to red shift in the presence of 1.0 M DEA.

From the IR data, photolysis of the non-hydrogen-bonded ketones should produce solvent-separated ion pairs, $\lambda_{\text{max}} = 770$ nm. Photolysis of the hydrogen-bonded ketones could produce either contact ion pairs or the hydrogen-bonded 4-phenylbenzophenone radical anion. If the hydrogen bond is not broken in the excited state, contact ion pair formation will be precluded; the thermodynamically more stable hydrogen-bonded anion will be formed immediately following the electron transfer. Deconvolution of the absorption band given in Figure 2 suggests that the absorbance arises from both hydrogen-bonded anion, $\lambda_{\text{max}} = 719$ nm, and the solvent-separated ion pair, in agreement with predictions based on the infrared analysis. Examining the time evolution of the transient absorption spectrum, we find that the component at 770 nm undergoes a hypsochromic shift with a half-life of 77 ps to 719 nm, indicating complete formation of the hydrogen-bonded 4-phenylbenzophenone ketyl. The rate of hydrogen-bond formation revealed by the shift in absorption maximum from 770 to 719 nm is approximately twice that observed for the benzophenone–DEA contact ion-pair separation in ethanol.

The photoreduction of benzophenone by DEA in ethanol proceeds through initial contact ion-pair formation in less than 25 ps. In addition to transient spectral data, the presence of the contact ion pair was confirmed by infrared studies which revealed a ground-state interaction between both hydrogen-bonded and non-hydrogen-bonded ketones and DEA in ethanol. However, no initial hydrogen-bonded anion is formed in the benzophenone–DEA system.

Relativistic Configuration Interaction Calculations for Several Low-Lying States of PbO: Comparison with Chemiluminescent Spectra

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Relativistic quantum calculations including configuration interaction and spin–orbit interaction are described for 11 low-lying states of PbO. Comparison calculations are presented for eight $A^2S$ states obtained in the absence of spin–orbit interaction. These calculations were carried out by 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$_2$, N$_2$O, 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 wave functions are discussed and comparisons made with SnO.

I. Introduction

The lead oxide molecule is of considerable experimental interest because of the chemiluminescence of the reaction of Pb with O$_2$. 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


tense band attributable to the allowed $\Delta$(0') → $X$(0') transition, where $X$(0') is the ground state and $\Delta$(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 → $X$(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 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 TH, Pb,$^8$ PbO,$^{10}$ SnO,$^{11}$ and SnO$_2$.

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 wave functions 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 of a $\tau$-electron to the $\pi^*$-antibonding orbital generates six $\Delta$-$\Sigma$ states which are split into ten $\omega$-$\omega$ states by spin-orbit interaction. The promotion of the $\sigma$-electron to a $\pi^*$-orbital generates $\Pi$ and $\Pi$ $\Delta$-$\Sigma$ states which are split into five $\omega$-$\omega$ states. Table I summarizes these low-lying electronic states. In Table II we show the dissociation limits of these electronic states.

The atomic states of the lead atom have been described in both $\Delta$-$\Sigma$ and $j$-$j$ coupling schemes in our earlier paper 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 $\Delta$-$\Sigma$ states that give rise to states of same $\omega$-$\omega$ symmetry mix in the presence of spin-orbit interaction. Thus the ground state is a mixture of $\Sigma^+, \Pi(0'), \Sigma^-(0'), \Sigma^- (\Pi(0'))$, etc. Similarly the 1(I) state is a linear combination of $\Sigma^+(1), \Sigma^+(1), \Sigma^- (\Pi(1))$, etc. The coefficients in the linear combination are determined variationally.

The lowest 0* state included $\sigma^4\pi^3\tau^*$, and $\sigma^3\pi^2\tau^*$ as reference configurations. Further, for the sake of electron correlation and to represent the molecule properly near the dissociation limits we included the $\sigma^2\pi^2\tau^2$, $\sigma^3\pi^*\tau^*$, $\sigma^2\pi^*\tau^*\tau^*$ 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 $\sigma^2\pi^*\tau^*, \sigma^2\pi^*\tau^*\tau^*$ 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 III summarizes the number of reference configurations and the total number of configurations included in our CI calculation.

Our SCF calculations were carried out by 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$^2$p$^2$) and all eight 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 IV.

The 1s orbital of the oxygen and all of 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 6 $\sigma$

TABLE V: Spectroscopic Properties of PbO

<table>
<thead>
<tr>
<th>state</th>
<th>$R_e$, Å</th>
<th>$T_e$, cm$^{-1}$</th>
<th>$\omega_e$, cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>calcd</td>
<td>exptl</td>
<td>calcd</td>
</tr>
<tr>
<td>1$\Sigma^+$(1), O+(1), X</td>
<td>2.02</td>
<td>1.92</td>
<td>0</td>
</tr>
<tr>
<td>2$\Sigma^+$, 1, b?</td>
<td>2.23</td>
<td>2.12</td>
<td>14 461</td>
</tr>
<tr>
<td>$\Pi$ 1, a</td>
<td>2.23</td>
<td>2.07</td>
<td>14 551</td>
</tr>
<tr>
<td>1, b?</td>
<td>2.23</td>
<td>2.07</td>
<td>15 205</td>
</tr>
<tr>
<td>1(II)</td>
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<td>2.07</td>
<td>15 360</td>
</tr>
<tr>
<td>4(II)</td>
<td>2.24</td>
<td>2.07</td>
<td>16 035</td>
</tr>
<tr>
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<td>2.07</td>
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<td>24 947</td>
</tr>
<tr>
<td>1(IV), C</td>
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<td>2.05</td>
<td>27 215</td>
</tr>
<tr>
<td>1*(II)(0*+(IV)), E</td>
<td>2.22</td>
<td>2.18</td>
<td>34 454</td>
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<tr>
<td>$\Sigma^+$</td>
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<td></td>
<td>682</td>
</tr>
<tr>
<td>$\delta$</td>
<td>2.21</td>
<td></td>
<td>16 610</td>
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</tr>
<tr>
<td>$\Sigma^+$</td>
<td>2.22</td>
<td></td>
<td>39 202</td>
</tr>
</tbody>
</table>

orbitals and 4$\pi$ orbitals.

Separate SCF calculations were carried out for the three configurations $\sigma^+$,$\sigma^-$,$\pi+\sigma^+\pi^*$, and $\pi+\sigma^*$-$\sigma^+$ $\pi^*$. The CI calculations were based on the most appropriate set of SCF orbitals. While the 0+(1), 0+(2), 0+(II), 2(2), and 2(II) states have been calculated by the above scheme, the higher roots of these symmetries have been calculated somewhat less accurately. Since our calculations were based on Cartesian orbitals in $C_{4v}$ symmetry, different $C_{4v}$ 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 not much less accurate. The 0+(II) state had all of the $\Pi$, $\Sigma^-$, and $\Sigma^-$ configurations with single and double excitations. The 0+(III) state included only the $\Sigma^+$, $\Pi$, and $\Sigma^-$ configurations with single and double excitations. The 0+(IV) and 0+(II) states included $\Sigma^+$, $\Pi$, and $\Sigma^-$ configurations. We allowed single and double excitations from these reference configurations. The 1(III) and 1(IV) states are mixtures of $\Pi$, $\Sigma^-$, and $\Pi$ and were not calculated accurately enough to be reported. The upper root of a calculation involving $\Pi$ and $\Pi$ configurations appears to be a reasonable estimate for $\Pi$($\Pi$) and is reported. Thus the spectroscopic properties of some of the highly excited states such as 0+(III), 0+(IV), 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 ten low-lying $\omega=\omega$ states and the corresponding eight $\Delta=S$ states (in the absence of spin-orbit interaction) are shown in Table V. Several authors 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 agreement with these experimental observations. This A(0) state is a mixture of the $\Pi(\Pi)$ and $\Sigma^+$ states. Linton and Broda have observed several new bands in the a(1)-X(0) and A(0)-X(0) emission systems which enabled calculation of $\omega$ values of these states. In Table III we show the $\omega$ and $\omega$ values calculated by these authors based on these new bands. Our calculated $\omega$ and $\omega$ values for the a(1) state which is our 1(I) state are in reasonable agreement with the values obtained in ref 3 and 5.

The a(1) state is assigned to $\Sigma^+$ by several authors. Our calculations confirm this assignment. The two components of the $\Sigma^+$ term are very substantially mixed by spin-orbit interaction. The 0 state is about 3/4 $\Sigma^+(0)$ and 1/4 $\Sigma^-$ while the 1 state is about 3/4 $\Sigma^+(1)$ and 1/4 $\Sigma^-(1)$. The mixing of $\Sigma^-(1)$, $\Pi(0)$, and $\Pi(1)$ is small. Our calculations give $\Sigma^+(1)$ a little higher than $\Sigma^-(0)$ whereas most other investigators have come to the opposite conclusion. The theoretical argument of Kurylo et al. 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 16 454 cm$^{-1}$ might arise from $\Delta(2)$ as well as from $\Sigma^-(0)$. 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 16 454 cm$^{-1}$ to $\Delta(2)$ should be considered as a possibility. An emission system B $\rightarrow$ X(0*) has been observed. The B state was assigned to $\Pi(1)$ state with a T$e$ value of 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 $\omega$ value is lower than the $\omega$ value of the 3 states obtained without spin-orbit operator. Thus the assignment of the B state to $\Pi(1)$ seems to be appropriate, although this state is certainly a mixture of $\Pi(1)$, $\Pi(1)$, and $\Sigma^-(1)$ with $\Pi(1)$ making a dominant contribution. The experimental $\omega$ value of the C state is 23 820 cm$^{-1}$. This state should be $\Sigma^+(0)$ and our calculated $\omega$ value is somewhat lower. The calculated $\omega$ 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 $\omega$ values of these states are 30 199 and 34 454 cm$^{-1}$. The D and E states correspond to our 1(V) and 0(IV) states. These states are dominantly $\Pi(1)$ and $\Sigma^+(1)$ states. The experimental $\omega$ value for the C($\Pi(1)$) state is shown in Table V, but we could not calculate the spectroscopic properties of this state with sufficient accuracy. The experimental $\omega$ and $\omega$ values...
the basis of the properties of the atomic states of Pb and Sn. While the $3p_0-3p_0$ separation for the tin atom is only 3.75 eV. Our calculated $R_N$ and $\omega_N$ values for the ground state are in good agreement with the experimental values and the values obtained by Basch, Stevens, and Krauss using a MCI calculation. The calculated $\omega_N$ and $R_N$ 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 VI and VII. A few potential energy curves are also shown in Figure 1.

4. The Nature of CI Wave Functions and Comparison with SnO

Spin--orbit interaction not only changes the $T_N$ values of several $\omega-\omega$ states in comparison to the $T_N$ values of the corresponding $\Lambda-S$ states but also mixes several $\Lambda-S$ 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 $3p_0-3p_0$ separation for the tin atom is only 13 mhartrees, the corresponding value for Pb is 43 mhartrees. 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 next discuss in some detail the nature of the CI wave function for some electronic states. The ground state 0$^+$ at the equilibrium bond length 3.75 bohr is populated 84% by $1\Sigma^+(II)$, 0.8% by $1\Pi$, and 3.0% by $3\Sigma^-$. The rest of the population is attributable to single and double excitations from the ground state. Thus this is dominantly a $1\Sigma^+ \Lambda-S$ state with considerable correlation. One can thus explain relatively small lowering of this state by spin--orbit interaction. At equilibrium bond distances the 1$\Pi$ state is a mixture of about $3/4$ $2\Sigma^+$ and $1/4$ $3\Sigma^+$ with a little $1\Delta$. The contribution of $1\Pi$ and $3\Pi$ states to this state is very small. The 0$^-(I)$ state is 74% $3\Sigma^-$ and $20\% 2\Sigma^-$. The contribution of $3\Pi$ at equilibrium bond distances is negligible. The 0$^+(II)$ and 0$^+(III)$ states are primarily $1\Pi$ and $3\Sigma^-$, respectively, but have nonnegligible coefficients for the $1\Sigma^+(I)$ and $1\Sigma^+(II)$ states. The 0$^-(II)$ state is 90% $3\Pi$ and $5.5\% 1\Sigma^-$ with an only small contribution from the $1\Sigma^-$. There are two striking differences in the CI wave function and electronic properties of PbO and SnO. First, the tin oxide molecule can be described reasonably well within $\Lambda-S$ coupling scheme. When the spin--orbit interaction was included the mixing of $\Lambda-S$ states that have different $\Lambda-S$ symmetry but the same $\omega-\omega$ 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 $T_N$ values of the excited states in com-

![Figure 1. Potential energy curves of three low-lying states of PbO.](image-url)
Effect of the Solvent on the Entropy of Formation of the Mercury/Solution Interface

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The temperature dependence of the dielectric properties of a monolayer of solvent dipoles at a polarizable interface, including the entropy of monolayer formation, are examined within the context of a multistate model in which the solvent molecules are represented as hard, polarizable spheres having a dipole moment which can take up specified orientations with respect to the field at the interface. Data are presented for the entropy of formation of the mercury/nonaqueous solution interface with methanol (MeOH), N-methylformamide (NMF), N,N-dimethylformamide (DMF), and propylene carbonate (PC) as solvents. When these results are considered within the context of the multistate model and the previously presented three-state model, it is clear that the simpler model is not able to account for the experimental results obtained with aprotic solvents. The experimental data are also discussed with respect to the classification of the interfacial solvent behavior proposed by Parsons.

Introduction

Solvent effects on the differential capacity, interfacial tension, and other thermodynamic properties of the mercury/solution interface have been well documented in the literature. The dependence of differential capacity on electrode charge density in the absence of specific adsorption has been attributed to a change in the dielectric properties of the solvent at the interface. In this regard, inner-layer-capacity curves have been analyzed on the basis of simple molecular models which assume that the solvent dipoles are present in a monolayer in which they can take up a finite number of orientations with respect to the electrode's field. Further experimental data are available regarding the temperature dependence of interfacial dielectric properties for nonaqueous solvents. The temperature dependence of the inner-layer capacity of the Hg/solution interface has been determined with dimethylformamide (DMF), propylene carbonate (PC), and propyl alcohol.

Acknowledgment.

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Registry No.

PbO, 1317-36-8; Pb, 7439-92-1; Os, 10028-15-6; N2O4, 1002-57-2.