PbO SPECTROSCOPY AND STUDIES OF THE INTERACTION OF SINGLET MOLECULAR OXYGEN WITH LEAD ATOMS BY LASER-INDUCED FLUORESCENCE AND BY HIGH-RESOLUTION FOURIER TRANSFORM SPECTROSCOPY

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PbO SPECTROSCOPY AND STUDIES OF THE INTERACTION OF SINGLET MOLECULAR OXYGEN WITH LEAD ATOMS BY LASER-INDUCED FLUORESCENCE AND BY HIGH-RESOLUTION FOURIER TRANSFORM SPECTROSCOPY

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The \(^1\Delta_g\) state of \(O_2\) has an extremely large radiative lifetime (~1 hour) and is quenched with a very low efficiency by collisions with various types of wall. The success of pumping the iodine atom by \(O_2\) \(^1\Delta_g\) in the Chemical Oxygen-Iodine Laser has led to the examination of its action on various atoms (1), and in particular on lead, because the lowest excited state \(^3\Sigma_u^+\) is in quasi-resonance with \(O_2\) \(^1\Delta_g\) (fig. 1).

The mixing of molecular oxygen and lead atoms in their ground states \((O_2\ ^3\Sigma_u^+\) and \(Pb\ ^1\Sigma_g^+)\) does not produce a reaction. With \(O_2\ ^1\Delta_g\) a rather bright flame appears. The

![Figure 1](http://dx.doi.org/10.1051/jphyscol:1987791)

**Figure 1** Energy levels of Pb, O₂ and PbO

![Figure 2](http://dx.doi.org/10.1051/jphyscol:1987791)

**Figure 2** Experimental arrangement.
emission comes mainly from the lowest excited states of \( \text{Pb} \) and \( \text{PbO} \). The abundant formation of \( \text{PbO} \) is a competing reaction which tends to hinder the achievement of population inversion in \( \text{Pb} \) atoms: it is therefore desirable to eliminate the formation of \( \text{PbO} \), and hence we need to know and understand the reactions involved.

We have undertaken a high resolution spectroscopic study of the \( \text{O}_2 \left( ^1 \Delta_g \right) \cdot \text{Pb} \) flame in order to obtain new spectroscopic data on the \( \text{PbO} \) molecule, and to determine the excited state populations in the steady state regime of the flame. A bright and stable flame was created with a Broida-type oven (fig. 2).

High resolution Fourier transform spectra were obtained using natural \( \text{Pb} \) (see fig. 3) and isotopically pure \( ^{208} \text{Pb} \) (fig. 4). We have investigated in detail the \( \text{A} \, 0^+ \rightarrow \text{X} \, 0^+ \), \( \text{A} \, 1^+ \rightarrow \text{X} \, 0^+ \) and \( \text{B} \, 1^+ \rightarrow \text{X} \, 0^+ \) transitions of \( \text{PbO} \) produced in the reaction of \( \text{O}_2 \left( ^1 \Delta_g \right) \) with \( \text{Pb} \).

\[ \text{Figure 3} \quad \text{A} \, 0^+ \rightarrow \text{X} \, 0^+ \quad \text{band head of natural PbO. The intensities are in agreement with the natural abundances:} \quad ^{204} \text{Pb} \ 52.3\%, \quad ^{207} \text{Pb} \ 22.6\% \quad \text{and} \quad ^{206} \text{Pb} \ 23.6\%. \quad \text{Recorded in 2 hours.} \]

The traditional spectroscopic constants characterizing the \( \text{A} \) and \( \text{X} \) states have been precisely determined for \( ^{208} \text{PbO} \) (Table 1). There were too many superpositions in the natural \( \text{PbO} \) spectra to obtain accurate data for the two other isotopes. Nevertheless, the classical Dunham isotope relations enable their line positions to be calculated from the \( ^{208} \text{PbO} \) constants. We have found that the non blended lines in the natural \( \text{PbO} \) spectrum are indeed recalculated to within the experimental accuracy (error ~ 0.005 - 0.010 cm\(^{-1}\)).

\[ \text{Table 1} \quad \text{Equilibrium constants (cm}^{-1}\text{) for the X 0^+ \text{ and A 0^+ states of} \quad ^{208} \text{PbO.} \]

The \( \omega_{X_A} \) parameter for the \( \text{A} \, 0^+ \) state is observed to be negative, explaining the variations amongst the values of \( \omega_{X_A} \) given by different authors (2).

<table>
<thead>
<tr>
<th>( X \text{-State} )</th>
<th>( A \text{-State} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \omega_e )</td>
<td>( 720.5980 ( \pm ) 36 )</td>
</tr>
<tr>
<td>( \omega_e \cdot x )</td>
<td>( 3.5161(11) )</td>
</tr>
<tr>
<td>( r_e )</td>
<td>( 1.9218 ) A</td>
</tr>
<tr>
<td>( B_e )</td>
<td>( 0.3073121(42) )</td>
</tr>
<tr>
<td>( \alpha_e )</td>
<td>( 0.19084(75) \times 10^{-2} )</td>
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</table>
The relative intensities of the rotational lines are well-determined in the $^{208}$PbC spectra. They show that the significantly populated vibrational levels of the A 0' state have a Boltzmann rotational distribution, corresponding to a temperature of 860 K (fig. 5). The comparison of the intensities between different bands show that the vibrational populations are in the ratio of the intensities: $\text{Int}(v=0) = 1.0$, $\text{Int}(v = 1) = 1.2$ and $\text{Int}(v = 2) = 0.7$. There is a small population inversion between $v=1$ and $v=0$ in the A state. The comparison of the bands' intensities, recorded at low resolution gave the same results. Simple multi-step processes possibly involved in the reaction cannot explain this inversion. Further investigations of the flame are now in progress.

Figure 4
Part of the non-apodised Fourier Transform record of the $^{208}$Pb-O$_2$ [A-X] flame at high resolution (0.04 cm$^{-1}$). Recorded in 2 hours.

Figure 5
Determination of the rotational temperature in the vibrational levels of the A state from the $^{208}$PbO spectrum.

References.