A Study of the Chemiluminescence of the Pb + O₃ Reactions*

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The chemiluminescent reaction of Pb + O₃ has been studied using both "cold" and vibrationally excited O₃. Emission from new states a and b has been observed in addition to the A and B states. The reaction of vibrationally excited O₃ with Pb to yield PbO(A) appears to be faster than that using "cold" O₃.

Key words: Chemiluminescence; electronic states; gas kinetics; laser enhanced reactions; O₃; PbO.

1. Introduction

The results of our recent studies on laser enhanced reactions have shown that vibrational energy in a reactant molecule can reappear as excitation in a product species. For example, emissions from both NO₂⁺ and SO₂⁺ produced in the reactions of NO and SO with O₃ were observed to shift to shorter wavelength when the O₃ was vibrationally excited using a CO₂ laser [1, 2]. Because of the spectroscopic complexities of the triatomic molecules, NO₂ and SO₂, our intention in the present study was to investigate a chemiluminescent reaction producing a diatomic product which would be, in principle, easier to characterize spectroscopically. The metal atom-oxidant systems represent a class of such reactions. A significant number of these have been investigated to date because of their potential as chemical lasers. We report herein some observations on the reaction

\[ \text{Pb} + \text{O}_3 \rightarrow \text{PbO} + \text{O}_2. \]  

While the information obtained from studying the infrared laser-enhanced reaction component is minimized by the overall reaction complexity, it does nevertheless provide some additional insight into this reaction system. This information coupled with new high pressure spectroscopic results complement the detailed low pressure investigation by Oldenborg, Dickson, and Zare (ODZ) [3].

2. Experimental Detail

The furnace, reaction cell, fast flow pumping system, CO₂ laser, and spectrometer are shown schematically in figure 1. Lead vapor, produced from a resistively heated crucible containing lead metal enters the glass reaction chamber in an Ar diluent stream. The effluent from a commercial O₃ generator, consisting of 4 percent O₃ in O₂ is mixed with Ar and flows past the cell windows (to eliminate window deposits) into the cell. There it diffusively mixes with the lead-argon flow. The temperature of the crucible (as measured by a thermocouple probe) ranges from 900–1000 K while the temperature in the flame reaction zone varies from 500–600 K. The total pressure in the cell varies from 1 to 5 torr (1 torr = 133.3 Pa) with the flow through the furnace being anywhere from 20 to 50 percent of the total flow.

The 0.5 cm diameter beam from a CO₂ laser tuned to the 9.6 μm P(30) transition is square wave chopped and traverses the flame exciting ν₃, the asymmetric stretching mode of O₃ (1043 cm⁻¹). The chemiluminescence from the Pb + O₃ reaction is monitored through a spectrometer-photomultiplier assembly. The photomultiplier output is fed through a series of pulse amplifiers and voltage discriminator into a dual counter, one channel of which records the "laser-on" signal and the other the "laser-off". A printout from these counters is synchronized with the spectrometer wavelength-scan-drive thereby facilitating the recording of the modulation spectrum vs wavelength. The normal spectral ("laser-off") emission is automatically obtained from the "laser-off" counter.

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†Figures in brackets indicate the literature references at the end of this paper.
3. Results

In contrast to the spatially sharp diffusion flame observed for the Ba\textsuperscript{+}O\textsubscript{3} (or N\textsubscript{2}O) reaction, the Pb\textsuperscript{+}O\textsubscript{3} flame is quite diffuse (apparently reaction limited). It is brightest in the high temperature zone at the furnace nozzle, diminishes with decreasing temperature (increasing distance from the nozzle), and persists for some two to three feet into the pumping system. These observations suggest a reaction rate for Pb\textsuperscript{+}O\textsubscript{3} which is considerably slower than gas kinetic.

The spectrum which we observe at several torr total pressure partly resembles the low pressure spectrum obtained by ODZ and reproduced by us in a similar quasi-beam apparatus. The short wavelength end of the more complete spectrum (fig. 2) can be identified from the low (submicron) pressure spectrum in that it is less diffuse. The long wavelength portion between 480 nm and 595 nm is almost entirely the new \textit{\textalpha} state recently characterized by ODZ. At still longer wavelengths, our spectrum differs from that of ODZ in that we observe a series of strong lines which do not agree with \textit{\textalpha} \rightarrow X, A \rightarrow X, or B \rightarrow X, but rather appear to originate from a new state observed via six weak lines by ODZ and identified as \textit{\textdelta} by them. This \textit{\textdelta} state is seen more intensely in our high pressure spectrum. This series of lines in our spectrum can be fit to the expression:

\[
\nu(\nu', \nu'') = 16315 + 441.0\nu' - \{717.7\nu'' - 3.53\nu''^2\}
\]

where the lower state constants have been taken from Rosen’s compendium [4]. The spectral constants given here and in tables 1 and 2 for the \textit{\textalpha}, A, and B state are not as well determined as previous values given in references [1] and [4].

### Table 1. Observed band heads and assignments in cm\textsuperscript{-1}

| \(\nu(\text{obs})\) | \(\nu(\text{calc})\) | assignment |
|-------------------|-------------------|------------|
| 24143             | 24116             | B (4.0)    |
| 23590             | 23640             | B (3.0)    |
| 23392             | 23402             | B (4.1)    |
| 23170             | 23157             | B (2.0)    |
| 22957             | 22926             | B (3.1)    |
| 22636             | 22665             | B (1.0)    |
| 22457             | 22443             | B (2.1)    |
| 22178             | 22166             | B (0.0)    |
| 21954             | 21951             | B (1.1)    |
| 21636             | 21660             | B (12.0)   |
| 21474             | 21452             | B (0.1)    |
| 21169             | 21211             | B (11.0)   |
| 21079             | 21065             | B (5.5)    |
| 20877             | 20870             | a (11.0)   |
| 20721             | 20745             | B (0.2)    |
| 20614             | 20616             | B (4.5)    |
| 20442             | 20445             | a (10.0)   |
| 20338             | 20314             | b (9.0)    |
| 20149             | 20156             | a (11.1)   |
| 20024             | 20014             | a (9.0)    |
| 19904             | 19867             | b (8.0)    |
| 19743             | 19731             | a (10.1)   |
| 19585             | 19578             | a (8.0)    |
| 19467             | 19449             | a (11.2)   |
| 19128             | 19138             | a (7.0)    |
| 19015             | 19023             | a (10.2)   |
| 18688             | 18692             | a (6.0)    |
| 18515             | 18530             | b (5.0) Sh.|
| 18305             | 18323             | a (10.3)   |
| 18238             | 18241             | a (5.0)    |
| 17986             | 17978             | a (6.1)    |
| 17790             | 17785             | a (4.0)    |
| 17615             | 17630             | a (10.4)   |
| 17535             | 17527             | a (5.1)    |
| 17319             | 17325             | a (3.0)    |
| 17212             | 17199             | b (2.0)    |
| 17108             | 17052             | b (8.4)    |
| 17033             | 17108             | b (5.2)    |
| 16915             | 16853             | b (6.3)    |
| 16858             | 16859             | a (2.0)    |
| 16773             | 16757             | b (1.0)    |
| 16614             | 16664             | b (4.2)    |
| 16488             | 16485             | b (2.1)    |
| 16434             | 16367             | b (10.5)   |
| 16297             | 16315             | b (0.0)    |
| 16215             | 16220             | b (3.2)    |
| 16108             | 16160             | b (6.4)    |
| 15773             | 15778             | b (2.2)    |
| 15623             | 15601             | b (0.1)    |
| 15672             | 15715             | b (5.4)    |
| 15363             | 15335             | b (1.2)    |

The calculated \(\nu\) have been generated from a least-squares treatment of the observed data using Rosen’s constants for the X state. The generating equations are:

a. \(\nu(\nu', \nu'') = 15912 + 478.4\nu' - 2.5\nu'^2 - \{717.7\nu'' - 3.53\nu''^2\}\)
b. \(\nu(\nu', \nu'') = 16315 + 441.0\nu' - \{717.7\nu'' - 3.53\nu''^2\}\)
B. \(\nu(\nu', \nu'') = 22166 + 502.0\nu' - 3.8\nu'^2 - \{717.7\nu'' - 3.53\nu''^2\}\)
levels are observed. The assignment hypothesized

\[ X \rightarrow \] 

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A definite vibrational assignment for an electronic
state, for which a rotational analysis has not been
observed, requires the measurement of a vibrational
isotope shift. Lacking data of this type one tries to

assign band heads such that both (0, 0') and (0', 0)
levels are observed. The assignment hypothesized by
ODZ on the basis of six observed transitions in a
(0, 0') transition has placed \( T_0 \) of the \( b \) state about one
vibrational quanta above \( T_0 \) of the \( a \) state. In this study
20 band heads have been observed that can be assigned
to \( b \) state. In addition to the (0', 0) band heads, other
bands have been observed with \( v' = 1, 2, 3, 4, 5 \). The
hypothesis regarding the separation of the \( a \) and \( B \)
states is supported by arguments given later.

Although considerable intensity is observed for \( B \rightarrow X \) transition, the zeroth level of this state lies very close
to the thermodynamic threshold for the reaction

\[ \text{Pb}(J=0) + O_3 \rightarrow \text{PbO}(B) + O_2. \]

The dissociation energy \( (D^0) \) of PbO is given by Rosen
[4] as 30,920 ±500 cm⁻¹. Using \( \Delta Hf^\circ(298 \text{ K}) \) of \( O_3 \)
and \( O \) as 34.1 and 59.5 kcal/mol as recommended
by Wagman et al. [5], one computes 22036 cm⁻¹ for the
exothermicity of the reaction.

\[ \text{Pb}(J=0) + O_3 \rightarrow \text{PbO}(X \Sigma^+) + O_2 \]

This to be compared to 22174 cm⁻¹ of the \( v(0,0) \) level of the \( B \) state. Oldenberg and Zare have suggested
that production of this state results from reaction of
\( \text{Pb}(J=1) \) present in their experiments due to an
electric discharge in their furnace. The strong \( B \rightarrow X \)
emission observed in our high pressure experiment was
found to vary markedly with the oven temperature.
The observed \( B \rightarrow X \) emission increase over that
emission from either \( a \) or \( b \rightarrow X \) with increasing
temperature obeyed an Arrhenius-type formulation
with an activation energy of some 10 kcal (i.e. nearly
equal to the energy difference between \( J=0 \) and \( J=1 \)
multiplet components of Pb). This observation suggests
that \( \text{Pb}(J=1) \) is produced thermally in our furnace
as opposed to its possible production via secondary
processes, e.g.

\[ \text{PbO}^* + \text{Pb}(J=0) \rightarrow \text{PbO} + \text{Pb}(J=1). \]

If PbO(B) is indeed produced through reaction of Pb
\( (J=1) \) with ozone, the rate of this reaction must be
extremely fast to compete with the deactivation process

\[ \text{Pb}(J=1) + O_2 \rightarrow \text{Pb}(J=0) + O_2 \]
since the deactivation proceeds with a high rate
constant and the \( O_2 \) pressure is twenty times that of \( O_3 \)
der under our usual experimental conditions.

Part of the modulation spectrum is reproduced in
figure 3. This spectrum, which has been smoothed,

![Smoothened modulation spectrum (the component of the emission which varies with laser excitation of O₃) of the Pb(ν) + O₂ reaction.](image)

**Table 2.** Observed band heads for the modulated spectrum (\( A \rightarrow X \)) in cm⁻¹

| \( \nu'(\text{obs}) \) | \( \nu'(\text{calc}) \) | \( \nu' \) | \( \nu'' \) |
|-----------------|-----------------|--------|--------|
| 17.252          | 17.599          | 0      | 3      |
| 18.513          | 18.293          | 0      | 2      |
| 19.015          | 19.065          | 0      | 1      |
| 19.701          | 19.720          | 0      | 0      |
| 18.005          | 18.041          | 1      | 3      |
| 18.748          | 18.741          | 1      | 2      |
| 17.765          | 17.789          | 2      | 4      |
| 18.478          | 18.482          | 2      | 3      |
| 19.216          | 19.182          | 2      | 2      |
| 19.985          | 19.889          | 2      | 1      |
| 20.644          | 20.603          | 2      | 0      |
| 18.925          | 18.923          | 3      | 3      |
| 18.611          | 18.623          | 3      | 2      |
| 20.305          | 20.375          | 3      | 1      |
| 19.701          | 19.764          | 4      | 5      |
| 18.642          | 18.670          | 4      | 4      |
| 19.384          | 19.363          | 4      | 3      |
| 20.064          | 20.063          | 4      | 2      |
| 20.773          | 20.770          | 4      | 1      |
| 21.463          | 21.465          | 4      | 0      |
| 19.826          | 19.803          | 5      | 3      |
| 20.917          | 20.904          | 5      | 2      |
| 21.911          | 21.211          | 5      | 1      |
| 18.783          | 18.864          | 6      | 5      |
| 19.554          | 19.550          | 6      | 4      |
| 20.226          | 20.243          | 6      | 3      |
| 20.947          | 20.943          | 6      | 2      |
| 21.737          | 21.650          | 6      | 1      |
| 20.024          | 19.990          | 7      | 4      |
| 18.408          | 18.392          | 8      | 7      |
| 19.015          | 19.064          | 8      | 6      |
| 20.434          | 20.429          | 8      | 4      |
| 18.854          | 18.831          | 9      | 7      |
| 19.497          | 19.502          | 9      | 6      |
| 17.940          | 17.946          | 10     | 9      |
| 18.573          | 18.604          | 10     | 8      |
| 19.230          | 19.299          | 10     | 7      |
| 19.964          | 19.941          | 10     | 6      |
| 20.584          | 20.619          | 10     | 5      |
| 21.350          | 21.305          | 10     | 4      |

The calculated \( \nu \) have been generated from a least-squares
treatment of the data using Rosen's constants for the
state. The generating equation is:

\[ \nu'(v', v'') = 19721 + 441.9 \nu' - 0.20 \nu'^2 - \{ 717.7 \nu'' - 3.53 \nu''^2 \} \]

**Figure 3.** Smoothed modulation spectrum (the component of the emission which varies with laser excitation of \( O_3 \)) of the Pb(\( \nu \)) + \( O_2 \) reaction.
of about $10^{-5}$ assuming Pb ($J=0$) and Pb ($J=1$) reacted with O$_3$ with the same rate constant. The observation of the decay of chemiluminescence over several feet in our flow tube points to a slow rate of reaction for Pb ($J=0$) while the fact that the reaction of Pb ($J=1$) must compete favorably with its deactivation channels speaks for a very fast (collision frequency) rate of reaction for Pb ($J=1$). Assuming a reaction efficiency of $10^{-2}$ for the Pb ($J=0$) reaction in the spectrometer observation zone increases the quantum yield for $a + b$ state production by a factor of 100 to $10^{-3}$. We compare this to the ODZ's upper limit of $10^{-2}$ obtained under the assumption of a fast reaction rate for Pb ($J=0$). A slower reaction rate would unfortunately raise their quantum yield (in greater disagreement with our $10^{-3}$ estimate). However, our observation of a large luminous region is not necessarily contradictory to ODZ's estimate of a fast reaction rate because of the different temperature regions of the two studies. In the quasi-beam configuration, Pb exits the furnace at very high temperature (>1000 K) and collides with O$_3$ with much higher kinetic energy than in our high pressure experiments (kinetic energy of 600 K at the nozzle tip and decreasing rapidly to 400 K downstream of the mixing zone).

4. Analysis and Conclusions

Oldenborgh et al. identify the two ($0^-, 1$) components of the $^3\Sigma^+$ as $b$ and $a$, respectively. This energy ordering is consistent with the present observations including an analysis of the relative intensities of the $a$ and $b$ transitions. A theoretical analysis can also be made of the spin-spin splitting constant of the $^3\Sigma^+$ state which shows that the $0^-$ component must be at a higher energy than the 1 component. The spin-spin splitting for a molecule containing a heavy atom is dominated by the second-order spin-orbit coupling to nearby electronic states. Spin-orbit coupling will occur for $\Delta\Omega=0$ and couple the $0^-$ component to $^3\pi(0^-, 1)$, $^1\Sigma^-(0^-)$ and the 1 component to $^3\pi(1)$, $^3\Sigma^-(1)$, $^1\pi(1)$. Note that there is no first-order spin-orbit coupling between the $^3\Sigma^+(1)$ and $^3\Delta(1)$ states. Using a Hamiltonian of the form

$$\sum_i l_i \cdot s_i,$$

the spin-orbit interaction is reduced [6] to the one-electron spin-orbit integrals given in table 3.

| Table 3. Molecular spin-orbit interactions |
|------------------------------------------|
| $\Omega = \sigma$                        |
| $^3\Sigma^+ - ^3\pi - 1/2\sqrt{2} < \pi || \sigma >$ |
| $^3\Sigma^+ - ^1\Sigma^- - 1/2 < \pi || \pi > + 1/2 < \pi^* || \pi^* >$ |
| $\Omega = 1$                             |
| $^3\Sigma^+ - ^3\pi + 1/2\sqrt{2} < \pi || \sigma >$ |
| $^3\Sigma^+ - ^1\Sigma^- - 1/2\sqrt{2} < \pi || \pi > + 1/2 < \pi^* || \pi^* >$ |

Interaction with the $^3\pi$ state shifts both components
equally and can be ignored. The $^1\pi(1)$ interaction is small both because the $\sigma$ and $\pi$ orbitals are primarily localized on the oxygen atom, and there is a large energy separation between the $^1\pi$ and $3\Sigma^-$ states. The spin-spin splitting constant is dominated by the difference between the $3\Sigma^+(1)$ and $1\Sigma^-(0^-)$ interactions. From Table 3 we see that the $3\Sigma^-$ interaction is necessarily the largest term. This demonstrates that the $3\Sigma^-(1)$ component is lower in energy than $3\Sigma^-(0)$.

Quantitative estimates of the spin-spin splitting cannot be made from molecular spin-orbit parameters since little is known for the PbO excited states. Using the atomic spin-orbit parameter [6], assuming atomic populations by comparing calculations on PbO [7] and CO [8], and excitation energies for the perturbing states [9], a spin-spin splitting of about $1000 \text{ cm}^{-1}$ is obtained. This qualitatively confirms the analysis of the emission spectrum and the assignment of the $a$ and $b$ states. Assuming that the molecular integrals will scale with the atomic spin-orbit parameters, the splitting in the case of SnO would be an order of magnitude less than the value for PbO while GeO is about two orders of magnitude less.

There are two mechanisms which could give intensity to the dipole forbidden $b \rightarrow X$ transition, spin-rotation and electronic rotational coupling. For large spin-spin splitting the spin-rotation coupling between the $a$ and $b$ states is negligible even for $J$ as large as 100 (one expects the most probable value of $J$ to be 24 for $T=500 \text{ K}$).

The electronic-rotation coupling matrix elements between a $3\Sigma^+$ and $3\pi$ state are given by Kovacs [11]. The coupling is proportional to $4B^2J(J+1)/\Delta E$ for the Hund case $a$ representation where $\Delta E$ is the difference in the electronic energies and $B$ is the rotational constant. Since $\Delta E \approx 5000 \text{ cm}^{-1}$ and $T \approx 500 \text{ K}$, this coupling is significant but can only be ascertained quantitatively if the complete mixing between $3\Sigma^+$ and $3\pi$ states is considered. It is likely that the $b$ state transition probability would increase with temperature.

Since all the observed transitions to the ground state ultimately derive their intensity from spin-orbit mixing to the higher singlet excited states, it is well to remember that the transitions between $3\pi$ and $3\Sigma^+$ states are electric-dipole allowed and should have significant intensity even though they are in the infrared ($\sim 5000 \text{ cm}^{-1}$).

The present results point to a slow overall reaction of Pb $(J=0)$ with O$_3$ as well as a small quantum yield for production of PbO excited electronic states. Since the reactant states can couple to only one final product state, adiabatically this must be PbO (X) and O$_2$ (X). Excited PbO states are the result of a nonadiabatic transition. The enhanced reactivity of Pb $(J=1)$ into the excited B state reflects the additional channels that are now available but the population yield of the various excited states remains puzzling.

Our observations at high pressure are somewhat different from those of Oldenborg et al. In particular, we find more intensity in the $b$ state than they did. Their observations were made before collisions took place. In the present case many collisions can occur before the emitted light is observed. Two general explanations can be advanced for the different observations. The effective rotational temperatures can be very different. Pressure effects can also be important both by collisionally deactivating other excited states into the $b$ state or by collisionally inducing the radiative transition.

Finally, we note that the enhancement of even initial formation of the A state by laser excitation of the ozone is not understood. In order to further unravel these questions, additional experiments must be carried out in conjunction with a more extensive theoretical investigation of the Group IV oxides.

5. References

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