Free-Jet Electronic Spectroscopy of the PO_2 Radical

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The laser fluorescence excitation spectrum of the jet-cooled PO_2 radical has been recorded in the wavelength range 325−284 nm. This work extends previous flash photolysis and laser fluorescence studies of the UV electronic transition in PO_2. Resolved emission spectra were recorded for excitation of a number of bands. The previous vibrational analyses of both the absorption and emission spectra were extended. The rotational structure of the bands was investigated and found to be very complicated, defying an analysis. The radiative decays of the excited vibronic levels were found to be nonexponential but could be fitted to a double exponential form. The lifetimes were found to be much shorter than those observed in a discharge-flow system by Hamilton [*J. Chem. Phys.* **1987**, *86*, 33]. The inferred dependence of the lifetime upon the degree of rotational excitation and the complicated rotational structure of the bands suggest that there is significant electronic state mixing, as in the isovalent NO_2 molecule.

1. Introduction

The oxidation of elemental phosphorus (see ref 1) and the combustion of phosphorus-containing molecules have been of interest for a long time. An understanding of the pyrolysis and combustion of organophosphorus compounds[2−4] is of particular interest because of the need to destroy chemical warfare agents, including organophosphorus agents. Additionally, phosphorus-containing compounds may be useful as potential fire suppressant agents.[5] The combustion chemistry of phosphorus is complicated,[6] and there is a need for the development of diagnostics for the detection of reactive intermediates.[7]

One of the key intermediates in phosphorus combustion chemistry is the PO_2 molecule, but spectroscopic information on this species is fairly sparse, in contrast to the extensive information available on the diatomic PO radical.[8,9] The PO_2 molecule was first spectroscopically detected by Verma and McCarthy[10] in a flash photolysis study. Several progressions of bands were observed in the region 312−268 nm and were assigned as electronic excitation to a $^2B_2$ state from the ground $\tilde{X}^2A_1$ state, in analogy with the 249 nm system in NO_2.[11] Hamilton[12] presented a study of the laser fluorescence excitation spectrum of this band system and measured excited-state decay lifetimes and collisional quenching rates. These two studies were carried out in a cell, with the internal excitation of the radical at approximately room temperature, and the rotational structure was not resolved.

Verma and McCarthy assigned the excited-state symmetry both by analogy with NO_2 and through their assignment of attributed K-structure to a $\Delta K = 0$ selection rule, corresponding to a type-A transition. High-resolution spectroscopic studies in the infrared and microwave regions have been reported,[13,14] and precise values for the rotational and spin-rotation constants are available for the ground vibronic and $v_3 = 1$ levels.[14] From the latter, a precise value for the antisymmetric P−O stretching fundamental (ν_3'') was determined. The electronic and vibrational spectrum of the PO_2 radical deposited in solid argon has also been examined.[15−17] Of relevance to the present study is the observation of absorption features in the range 301−284 nm.[17]

The ground $\tilde{X}^2A_1$ electronic state of PO_2 is well-known from both experimental[13,14] and theoretical[18−22] studies to be strongly bent, with the following experimental r_0 geometry: $r(\text{P−O}) = 1.4665 \pm 0.0041$ Å, $\theta(\text{O−P−O}) = 135.3 \pm 0.8°$.[13] Several of the ab initio studies also investigated excited electronic states of PO_2 in order to understand its electronic spectrum.[18,20,22] Kabbadj and Lievin[20] computed equilibrium geometries, vibrational frequencies, and excitation energies, and investigated the dependence of the energies on the bond angle, for the ground and the low-lying 1^2B_2, 1^2A_2, and $1^2\Pi_u$ (1^2B_1, 2^2A_1) electronic states at the SCF and MCSCF levels, with small basis sets. The most complete study to date of the excited electronic states of PO_2 is that by Cai et al.,[22] who considered 18 electronic states at the MRD-CI level and computed vertical excitation energies and oscillator strengths. In addition, these workers computed equilibrium geometries, vibrational frequencies, and adiabatic excitation energies for the lowest excited states (1^2B_2, 1^2A_2, 1^2B_1). In early work, Lohr[18] estimated the excitation energy of the 1^2B_1 ($1^2\Pi_u$) state.

The excited states in the first set (1^2B_2, 1^2A_2) are predicted to be even more strongly bent than the ground state, but their energies are too low to be candidates for the upper state of the observed electronic transition. Based on Lohr's calculations,[18] Hamilton[12] assigned the upper state of the observed electronic transition in the UV as the 1^2B_1 state, in contrast to the assignment of a $^2B_2$ upper state by Verma and McCarthy.[10] Other workers[22,17] have concurred with Hamilton's assignment.

To reduce the spectral congestion, we have recorded the laser fluorescence excitation spectrum of the PO_2 radical, prepared in a supersonic molecular beam. The resultant low internal temperature leads to a considerable reduction in the spectral congestion. This should allow, for example, distinguishing between a linear and nonlinear excited electronic state from the rotational structure of bands involving even and odd quanta of bend vibrational excitation.[23] We have observed the bands reported by Verma and McCarthy, as well as bands at longer wavelength, almost to the previously estimated[10] band origin. We have also recorded resolved emission spectra with greater spectral resolution than in the study by Hamilton.[12] With these

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data, improved vibrational analyses of the upper and lower electronic states are reported. The rotational structure of many bands was investigated and found to be complex, even for the low rotational temperatures of the supersonic beam. It has not been possible to carry out a rotational analysis. Finally, we report decay lifetimes for a number of excited vibronic levels.

2. Experimental Section

The apparatus employed in this work is similar to those that have been employed in this laboratory for previous spectroscopic studies of weakly bound complexes and transient molecules.[24−26] A supersonic beam containing PO_2 radicals was produced in a pulsed free-jet expansion (0.02 cm diam orifice) of mixtures, seeded in argon, of phosphorus trichloride (Aldrich, 98%) and oxygen which were photolyzed with focused 193 nm excimer laser radiation at the nozzle. The experimental chamber that houses the molecular beam was evacuated by a water-baffled 10 in. diffusion pump. The backing gas pressure was ca. 12 atm, with typical PCl_3 and O_2 partial pressures of 0.13 and 0.20 atm, respectively.

Fluorescence excitation spectra were recorded 1.5 cm downstream of the nozzle using the frequency-doubled output of an XeCl excimer laser pumped dye laser (Lambda Physik). The dye laser was operated both in the low- and high-resolution modes, with the installation of an intracavity Etalon for the latter. The spectral bandwidth was $\sim$0.4 cm^{-1} in the low-resolution mode and $\sim$0.12 cm^{-1} in the high-resolution mode. UV pulse energies for the recording of excitation spectra were $<$100 μJ in a 0.2 cm diam beam.

The laser-induced fluorescence signal was imaged onto the entrance slit of a 1/4 m monochromator, and the light passing through the monochromator was detected with a photomultiplier (Thorn EMI 9813QB), whose output was directed to a gated integrator and then to a computer. Resolved fluorescence emission spectra were recorded with 150 μm slits installed in the monochromator (0.8 nm resolution). The excitation spectra were calibrated using the fluorescence spectrum of molecular iodine.[27]

Decay lifetimes of excited vibronic levels were measured in a slightly modified optical arrangement. The monochromator was replaced by a combination of an interference filter (490 nm center wavelength, 10 nm full width at half-maximum, 1 in. diam) and several color filters. In this way, emission from the excimer and excitation lasers could be blocked while minimizing flyout of the molecules from the fluorescence detection zone. With this geometry, emission up to $\sim$10 μs after the excitation laser pulse could be detected. Light passing through the filters was detected with a photomultiplier (Thorn EMI 9813QB) which was not gated to block the excimer laser. The photomultiplier was directly connected to the 300 MHz input of a LeCroy model 9360 digital oscilloscope, which was triggered by scattered light from the excitation laser using a fast photodiode. Each waveform was averaged over 2000 laser shots to increase the dynamic range and the signal-to-noise ratio. Background waveforms were collected with the excitation laser beam blocked and were subtracted from the fluorescence decay waveforms.

3. Results

3.1. Excitation Spectra. Laser fluorescence excitation spectra were recorded in the wavelength range 325−284 nm. This covers the longer-wavelength portion of the spectral region in which Verma and McCarthy[10] observed PO_2 bands and extends to even longer wavelength. As noted by Hamilton,[12] the fluorescence emission also occurs over a wide wavelength range.

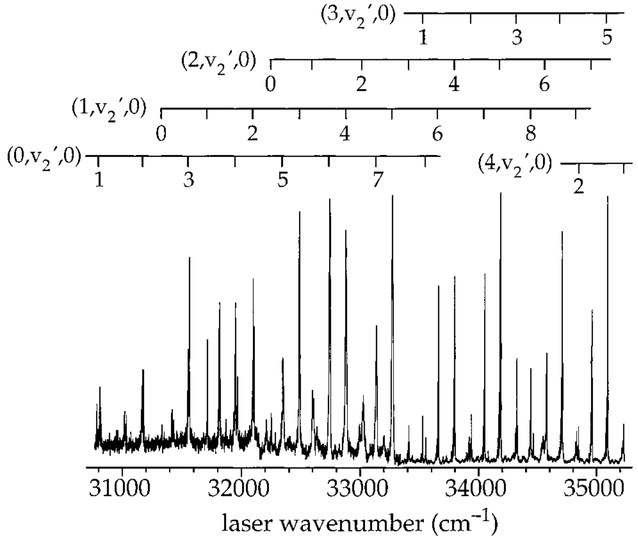

Figure 1. Survey of the laser fluorescence excitation spectrum of the jet-cooled PO_2 radical. Progressions in the upper-state bend vibrational mode ν_2' are indicated. The spectrum was constructed from a composite of several scans and has not been normalized for the laser power. The sensitivity was progressively increased toward lower wavenumbers.

TABLE 1: Transition Wavenumbers for the Observed (v_1',v_2',0) − (000) Bands of PO_2 (in cm^{-1})[a]

	v_1'				
v_2'	0	1	2	3	4
0		31331.1	32251.2		
1	30782.0	31713.0	32635.6	33551.0	
2	31177.0	32097.3	33027.3	33937.5	34845.9
3	31562.4	32491.4	33409.6	34321.7	35231.5
4	31947.3	32879.6	33795.5	34707.5	
5	32346.5	33271.5	34179.0	35094.7	
6	32742.2	33659.4	34574.5		
7	33136.7	34050.9	34960.8		
8	33526.7	34439.4			
9		34828.5			

[a] Estimated absolute accuracy ±0.5 cm^{-1}.

Figure 1 presents a survey scan of the laser-induced fluorescence signal as a function of the excitation wavenumber. This scan was constructed from a composite of several spectra. A large number of bands, all assignable to PO_2, are seen in this scan. We observe the bands reported by Verma and McCarthy,[10] as well as weaker bands to the red. The widths of the bands are considerably less than in the laser fluorescence spectra reported by Hamilton,[1] consistent with the much colder rotational temperature of our supersonic beam than in his discharge-flow experiment. A long excited-state progression in the bending vibrational mode ν_2' is observed. This suggests that the bond angle changes significantly upon electronic excitation.

Table 1 presents the transition wavenumbers of our observed bands. The reported wavenumbers refer to the strongest feature within the rotational contour in low-resolution scans of each band. In general, we find good agreement with the previously reported[10] transition wavenumbers. As verified through resolved emission spectra for many of the bands, presented below, all assigned bands involve transitions out of the ground vibronic level. In the following, we use the labeling of the vibrational modes given previously.[10,22]

Our band transition wavenumbers for the assigned bands can be fitted, following the vibrational assignments of Verma and

TABLE 2: Vibrational Constants and Excitation Energy for the Ground and Excited Electronic States of PO_2 (in cm^{-1})[a]

	electronic state	
parameter	X^2A_1	upper
T_0	0	30392.8(19)
ω_1	1075.4(50)	935.9(14)
ω_2	397.3(43)	389.53(68)
x_{11}	−1.6(9)	−3.25(28)
x_{22}		0.26(7)
x_{12}		−2.17(20)

[a] Quoted uncertainties are one standard deviation in units of the last significant digit. The spectroscopic parameters for the ground $\tilde{X}^2A_1$ and the upper electronic states were determined from spectroscopic analyses of resolved fluorescence emission and laser fluorescence excitation spectra, respectively.

McCarthy, as indicated in Table 1. The observed bands involve excitation of the symmetric P−O stretch (ν_1') and/or the bend (ν_2'). The energies of the excited vibronic levels can be expressed as[23]

$$T_v' = T_0 + \sum_i \omega_i' v_i' + \sum_{i,j} x_{ij}' v_i' v_j' \qquad (1)$$

A least-squares fit of the transition wavenumbers yielded the spectroscopic constants reported in Table 2. These parameters are in reasonable agreement with those reported by Verma and McCarthy.[10] Several of the weaker observed bands at lower transition wavenumbers could not be vibrationally assigned. These include the bands at 31017, 31419, and 31713 cm^{-1}.

3.2. Resolved Fluorescence Spectra. Resolved fluorescence emission spectra were recorded for excitation of a number of the bands shown in Figure 1. Fluorescence spectra to low-lying vibrational levels in the ground state were recorded with the monochromator in the second diffraction order. Typical spectra, for emission to $\tilde{X}^2A_1$ vibrational levels with energies ≤4000 cm^{-1}, are shown in Figure 2. In these spectra, as well as in other recorded spectra, no emission was observed to the blue of the excitation wavenumber. This indicates that the bands involve transitions out of the $PO_2(\tilde{X}^2A_1)$ ground vibrational level. The spectral resolution here is significantly better than that obtained by Hamilton.[12]

As in the excitation spectra reported in the previous section, emission occurred to levels involving excitation of the symmetric P−O stretch (ν_1'') and the bend (ν_2'') only. Table 3 presents measured vibrational energies in the $\tilde{X}^2A_1$ state for those levels for which a confident vibrational assignment could be made. To determine vibrational constants for the $\tilde{X}^2A_1$ state, the energies reported in Table 3 were fitted to eq 1. The derived parameters are reported in Table 2. It can be seen that both the symmetric P−O stretch and the bend vibrational frequencies are somewhat larger in the ground electronic state than in the excited state. The harmonic frequencies ω_1'' and ω_2'' are in reasonable agreement with the best estimates from ab initio calculations for the $\tilde{X}^2A_1$ state. Cai et al.[22] report values of 1052 and 389 cm^{-1}, respectively, from calculations at the MRD-CI level.

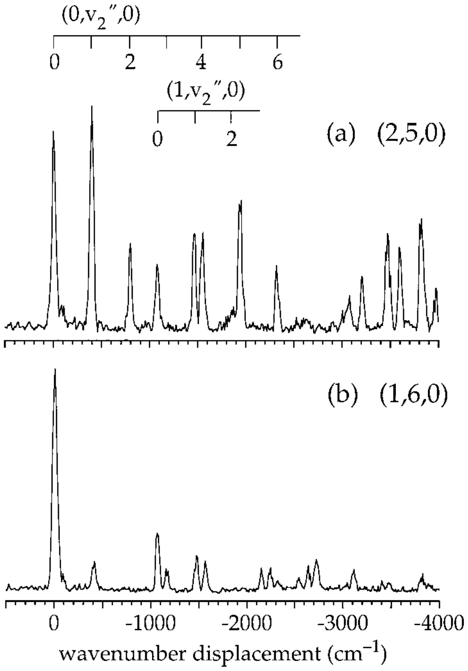

Figure 2. Resolved emission spectrum (in the second diffraction order of the spectrometer) for excitation of the (a) (2,5,0) and (b) (1,6,0) excited vibronic levels, plotted as a function of the displacement of the emission wavenumber from the excitation wavenumber. Progressions in the lower-state bend vibrational mode ν_2'' are indicated.

TABLE 3: Vibrational Energy Levels in the $PO_2(X^2A_1)$ Electronic State (in cm^{-1})[a]

(v_1'',v_2'',v_3'')	energy (cm^{-1})
(0,1,0)	397
(0,2,0)	794
(1,0,0)	1076
(0,3,0)	1175
(1,1,0)	1470
(0,4,0)	1560
(1,2,0)	1866
(0,5,0)	1948
(2,0,0)	2144
(0,6,0)	2328

[a] As determined from resolved emission spectra. The energies were determined to a standard deviation of 12 cm^{-1}.

The fluorescence emission to the excited vibronic levels actually extends far from the excitation wavenumber. Figure 3 presents the emission spectrum for preparation of the (2,5,0) excited vibronic level, recorded in the first diffraction order. The emission appears to reach a maximum intensity at a displacement of ca. 12000 cm^{-1} and extends as far as 17000 cm^{-1} to the red of the excitation wavenumber. The fluorescence spectrum thus undoubtedly involves transitions to low-lying electronic states, as well as to excited vibrational levels in the ground $\tilde{X}^2A_1$ state.

3.3. Rotational Structure. We also recorded high-resolution scans of a number of the observed bands. Figure 4 presents several such scans. These spectra illustrate the complicated rotational profiles that we observe for the excitation of the PO_2 bands. Based on our previous spectroscopic studies of jet-cooled iron-containing molecules in this apparatus,[28] we estimate that the PO_2 rotational temperature should be 15−20 K. No hint of the *K*-structure assigned by Verma and McCarthy[10] is discernible in the spectra displayed in Figure 4 or in recorded spectra of other bands. It should be noted that the ratio of the populations of the $PO_2(\tilde{X}^2A_1)$ $K'' = 1$ to $K'' = 0$ manifolds is calculated to equal 1.4 for a temperature of 15 K. In all cases, the feature assigned by Verma and McCarthy as the $K' = 0 \leftarrow K'' = 0$ subband appears as the strongest feature in our spectra.

Our analysis of these bands should be facilitated by the availability[13,14] of precise spectroscopic constants for the $\tilde{X}^2A_1$ ground vibrational level. We have compared our recorded spectra with simulated[29] spectra, based on the assumption of a type-A transition ($^2B_2$ excited state) or a type-C transition ($^2B_1$ excited state) and various values for the excited state rotational

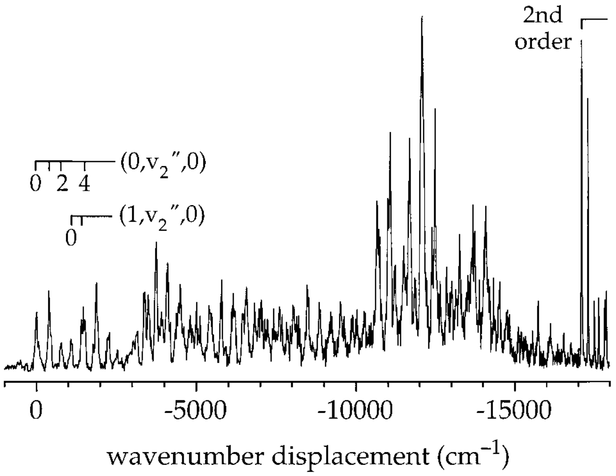

Figure 3. Resolved emission spectrum (in the first diffraction order of the spectrometer) for excitation of the (2,5,0) excited vibronic level, plotted as a function of the displacement of the emission wavenumber from the excitation wavenumber. Progressions in the lower-state bend vibrational mode ν_2'' are indicated. The onset of emission in the second diffraction order (displayed in Figure 2a) is indicated. The intensities were not corrected for the wavelength response of the detection system.

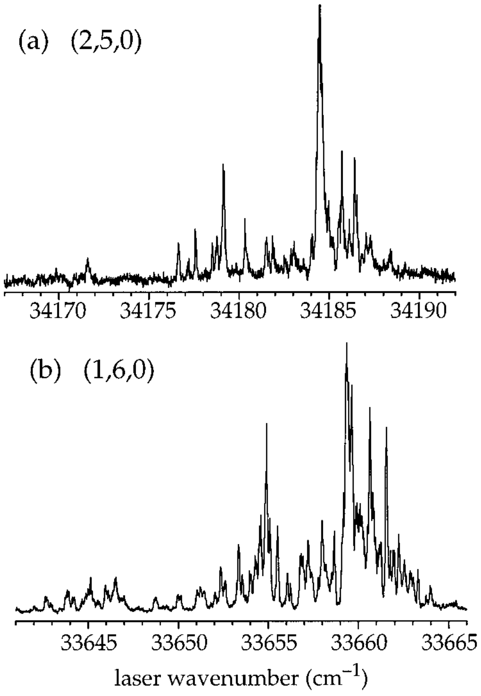

Figure 4. High-resolution scans of the transitions to the (a) (2,5,0) and (b) (1,6,0) excited vibronic levels.

constants. In no case was a satisfactory, even qualitatively correct, simulation of the experimental spectra achieved. It was also not possible to make confident line assignments by ground-state combination differences.

The complicated appearance of the rotational contours both in the spectra displayed in Figure 4 and in recorded spectra of other bands strongly suggests that the rotational structure in the excited vibronic levels is irregular. Hence, a definite assignment of the symmetry of the excited state could not be made. We note, in particular, that the spectrum is not consistent with the assumption of a linear excited state, e.g., 1^2B_1 ($1^2\Pi_u$). In this case, the rotational contours of levels with even and odd quanta of the bend vibrational excitation (ν_2') should be different.[23] Also, with our low beam rotational temperature, the intensities of bands involving even and odd values of ν_2' should be different since these bands will involve mainly excitation of $K'' = 1$ and 0 levels, respectively. Such systematic variations were not observed in our spectra.

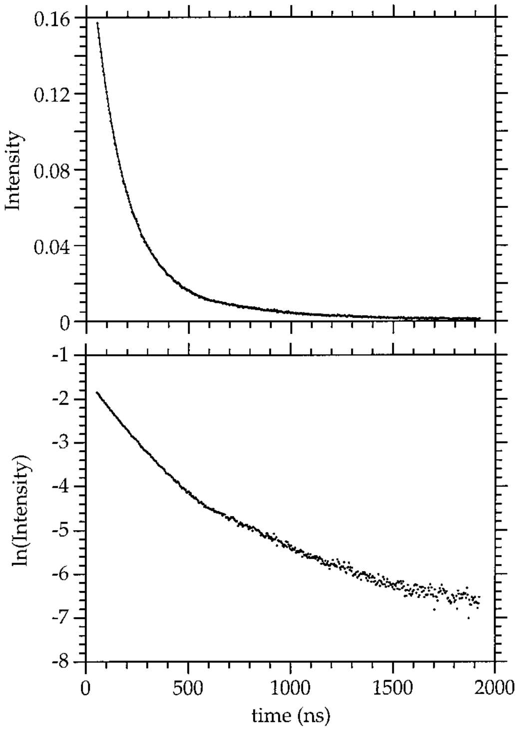

Figure 5. Fluorescence decay waveform for excitation of the (2,5,0) excited vibronic level (first entry for this vibronic level in Table 4). The top panel displays the waveform (solid circles), while the solid line is the curve computed with parameters from the least-squares fit to eq 1. The bottom panel presents a semilogarithmic plot of the same experimental data.

3.4. Decay Lifetimes. Decay lifetimes for a number of excited vibronic levels were determined from recorded fluorescence decay waveforms. The acquisition of these waveforms is described in the Experimental section. All of the waveforms displayed nonexponential behavior, as illustrated by the waveform and a semilogarithmic plot displayed in the two panels of Figure 5.

The waveforms were fitted to a double exponential of the form

$$I(t) = A \exp(-t/\tau_1) + B \exp(-t/\tau_2) \qquad (2)$$

where τ_1 and τ_2 are the short and long lifetimes, respectively, of the two components, and A and B are their respective amplitudes. A nonlinear least-squares fit of the decay profile to eq 2 was performed in order to derive the lifetimes. In all cases, the short lifetime τ_1 was more precisely determined and varied from 80 to 250 ns. These lifetimes are tabulated in Table 4 as a function of the excited-state vibrational quantum numbers v_1' and v_2'.

The relative intensity of the long-lived component [i.e., ratio B/A, see eq 2] was less than 10%, and there was significant uncertainty in the determined values of τ_2, which ranged from 480 to 1000 ns. Under our experimental conditions, collisional electronic quenching is not significant for the determination of decay (radiative) lifetimes of the order of 100 ns unless the quenching cross section is larger than 100 Å^2, based on the estimated[30] collision frequency within the molecular beam. The possible flyout of the molecules from the detector field of view was discussed in the Experimental section.

TABLE 4: Decay Lifetimes (in ns) for Electronically Excited PO_2 Vibronic Levels[a]

ν_2'	ν_1'				
	0	1	2	3	4
0			133 ± 23		
1			137 ± 6[b] 106 ± 6	192 ± 13	
2		84 ± 3	168 ± 11 134 ± 4[b]	128 ± 3	85 ± 2[b] 117 ± 8
3		148 ± 7	168 ± 8[b] 139 ± 4	129 ± 4[b] 97 ± 4	
4	97 ± 6	102 ± 6[b] 90 ± 3	173 ± 4[b] 172 ± 8	130 ± 3[b] 136 ± 10	
5	210 ± 21	173 ± 16 157 ± 3[b]	149 ± 2[b] 164 ± 12 147 ± 11	171 ± 16	
6	144 ± 10[b] 170 ± 11	185 ± 8[b] 172 ± 18	274 ± 59 192 ± 8[b]		
7	185 ± 13[b] 214 ± 9	85 ± 2 170 ± 14[b] 205 ± 32 110 ± 5	157 ± 7 200 ± 24 138 ± 7[b]		
8	163 ± 10[b] 101 ± 5	84 ± 3[b] 239 ± 36			
9		172 ± 26			

[a] Within each vibrational level, the lifetimes τ_1 of the fast components [see eq 2] are reported in order of decreasing excitation wavenumbers. [b] For vibronic levels for which more than one lifetime is reported, this value corresponds to excitation of the strongest feature in the rotational contour.

The lifetimes τ_1 of the short-lived component, presented in Table 4, do not display any obvious systematic variation with the excited-state vibrational quantum numbers. For all excited vibrational levels, lifetime measurements were carried out with excitation of the strongest feature in the rotational contour. Based on the high-resolution scans reported in the previous section, several excited rotational levels were prepared in this excitation scheme. In addition to excitation of the strongest feature, for many bands, several additional features were excited within the rotational contour, and lifetimes for the relevant upper levels determined. These are also reported in Table 4. It can be seen that the variation of the lifetimes for excitation of different groups of rotational levels within a given vibrational level is comparable to the variation of the lifetimes for different vibrational levels. This, as well as the observed nonexponential decay, indicates that the lifetimes depend strongly on the rotational level excited.

4. Discussion

In this paper, an investigation of the UV transition in the PO_2 radical was carried out through laser fluorescence excitation spectroscopy with a jet-cooled beam containing the radical. This work extends previous flash photolysis absorption[10] and laser fluorescence excitation[12] studies. A number of bands were newly observed in the excitation spectrum, in particular at transition wavenumbers less than those of the previously observed bands. The vibrational assignment of Verma and McCarthy[10] could be extended to the newly observed bands.

Despite the relatively low beam rotational temperature, the rotational contours of the bands defied analysis. The rotational structure of the excited state appears to be irregular, and we could not deduce the symmetry of the excited state. These observations suggest that there is significant electronic state mixing in the excited vibronic levels. This point is addressed further in our discussion below of the excited-state lifetimes.

In the resolved fluorescence spectra, we observed emission to excited vibrational levels in the ground $\tilde{X}^2A_1$ electronic state. The energies of the lower vibrational levels were determined, and an improved vibrational analysis was carried out. In both the excitation and emission spectra, vibrational activity was found only in the symmetric P−O stretch (ν_1) and the bend (ν_2). A precise value for the asymmetric P−O stretch (ν_3'') in the ground electronic state was previously determined in a high-resolution infrared study.[14]

The most intense portions of the emission spectra appear at approximately 12000 cm^{-1} to the red of the excitation wavenumber. This emission appears to involve transitions to low-lying excited electronic states. From the emission spectra and the excitation wavenumber, the energy of these states is estimated to be ca. 22000 cm^{-1}, or 2.7 eV, above that of the ground vibronic level. This is quite close to the calculated vertical excitation energies of the low-lying 1^2B_2 and 1^2A_2 states, whose excitation energies are calculated by Cai et al.[22] to equal 2.59 and 2.63 eV, respectively. This strongly suggests that this red-shifted emission involves a transition from the upper level of the UV transition to one or both of these low-lying electronic states.

Despite the low internal temperature of the supersonic beam, the rotational structure of the bands was found to be quite complicated, and it was not possible to carry out a rotational analysis of the bands. It should be noted that the identity of the molecular carrier of these bands seems firm. The bands we observe are undoubtedly identical with those originally reported in the original flash photolysis study of Verma and McCarthy[10] and the laser fluorescence study of Hamilton.[12] Through ^{18}O isotope substitution, Verma and McCarthy proved that the carrier possesses oxygen atoms. The presence of a phosphorus atom in the carrier is firm since identical spectra were observed with PCl_3 and PBr_3 precursor. Their production method was similar to ours, though at higher total pressure, i.e., photolysis of mixtures containing PCl_3 or PBr_3 and O_2.

In addition to characterizing the three lowest excited electronic states, Cai et al.[22] also computed vertical excitation energies of a number of excited states. Within the energy range under consideration, they report a state of $^2B_2$ symmetry which lies only 0.1 eV above the 1^2B_1 state. These two states are both strong candidates for the excited state of the UV transition. Cai et al.[22] computed vibrational frequencies $\omega_1' = 926$ and $\omega_2' = 400$ cm^{-1} for the 1^2B_1 state. These values are in reasonable agreement with our experimental values, reported in Table 2. Unfortunately, there is no theoretical calculation available for the equilibrium geometries and vibrational frequencies of the 2^2B_2 state.

It should also be noted that the energy of the upper state of the UV transition is below that of the $PO_2 \rightarrow PO + O$ dissociation limit, which equals 5.24 eV.[31] This implies that the ground electronic state is bound at the energies of the upper state of the UV transition. The observed complex rotational structure of the bands can be explained by mixing of the excited electronic state(s) with highly excited $\tilde{X}^2A_1$ vibrational levels. This is similar to the situation in the isovalent NO_2 molecule,[32,33] for which the electronic state mixing is so strong that the vibronic structure is also irregular. This point is addressed in further detail by examination of the measured excited-state radiative lifetimes.

It is of interest to compare the decay lifetimes measured in this work with those reported by Hamilton.[1] In his experiment, the decay waveforms were recorded as a function of the total pressure, and the zero-pressure radiative decay rates and electronic collisional quenching rate constants were derived. For each excited vibronic level, laser excitation was carried out at the band head, and it should be noted that the rotational temperature of the PO_2 was approximately room temperature in the discharge-flow apparatus. As in the present study, the decay profiles were found to be nonexponential and were fitted to the biexponential form given in eq 2. The relative contribution of the long-lifetime component to the decay profile was found to be greater [i.e., larger values of the ratio B/A, see eq 2] than in the present study.

There is considerable overlap of the excited vibronic levels for which decay lifetimes are reported by Hamilton[1] and in the present study. The zero-pressure lifetimes τ_1 of the fast-decay components reported by Hamilton range from 0.24 to 1.4 μs and hence are considerably longer than the values reported in Table 4. Moreover, in contrast to our measurements, Hamilton observed that there was a tendency toward longer lifetimes τ_1 with increasing bend vibrational excitation v_2'. In addition, the short lifetimes τ_1 showed a correlation with the ratio B/A of the long and short components of the fitted biexponential decay.

There is no necessary disagreement between our lifetime measurements and those of Hamilton[1] because of the different degrees of rotational excitation of the excited PO_2 molecules in the two experiments. As already noted in our measurements of lifetimes for excitation of different rotational features within the same band, there appears to be a strong dependence of the excited-state lifetime upon the degree of rotational excitation of the excited PO_2 molecules. Because the molecules were excited from an approximately room-temperature rotational state distribution in Hamilton's experiment and a 15−20 K distribution in our study, we expect that lifetimes reported by Hamilton refer to excited molecules with a higher degree of rotational excitation than in the present study. This implies that the excited-state lifetimes increase with increasing rotational excitation.

The observation of increasing radiative lifetimes with increasing rotational excitation allows us to draw some conclusions about the excited-state mixing. Based on the calculations of Cai et al.,[22] the excited-state accessed in the electronic transition can be the 1^2B_1 or 2^2B_2 states, or possibly a mixture of the two. Both of these states have reasonable oscillator strengths from the ground $\tilde{X}^2A_1$ state. From the vertical oscillator strengths, radiative lifetimes of 224 and 37 ns were computed for the transitions to the 1^2B_1 or 2^2B_2 states, respectively.[22]

As noted above, the ground $\tilde{X}^2A_1$ state is bound at the excitation energies of the excited vibronic levels accessed. Increasing rotational excitation would be expected to lead to increased electronic state mixing through Coriolis coupling. Mixing of $\tilde{X}^2A_1$ electronic character into the excited-state wave function would have the effect of increasing the radiative lifetime of the excited vibronic levels. This would provide an explanation for the differences in the radiative lifetimes measured in the present study and those reported by Hamilton.[1] Mixing of the 1^2B_1 and 2^2B_2 states could also be present, but this would be expected to be weaker because of their lower state densities. Moreover, this mixing of these electronic states would not be expected to have such a dramatic effect on the excited-state radiative lifetimes.

In this study, we have found an irregular rotational structure in the excited vibronic manifolds accessed by the UV transition in PO_2. This irregular structure, along with an inferred strong dependence of the excited-state radiative lifetimes on the degree of rotational excitation, strongly suggests that there is electronic state mixing with high vibrational levels of the ground electronic state. This state mixing is strongly reminiscent of the well-known state mixing in the isovalent NO_2 molecule. The radiative decay of nitrogen dioxide excited with visible radiation has been the subject of numerous studies over a number of decades, and this body of work has been reviewed by Johnston and coworkers.[34] There is a strong nonadiabatic interaction in NO_2 between the ground $\tilde{X}^2A_1$ and excited $\tilde{A}^2B_2$ states.[32,33,35] This mixing strongly affects the $\tilde{B}^2B_1 \leftarrow \tilde{X}^2A_1$ electronic transition, which leads to a chaotic vibronic structure by an excitation energy of $\sim$16000 cm^{-1}. By contrast, in the case of the upper level of the PO_2 UV transition, the state mixing is not so severe as to disrupt the vibronic structure.

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