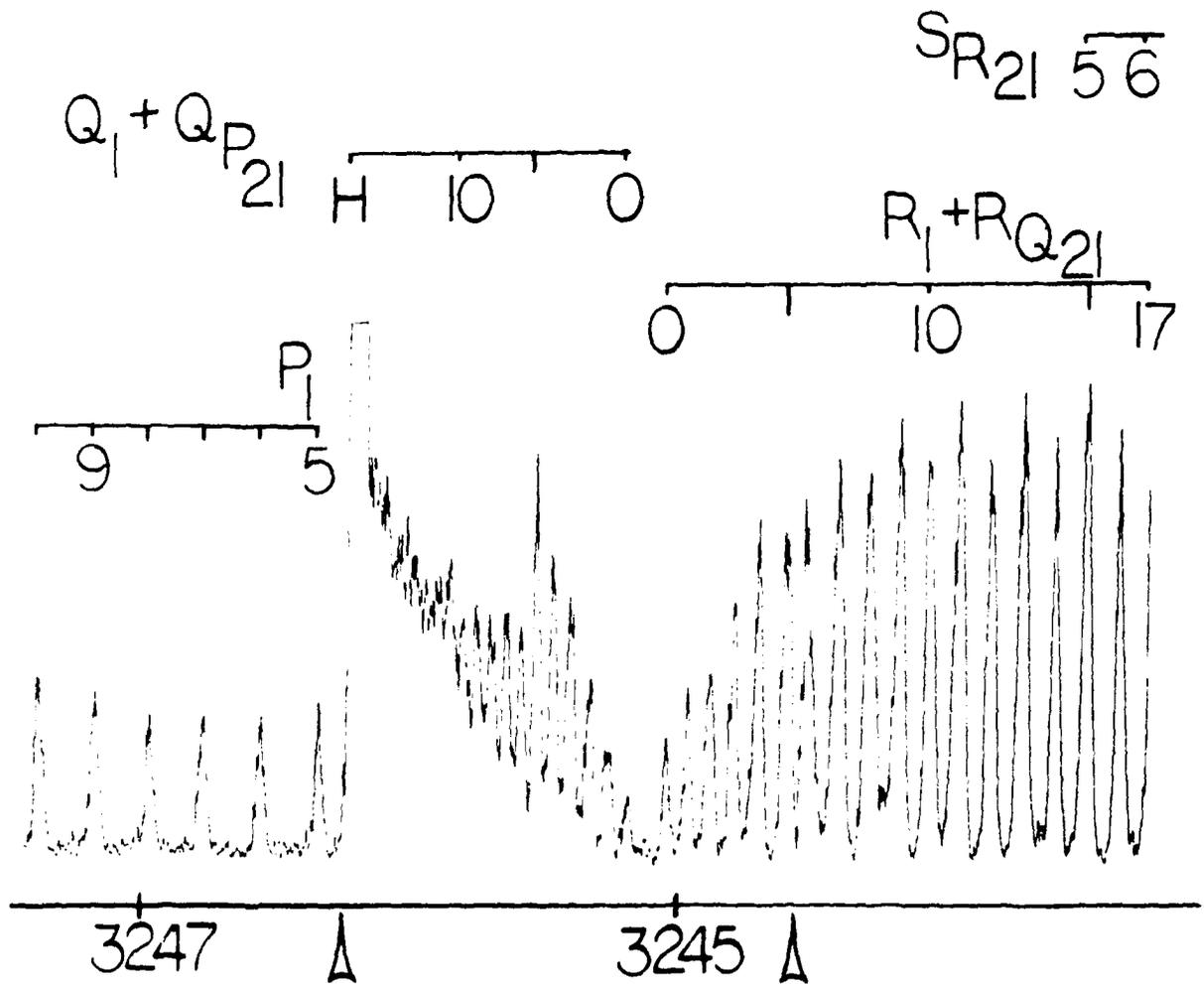


Figure 1b. A Laser Excitation Scan Through The (0,0) Band Of The $B^2\Sigma^+ + X^2\Pi$ System Of PO. Triangles On The Wavelength Scale Indicate Laser Etalon Reset Positions, An Artifact Of The Tuning Mechanism. B. The $B^2\Sigma^+ + X^2\Pi_{1/2}$ Subband. The O_1 Branch, From $N''=6$ To The Head, Was Recorded At A Sensitivity About Two Times Lower Than The Rest Of The Subband. (Continued)

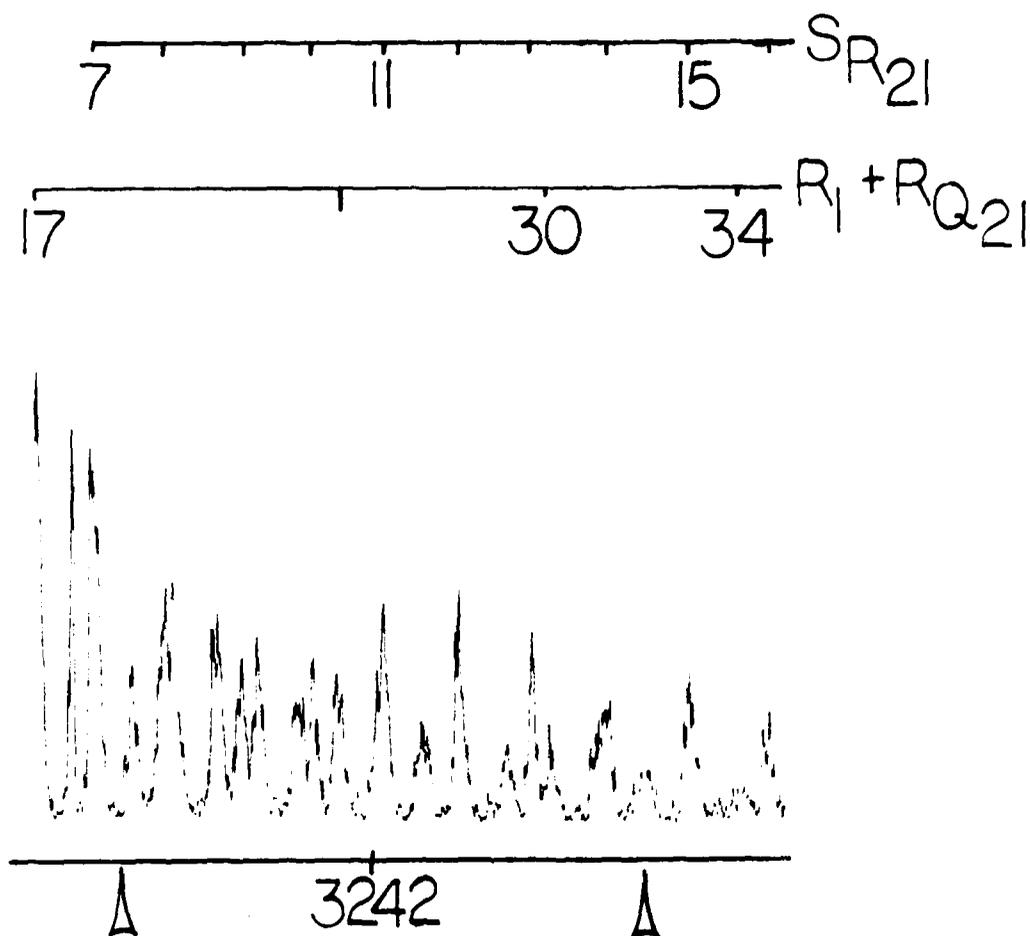


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The earlier work on PO contains a discrepancy as to the rotational numbering of the P_1 branch in the $(0,0)$ band.^{2,3,6} For this reason, the measured line positions were refitted¹⁰ using a weighted nonlinear least squares routine and standard doublet Hamiltonian.¹¹ The results indicate the original P_1 branch assignments^{2,3b} were correct.* Therefore, the rotational assignments in Refs. 2, 3b should be retained. The assignments of the P_1 branch in Figure 1, Reference 3a and Figure 2, Reference 6 should be increased by one unit.** The correct assignments are shown in our Figure 1b.

The fitting of the band has led to predicted bandhead positions and the corresponding values of J'' at which they occur. The J'' values at which the various branches turn have not appeared previously because of the difficulty in resolving this very dense region of the spectrum. The J'' value at which the branches reverse and the calculated wavelength of the appropriate transition are given in Table 1. The observed bandheads from Reference 3a are also given for comparison.

Franck-Condon Factors for $v'=0$

For the measurement of FCFs, the laser wavelength was fixed on the strongest feature of the excitation spectrum, the $Q_1 + Q_{P_{21}}$ bandhead (see Figure 1 and Table 1). The monochromator was then scanned to obtain relative intensities of the vibrational bands originating from $v'=0$. Signals were obtained for $v''=0, 1, \text{ and } 2$, but not for $v''=3$. Since the FCFs are expected to

^{10a}A.J. Kotlar, "An Evaluation of the PO $(0,0)$ $B^2\Sigma^+ - X^2\Pi_r$ Spectroscopic Parameters for Diagnostic Applications," Chemical Research and Development Center Scientific Conference on Chemical Defense Research, Aberdeen Proving Ground, MD, November 1983.

^bA.J. Kotlar, BRL Report to be published.

¹¹A.J. Kotlar, R.W. Field, J.I. Steinfeld, and J.A. Coxon, "Analysis of Perturbations in the $A^2\Pi - X^2\Sigma^+$ 'Red' System of CN," J. Mol. Spectrosc., Vol. 80, p. 86, 1980.

*The discrepancy apparently arose from an accidental mislabeling of the P_1 branch in Figure 1 of Reference 3a. Cross checks of our result by M. Heaven¹² and R.D. Verma¹³ were in agreement.

¹² M. Heaven, private communication.

¹³ R.D. Verma, private communication.

** Some confusion could result because in the text of Reference 6, the authors state that the P_1 branch assignments of Singh² must be increased by one unit. However, in their Figure 2 of Reference 6, as in the similar Figure 1 of Reference 3a, the numbering is lowered by one unit. Therefore, we do indeed mean the numbering in their figure must be increased by one unit. It should be noted that the rotational assignments given in tabular form by Singhal^{3b} are in excellent agreement with those of Singh.

Table 1. Bandhead Positions in the (0,0) Band of the B-X System of PO^a

<u>Wavelength (Å)</u>		<u>Assignment</u>
<u>Observed</u>	<u>Calculated</u>	
3246.1	3246.2	Q ₁ (27.5)
	3246.2	Q _{P21} (27.5)
3270.4	3270.4	P ₂ (44.5)
	3270.5	P _{Q12} (45.5)

a - Observed values were taken from Reference 3a.

decrease for higher v'' , higher values were not checked. Magnitudes of the signal levels observed for $v''=0$ and 2 necessitated usage of different voltages (an uncalibrated gain change) on the photomultiplier. Therefore, the band intensity ratios were obtained in pairs with the (0,0):(0,1) ratio at low and the (0,1):(0,2) ratio at high sensitivity. At least four scans were obtained for each band at the necessary sensitivities. A representative pair of bands is shown in Figure 2. Areas under these curves were obtained by computer integration (trapezoidal summation) and averaged for the four runs. The area under the (0,0) bands was then corrected for a small amount of laser scatter from the cell walls and windows whose magnitude was obtained from runs with the microwave discharge off (see Figure 2). Finally, the combined lensing, monochromator-photomultiplier system's spectral sensitivity was calibrated using an NBS traceable tungsten standards lamp. The ratios of Einstein band emission coefficients thus obtained were $A_{0,1}:A_{0,0} = 0.0690 \pm 0.0073$ and $A_{0,2}:A_{0,1} = 0.0824 \pm 0.0119$. These ratios may be used irrespective of any assumptions about the electronic transition moment. If one assumes the electronic transition moment is constant over the range of internuclear distance sampled in the three vibrational bands, then by doing the appropriate algebraic manipulations, FCFs may be derived from these Einstein coefficient ratios. These are shown in Table 2.

Table 2. Measured and Calculated Franck-Condon Factors for the $v'=0$ Progression in the B-X System of PO. The electronic transition moment was assumed constant in the derivation of FCFs from experimental data (see text).

<u>(v', v'')</u>	<u>q_{v', v''} (meas.)</u>	<u>q_{v', v''} (RKR calc.)</u>
(0,0)	0.9213 ± 0.0071	0.9776
(0,1)	0.0720 ± 0.0076	0.0194
(0,2)	0.0067 ± 0.0012	0.0028
(0,3)	Not detected	0.0001

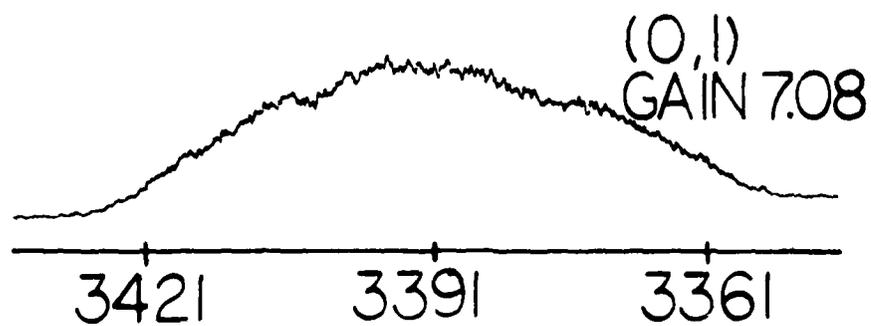
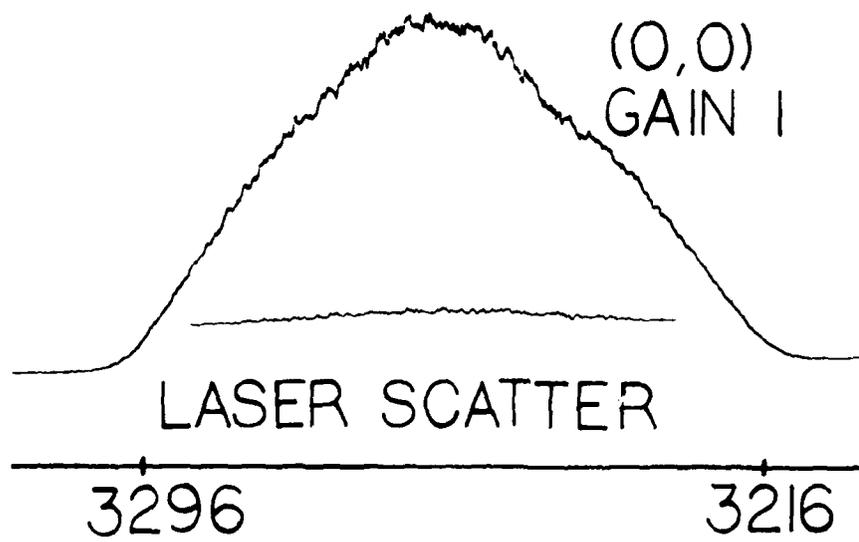


Figure 2. Fluorescence Scans Of The (0,0) And (0,1) Vibrational Bands. Wavelengths In Angstroms. Note That The Baseline For The Laser Scatter Scan Is Displaced Upwards From That For The Scan Of The (0,0) Band. The Scattering Correction To The (0,0) Intensity Is Actually Quite Small.

FCFs were also obtained from theoretical calculations for the entire v' , v'' array using the RKR potentials. Subsequent to these calculations, it was discovered that similar calculations had been performed previously by Singhal^{3b} and concurrently by Smyth and Mallard.⁷ All of these results are in excellent quantitative agreement for the $v'=0$ progression. The present theoretical results for the $v'=0$ progression are shown in Table 2 for comparison with the experimental results. Note that though the qualitative trends are quite similar, the quantitative agreement is poor, especially for the small FCFs. Small FCFs are especially difficult to calculate because they result from the cancellation of many positive and negative contributions in the integration of the vibrational wavefunctions; that is, they result essentially from the difference of two large, nearly equal numbers. Such problems have been suggested previously as the cause of a several orders of magnitude difference in measured and calculated FCFs in the A-X system of NH.¹⁴ Along these lines it is also worth noting that Smyth and Mallard state⁷ that their multiphoton ionization results could perhaps be better explained if the RKR calculational procedure underestimates several of the smaller FCFs. Unfortunately, the sketchy data presently available do not allow one to be certain whether problems with the FCF calculations or changes in the electronic transition moment with internuclear distance, as is known to occur in the A-X system of OH,¹⁵ are responsible for the poor agreement in Table 2. In any event, the Einstein emission coefficient ratios may be used irrespective of any assumptions about the form of the transition moment. The measured Einstein coefficients are to be preferred over those calculated from the theoretical FCFs, especially for rotational quanta near $N'=27$ (turning point of the Q_1 bandhead) where the measurements were performed.

Concentration of PO

A rough estimate of the density of PO in the excitation region was obtained using a procedure entirely analogous to that used previously for C_2 and CN,¹⁶ and NCO¹⁷ in a flame with changes appropriate to the tunable, pulsed laser. In the present work, the absolute fluorescence intensity in the (0,0) band was directly measured rather than referenced to N_2 Raman signals as was

¹⁴W.R. Anderson and D.R. Crosley, "Laser-Excited Fluorescence in the A-X System of NH," Chem. Phys. Lett., Vol. 62, p. 275, 1979.

^{15a}D.R. Crosley and R.K. Lengel, "Relative Transition Probabilities and the Electronic Transition Moment in the A-X System of OH," J. Quant. Spectrosc. Radiat. Transfer, Vol. 15, p. 579, 1975.

^bD.R. Crosley and R.K. Lengel, "Relative Transition Probabilities in the A-X System of OD," J. Quant. Spectrosc. Radiat. Transfer, Vol. 17, p. 59, 1977.

¹⁶J.A. Vanderhoff, R.A. Beyer, A.J. Kotlar, and W.R. Anderson, "Ar⁺ Laser-Excited Fluorescence of C_2 and CN Produced in a Flame," Combust. Flame, Vol. 49, p. 197, 1983.

¹⁷W.R. Anderson, J.A. Vanderhoff, A.J. Kotlar, M.A. DeWilde, and R.A. Beyer, "Intracavity Laser Excitation of NCO Fluorescence in an Atmospheric Pressure Flame," J. Chem. Phys., Vol. 77, p. 1677, 1982.

done previously. The Einstein coefficients were obtained using the B state lifetime, 250 nsec, measured in Reference 6 and the measured FCFs. Linestrengths necessary for the calculation of absorption coefficients for the resolved rotational lines were obtained using formulae of Earls.¹⁸ The pumping transition(s) was assumed to be Doppler broadened at 400 K, a temperature typical of our flow system. The measurement was made by pumping in the Q₁ bandhead where the laser line overlaps several rotational lines of PO. To estimate the effective number of transitions pumped, the relative intensities of R₁(27) and the Q₁ bandhead, which occurs near N''=27, were obtained from the excitation scan. After correcting for rotational linestrengths, it was found that the laser effectively overlaps 6.9 transitions.* Finally, the importance of quenching was ascertained. It is expected that the quench rate of B state PO by Ar is certainly less than that of N₂ measured in the previous LEF study⁶ and found to be gas kinetic. Now, in comparing the Einstein emission coefficients, A_{v,v''}, to the quench rate, Q, for N₂ at 1 torr, it is found that the radiative and quench rates are nearly equal. Saturation checks were run using the ratioing boxcar averager so that stimulated emission is known to be unimportant. The fluorescence rate under these conditions is proportional to A_{v,v''}/[(Σ_v A_{v,v''}) + Q] rather than A_{v,v''}/Q as in Eq. (3) of Reference 16. The quench rate actually used was that of N₂. However, if the quench rate of Ar is much less than for N₂, the effect would reduce the estimated PO density by only a factor of about 2. The density estimated in this manner was about 1 x 10¹⁰ cm⁻³. Thus, about 1 x 10⁻⁵ of the phosphorus was present as PO. Because of the various uncertainties involved in these estimates, they are believed to be good only to within a factor of 10.**

IV. CONCLUSIONS

In these experiments, PO was obtained for fluorescence studies using organophosphonate esters as precursors. Discovery of these sources should aid in further research on PO as they are more easily handled than earlier precursors. The measurement of FCFs, together with the previous lifetime measurements, now makes quantitative determination of PO using absorption or fluorescence techniques possible.

¹⁸L.T. Earls, "Intensities in 2_π - 2_Σ Transitions in Diatomic Molecules," Physical Review, Vol. 48, p. 423, 1935.

*This procedure is valid because the Boltzmann fractions and normalized rotational linestrengths, and, hence, Einstein coefficients, do not vary significantly around N''=27. The result is similar to that obtained by dividing the laser linewidth, 0.3 cm⁻¹, by the density of lines in the region of the Q₁ bandhead.

**This uncertainty limit could have been reduced to about a factor of 2.5, even in the absence of further quench rate information, if a more careful laser power measurement had been available at the time of the experiment. The result shows that good quantitative measurements of PO could be made even in the absence of very precise quench rate information.

ACKNOWLEDGEMENTS

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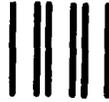
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