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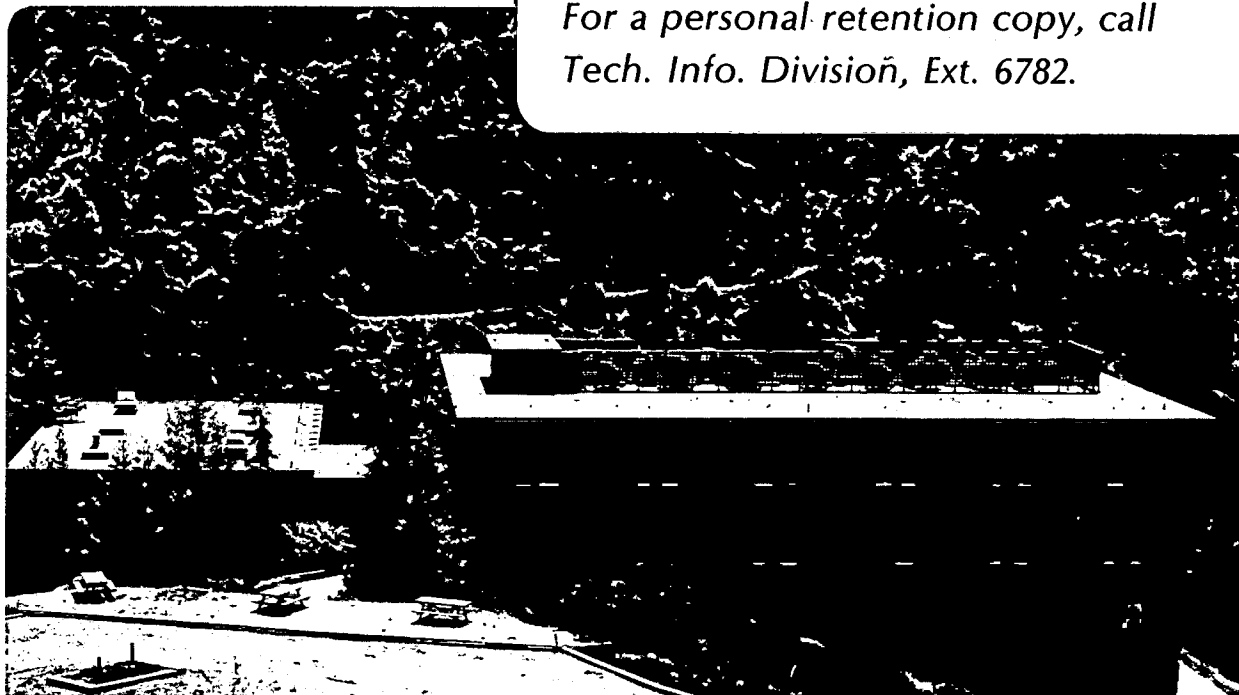LIBRARY AND
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RELATIVISTIC CONFIGURATION INTERACTION CALCULATIONS
FOR SEVERAL LOW LYING STATES OF PbO: COMPARISON
WITH CHEMILUMINESCENT SPECTRA

K. Balasubramanian and Kenneth S. Pitzer

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Relativistic Configuration Interaction Calculations for Several Low Lying

States of PbO: Comparison with Chemiluminescent Spectra

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Abstract

Relativistic quantum calculations including configuration interaction and

spin-orbit interaction are described for eleven low lying states of PbO.

Comparison calculations are presented for 8 Λ-S states obtained in the

absence of spin-orbit interaction. These calculations were carried out

using relativistic effective core potentials. Spectroscopic properties

of these low lying states of PbO are computed and compared with the

spectra resulting from chemiluminescent reactions of Pb with O_3, N_2O,

etc. Possible assignments of the experimentally observed bands are

suggested. Spectroscopic properties are predicted for several low

lying electronic states that have not yet been observed experimentally.

The effect of spin-orbit interaction and the nature of CI wavefunctions

are discussed and comparisons made with SnO.

1. Introduction

The lead oxide molecule is of considerable experimental interest because of the chemiluminescence of the reaction of Pb with O_3. The electronic spectra[1-7] of PbO reveals the existence of several emission systems in the visible and ultraviolet region. One of the important bands is the intense band attributable to the allowed $A(0^+) \rightarrow X(0^+)$ transition, where $X(0^+)$ is the ground state and $A(0^+)$ is an excited state of same symmetry as the ground state in the double group symmetry of the molecule. Several other less intense systems such as $a \rightarrow X(0^+)$, $b \rightarrow X(0^+)$ etc. have been observed. One of the objectives of this theoretical investigation is to compute the spectroscopic properties of several low lying electronic states with the intent of assigning the emission systems observed experimentally to the appropriate electronic states.

The calculations presented here were carried out with the method formulated by Christiansen, Balasubramanian and Pitzer[8] for diatomics containing very heavy atoms. This method was found to be quite successful for the computation of the spectroscopic properties of several low lying electronic states of the molecules such as TℓH,[8] Pb_2,[9-10] Sn_2,[10] and SnO.[11]

In Section 2 the method of our calculations is described. In Section 3 we compare the calculated spectroscopic properties of several electronic states with available experimental spectra. In the last section the nature of CI wavefunctions for several states is discussed and compared with those of the tin oxide (SnO) molecule.

2. Method of calculations

The lead oxide molecule has a closed shell ground state $\sigma^2\pi^4$ (considering only p electrons and ignoring the s and d electrons of the lead and oxygen atoms). Promotion/a π-electron to the π^* antibonding orbital generates 6 Λ-S states which are split into 10 ω-ω states by spin-orbit interaction. The promotion of the σ-electron to a π^* orbital generates $^3\Pi$ and $^1\Pi$ Λ-S states which are split into 5 ω-ω states. Table 1 summarizes these low lying electronic states. In Table 2 we show the dissociation limits of these electronic states.

The atomic states of the lead atom have been described in both ℓ-S and j-j coupling schemes in our earlier paper[10] on Pb_2 and Sn_2. As reported there, our calculations for the atoms reproduce the atomic energy levels quite satisfactorily.

We will now consider the selection of configurations for our relativistic CI calculations. All Λ-S states that give rise to states of same ω-ω symmetry mix in the presence of spin-orbit interaction. Thus the ground state is a mixture of $^1\Sigma^+$, $^3\Pi(0^+)$, $^3\Sigma^-(0^+)$, $^1\Sigma^+(II)(0^+)$ etc. Similarly the 1(I) state is a linear combination of $^3\Sigma^+(1)$, $^3\Sigma^-(1)$, $^3\Delta(1)$, $^3\Pi(1)$, and $^1\Pi(1)$. The coefficients in the linear combination are determined variationally.

The lowest 0^+ state included $\sigma^2\pi^4$, $\sigma^2\pi^3\pi^*$, and $\sigma\pi^4\pi^*$ as reference configurations. Further, for the sake of electron correlation and to represent the molecule properly near the dissociation limits we included the $\sigma^2\pi^2\pi^{*2}$, $\sigma^2\pi\pi^{*3}$, $\sigma^2\pi^{*4}$, $\sigma\sigma^*\pi^2\pi\pi^*$ configurations were added. An extensive array of single and double excitations from these configurations were allowed. To compute the properties of the lowest 1 state we included the $\sigma^2\pi^3\pi^*$, $\sigma\pi^4\pi^*$ configurations with spin and angular momentum chosen appropriately to yield the 1 state. Single and double excitations were

allowed. The lowest 0^- and 2 states were also represented in a like manner. Our calculations were carried out with a molecular program that uses Cartesian Slater type orbitals in C_{2v} symmetry. The above configurations were expanded to the Cartesian basis. Table 3 summarizes the number of reference configurations and the total number of configurations included in our CI calculation.

Our SCF calculations were carried out using relativistic effective potentials for the lead atom obtained from relativistic numerical Dirac-Fock calculations of the atom. Fourteen electrons of the lead atom $(d^{10}s^2p^2)$ and all 8 electrons of oxygen were included in our SCF calculations. The relativistic effective potentials were averaged with respect to spin at the SCF stage. We employed a double zeta basis set of Slater functions. The Slater exponents were optimized for the ^3P lead and oxygen atoms. The optimized exponents are shown in Table 4. The 1s orbital of the oxygen and all the primarily d orbitals of the lead atom were frozen after the SCF stage to limit the number of configurations. Our final CI calculations included 6σ orbitals and $4\pi_x$ and $4\pi_y$ orbitals.

Separate SCF calculations were carried out for the three configurations $\sigma^2\pi^4$, $\sigma^2\pi^3\pi^*$ and $\sigma\pi^4\pi^*$. The CI calculations were based on the most appropriate set of SCF orbitals.

While the $0^+(I)$, $1(I)$, $0^-(I)$, $0^-(II)$, $2(I)$ and $2(II)$ states have been calculated using the above scheme the higher roots of these symmetries have been calculated somewhat less accurately. Since our calculations were based on Cartesian orbitals in C_{2v} symmetry, different $C_{\infty v}$ symmetries involve the same Cartesian orbitals but with different sign relationships among the coefficients. While our CI program, in principle, maintains the symmetry as determined by our input any asymmetry from the SCF orbitals or round-off errors can cause a collapse from a high

energy root of the desired symmetry to a lower root of another symmetry.

For example, a 2 state has the same set of configurations as an 0^- state

but with different sign relationship. Thus a 2 state could collapse to

an 0^- state. In some cases this collapse could be avoided by calculations

with fewer configurations, but the results are now much less accurate.

The $0^+(II)$ state had all of the $^3\Pi(0^+)$, $^1\Sigma^+(0^+)$, and $^1\Sigma^+(II)(0^+)$ refer-

ence configurations with single and double excitations. The $0^+(III)$

state included only the $^1\Sigma^+$, $^3\Sigma^-$, and $^1\Sigma^+(II)$ configurations with single

and double excitations. The $1(I)$ and $1(II)$ states included $^3\Sigma^+(1)$,

$^3\Delta(1)$, $^3\Sigma^-(1)$, $^3\Pi(1)$, and $^1\Pi(1)$ state reference configurations. We

allowed single and double excitations from these reference configurations.

The $1(III)$ and $1(IV)$ states are mixtures of $^3\Pi$, $^3\Sigma^-$, and $^1\Pi$ and were not

calculated accurately enough to be reported. The upper root of a calcu-

lation involving $^3\Pi$ and $^1\Pi$ configurations appears to be a reasonable

estimate for $1(V)(^1\Pi)$ and is reported. Thus the spectroscopic properties

of some of the highly excited states such as $0^-(III)$, $0^+(III)$, $1(V)$, etc.,

are only estimates and should not be regarded as accurate calculations.

3. Results and Interpretation of Experimental Spectra of PbO

Our calculated spectroscopic properties of 10 low lying $\omega-\omega$ states

and the corresponding 8 Λ-S states (in the absence of spin-orbit inter-

action are shown in Table 5. Several authors[7] have observed the $A(0^+) \rightarrow$

$X(0^+)$ emission system of PbO at about 19,863 cm^{-1}. Our calculated value

for the $A(0^+) \rightarrow X(0^+)$ separation is 18,890 cm^{-1} which is in good agree-

ment with these experimental observations. This $A(0^+)$ state is a

mixture of the $^3\Pi(0^+)$ and $^1\Sigma^+$ states. Linton and Broida[5] and Oldenborg,

et al.,[3] have observed several new bands in the $a(1) - X(0^+)$ and $A(0^+) -$

$X(0^+)$ emission systems which enabled calculation of ω_e values of these

states. In Table 3 we show the ω_e and T_e values calculated by these authors based on these new bands. Our calculated T_e and ω_e values for the a(1) state which is our 1(I) state are in reasonable agreement with the values obtained in Refs. 3 and 5.

The a(1) state is assigned to $^3\Sigma^+(1)$ by several authors. Our calculations confirm this assignment. The two components of the $^3\Sigma^+$ term are very substantially mixed by spin-orbit interaction. The 0^- state is about $\frac{3}{4}$ $^3\Sigma^+(0^-)$ and $\frac{1}{4}$ $^1\Sigma^-$ while the 1 state is about $\frac{3}{4}$ $^3\Sigma^+(1)$ and $\frac{1}{4}$ $^3\Sigma^-(1)$. The mixing of $^3\Delta(1)$, $^3\Pi(0^+)$, and $^3\Pi(1)$ is small. Our calculations give $^3\Sigma^+(1)$ a little higher energy than $^3\Sigma^+(0^-)$ whereas most other investigators[3,4] have come to the opposite conclusion. The theoretical argument of Kurylo, et al.,[4] appears to be valid for small mixing, but higher order effects might arise for such large mixing as we find. Experimentally, the weak and presumably "forbidden" transition at 16454 cm^{-1} might arise from $^3\Delta_2$ as well as from $^3\Sigma^+(0^-)$. The approximations in our calculations are such that we cannot draw a definite conclusion, but we believe that the alternate assignment of the b state at 16454 to $^3\Delta_2$ should be considered as a possibility. An emission system B $\rightarrow$ X(0^+) has been observed. The B state was assigned to B($^3\Pi_1$) state with a T_e value 22,285 cm^{-1} by several investigators. As noted above, we could not calculate with accuracy the 1(III) state, but we know that its T_e value is lower than the T_e value of the $^3\Pi$ state obtained without spin-orbit operator. Thus the assignment of the B state to $^3\Pi_1$ seems to be appropriate, although this state is certainly a mixture of $^3\Pi_1$, $^1\Pi_1$ and $^3\Sigma^-(1)$ with $^3\Pi_1$ making a dominant contribution. The experimental T_e value of the C state is 23,820 cm^{-1}. This state should be $^3\Sigma^-(0^+)$ and our calculated T_e value is somewhat lower. The calculated

ω_e value (613 cm^{-1}) is in good agreement with the experimental value. The D $\rightarrow$ X(0$^+$) and E $\rightarrow$ X(0$^+$) emissions have also been observed experimentally. The experimental T_e values of these states are 30,199 cm^{-1} and 34,454 cm^{-1}. The D and E states correspond to our 1(V) and 0$^+$(IV) states. These states are dominantly $^1\Pi(1)$ and $^1\Sigma^+$(II) states. The experimental T_e value for the 1(IV) state is shown in Table V, but we could not calculate the spectroscopic properties of this state with sufficient accuracy. The experimental T_e and ω_e values of this state are close to those of C(0$^+$(III)). Since C(0$^+$(III)) is dominantly $^3\Sigma^-$(0$^+$), we believe that this state should be $^3\Sigma^-$(1) state.

Our T_e values of the excited states are somewhat lower than the experimental values. We believe that this is attributable to a poor π^* antibonding orbital for the ground state which was optimized only for the excited states. This could have led to imbalance in the amount of correlation in the ground state and excited states.

Our calculated dissociation energy of 3.0 eV fot the PbO molecule is based on the molecular calculation at 8.0 Bohr. This is in reasonable agreement with the experimental value of 3.83 eV. Our calculated R_e and ω_e values for the ground state are in good agreement with the experimental values and the values obtained by Basch, Stevens and Krauss using a MCSCF calculation.[12] The calculated ω_e and R_e values for the excited states are also in good agreement with the available experimental results. As one can see from Table V spin-orbit interaction is quite large and important for the lead oxide molecule.

The original calculated energy values for the several low-lying electronic states mentioned above are shown in Tables 6 and 7. A few potential energy curves are also shown in Figure 1.

4. The Nature of CI Wavefunctions and Comparison with SnO

   Spin-orbit interaction not only changes the T_e values of several $\omega-\omega$

states in comparison to the T_e values of the corresponding Λ-S states

but also mixes several Λ-S states that have the same $\omega-\omega$ symmetry. This

effect is larger for PbO than SnO. This difference can be explained on

the basis of the properties of the atomic states of Pb and Sn. While

the $^3P_0$ - ^3P separation for the tin atom is only 13 milihartrees, the

corresponding value for Pb is 43 milihartrees. In general the lower

root of a given $\omega-\omega$ symmetry is stabilized by spin-orbit interaction

but this lowering is smaller for the molecule in comparison to the atom.

   We will next discuss in some detail the nature of the CI wavefunction

for some electronic states. The ground state 0^+ at the equilibrium bond

length 3.75/is populated 84% by $^1\Sigma^+$, 0.8% by $^3\Pi_{0^+}$ and 3.0% by $^3\Sigma^-$. The

Bohr

rest of the population is attributable to single and double excitations

from the ground state. Thus this is dominantly a $^1\Sigma^+$ Λ-S state with

considerable correlation. One can thus explain relatively small lowering

of this state by spin-orbit interaction. At equilibrium bond distances

the 1(I) state is a mixture of about $\frac{3}{4}$ $^3\Sigma_1^+$ and $\frac{1}{4}$ $^3\Sigma_1$ with a little $^3\Delta_1$.

The contribution of $^3\Pi_1$ and $^1\Pi_1$ states to this state is very small. The

0^-(I) state is 74% $^3\Sigma^+(0^-)$ and 20% $^1\Sigma^-(0^-)$. The contribution of $^3\Pi_{0^-}$ at

equilibrium bond distances is negligible. The 0^+(II) and 0^+(III) states

are primarily $^3\Pi$ and $^3\Sigma^-$, respectively, but have non-negligible coeffi-

cients for the $^1\Sigma^+$(I) and $^1\Sigma^+$(II) states. The 0^-(II) state is 90% $^3\Pi_{0^-}$

and 5.5%. $^3\Sigma^+(0^-)$ with an only small contribution from the $^1\Sigma^-(0^-)$.

   There are two striking differences in the CI wavefunction and elec-

tronic properties of PbO and SnO. First, the tin-oxide molecule can be

described reasonably well within Λ-S coupling scheme. When the spin-orbit

interaction was included the mixing of Λ-S states that have different Λ-S symmetry but the same ω-ω symmetry has a negligible effect on the energy (but may be important for transition probabilities). This mixing is much larger for PbO as discussed above. Secondly, there is a significant lowering of the T_e values of the excited states in comparison to the T_e values of the corresponding Λ-S states. This can be explained on the basis of the nature of the π^* anti-bonding orbital. While the π bonding orbital is mainly on the oxygen atom with only a small contribution from the heavier atom, the π^* orbital is mainly on the heavier atom. Thus promotion of a σ or π electron to the antibonding π^* orbital picks up the large spin-orbit interaction on the heavy atom. Of course, as discussed above, this effect is noticeably large for the lead atom in comparison to the tin atom. Consequently, spin-orbit interaction stabilizes most of the excited states which arise from the promotion of an electron to the π^* orbital. However, the $^1\Pi_1$ state is a mixture of $^3\Pi(1)$ and $^1\Pi(1)$ lowering the T_e value of $^3\Pi(1)$ and increasing the T_e value of $^1\Pi_1$. Thus our 1(V) state has a higher T_e value in comparison to the T_e value of the $^1\Pi$ Λ-S state.

The ω_e values of the various electronic states of PbO (and SnO) are very sensitive to the basis sets although the T_e and R_e values do not change appreciably in different basis sets. If we employ a single zeta basis for the oxygen 1s and 2s and a double zeta basis for the oxygen 2p orbital (the basis set for the heavy atom being the same as in Table 3). The ground state ω_e values for PbO and SnO are 900 cm^{-1} and 1000 cm^{-1}, respectively. The ω_e values of the excited states are in the region of 650-950 cm^{-1} for PbO and the corresponding range for SnO is 700-1000 cm^{-1}. Thus a smaller basis set tends to increase the ω_e value. This

dependence of ω_e value on the basis sets was also noted by Datta, Van Wazer and John[13] for the ground state of PbO molecule.

There is an avoided crossing of the states arising from $\pi^3\pi^*$ configuration of a given symmetry with a compatible $^3\Pi$ state of the same $\omega-\omega$ symmetry. For example, the 1(I) state is dominantly $^3\Pi_1$ at shorter distances and it becomes dominantly $^3\Sigma^+$(1) at equilibrium bond distances. This avoided crossing is also observed for the 0^-(I) and 0^+(II) states in the repulsive regions. This crossing occurs at 3.5 Bohr for PbO and 3.25 Bohr for SnO. The crossing in SnO is sudden because of the small mixing of $^3\Pi$ and $^3\Sigma^+$ states. However, there is significant $^3\Pi$ and $^3\Sigma^+$ interaction in the 1(I) and 0^-(I) states of PbO in this region since spin-orbit effects are quite large for the lead atom.

Acknowledgment

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Table 1. A Few MO Configurations of PbO and the
          Terms Arising from them in Λ-S and ω-ω
          Coupling Schemes

Configuration	Λ-S State	ω-ω State
$\sigma^2\pi^4$	$^1\Sigma^+$	0^+
$\sigma\pi^4\pi^*$	$^3\Pi$	$0^+,0^-,1,2$
	$^1\Pi$	1
$\sigma^2\pi^3\pi^*$	$^3\Sigma^+$	$0^-,1$
	$^3\Delta$	$1,2,3$
	$^3\Sigma^-$	$0^+,1$
	$^1\Sigma^+$	0^+
	$^1\Delta$	2
	$^1\Sigma^-$	0^-

Table 2: Molecular States of PbO Related to Atoms

Molecular States	Dissociation Limit O/Pb	Atomic Energies in cm^{-1} Pb + O
0^+, 1, 2	$^3P_2 + {}^3P_0$	0.0
0^-, 1	$^3P_1 + {}^3P_0$	158.5
0^+	$^3P_0 + {}^3P_0$	385
0^+, 0^-(2), 1(3), 2(2), 3	$^3P_2 + {}^3P_1$	7819.4
0^+(2), 0^-, 1(2), 2	$^3P_1 + {}^3P_1$	7978
0^-, 1	$^3P_0 + {}^3P_1$	8204

Table 3. Number of Reference and Total Configurations
Included in CI Calculations for the Lowest-
energy State of Each Symmetry

State	RC[a]	Total
$^1\Sigma^+(0^+)$	19	2480
$^3\Sigma^+(1)$	8	1492
$^3\Sigma^+(0^-)$	12	2137
$^3\Delta(2)$	12	2137

[a] RC stands for the number of reference configurations.

Table 4: Orbital Exponents in Slater Type Basis Functions Optimized for the ^3P Oxygen and Lead Atoms. The Principal Quantum Numbers are Shown in Parentheses

|	Pb	O
s	1.9021(4)	9.6982(1)
		6.9562(1)
	.8482(4)	2.6786(2)
		1.6927(2)
p	1.5189(4)	3.7183(2)
	0.8599(4)	1.6671(2)
d	3.5804(4)	—
	1.6047(4)	

Table 5: Spectroscopic Properties of PbO

State	R_e(Å)		T_e(cm^{-1})		ω_e(cm^{-1})	
	Calcd.	Expt.	Calcd.	Expt.	Calcd.	Expt.
0^+(I)	2.02	1.92	0	0	715	721
$^3\Sigma^+$ $\{$ 0^-	2.23		14 461	16 454?		441?
1	2.23	2.12	14 551	16 025	487	482
$^3\Delta$ $\{$ 2	2.23		15 205	16 454?	540	441?
1(II)	2.24		15 360		472	
$^1\Delta$ (2(II))	2.24		16 035		451	
$^3\Pi$ $\{$ 0^-(III)?	2.14		18 758		576	
0^+(II)	2.13	2.09	18 890	19 863	528	444
1(III)	–	2.07	–	22 285	–	498
$^3\Sigma^-$ $\{$ 0^+(III)	2.23		20 747	23 820	612	532
1(IV)	–		–	24 947	–	494
$^1\Pi$ (1(V))	2.14	2.05	27 215	30 199	521	530
$^1\Sigma^+$(II)(0^+(IV))	–	2.18	–	34 454	–	454
$^1\Sigma^+$	2.02	–	682	–	706	
$^3\Sigma^+$	2.21	–	16 610	–	503	
$^3\Delta$	2.24	–	18 267	–	485	
$^3\Sigma^-$	2.23	–	20 292	–	600	
$^1\Sigma^-$	2.22	–	20 477	–	594	
$^3\Pi$	2.13	–	22 469	–	514	
$^1\Pi$	2.15	–	24 771	–	505	
$^1\Sigma^+$(II)	2.22	–	39 202	–	703	

Table 6:   Potential Energy Curves of PbO

R	$0^+(I)$ 1_Σ^+	$0^-(I)$ 3_Σ^+	$1(I)$ 3_Σ^+	$2(I)$ 3_Δ	$1(II)$ 3_Δ	$2(II)$ 1_Δ	$0^-(II)$ 3_Π	$0^+(II)$ 3_Π	$1(III)$ 3_Π	$0^+(III)$ 3_Σ^-	$1(IV)$ 1_Π	$0^+(IV)$ $1_\Sigma^+(II)$
3.0	.0944	.1994	.2065	-	.2345	-	-	.2061	.2428	.3034	-	-
3.25	-.0151	.0744	.0795	.1267	.0819	-	-	.0792	.0823	.1413	.1163	.2186
3.5	-.0915	.0086	.0195	.0161	.0244	.0325	-	.0135	.0169	.0518	.0511	.1361
3.65	-.1053	-	-.0093	-	-	-	-	-	-	-	-	-
3.75	-.1095	-	-.0207	-.0180	-	-	-	-.0157	-.0019	+.0067	.0222	.0929
3.85	-.1099	-.0323	-.0319	-.0286	-.0264	-.0228	-.0207	-.0211	-.0115	-.0037	.0171	.0827
4.0	-.1066	-.0407	-.0405	-.0371	-.0357	-.0325	-.0244	-.0240	-.0184	-.0121	.0140	.0732
4.1	-	-.0433	-.0430	-.0400	-.0387	-.0357	-.0244	-.0236	-.0195	-.0149	.0142	.0696
4.2	-	-.0442	-.0438	-.0372	-.0400	-	-	-	-	-	-	-
4.5	-.0713	-.0404	-.0394	-.0349	-.0368	-.0348	-.0078	-.0054	-.0040	-.0050	.0308	.0835
8.0	0.0	-	-	-	-	-	-					

Table 7: Potential Energy Curves of PbO Calculated Without the Spin-Orbit Effect

R	$^1\Sigma^+$	$^3\Sigma^+$	$^3\Delta$	$^3\Sigma^-$	$^1\Sigma^-$	$^3\Pi$	$^1\Pi$	$^1\Sigma^+(II)$
3.0	.1026	-	-	.3037	.3042	.2163	.2373	-
3.25	-.0123	.1324	.1455	.1415	.1421	.0923	.1087	.2186
3.5	-	.0287	.0403	.0516	.0523	.0283	.0421	.1361
3.65	-.1024	-	-	-	-	-	-	-
3.75	-.1064	-	-	.0061	.0068	.0001	.0121	.0929
3.85	-.1068	-.0235	-.0139	-.0046	-.0039	-.0050	.0066	.0827
4.0	-.1034	-.0317	-.0227	-.0133	-.0127	-.0077	.0030	.0732
4.1	-	-.0339	-.0256	-.0165	-.0158	-.0073	.0029	.0696
4.2	-	-.0344	-.0268	-	-	-	-	-
4.5	-.0679	-.0289	-.0230	-.0089	-.0082	.0102	.0188	.0835
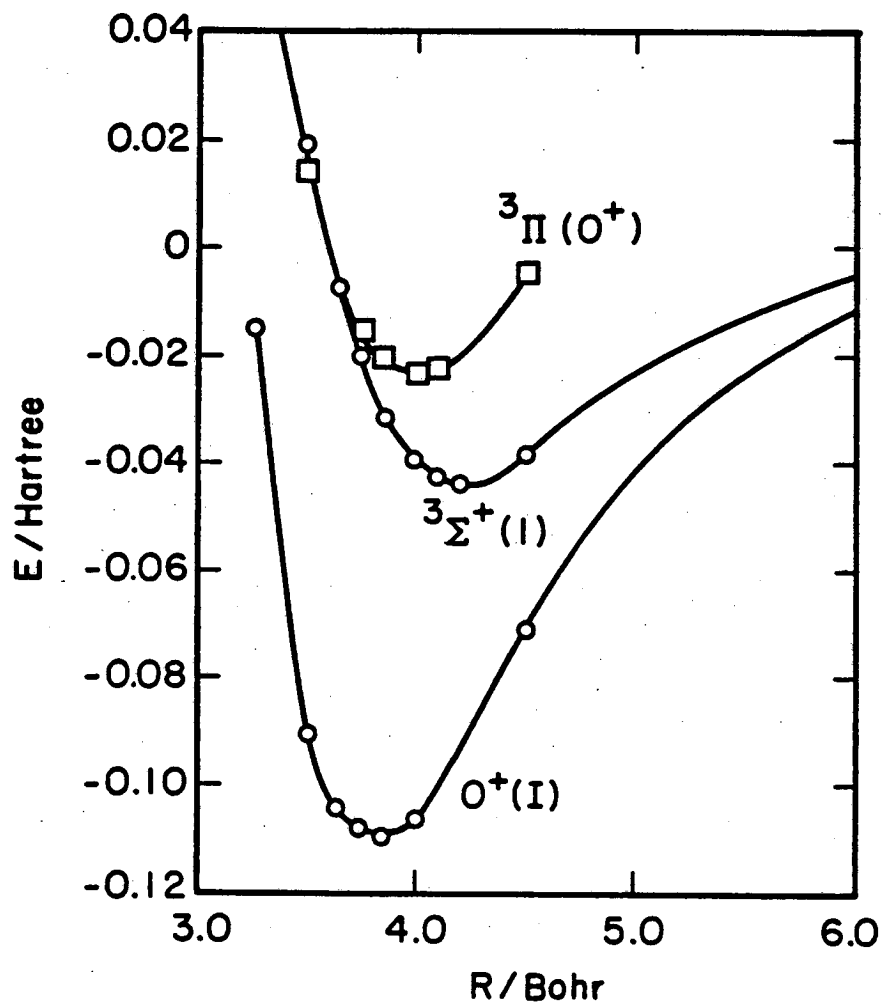
Figure 1. Potential energy curves of three low-lying
           states of PbO.

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