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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J. Bachar, R. Bacis, S. Churassy, F. Martin, S. Rosenwaks, et al.. 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. Journal de Physique Colloques, 1987, 48 (C7), pp.C7-381-C7-383. 10.1051/jphyscol:1987791 . jpa-00227096

HAL Id: jpa-00227096

<https://hal.science/jpa-00227096>

Submitted on 1 Jan 1987

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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 [$= O_2(^1\Delta_g)$] 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 3P_1 is in quasi-resonance with $O_2(^1\Delta_g)$ (fig 1).

The mixing of molecular oxygen and lead atoms in their ground states ($O_2(^3\Sigma_g^-)$ and $Pb(^3P_0)$) does not produce a reaction. With $O_2(^1\Delta_g)$ a rather bright flame appears. The

Figure 1 Energy levels of Pb, O_2 and PbO

Figure 2 Experimental arrangement.

emission comes mainly from the lowest excited states of Pb and PbO. The abundant formation of PbO is a competing reaction which tends to hinder the achievement of population inversion in Pb atoms: it is therefore desirable to eliminate the formation of PbO, and hence we need to know and understand the reactions involved.

We have undertaken a high resolution spectroscopic study of the $O_2 [^1\Delta_g] - Pb$ flame in order to obtain new spectroscopic data on the 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 Pb (see fig 3) and isotopically pure ^{208}Pb (fig. 4). We have investigated in detail the $A 0^+ - X 0^+$, $a 1 - X 0^+$ and $B 1 - X 0^+$ transitions of PbO produced in the reaction of $O_2 [^1\Delta_g]$ with Pb.

Figure 3 $A0^+ - X0^+$ (0-3) band head of natural PbO. The intensities are in agreement with the natural abundances: ^{208}Pb 52.3%, ^{207}Pb 22.6 % and ^{206}Pb 23.6 %. Recorded in 2 hours.

The traditional spectroscopic constants characterizing the A and X states have been precisely determined for ^{208}PbO (Table 1). There were too many superpositions in the natural 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}PbO constants. We have found that the non blended lines in the natural PbO spectrum are indeed recalculated to within the experimental accuracy (error $\sim 0.005 - 0.010 \text{ cm}^{-1}$).

Table 1 Equilibrium constants (cm^{-1}) for the $X 0^+$ and $A 0^+$ states of ^{208}PbO .

The $\omega_e x_e$ parameter for the $A 0^+$ state is observed to be negative, explaining the variations amongst the values of $\omega_e x_e$ given by different authors (2).

	X State	A State
ω_e	720.9580 (36)	442.897(37)
$\omega_e x_e$	3.5161(11)	-0.123(25)
r_e	1.9218 Å	2.0950 Å
B_e	0.3073121(42)	0.258596(19)
α_e	$0.19084(75) \times 10^{-2}$	$0.1270(45) \times 10^{-2}$

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 $\text{A}0^+$ state have a Boltzmann rotational distribution, corresponding to a temperature of 860K (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 $^{208}\text{Pb-O}_2 [^1\Delta_g]$ flame at high resolution (0.044 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.

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