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Detection of the infrared laser spectrum of the PO_2 radical in the gas phase

Hai-Bo Qian^a, Paul B. Davies^a, Imtiaz K. Ahmad^b, Peter A. Hamilton^b

^a Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK ^b Department of Chemistry, Queen Mary and Westfield College, Mile End Road, London E1 4NS, UK

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Abstract

The infrared laser absorption spectrum of the PO₂ free radical has been detected in the reaction of oxygen atoms with white phosphorus. Over 300 lines of the ν_3 fundamental band of the ${}^{2}A_{1}$ ground state have been measured and assigned between 1300 and 1345 cm⁻¹. Rotational, centrifugal distortion and spin-rotation constants for the $\nu_3 = 1$ level have been obtained from fitting the lines to an asymmetric rotor Hamiltonian, with the ground state constants held at their microwave/laser magnetic resonance values. The band origin is 1327.53452(69) cm⁻¹.

1. Introduction

The oxidation of white phosphorus, and its accompanying chemiluminescence, has been extensively studied almost since the isolation of elemental phosphorus in 1669. It is only relatively recently, however, that the mechanism of the chemiluminescence has been elucidated [1-3]. A considerable number of reactive intermediates have been identified or proposed as important in the reaction. Andrews and co-workers have carried out an extensive study of the reactions of phosphorus compounds using matrix isolation methods to trap the reactive intermediates, and successfully identified many of them using FTIR spectroscopy [4-6]. Phosphorus oxides which have been identified using matrix IR include PO, PO₂, P₂O and many higher oxides [5,6]. Of these only PO has been observed previously in the infrared region in the gas phase [7].

The PO_2 radical has long been associated with the extensive continuous visible chemiluminescence [3,8]

from phosphorus oxidation. In contrast to NO2, no banded-visible absorption system of PO2 has been observed [9,10]. An absorption system of PO_2 in the near UV with clear rotational structure was identified using flash photolysis by Verma and Singhal [9] and this system was subsequently examined by LIF [8]. Single vibronic level fluorescence was used to obtain vibrational intervals of 387 and 1117 cm⁻¹ for ν_2 and ν_1 modes of PO₂ in its ground ²A₁ electronic state. Hirota and co-workers detected the pure rotational spectrum of PO₂ in the vibronic ground state using far-infrared laser magnetic resonance (LMR) and microwave spectroscopy [11] and accurately determined the molecular constants in this state. They estimated vibrational intervals of 377 and 1090 cm^{-1} for the ν_2 and ν_1 vibrational modes from the centrifugal distortion constants. Ab initio calculations on PO_2 by Lohr [12] gave harmonic frequencies of $\omega_1 = 1048 \text{ cm}^{-1}, \ \omega_2 = 396 \text{ cm}^{-1}, \text{ and } \omega_3 = 1260$ cm^{-1} , in fair agreement with the results from LIF [8], and far-infrared LMR and microwave spectra [11]. In the matrix studies Andrews and co-workers [4-6] were only able to identify the ν_3 band of PO₂, which occurs in an argon matrix at 1319 cm⁻¹, suggesting that it is the most intense of the three fundamentals. PO₂ is a near prolate asymmetric rotor and the ν_3 band is an A type band which should resemble the parallel band of a symmetric rotor. This study reports the detection of this band in the gas phase by diode laser absorption spectroscopy.

2. Experimental details

PO2 radicals were generated by reacting the vapour from solid white phosphorus with oxygen atoms in situ in a long path multiple-reflection White cell evacuated by a rotary and Roots blower pumping system. The oxygen atoms were formed by a microwave discharge in He/O2 in one side arm of the cell. The white phosphorus vapour was entrained in helium at room temperature and injected through a second side arm, opposite to the O atom inlet and near the middle of the cell. This position corresponded to minimum deposition of phosphorus oxides on the White cell mirrors. The phosphorus injection tube was directed against the flow direction to achieve rapid and uniform mixing which was found to substantially improve the signal. Spectra were recorded using diode current modulation at 1 kHz. The signal to noise ratio of the strongest lines was 30:1.

The diode laser spectrometer and the multiple-reflection cell have been described previously [13]. The laser beam was passed through the 1 m long cell 40 times. From the chemiluminescence, however, it was clear that the reaction was limited to the central region of the cell, giving an effective absorption pathlength of 20 meters. The spectra of PO₂ were recorded simultaneously with the spectra of a reference gas and the fringes from an evacuated confocal etalon (fsr = 0.0098 cm⁻¹). N₂O [14] was used as a reference gas in the region from 1290 to 1336 cm^{-1} and CH₃OH from 1336 to 1350 cm⁻¹. The wavenumbers of the CH₃OH lines were measured on a Bomem DA 3.002 Fourier Transform Spectrometer with an absolute accuracy of about 0.001 cm^{-1} . The absolute accuracy of PO₂ line positions was therefore limited by the CH₃OH line calibration data.

3. Analysis and results

The oxidation of white phosphorus vapour (\mathbf{P}_{4}) is known to proceed by a complex chain reaction [15] which involves a variety of oxide species. The dominant species under steady state conditions depend critically on the relative oxygen and phosphorus concentrations. Although the $O/O_2/P_4$ reaction is known [8] to be a source of PO_2 , the exact chemistry and mixing conditions for our flow system were unknown. The infrared spectrum of PO has previously been observed using a diode laser (in a microwave discharge of $H_2/He/O_2$ mixtures over solid red phosphorus [7]) and so its spectrum was used to optimize our reaction conditions. The spectrum of PO near 1200 cm⁻¹ was readily observed and optimized. A factor of ≈ 10 increase in signal strength was achieved during this optimization procedure which was crucial for the initial detection of the much weaker PO₂ spectrum. The strongest signals for PO were observed at a total pressure of 240-250 mTorr with an oxygen partial pressure of $\approx 8-10$ mTorr and with the He gas through the oxygen and phosphorus inlets at a pressure ratio of 3:5. The search for PO₂ was first undertaken in the region of 1320 cm⁻¹ near the predicted ν_3 band origin with similar flow conditions to that used for PO but with a slightly higher oxygen concentration. Eventually the optimum signal for the new spectrum was obtained at a total pressure of 330-350 mTorr with 40-50 mTorr of O_2 and with the He flow divided equally between the oxygen and phosphorus inlets. Under these conditions a dense spectrum of lines was observed between 1300 and 1345 cm^{-1} . The oxygen-phosphorus chain reaction is self-sustaining and so both the PO spectrum and the new spectrum were observable, although at lower intensity, when the discharge producing atomic oxygen was extinguished (Fig. 1). The self-sustaining nature of the reaction under similar chemical conditions to those observed in the LIF study of PO₂, which also used the $O/O_2/P_4$ source, strongly supported the assignment of the new spectrum to PO_2 .

The large number of lines observed in the 1300 to 1345 cm^{-1} region had identical chemical behaviour but no apparent branch structure. While it was almost certain from the chemical behaviour of the signal and the expected appearance of the spectrum



Fig. 1. Representative diode laser spectra of (a) PO and (b) PO_2 . Upper pair of scans with the atomic oxygen microwave discharge source turned on. Lower pair of scans with the discharge off but with the same inflow of molecular oxygen and phosphorus vapour.

that the carrier was PO_2 , a definitive assignment of quantum numbers at first proved very elusive. As the nuclear spin of ¹⁶O is zero only levels with $(K_a +$ $(K_c)_{even}$ for A₁ vibrational states and $(K_a + K_c)_{odd}$ for B₁ vibrational states are permitted in PO₂ by nuclear spin statistics. As a result, the characteristic asymmetry doubling for each value of K_a is absent and only a shift from the regular symmetric rotor pattern is observed. By analogy with NO_2 [16] the difference in the A rotational constant (A' - A'') is expected to be large for the ν_3 A type band and so the K_a sub-bands for each N in the P and R branch will be widely spaced and essentially appear randomly over the short diode laser modes. The unpaired electron in the electronic ground ${}^{2}A_{1}$ state should, however, give rise to an observable spin-rotation splitting of lines at low N and high K_a [17]. Initially few low N and high K_a transitions were detected and a more typical recording of a P branch region showing the spin-rotation splitting for weak, high K_a lines is shown in Fig. 2.

In contrast to the P and R branches the spacing of the lines within a Q branch with a single value of K_a



depends mainly on $\Delta(\frac{1}{2}(B+C))$, which was estimated to be very small and predicted to give rise to regular structure within a single diode laser mode. Three obvious Q branch structures close to each other, such as the one shown in Fig. 3, were eventually found and provided the key to start the assignment. For initial assignment the K_a values of the



Fig. 3. The $Q_7(N)$ branch of PO₂, showing resolved spin-rotation splitting.

three Q branches were estimated from the magnitude of the spin-rotation splitting. The upper state rotational constants were estimated from the known ground state values by comparison to NO₂, and the distortion constants and spin-rotation constants were fixed at their microwave/LMR values. The ground state combination differences calculated from the accurately determined ground state constants were used to independently confirm the initial assignments. Once the first set of upper state constants was obtained the analysis proceeded iteratively with additional assignments, revised constants and prediction of new transition frequencies. In this way an unambiguous assignment of quantum numbers of all observed lines was obtained. The Hamiltonian used in the analysis was that described by Sears [18,19]. It was used to fit about 300 lines in the final fit in which the ground state constants were fixed at the microwave/LMR values. The RMS value obtained in the fit was 0.0007 cm^{-1} which is similar to the estimated experimental error. Lines with N as high as 45 and K_a up to 10 were included in the fit which gave the 15 floated effective parameters listed in Table 1.

4. Discussion

The origin of the ν_3 band is 1327.53452 cm⁻¹, a blue-shift of around 8.5 cm⁻¹ from the matrix value. This is fairly large for a matrix shift but is well within the 1320 ± 10 cm⁻¹ range suggested as reasonable by Andrews and co-workers [6]. The shift is in the same direction as that observed for PO which exhibits a 2 cm⁻¹ shift. The A, B, and C rotational constants are all of the magnitude expected for PO₂ and decrease from their ground state values by a similar percentage to that observed for the ν_3 band of NO₂ [16]. In particular, the A rotational constant exhibits a relatively large 2.2% shift on excitation which is similar to the 2.8% change observed from A" to A' in the ν_3 band of NO₂. With the exception of Δ_K and H_K the centrifugal distortion constants also show very little change from their ground state values. The three spin-rotation parameters are all well determined in the fit, even though the spin-rotation splitting was not resolved for all the lines, and are very close to the ground state values.

Table 1

Molecular constants (cm⁻¹) for the ground and $v_3 = 1$ states of PO₂ (1 σ uncertainties given in parentheses)

Parameters	Ground state ^a	v ₃ = 1
$\overline{\nu_0}$		1327.53452(69)
A	3.4859769(4)	3.408323(69)
В	0.28680775(6)	0.2859130(43)
С	0.26422995(4)	0.2630616(43)
$\Delta_N \times 10^6$	0.15424(19)	0.1588(13)
$\Delta_{NK} \times 10^4$	-0.12987(4)	-0.12954(56)
$\Delta_K \times 10^3$	0.95354(9)	0.9077(33)
$\delta_N \times 10^7$	0.32916(13)	0.3391(96)
$\delta_{\kappa} \times 10^5$	0.1538(9)	0.166(57)
$\hat{H_N} \times 10^{11}$	-0.343(14)	-0.343
$\dot{H_{NK}} \times 10^9$	-0.183(6)	-0.183
$H_{\kappa N} \times 10^8$	-0.987(9)	-0.903(82)
$H_{\kappa} \times 10^6$	0.8892(22)	0.831(56)
$h_N \times 10^{12}$	0.31(7)	0.31
$h_{NK} \times 10^9$	-0.20(4)	-0.20
$L_K \times 10^8$	-0.1014(19)	-0.103(29)
ϵ_{aa}	0.054586(4)	0.05317(14)
ϵ_{bb}	0.0007167(4)	0.000713(93)
ϵ_{cc}	-0.0014818(4)	-0.001484(93)
σ		0.0007

^a The ground state constants were fixed to those of Ref. [11].

The inertial defect in the $v_3 = 1$ state is 0.176 u Å² which is very similar to that for the ground state (0.186 u Å²) indicating that this band is not strongly perturbed by Coriolis coupling to other vibrational levels. This is reasonable as the v_1 band is expected to lie about 210 cm⁻¹ away near 1117 cm⁻¹ [8]. Detection of the v_1 band should be feasible with our current apparatus if the intensity is no more than a factor of 4 less than the v_3 band. Observation of the v_1 band and simultaneous fitting of all the available data (microwave, LMR, and IR) should allow the stretching vibrations of PO₂ and any possible coupling between them to be fully characterized.

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