



# Lifetimes and quenching of B 2Σ+ PO by atmospheric gases

Koon Ng Wong, William R. Anderson, Anthony J. Kotlar, Mark A. DeWilde, and Leon J. Decker

Citation: The Journal of Chemical Physics **84**, 81 (1986); doi: 10.1063/1.450136 View online: http://dx.doi.org/10.1063/1.450136 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/84/1?ver=pdfcov Published by the AIP Publishing

## Articles you may be interested in

Quenching of OD (A 2Σ+,v'=0 and 1) by various gases J. Chem. Phys. **87**, 7050 (1987); 10.1063/1.453350

Collisionfree lifetimes and quenching of the A  $2\Sigma$ + state of HS and DS radicals J. Chem. Phys. **79**, 130 (1983); 10.1063/1.445572

Fluorescence excitation spectra, lifetimes, and quenching of S2(B  $3\Sigma u -$ ) in the wavelength region 280–315 nm J. Chem. Phys. **74**, 4951 (1981); 10.1063/1.441748

Quenching of the B 2Σ+ State of the CN Radical J. Chem. Phys. **56**, 95 (1972); 10.1063/1.1676944

Measurement of Lifetimes and Quenching Cross Sections of the B State of I2 J. Chem. Phys. **46**, 2666 (1967); 10.1063/1.1841097



# Lifetimes and quenching of B $^{2}\Sigma^{+}$ PO by atmospheric gases

Koon Ng Wong,<sup>a)</sup> William R. Anderson,<sup>b)</sup> Anthony J. Kotlar, Mark A. DeWilde, and Leon J. Decker

U. S. Army Ballistic Research Laboratory, Aberdeen Proving Ground, Maryland 21005-5066

(Received 14 August 1985; accepted 20 September 1985)

Pulsed laser excited fluorescence in the  $B^2\Sigma^+ \leftarrow X^2\pi$  system of gas phase PO was used to measure the lifetime for v' = 0 of the B state. Rotationally resolved measurements for a few selected J' levels, at Ar or He carrier gas pressures of  $\sim 2$  Torr, reveal no dependence of the lifetime on the rotational level excited. Earlier measurements of relative fluorescence intensities in the v' = 0 vibrational progression were reinterpreted to extract the dependence of the electronic transition moment on internuclear distance. Using this transition moment, no lifetime dependence on rotational level is to be expected, even at low pressures. Rate constants for quenching of the B state PO by N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, and H<sub>2</sub>O, and upper limits thereof for He and Ar are reported. O<sub>2</sub> was found to react with ground state PO. A crude measurement of the rate constant was performed. The result is compared to two other known measurements. The rate constant is in excellent agreement with the previous measurement, but in poor agreement with that of a concurrent study. Further work is required to determine the reason for the discrepancy. A cathode ray-vidicon type waveform digitizer was found to lend itself readily to the lifetime measurements, wherein a low repetition rate laser was used. Unfortunately, it was discovered that small nonlinearities ( $\sim 1\%$  of full scale) in the digitizer response have a marked effect on the fits to the exponential lifetime decays and, especially, the quenching rate constants. We believe this problem is not commonly recognized. A simple method for calibration of this type of digitizer and removal of these effects is presented.

### **I. INTRODUCTION**

The emission and absorption spectra of PO have been studied extensively for over 50 years.<sup>1,2</sup> The many studies of Verma and co-workers<sup>3</sup> and of Coquart and co-workers<sup>4</sup> have been of special value in determining the relevant electronic states and rotational-vibrational structure of the molecule. In more recent years, other experimental techniques including chemiluminescence, laser excited fluorescence (LEF), multiphoton ionization (MPI), matrix isolation, laser magnetic resonance (LMR), microwave spectroscopy, and infrared diode laser spectroscopy have been brought to bear on the molecule. In 1976 Van Zee and Khan<sup>5</sup> reported the chemiluminescence spectra of phosphorus burning at atmospheric pressure in air with added  $H_2O$  (or  $D_2O$ ) vapor. Temperature dependent studies of the PO  $A^{2}\Sigma^{+} \rightarrow X^{2}\pi (\sim 247.0 \text{ nm})$  and  $B^{2}\Sigma^{+} \rightarrow X^{2}\pi (\sim 325.0 \text{ nm})$ nm) emissions, the HPO (or DPO)  $\widetilde{A} {}^{1}A {}^{"} \rightarrow \widetilde{X} {}^{1}A {}^{'}$  emission  $(\sim 525.0 \text{ nm})$ , and of a broadband underlying continuum  $(\sim 350-650 \text{ nm})$  were performed. The continuum was tentatively assigned to a (PO)<sup>\*</sup> excimer. Clyne and Heaven<sup>6</sup> first reported LEF of the PO radical, pumped in the B-X system, and measured the B state lifetime and quenching rate by  $N_2$ . More recently, we formed PO in a microwave discharge through dimethyl-methylphosphonate [DMMP, (CH<sub>3</sub>O)<sub>2</sub>  $(P = O)CH_3$ ]. The LEF technique was used to measure relative intensities emitted upon pumping v' = 0 in the B state<sup>7</sup> and lifetimes for both the A and B states.<sup>8</sup> Long and coworkers<sup>9</sup> used LEF of PO in the A-X system to study KrF

J. Chem. Phys. 84 (1), 1 January 1986

0021-9606/86/010081-10\$02.10

lifetime measured for the A state was in good agreement with our measurement. In addition, the quenching rates of the A state by  $N_2$  and  $O_2$ , the reaction of PO with  $O_2$  and the photofragmentation dynamics were studied. MPI spectra of PO were first observed by Smyth and Mallard.<sup>10</sup> PO was formed from phosphine (PH<sub>3</sub>), present as a trace impurity, in an acetylene-air flame. Wittig and co-workers<sup>11</sup> later used MPI spectra of the PO radical to study the infrared  $(CO_2 \text{ laser})$ photofragmentation dynamics of a number of organophosphorus compounds. A high degree of similarity was found in the PO spectra for the different compounds indicating similar photofragmentation dynamics for each. Larzilliere and Jacox<sup>12</sup> used low temperature matrix isolation to study PO, as well as other radicals, formed by vacuum ultraviolet irradiation of Ar/PH<sub>3</sub>/N<sub>2</sub>O mixtures and by reaction of PH<sub>3</sub> with the microwave discharge products of O2. Finally, Hirota and co-workers<sup>13,14</sup> have used far-infrared LMR, microwave spectroscopy, and infrared diode laser spectroscopy to measure molecular constants for the ground state.

(248 nm) and Ar F (193 nm) laser photolysis of DMMP. The

There have been several *ab initio* studies concerning the ground and excited electronic states of PO.<sup>15-20</sup> The bound nature of the  $B^2\Sigma^+$  state of PO has been of particular interest. For NO a bound state equivalent to the *B* state of PO is not observed. The earliest study concluded that the *B* state is a valence state.<sup>15</sup> Another study, however, concluded that this state is of at least partial Rydberg character.<sup>17</sup> Later calculations showed that a bound  ${}^{2}\Sigma^+$  state would result if atomic Rydberg orbitals were included in the basis set.<sup>18</sup> However, Ghosh and Verma<sup>3(c)</sup> did not include the *B* state in their assignments of  ${}^{2}\Sigma^+$  Rydberg states leading to  ${}^{1}\Sigma^+$  PO<sup>+</sup>. Moreover, because of their very diffuse nature, large

<sup>\*)</sup> NAS-NRC Postdoctoral Research Associate.

<sup>&</sup>lt;sup>b)</sup> Author to whom correspondence should be addressed.

energy shifts from the gas phase values are expected for Rydberg states in matrix isolation experiments.<sup>12(b)</sup> Only a small shift is observed for the *B* state of PO. The most recent theoretical work which includes excited state calculations<sup>19</sup> has arrived at the conclusion that this state owes its bound nature to diffuse molecular orbitals, although it is not a Rydberg state. Evidently if this is the case, the state is not diffuse enough to interact appreciably with the Ar matrix. In a crossing allowed model, the *B* state would dissociate to  $P(^2D) + O(^3P)$ . However, because of avoided curve crossings, the calculations indicate that this state dissociates to  $P(^4S) + O(^3P)$ , the ground state atoms. Note that these are all valence products, indicating the *B* state is *not* a Rydberg state.

We are interested in the PO radical because of its importance in several proposed laser photolysis detection schemes for organophosphonate esters under atmospheric conditions. For this reason, interactions of the radical with atmospheric constituents were studied. Lifetimes for the B state and its quenching rate constants by N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, and H<sub>2</sub>O were measured. Upper limits were also determined for quenching rates by Ar and He. In addition, PO was found to react with O<sub>2</sub>. A crude measurement of the reaction rate constant at 300 K was performed and is compared to two other measurements of this constant. In preliminary measurements,<sup>21</sup> the lifetimes and, hence, quenching rate constants were known to be affected by a slight nonlinearity in the waveform digitizer (Tektronix model 7912 AD) used for the experiments. The waveform digitizer has been calibrated making it possible to deconvolute the data and extract the correct lifetimes. Corrections of up to 15%-20% in the quenching rate constants were found. Details of the deconvolution procedure will be presented. In addition, a much more detailed description of the apparatus and discussion of results is given than appeared previously.

#### **II. EXPERIMENTAL**

For the production of PO an inert carrier gas was bubbled through a U tube containing DMMP. After bubbling through the DMMP, additional carrier gas was added to the system to optimize conditions for the production of PO. Except for the inert gas quenching rate constant measurements, usually about 2 Torr of carrier gas was used. Ar was used as the carrier gas in most of the experiments except for the measurement of the He quenching rate when He was used. The inert gas-DMMP mixture flowed through a microwave discharge (2450 MHz) where PO was formed. Quencher gases were introduced to the flow through a needle valve 9 cm downstream from the discharge. A further 9 cm downstream fluorescence of PO was excited by the output of a Nd:YAG pumped dye laser system. Pressures were measured using a Datametrics capacitance manometer mounted next to the laser excitation point. Prior to the experiments the manometer was checked against another capacitance manometer and against an NBS traceable calibrated thermocouple gauge. In one experiment the temperature at the laser excitation point was measured under typical flow conditions using a Chromel-Alumel thermocouple and found to be  $303 \pm 5$  K.

The present experimental arrangement allows for a much higher partial pressure of DMMP to be added to the flow than in our earlier experiments<sup>7</sup> and for much greater control over the flows. In the earlier work, DMMP contained in a glass bulb was simply allowed to vaporize into the inert gas flow. For that work we quoted a DMMP partial pressure of about 70 mTorr. However, the thermocouple pressure gauge used for the measurement was unreliable. We are quite certain that the previous measurement is in error. From comparative sizes of the PO fluorescence signals it is known that the present bubbling technique allows us to get a much higher partial pressure of DMMP into the system. The present experimental arrangement does not allow for a direct measurement of the partial pressure. By weighing a sample of DMMP, running the system under typical operating conditions for a known period of time and then measuring the sample loss, we find the pressure of DMMP in the present experiments is less than 1 mTorr. The earlier measurement<sup>7</sup> of 70 mTorr of DMMP for the bulb vaporization system, and the calculation of the PO yield from DMMP passed through the microwave discharge which was based upon this partial pressure, should not be trusted.

The exact purity of the Ar and He carrier gases is unknown but, as will be seen, these gases caused no quenching within our error limits so that their purity is not a major concern. The CO<sub>2</sub> was greater than 99.9% pure. The N<sub>2</sub> used was purified by passage through a Matheson model 462 gas purifier which removes heavy hydrocarbons and water. This should result in a purity of greater than 99.9%. No difference was found in quenching rates with or without purification. Since O<sub>2</sub> was found to react with PO, very low O<sub>2</sub> pressures had to be used in the system (<60 mTorr) in order to get sufficient PO signal for analysis. These low pressures required that the backing pressure of O<sub>2</sub> be lower than required for use of the Matheson purifier. Therefore, the purifier could not be used. The O2 was checked by gas chromatographic analysis and found to be  $\sim 99.9\%$  pure.<sup>22</sup> For the addition of H<sub>2</sub>O, distilled H<sub>2</sub>O in a bulb was pumped upon until it had boiled for several minutes to remove absorbed gases. An electrical heating pad was used during the experiments to maintain steady H<sub>2</sub>O backing pressure.

The PO was excited in the B-X (0, 0) band at ~ 325 nm. The output of a Nd:YAG pumped dye laser (Quantel, model TDL III) using Rhodamine 6G dye was frequency doubled to obtain ~ 286 nm radiation. The fundamental and doubled beams were passed collinearly through a hydrogen Raman shifter cell (Quanta-Ray, model RS-1). Bischel *et al.*<sup>23</sup> have found shifter cell conversion efficiencies of a 314 nm beam from doubled Rhodamine 640 to be 4-5 times greater if the fundamental beam is included than if it is not. We observed similar enhancement at our wavelength. The 325 nm radiation was obtained as the first Stokes shifted beam. The output was pulsed at 10 Hz. The pulses had a duration of ~ 10 ns and, under ideal conditions, an energy of ~ 1 mJ. The linewidth was about 0.3 cm<sup>-1</sup>.

PO fluorescence exiting the system at right angles to the laser beam was imaged onto a bandpass filtered photomultiplier (PMT). The filtered PMT configuration was used for all of the present lifetime measurements. The filter passed the PO B-X fluorescence with a transmission of about 50%. The PMT was an RCA type 4832 wired for fast time response.<sup>24</sup> Care was taken to avoid saturating the PMT. Output from the PMT was analyzed by a Tektronix model 7912AD waveform digitizer with 7A19 vertical amplifier and 7B90P timebase. The detection system had an overall response time of about 1.5 ns. The waveform digitizer output was averaged and stored for later analysis by a PDP 11/03 computer.

#### **III. WAVEFORM DIGITIZER CALIBRATION**

The 7912AD digitizer sweeps an electron beam, controlled much like an ordinary oscilloscope beam, across the face of a vidicon detector array. The waveform thus stored is read back and digitized by the vidicon electronics using a raster type scanning format under the control of an internal microcomputer. The raster scan divides the vidicon screen into a  $512 \times 512$  format. The digitizer then determines the position of the waveform in each of the 512 X (time) "channels". The digitizer sends the waveform to the laboratory computer as a vector of 512 numbers.<sup>25</sup> It should be noted that because of a small amount of random noise in the input stage of the digitizer, computer averaging of waveforms from a large number of laser pulses generally results in a resolution much better than 1 part in 512, the limitation for a single sweep. This type of waveform digitizer has the advantage that very high sweep rates can be used for waveform storage. The waveform may then be read back and digitized at a slower rate. In addition, the entire decay curve for a given laser pulse is captured and stored. The latter advantage is very important when one is using low repetition rate lasers because it greatly reduces the waveform acquisition time. Thus, it is very desirable to be able to use this type of instrument for lifetime measurements. Unfortunately, as mentioned in the introduction, a slight nonlinearity in the waveform digitizer response (up to 1% of full scale) is inherent in this type of digitizer. As will be seen, the effect somewhat complicates data analysis. The nonlinearity was observed to have large effects on the lifetimes extracted from the fluorescence decay curves. The effect was first discovered as an inconsistency in the lifetimes extracted on different days. The lifetimes differed by up to 20%, depending on signal levels used, for no apparent reason. The problem was traced to the digitizer by using a decay curve which covered approximately one fourth of vertical full scale. This decay curve was moved alternately to the top and bottom halves of the vidicon screen without changing experimental conditions. The decay was measured (100 laser pulse averages) in both positions several times in an alternate fashion in order to eliminate the possibility that systematic drifts might affect the results. The decay curves were fitted using a nonlinear least-squares routine<sup>27</sup> to the functional form

$$I = A \exp(-t/\tau) + B, \tag{1}$$

where A is the waveform amplitude, t is the time after the laser pulse,  $\tau$  is the observed lifetime, and B is the base line. A,  $\tau$ , and B are allowed to vary in the fit. Some typical results are shown in Table I in the "uncorrected" column. The average and spread in the results (one standard deviation) are also shown. Note that the fitted  $\tau$ 's differ systematically by  $\sim 8\%$ 

	Position on digitizer screen	$\tau(ns)$		
Run		Uncorrected	Corrected	
1	······································	245.6	256.0	
2	Upper half	255.4	265.9	
3	• • • •	256.4	265.9	
	Average	$252.5 \pm 6.0$	262.6 ± 5.7	
4		278.3	269.8	
5	Lower half	269.7	263.5	
6		269.8	267.4	
	Average	272.6 ± 4.9	266.9 ± 3.2	

<sup>a</sup> The data were taken upon pumping in the  $Q_1 + {}^{Q}P_{21}$  head of the *B*-X (0,0) band. About 2 Torr of Ar carrier gas was used. The digitizer settings were 500 mV/div vertical and 100 ns/div horizontal.

and the averages do not agree within one standard deviation. This was consistently found to be the case for a large number of runs, though the differences in extracted lifetimes were sometimes larger depending on the experimental conditions, in particular the size of the waveform.

The waveform digitizer was calibrated and the waveforms were corrected for distortion produced by the nonlinearity in the following manner. First, a time mark generator (Tektronix model TG501), which generates very precisely and accurately spaced, short pulses, was used to check for nonlinearities in the X coordinate. It was determined by displacing the time mark generator trace vertically to several different positions that the time mark pulses always appeared in the same X channel no matter what vertical displacement was used. This fact is very important because it means that distortions in the X and Y (vertical) directions are decoupled which vastly simplifies calibration and deconvolution procedures. The X direction was calibrated by fitting the channel numbers at which the leading edges of about 10 time marks were observed to a simple quadratic equation

$$t = a_0 + a_1 X + a_2 X^2, (2)$$

where t is the known time at which a given time mark should be observed, X is the channel number at which the leading edge of the pulse was observed and the  $a_i$ 's are fitting constants. Note that the value of  $a_0$  fitted in this manner is somewhat arbitrary, but this does not affect the results. [It was later discovered after the Y calibration described below was performed that upon deconvolution equivalent values of  $\tau$ were obtained from any curve whether a linear or quadratic form was chosen for Eq. (2). The quadratic term was therefore dropped in later work.] The Y response was calibrated using a variable power supply hooked in parallel to a  $4 \frac{1}{2}$ digit voltmeter. About 20 different voltages covering the Y scale were then selected as input for the digitizer. For each voltage 100 sweeps of the digitizer were averaged. The observed digitizer response for each of the 512 X channels to the known voltages was then fitted to a fifth order polynomial.

$$V_i = \sum_{j=0}^{5} b_j y_{ij}^{j}, \quad i = 1, 2, \dots, 512,$$
(3)

TA	BLE	II. R6	C circuit	decay	constant	measurement.*
----	-----	--------	-----------	-------	----------	---------------

<b>n</b> 1.1	$RC$ constant ( $\mu$ s)		
Position on digitizer screen	Uncorrected	Corrected	
Upper half	0.91	1.01	
Middle	0.99	1.02	
Lower half	1.04	1.01	

<sup>a</sup> The data were taken using digitizer settings of 1 V/div vertical and 1  $\mu$ s/ div horizontal. The value of RC found by separately measuring R and C in the input circuit was  $1.04 \pm 0.02 \,\mu s$ .

where *i* is the channel number,  $V_i$  is the input voltage,  $y_{ij}$  is the digitizer response, and the  $b_i$ 's are fitting constants. Evaluation of the  $a_i$  and  $b_i$  completed the calibration procedure. For a given output waveform from the digitizer, the input waveform was reconstructed by substituting the output waveform into Eqs. (2) and (3) using the fitting constants obtained for the appropriate voltage and timescales.

To illustrate the validity of our technique an RC circuit of known decay constant was used. The resistance and capacitance were separately measured yielding an RC constant of  $1.04 \pm 0.02 \,\mu$ s. A pulse generator's square wave used as input to this simple circuit resulted in a repetitive pulse with the exponential decay constant given above. This waveform had extremely high signal to noise ratio, was very reproducible and was adjusted to cover  $\sim 1/4$  of full scale on the digitizer. Three 100 pulse averages were taken, one each near the top, middle and bottom of the digitizer screen. The decay constants which resulted from fits of the waveforms to Eq. (1) prior to deconvolution are shown in Table II in the column labeled "uncorrected." Note that the spread in the results is  $\sim 12\%$ . These three waveforms were then deconvoluted using Eqs. (2) and (3) and the resulting corrected waveforms fitted to Eq. (1). The resulting spread in decay constants is less than 1% (see Table II). In addition, the average of the three results,  $1.01 \pm 0.01 \,\mu$ s, is in good agreement with the predicted decay constant of  $1.04 \pm 0.02 \,\mu$ s. Thus



FIG. 1. Observed fluorescence decay pulse from one of the earliest runs, corrected for waveform distortion. The smooth curve is the least-squares fit to the data. This early run was chosen because it has a much lower signal to noise ratio than later runs, allowing one to clearly see the difference between the observed data and the fit. The fit results in a lifetime of about 260 ns.

encouraged by the agreement among results for our known decay circuit, we then deconvoluted the uncorrected fluorescence data in Table I using the same procedure. The results are shown in the column labeled "corrected." Note that the resulting lifetimes are quite close to each other for data taken at either position on the digitizer. The averages of the results for the two positions on the digitizer overlap within one standard deviation after deconvolution of the waveforms. The agreement in the resulting fluorescence lifetimes and between the predicted and observed decay constants for the RC circuit is strong evidence that the deconvolution procedure yields correct results for the lifetimes. This procedure was used for all of the lifetime measurements in this paper. A corrected decay pulse and least-squares fit from one of the earliest runs is shown in Fig. 1. This fairly simple calibration technique has made it possible to use our digitizer for lifetime studies with confidence.

#### **IV. RESULTS AND DISCUSSION**

### A. Free radiative lifetimes and the electronic transition moment variation with internuclear distance

As will be discussed in Sec. IV B, the excited state of PO is not quenched by Ar, He, or the precursor gas at the pressures used. Therefore, the average of the six corrected lifetimes in Table I represents the free radiative lifetime,  $\tau_r$ , of the PO B state (v' = 0) upon pumping in the  $Q_1 + {}^Q P_{21}$  head of the (0, 0) band. Pumping in the  $Q_1 + {}^QP_{21}$  head results<sup>7</sup> in excitation of rotational levels near J' = 27.5. The resulting free radiative lifetime<sup>28</sup> reported here is  $264.8 \pm 4.8$  ns. This result is in excellent agreement with the only previous measurement,  $\tau_r = 250 \pm 10$  ns, reported by Clyne and Heaven.<sup>6</sup> They similarly excited the B state in the  $Q_1 + {}^QP_{21}$  head of the (0, 0) band.

In preliminary work we reported that some excited state rotational level dependence of the lifetime was observed.<sup>8,21</sup> The lifetimes were observed to increase slowly by about 10% between J' = 5.5 and 20.5. The increase in lifetimes with J' could have been attributed to a decrease in electronic transition moment with increasing internuclear distance. Such a decrease coupled with centrifugal distortion leads to an increase in lifetimes with J' for OH<sup>29</sup> and NH.<sup>30</sup> In fact, as will be shown shortly, a comparison of the measured vibrational band intensities for the v' = 0 progression to calculated Franck-Condon factors (FCFs) leads to the conclusion that the electronic transition moment indeed does decrease with increasing internuclear distance. The lifetimes rapidly decreased above J' = 20.5, which we could not explain. However, after the decay curves were corrected for waveform digitizer distortion, the variation in lifetimes with J' was found to be negligible. Results for a few selected rotational levels excited in the  $P_1$  branch<sup>31</sup> are shown in Table III. Ar carrier was used to obtain the results in the table. Similar results are found for He carrier. Note that given the demonstrated standard deviation of  $\pm 4.8$  ns for measurements from excitation in the  $Q_1 + {}^Q P_{21}$  head, the lifetimes in Table III are all the same. The preliminary report of a smooth variation in the lifetimes with J' is attributed to the waveform digitizer distortion coupled with the smooth variation in the absolute fluorescence decay curve intensities.

TABLE III. Variation of radiative lifetime with rotational level for PO  $(B^2\Sigma^+, v'=0)$ .<sup>a</sup>

J'	$\tau_r$ (ns)	
5.5	258.6	
11.5	256.6	
15.5	262.5	
18.5	265.3	
21.5	262.4	
24.5	257.3	
27.5	264.3	
30.5	262.9	

<sup>a</sup> It should be noted that 2 Torr of Ar carrier gas was used in these measurements, which may cause some rotational relaxation in the excited state (see the text). Excitation was in the  $P_1$  branch of the (0,0) band.

Since rotational relaxation in the excited state will tend to remove any variation in lifetimes with J', attempts were made to measure the lifetimes at very low pressure (< 20mTorr) to minimize relaxation. (A differentially pumped flow system similar to those used previously on OH<sup>32</sup> was tried.) These attempts failed due to low signal levels. However, one can reasonably argue that the rotational relaxation should be far from complete. Studies on OH, NH, CH, C<sub>2</sub>, CN, NCO, and NH<sub>2</sub> fluorescence in atmospheric pressure flames show that although a large amount of rotational redistribution does occur, a large fraction of the excited state population remains in the originally pumped level.<sup>33</sup> One would expect this to be the case at lower pressures as well. Therefore, if there were any large variation in lifetimes with rotational level (say 10%) one would expect some variation in the  $\tau_r$ 's of Table III. Two points further support this argument. First, as previously mentioned, similar results for  $\tau_r$ , vs J' were found for  $\sim 2$  Torr of both Ar and He carrier gases. One would expect these gases to have different cross sections for rotational transfer. Second, as will be discussed in the next section, there is no significant change in the observed lifetime with pressure of Ar or He carrier gases over a range from 0.5–10 Torr while pumping in the  $Q_1 + {}^QP_{21}$  head. We therefore conclude that any variation in  $\tau$ , with J' must be small. McDermid and Laudenslager<sup>34</sup> found a similar lack of variation for rotational levels in v' = 0 of  $A^2 \Sigma^+$  NO.

The lifetimes exhibit little dependence on the rotational level studied but, as previously stated, comparison of the observed vibrational band intensities<sup>7</sup> to calculated FCFs leads to the conclusion that the electronic transition moment decreases as internuclear distance, r, increases. One naturally asks the question why no effect is seen on the rotational state lifetimes. In order to explain this, we present a derivation of the electronic transition moment variation with r and estimate the expected lifetime change with rotational level. The derivation closely follows that presented by Crosley and Lengel.<sup>35</sup> It is well known that the intensity of fluorescence in a given vibrational band, averaged over the rotational levels, is proportional to the Einstein band emission coefficients

$$\mathbf{A}_{v'v'} = (64\pi^4/3hc^3)v_{v'v'}^3 p_{v'v'}, \qquad (4)$$

where h is Planck's constant, c is the speed of light, and  $v_{v'v'}$  is the band frequency. The vibrational transition probability

TABLE IV. Data for the v' = 0 progression in the *B*-X system of PO.

Vibrational band	Normalized $p_{v'v}$ . * (measured)	$q_{v'v^*}$ (RKR calc)	₹ (Å) (RKR calc)
(0,0)	0.9213 ± 0.0071	0.9776	1.47
(0,1)	$0.0720 \pm 0.0076$	0.0194	1.21
(0,2)	$0.0067 \pm 0.0012$	0.00285	1.31
(0,3)	Not detected	0.00014	1.15

\* From Ref. 7.

is given by

$$p_{v'v''} = |\langle \psi_{v'} | R_e(r) | \psi_{v'} \rangle|^2, \qquad (5)$$

where  $R_e(r)$  is the electronic transition moment and  $\psi_{v'}$  and  $\psi_{v'}$  are the excited and ground state vibrational wave functions, respectively. It is often assumed that  $R_e(r)$  is constant in which case one finds

$$p_{v'v''} = R_e^2 q_{v'v''}, (6)$$

where the  $q_{v'v'}$  are the FCFs for the system. In a better approximation one uses the *r* centroids

$$\bar{r}_{v'v^*} = \langle \psi_{v'} | r | \psi_{v^*} \rangle / \langle \psi_{v'} | \psi_{v^*} \rangle.$$
<sup>(7)</sup>

A functional form for  $R_e(r)$  is then chosen. One of the most common is the linear form

$$R_e(r) = c(1 - \rho r), \tag{8}$$

where c and  $\rho$  are constants. Substituting Eq. (8) into Eq. (5), one finds

$$p_{v'v''} = c^2 (1 - \rho \overline{r})^2 q_{v'v''} = R_e^2(\overline{r}) q_{v'v''} . \qquad (9)$$

In our earlier measurements of FCFs the assumption of a constant  $R_e(r)$  was made.<sup>7</sup> The measured "FCFs" reported in Ref. 7 are therefore actually normalized  $p_{v'v'}$  [see Eqs. (4) and (6) which were used with the normalization  $\Sigma_{v'} q_{v'v'} = 1$  to derive the FCFs]. The  $q_{v'v'}$  calculated from the RKR curves<sup>7</sup> are actually better representations of the FCFs for the system. In addition, the RKR calculation yields results for the *r*-centroids. The normalized  $p_{v'v'}$  from the earlier relative intensity measurements, calculated  $q_{v'v'}$  and *r*-centroids for the v' = 0 progression are given in Table IV. From Eq. (9) it is obvious that a plot of  $(p_{v'v'}/q_{v'v'})^{1/2}$  vs  $\bar{r}$  will yield  $\rho$ . Such a plot is given in Fig. 2. The result for  $\rho$  is 0.577  $\pm$  0.010 Å<sup>-1</sup>. This may be compared to  $\rho \simeq 0.7$  Å<sup>-1</sup> for OH<sup>35</sup> and  $\rho \simeq 0.5$  Å<sup>-1</sup> for NH.<sup>36</sup> In order to use this result to predict how much the lifetime will vary with J', one notes that lifetimes for an individual v', J' level are given by

$$\tau_{v'J'}^{-1} = \sum_{v'',J''} A_{v'J'}^{v'J'} , \qquad (10)$$

where the summation over J'' extends over all allowed transitions. Here  $A_{v'J'}^{\nu'J'}$  denotes the Einstein emission coefficient for an individual rotational transition within the (v',v'') band. The effect of centrifugal distortion on r may be calculated for a given rotational level<sup>37</sup> using the molecular constants. (Here, we assume that since selection rules do not allow J''values to be much different than J', it is a reasonable approximation for the present purposes to use an average centrifugal distortion for the entire set of allowed transitions from a given J'.) One finds that J' = 30.5 has r only 0.002 Å



FIG. 2. Plot of  $(p_{v'v^*}/q_{v'v^*})^{1/2}$  vs  $\bar{r}$  for the v' = 0 progression of the *B*-X transition of PO.

longer than J' = 0.5 for B state PO. Now, since most of the emission from v' = 0 is in the (0,0) band (see Table IV) the effects of this amount of centrifugal stretching on  $\tau_r$  may be readily estimated by assuming that  $\bar{r}$  for J' = 0.5 is  $\sim 1.470$ Å (from Table IV) and  $\bar{r}$  for J' = 30.5 is  $\sim 1.472$  Å. The relative values of  $R_e^2(\bar{r})$  for each J' are readily calculated from Eq. (9). One finds  $R_e^2(\bar{r})$  drops by only about 2% as one increases J' from 0.5 to 30.5. Thus,  $\tau_r$  is expected to increase by only about 2% in this range of J'. This is too small an effect to observe in our experiments. It is, therefore, not surprising that  $\tau_r$  exhibits negligible dependence on J'. Since centrifugal stretching is much larger for hydrides, the effect on the lifetimes is observed.

The results of Smyth and Mallard<sup>10</sup> deserve some comment in regard to the r dependence of the electronic transition moment. The two photon ionization spectrum of the B-X system of PO, where the first photon excited the B state and the second caused ionization of this state, was studied in an atmospheric pressure flame in their work. The intensities of bandheads within a number of vibrational bands were measured. In order to determine the relative cross section for the ionization step, the intensity dependence of the absorption cross section for the first photon was factored out by dividing the observed intensities by  $v_{v'v'}^3 q_{v'v''}$ . The  $q_{v'v''}$  were calculated using RKR curves. Heads of the (5,4) and (6,5) transitions appeared to have abnormally high ionization cross sections in comparison to heads of other bands. Smyth and Mallard tentatively ascribed these high cross sections to the excitation of autoionizing states. Several warnings were given concerning their tentative interpretation. One of these was that it is rather difficult to calculate small FCFs for large values of v' and v'' with a high level of accuracy. This problem results because the FCFs represent the difference in the overlap integral of two wave functions with many positive and negative contributions. Indeed, although our RKR calculations yield results for the v' = 0 progression which agree very well with those in Ref. 10, results for the (5,4) and (6,5)

bands do not agree nearly so well. Smyth and Mallard obtained  $q_{v'v''}$  values of  $4.76 \times 10^{-3}$  and  $1.49 \times 10^{-4}$  while we obtain  $7.17 \times 10^{-3}$  and  $1.83 \times 10^{-4}$ , respectively, for these bands. Note that these values disagree by almost a factor of 2 in the case of the (5,4) band.<sup>38</sup> Thus, there is indeed some difficulty in computing these small FCFs accurately. But Smyth and Mallard point out  $q_{5,4}$  and  $q_{6,5}$  would have to be low by 2-3 orders of magnitude to explain the anomalously large ionization cross sections found for heads of these bands. The agreement between the two calculations is much better than this. However, it is the  $p_{y'y'}$  which should be used for calculation of relative cross sections for absorption of the first photon, rather than  $q_{\mu'\nu'}$ . Our RKR calculations yield r-centroids for the (5,3), (5,4), (5,5), (6,4), (6,5), and (6,6) bands of 1.51, 2.33, 1.53, 1.55, 6.80, and 1.54 Å, respectively.<sup>39</sup> Using Eq. (9), one finds the ionization cross sections determined by Smyth and Mallard for heads within the (6,5) band should be reduced by a factor of about 700 relative to cross sections for the (6,4) and (6,6) bandheads. Thus, the very large ionization cross section modulation for the v' = 6progression is removed. Ionization cross sections for the (5,4) bandheads are reduced by only about a factor of 8 relative to those for the (5,3) and (5,5) heads. The large intensity modulation is not entirely removed for heads in the v' = 5 progression, but it is very much reduced. In fact, the ionization cross section for one of the heads of the (5,4) band fits very nicely into the sequence for v' = 5. It is, therefore, highly likely that the dependence of the electronic transition moment on internuclear distance, rather than autoionization, is responsible for the high intensities of the (5,4) and (6,5) bands.

#### B. Quenching of $B^2\Sigma^+$ PO

Quenching rates for  $B^2\Sigma^+$  PO were measured for Ar, He, N<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>O, and O<sub>2</sub>. All of the quenching measurements were made upon excitation in the  $Q_1 + Q_{P_{21}}$  head of the (0,0) band which populates excited state levels near N' = 27. Lifetimes were measured as a function of pressure. These were then fitted using the nonlinear least squares routine to the Stern-Volmer equation cast in the form

$$\tau = (1/\tau_r + k_a P)^{-1}, \tag{11}$$

where  $\tau$  is the observed lifetime,  $k_a$  is the quenching rate constant, and P is the quencher partial pressure. Both  $\tau_r$ , and  $k_a$  are fitted constants, as they are in the more usual linear least squares fits to the inverse form of (11).40 For Ar and He, the lifetimes were determined simply by using Ar or He as inert carrier and varying the carrier gas pressure over the range 0.5-10 Torr. No variation in the lifetimes was observed within error limits. Therefore, only upper limits to the inert gas quenching rates could be determined. The possibility of quenching by the DMMP precursor, or its microwave products, was also checked. This was done by varying flow conditions so that the DMMP partial pressure changed at least a factor of 2 (verified by observing the PO signal level). No effect on the lifetime was observed. This is not surprising since the DMMP partial pressure is less than 1 mTorr. Lifetimes for the other gases were measured by using  $\sim$ 2 Torr of Ar as the carrier gas and adding the desired quenching gas  $(N_2, CO_2, H_2O, or O_2)$  to the flow. The results



FIG. 3. Representative plots of  $1/\tau$  vs. quencher partial pressure. The data are plotted in linear form, but the least-squares lines drawn are from the results of nonlinear fits using Eq. (11).

were similarly fitted to Eq. (11). A few runs were plotted in linear form for purposes of presentation. Results for representative runs for  $N_2$ ,  $CO_2$ , and  $H_2O$  are shown in Fig. 3. The results for all of the gases are summarized in Table V.

There are several comments to make regarding Table V. First, as mentioned earlier, these results differ by up to 15% from those given in our preliminary paper<sup>21</sup> because the systematic effects of waveform digitizer distortion were not previously taken into account. Second,  $k_q$  for  $N_2$  is in reasonable agreement with the result of Clyne and Heaven,<sup>6</sup>  $2.7 \pm 0.1 \times 10^{-10}$  cm<sup>3</sup>/molecule s. Third, results for the molecular species are all very close to the hard sphere collisional rate constants. On the other hand, quenching constants for the inert, monatomic gases are quite small. This is usually found to be the case for quenching of diatomic molecules by inert gases. Finally, the result for O<sub>2</sub> has a very large error limit because O<sub>2</sub> was found to react with ground state PO, as will be discussed further in the next section. The experiments had to be restricted to O<sub>2</sub> pressures of 60 mTorr or less in order to achieve usable signal levels. The large error limit is the result of the lower signal levels and the smaller pressure range used.

TABLE V. Quenching rate constants for atmospheric gases (300 K).

Quencher	$k_Q$ (cm <sup>3</sup> /molecule s)	
N2	$3.28 \pm 0.12 \times 10^{-10}$	
CO	$2.19 \pm 0.09 \times 10^{-10}$	
H-O	$8.44 + 0.29 \times 10^{-10}$	
Ô,	$5.7 + 1.2 \times 10^{-10}$	
Ar	$< 8.0 \times 10^{-13}$	
He	<3.0×10 <sup>-12</sup>	

#### C. Reaction of $X^2 \pi$ PO with O<sub>2</sub>

As noted in the previous section, ground state PO was found to react with O<sub>2</sub>. This is known to be the case because  $I_0$ , the fluorescence intensity at the laser pulse, was found to decrease sharply when small amounts of O2 were added to the system. (Note that the decrease in  $I_0$  cannot be attributed to excited state reactions since such reactions merely affect the excited state quenching rate.) No significant reaction was observed for any of the other quenching gases. It is interesting to note that in their first attempts to make PO for LEF studies Clyne and Heaven<sup>6</sup> used a microwave discharge in  $O_2$  to make  $O({}^3P)$  atoms. They then attempted to make PO by reacting the O atoms with PH<sub>3</sub>. However, no LEF of PO could be found in this way and a different method for PO production had to be used. The original attempts probably failed because of the reaction of PO with O<sub>2</sub>. A yellow-green chemiluminescence was observed in the region where O atoms and PH<sub>3</sub> were mixed. The mixing region was upstream from the laser probe region. The chemiluminescence was probably similar to that seen by Van Zee and Khan<sup>5</sup> and ascribed to the (PO)<sup>\*</sup><sub>2</sub> excimer. One would speculate that PO is also present in this region since Van Zee and Khan observed its emission there.

In the present experiments the concentrations of  $O_2$ used were much higher than the concentration of PO, estimated at ~  $10^{12}$  cm<sup>-3</sup>. In addition, the partial pressure of Ar carrier gas, ~2.4 Torr, was much higher than the highest  $O_2$ pressure used. Thus, the overall pressure and flow rate does not vary appreciably with  $O_2$  partial pressure. It seems reasonable to assume that the loss of PO is due to the reaction

$$\mathbf{PO} + \mathbf{O}_2 \rightarrow \mathbf{PO}_2 + \mathbf{O} \,. \tag{12}$$

Since the concentrations of  $O_2$  used were much greater than that of PO, Reaction (12) is in the pseudo-first-order regime.



FIG. 4. Plot of  $\ln(I_0)$  vs partial pressure of  $O_2$  at a constant input concentration of PO and laser flux.

One may easily show that given these assumptions and a constant input pressure of PO, a plot of  $\ln(I_0)$  vs pressure of  $O_2$  should have a slope of  $k_r \Delta t$ .<sup>41</sup> Here  $k_r$  is the reaction rate constant of (12) at our measured temperature of  $303 \pm 5$  K and  $\Delta t$  is the contact time of the reactants, that is, the time it takes the gases to flow from the point of addition of O2 to the point at which the fluorescence is excited by the laser. Thus, the present results may be used to yield a crude estimate of the reaction rate constant. An example plot for one of the runs made is shown in Fig. 4. (The zero O<sub>2</sub> pressure point was not measured in this run because of dynamic range problems in the detection system. A separate run over the range of 0-30 mTorr was made and indicates that the zero  $O_2$  intercept is at the correct point.) A rough estimate of the flow rate was made using a rotameter. The flow rate implies a contact time of  $\sim 6$  ms for the experimental conditions. This measurement is believed to be good to within a factor of 2. The resulting rate constant is shown in Table VI and compared to the only other known measurements. The present result is in excellent agreement with a prior flow system measurement by Aleksandrov et al.<sup>42</sup> However, Sausa et al.,<sup>9(b)</sup> in work performed at our laboratory, photolyzed DMMP in the presence of O<sub>2</sub> using a KrF laser to produce PO. The PO was monitored as a function of time after the laser pulse using LEF in the A-X system. They obtained a rate constant about

TABLE VI. Measured reaction rate constants for PO +  $O_2 {\rightarrow} \text{products}$  at  $\sim 300$  K.

$k_r$ (cm <sup>3</sup> /molecule s)	Source	
$2.2 \pm 1.0 \times 10^{-13}$	Aleksandrov et al. (Ref. 42)	
1.1 × 10^{-11}	Sausa et al. [Ref. 9(b)]	
$2^{+2}_{-1} \times 10^{-13}$	Present work	

50 times larger than the flow system measurements. At present we are unable to explain the discrepancy in these results.

A possible systematic error which could lead to rate constants which are too small in the flow system measurements is the depletion of the O<sub>2</sub> concentration prior to (or during) the reaction. One way the  $O_2$  could be depleted is if the microwave discharge region reached downstream to the addition point of the O<sub>2</sub> resulting in conversion to O atoms. We checked for this possibility by placing a metal collar around the quartz tube in which the discharge was sustained. downstream from the discharge cavity. We noted by visual inspection of the emission that the collar effectively blocked the discharge from extending downstream. The rate constant obtained with this configuration was identical to that without the collar. Therefore, we concluded that the O<sub>2</sub> concentration was not affected by the discharge. A second way the O<sub>2</sub> could be depleted is if enough highly reactive atoms or radicals are formed in the discharge to significantly alter the O<sub>2</sub> concentration. However, the pressure of DMMP precursor used in the present experiments (<1 mTorr) was much lower than the pressures of O<sub>2</sub> used (10-60 mTorr). It therefore seems unlikely that there could be significant depletion by precursor products. Unfortunately, Aleksandrov et al. do not give enough details concerning precursor pressures to tell whether microwave products could possibly have affected their  $O_2$  concentrations significantly. However, it is worth noting that the precursors used to study reaction (12) were quite different than that of the present work.

It should be noted that the time scales and  $O_2$  partial pressures used in the two flow system measurements were similar. The photolysis-LEF experiment was performed using a much shorter time scale ( $\sim 2 \ \mu s$ ) and much higher pressures (DMMP  $\sim 300 \text{ mTorr}$ ,  $O_2 \ 1-10 \text{ Torr}$ ). In all cases the data were interpreted under the assumption that only reaction (12) is responsible for the loss of PO. However, if the reaction mechanism is more complicated than assumed, the difference in time scales and pressure ranges used may account for the discrepancy. We attempted to investigate this question by considering other possible mechanisms, but quickly ran into trouble after only two or three reactions because the products were not known. (Some possibilities are discussed in Ref. 42 and references therein.) A very simple mechanism, namely reaction (12) and its reverse followed by

$$PO_2 + O_2 \rightarrow products$$
 (13)

was tried. If the experimental conditions were such that reaction (13) was very slow in comparison to the equilibration of reaction (12), then perhaps PO and PO<sub>2</sub> are in a superequilibrium.<sup>43</sup> The forward rate constant measured for reaction (12) would then be affected by the rate of reaction (13). Because of the comparatively long time scales used in the flow system vs photolysis measurements, we investigated this possibility. We noted that O atoms may be a product of reaction (13), but assumed the reaction is slow enough that it does not appreciably contribute to their concentration. We first tried the assumption that reaction (12) proceeds to equilibration and no further reactions occur. We later tried the assumption that reaction (12) proceeds rapidly to equilibrium and reaction (13) then occurs slowly. The functional forms found for (PO) vs (O<sub>2</sub>) in either case do not fit the observed data at all. In addition, recall that the correct zero [O<sub>2</sub>] intercept was observed for plots similar to Fig. 4 for the range 0-30 mTorr. This fact makes hypothetical arguments that PO may quickly reach a super equilibrium according to some mechanism of very fast reactions, and that some key species in the super equilibrium with PO is then slowly destroyed in another reaction, seem unlikely. We conclude that if a global mechanism leads to systematically small values of  $k_r$ , in the flow system studies, it must be rather complicated. Further experimentation will be necessary to resolve the discrepancy in results.

In view of the fact that Van Zee and Khan<sup>5</sup> observed strong emission of HPO upon burning phosphorus in air with a trace of added  $H_2O$ , it was initially surprising to us that no reaction of PO with H<sub>2</sub>O was observed. The heats of reaction of PO with O<sub>2</sub> and H<sub>2</sub>O explain the results. Using the tables compiled by Benson<sup>44</sup> and  $\Delta H_{f,298 \text{ K}}$  of  $PO_2 = -60.5 \pm 2.9$  kcal/mol from the work of Guido et al.,<sup>45</sup> one finds that  $\Delta H_{r,298 \text{ K}}$  for reaction (12) is  $1.6 \pm 4.0$ kcal/mol, that is, the reaction is thermoneutral within error limits. If the activation energy is small, reaction at room temperature is guite possible. On the other hand, one may show that

$$PO + H_2O \rightarrow HPO + OH$$
 (14)

is quite endothermic. The heat of formation of HPO was not readily available to us. One may place a lower limit on this heat of formation of about 0 kcal/mol by making the assumption that the H-P bond dissociation energy in HPO is less than that of the H-N bond in HNO. Using this lower limit one finds that reaction (14) is at least 70 kcal/mol endothermic. It is, therefore, not surprising that no reaction was observed at room temperature.

#### **V. CONCLUSIONS**

Lifetimes and quenching rate constants of  $B^2\Sigma^+$  PO by atmospheric constituents were measured. Quenching by the molecular species is found to approach the gas kinetic collision frequency. Quenching by Ar and He inert gases is, not surprisingly, found to be much slower. These measurements, coupled with earlier relative intensity measurements,<sup>7</sup> should make it possible to quantitatively determine concentrations of PO formed by laser photolysis of organophosphorus compounds in the atmosphere. Either absorption or LEF techniques could be used. It would be of interest to compare the interactions of excited state PO to those of NO (although the  $A^{2}\Sigma^{+}$  state of NO is not analogous to the  $B^{2}\Sigma^{+}$  state of PO, as one might at first think).

The discrepancy in measured reaction rate constants for  $PO + O_2 \rightarrow PO_2 + O$  between the two flow system results and the photolysis measurement is not understood. This reaction should be studied further because of its analogy to the  $NO + O_2 \rightarrow NO_2 + O$  reaction. The latter is known<sup>46</sup> to be very slow below 1000 K, primarily because the reaction is about 46 kcal/mol endothermic.

Note added in proof: The rate constant for reaction (12) has recently been measured [S. R. Long, S. D. Christesen, and A. P. Force (to be published)] with an apparatus very similar to that used in Ref. 9(b). Instead of the KrF excimer

laser, a CO<sub>2</sub> laser was used as the photolysis source to make PO. The pressures and time scales were similar to those of Ref. 9(b). The resulting rate constant is  $2 \times 10^{-11}$  cm<sup>3</sup>/molecule s.

#### ACKNOWLEDGMENTS

The authors would like to thank Dr. John D. Powell, Dr. John A. Vanderhoff, Dr. David R. Crosley, and the authors of Ref. 9 for stimulating discussions. We are also indebted to Mr. Calvin E. Weaver for wiring the photomultiplier tube and to Dr. Shirley A. Liebman for performing the gas chromatographic analysis of the O<sub>2</sub>. The authors thank the Chemical Research and Development Center Electro-Optics Laboratory for the loan of the Raman shifter cell used in this work. Financial support by the Chemical Research and Development Center is also gratefully acknowledged.

- <sup>2</sup>K. P. Huber and G. Herzberg, Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules (Van Nostrand Reinhold, New York, 1979).
- <sup>3</sup>(a) R. D. Verma, M. N. Dixit, S. S. Jois, S.Nagaraj, and S. R. Singhal, Can. J. Phys. 49, 3180 (1971), and references therein; (b) R. D. Verma and S. R. Singhal, ibid. 53, 411 (1975); (c) S. N. Ghosh and R. D. Verma, J. Mol. Spectrosc. 72, 200 (1978).
- <sup>4</sup>B. Coquart, M. DaPaz, and J. C. Prudhomme, Can. J. Phys. 53, 377 (1975), and references therein.
- <sup>5</sup>R. J. Van Zee and A. U. Khan, J. Chem. Phys. 65, 1764 (1976).
- <sup>6</sup>M. A. A. Clyne and M. C. Heaven, Chem. Phys. 58, 145 (1981).
- <sup>7</sup>W. R. Anderson, S. W. Bunte, and A. J. Kotlar, Chem. Phys. Lett. 110, 145 (1984).
- <sup>8</sup>W. R. Anderson, L. J. Decker, A. J. Kotlar, and M. A. DeWilde, 39th Symposium on Molecular Spectroscopy, Columbus, OH, June 1984, Paper RC8.
- (a) S. R. Long, R. C. Sausa, and A. W. Miziolek, Chem. Phys. Lett. 117, 505 (1985); (b) R. C. Sausa, A. W. Miziolek, and S. R. Long, J. Phys. Chem. (submitted).
- <sup>10</sup>K. C. Smyth and W. G. Mallard, J. Chem. Phys. 77, 1779 (1982).
- <sup>11</sup>(a) J. S. Chou, D. Sumida, and C. Wittig, Chem. Phys. Lett. 100, 397 (1983); (b) J. Chem. Phys. 82, 1376 (1985); 83, 2003 (1985).
- <sup>12</sup>(a) M. Larzilliere and M. E. Jacox, Proc. Mater. Res. Symp. Natl. Bur. Stand. Spec. Publ. 561, (1979), p. 529; (b) J. Mol. Spectrosc. 79, 132 (1980)
- <sup>13</sup>K. Kawaguchi, S. Saito, and E. Hirota, J. Chem. Phys. 79, 629 (1983).
- <sup>14</sup>J. E. Butler, K. Kawaguchi, and E. Hirota, J. Mol. Spectrosc. 101, 161 (1983).
- <sup>15</sup>F. Ackermann, H. Lefebvre-Brion, and A. L. Roche, Can. J. Phys. 50, 692 (1972).
- <sup>16</sup>A. L. Roche and H. Lefebvre-Brion, J. Chem. Phys. 59, 1914 (1973).
- <sup>17</sup>T. J. Tseng and F. Grein, J. Chem. Phys. 59, 6563 (1973).
- <sup>18</sup>J. E. Grabenstetter and F. Grein, as discussed in M. Bialski and F. Grein, J. Mol. Spectrosc. 61, 321 (1976).
- <sup>19</sup>F. Grein and A. Kapur, J. Chem. Phys. 78, 339 (1983). A relevant comment appears in H. Lefebvre-Brion and F. Grein, J. Chem. Phys. 79, 1102 (1983).
- <sup>20</sup>L. L. Lohr, J. Phys. Chem. 88, 5569 (1984).
- <sup>21</sup>K. N. Wong, W. R. Anderson, A. J. Kotlar, and M. A. DeWilde, Proceedings of the 1984 Scientific Conference on Chemical Defense Research, Special Publication CRDC-SP-85006, June 1985, p. 239.
- <sup>22</sup>A sample was found to contain 50-100 ppm H<sub>2</sub>O, less than 50 ppm CO<sub>2</sub>, less than 0.1 ppm hydrocarbons, and less than 0.1% total of Ar, Ne, H<sub>2</sub>, N<sub>2</sub>, and CO.
- <sup>23</sup>W. K. Bischel, B. E. Perry, and D. R. Crosley, Appl. Opt. 21, 1419 (1982)
- <sup>24</sup>J. M. Harris, F. E. Lytle, and T. C. McCain, Anal. Chem. 48, 2095 (1976).
- <sup>25</sup>Actually, averaging of  $2^n$  pulses, where n = 0-6 as selected under computer control, takes place within the digitizer prior to communication of the waveform vector to the computer. However, this detail is unimportant

<sup>&</sup>lt;sup>1</sup>Spectroscopic Data, Volume I: Heteronuclear Diatomic Molecules, edited by S. N. Richards (IFI/Plenum, New York, 1975).

to the present discussion. The experiment may be viewed as though one vector of 512 numbers is sent to the computer for each laser pulse. The software written to handle the transfer allows one to average over 30 000 pulses. The program and interfacing hardware will be presented and discussed in detail in Ref. 26.

- <sup>26</sup>M. A. DeWilde and C. E. Weaver, BRL Report (to be published).
- <sup>27</sup>A. J. Kotlar, R. W. Field, J. I. Steinfeld, and J. A. Coxon, J. Mol. Spectrosc. **80**, 86 (1980).
- <sup>28</sup>All error limits reported in this paper are one standard deviation.
- <sup>29</sup>T. Bergeman, P. Erman, Z. Haratym, and M. Larson, Phys. Scr. 23, 45 (1981), and references therein.
- <sup>30</sup>W. H. Smith, J. Brzozowski, and P. Erman, J. Chem. Phys. **64**, 4628 (1976).
- $^{31}$ It should be noted that figures from Refs. 3(b), 6, and 11(b) contain an error in the assignment of N " for this branch due to an accidental mislabeling of the figure in the earliest reference. See Ref. 7 for the correct assignment which was used here.
- <sup>32</sup>See, for instance, I. S. McDermid and J. B. Laudenslager, J. Chem. Phys. **76**, 1824 (1982).
- <sup>33</sup>See D. R. Crosley, Opt. Eng. 20, 511 (1981) for a review on OH, NH, CH, C<sub>2</sub>, and CN. Additional measurements on C<sub>2</sub> and CN will be presented in K. N. Wong, W. R. Anderson, A. J. Kotlar, and J. A. Vanderhoff (to be published). Measurements on NCO were published in W. R. Anderson, J. A. Vanderhoff, A. J. Kotlar, M. A. DeWilde, and R. A. Beyer, J. Chem. Phys. 77, 1677 (1982). Evidence for retention of excited NH<sub>2</sub> in the originally pumped level appears in R. A. Copeland, D. R. Crosley, and G. P. Smith, 20th Symposium (International) on Combustion, Ann Arbor, MI, August 1984, and in K. N. Wong, W. R. Anderson, J. A. Vanderhoff, and A. J. Kotlar (to be published).
- <sup>34</sup>I. S. McDermid and J. B. Laudenslager, J. Quant. Spectrosc. Radiat. Transfer 27, 483 (1982).
- <sup>35</sup>(a) D. R. Crosley and R. K. Lengel, J. Quant. Spectrosc. Radiat. Transfer 15, 579 (1975); (b) 17, 59 (1977).
- <sup>36</sup>P. W. Fairchild, G. P. Smith, and D. R. Crosley, Chem. Phys. Lett. 107, 181 (1984).
- <sup>37</sup>G. Herzberg, Molecular Spectra and Molecular Structure. I. Spectra of

Diatomic Molecules (Van Nostrand Reinhold, New York, 1950), p. 104. <sup>38</sup>Since the FCFs are rather sensitive to the exact choice of molecular constants, the differences are probably ascribable to a choice of slightly different molecular constants. Results for the larger FCFs agree quite well.

- <sup>39</sup>The entire FCF and *r*-centroid array, along with a rotational analysis of previous measurements for the (0,0) band, will appear in A. J. Kotlar, BRL Report (to be published).
- <sup>40</sup>In almost all quenching work the inverse of Eq. (11) is used. The resulting linear form can easily be fitted using linear least squares routines. However, we point out that  $\tau$  is the quantity which is actually measured, not  $1/\tau$ . Because least squares routines will weight the data differently depending on the form of equation chosen, results of the fits are found to differ, especially the error limits. Therefore fits to the nonlinear form, as in Eq. (11), are to be preferred.
- <sup>41</sup>It should be noted that because there is some quenching competing with radiative decay when  $O_2$  is present,  $I_0$  is not strictly proportional to [PO]. However, the error limit which must be reported for  $k_r$ , will be seen to be very large. The corrections required to  $I_0$  for quenching result in negligible changes in  $k_r$ , within its large error limits.
- <sup>42</sup>E. N. Aleksandrov, V. S. Arutyunov, I. V. Dubrovina, and S. N. Kozlov, Dokl. Akad. Nauk SSSR 267, 110 (1982).
- <sup>43</sup>It may be shown that reaction (12) proceeds very rapidly to equilibrium in the pressure regime and time scale of the flow system measurements if one assumes  $k_r \simeq 10^{-11}$  cm<sup>3</sup>/molecule s. On the other hand, the reverse reaction rate of (12) is not appreciable on the flow system time scale if one assumes  $k_r \simeq 2 \times 10^{-13}$  cm<sup>3</sup>/molecule s. [For these calculations, one uses an estimated  $\Delta G_{r,298K} = -4.4 \pm 5.0$  kcal/mol for reaction (12) and an estimated PO concentration of  $10^{12}$  cm<sup>-3</sup>.]
- <sup>44</sup>S. W. Benson, Thermochemical Kinetics (Wiley, New York, 1968).
- <sup>45</sup>M. Guido, G. Balducci, G. DeMaria, and G. Gigli, J. Chem. Soc. Faraday Trans 1 73, 121 (1977).
- <sup>46</sup>Evaluated Kinetic Data for High Temperature Reactions. II. Homogeneous Gas Phase Reactions of the H<sub>2</sub>-N<sub>2</sub>-O<sub>2</sub> System, compiled by D. L. Baulch, D. D. Drysdale, and D. G. Horne (Chemical Rubber, Cleveland, 1973).