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Relativistic Molecular Structure Calculations
Including CI for Several Low Lying States of SnO

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Relativistic quantum calculations including configuration interaction and spin-orbit interaction are described for seven low lying Λ -S states of SnO and the corresponding ω - ω states with spin-orbit interaction. Spectroscopic properties of these states are computed and compared with experimental results. Properties are predicted for several low lying electronic states that have not yet been observed experimentally.

1. Introduction

The tin oxide (SnO) molecule has been a subject of experimental interest for several years.¹⁻³ Chemiluminescent spectra of SnO have revealed the existence of several emission systems in the visible and ultraviolet region. The tin oxide molecule is a candidate for chemical lasers because of the high photon yields (~50%) of the $\text{Sn} + \text{N}_2\text{O}$ reaction.³ As pointed out by Huber and Herzberg⁴ several bands observed in the visible and near UV region for SnO have not been interpreted satisfactorily. Theoretical studies of excited states of SnO molecule have not been undertaken so far. Our present efforts are directed towards filling this gap.

Calculations also near completion for PbO and the present results will be of interest in comparison.

The tin oxide molecule has a closed shell ground state. Promotion of either a σ or a π electron to the antibonding π^* orbital leads to 8 Λ -S states which are split by spin-orbit interaction into 15 ω - ω states.

Our calculations were carried out with the method formulated by Christiansen, Balasubramanian and Pitzer for diatomics containing very heavy atoms.⁵ This method was found to be very successful for computing the spectroscopic properties of the several low lying electronic states of TlH ⁵, Pb_2 and Sn_2 .^{6,7} Relativistic quantum chemical calculations have been reviewed recently;⁸ an earlier review⁹ discusses more broadly the effect of relativity on chemical properties.

2. Method of Calculations

First we show in Table 1 the symmetry relationship and the dissociation limits of a few low lying electronic states of the tin oxide molecule. In that table we have shown the possible electronic states in both Λ -S and ω - ω coupling schemes. Table 2 shows the dissociation limits of these electronic states.

The properties of the atomic states of both Sn and Pb atom have been described in our earlier paper on the Pb_2 and Sn_2 molecules.⁷ Readers are referred to that paper for the description of the atomic states in both L-S and j-j coupling. The spin-orbit interaction for the oxygen atom is very small and can be ignored for our purposes.

We next consider the selection of configurations for the relativistic CI calculations. In general all Λ -S states that give rise states of the same ω - ω symmetry mix in the presence of spin-orbit interaction. The ground state can thus be described as a linear combination of $^1\Sigma^+(0^+)$, $^3\Sigma^-(0^+)$, $^3\Pi(0^+)$ and $^1\Sigma^+(\Pi)(0^+)$ with the coefficients determined variationally.

Thus, for 0^+ there are contributing configurations from $\sigma^2\pi^4$, $\sigma^2\pi^3\pi^*$, and $\sigma\pi^4\pi^*$ at relatively low energy. For electron correlation and to better represent the molecule near dissociation the $\sigma^2\pi^2\pi^{*2}$, $\sigma^2\pi\pi^{*3}$ and $\sigma^2\pi^{*4}$ configurations were added. The calculations were carried out with a molecular program based on Cartesian Slater-type orbitals in C_{2v} symmetry. Thus these configurations in $C_{\infty v}$ were expanded to the Cartesian basis yielding 19 reference configurations (RC). With an extensive array of single and double excitations this led to a total of 2480 configurations for 0^+ as shown in Table 3. For other symmetries there are somewhat fewer states mixed by the spin-orbit interaction; also we made less effort to account for electron correlation over the full dissociation process. Thus the numbers of configurations for other symmetries are somewhat smaller as shown in Table 3.

Our SCF calculations were carried out using relativistic effective potentials for the Sn atom obtained from numerical Dirac-Fock calculations. Fourteen electrons of the Sn atom ($d^{10}s^2p^2$) and all 8 electrons of oxygen were included in the SCF calculations. The relativistic potentials were averaged with respect to spin at the SCF stage. The basis sets employed

in this calculation were double zeta Slater functions. The optimized exponents are shown in Table 4. The 1s and 2s orbitals of oxygen and all of the primarily d orbitals of the Sn atom were frozen after the SCF stage of the calculations with the intent of limiting the number of configurations.

Separate molecular SCF calculations were carried out for the three configurations $\sigma^2 \pi^4 ({}^1\Sigma^+)$, $\sigma^2 \pi^3 \pi^* ({}^3\Sigma^+)$ and $\sigma \pi^4 \pi^* ({}^3\Pi)$. The CI calculations were based on the most appropriate set of SCF orbitals.

Calculations were made both with and without the spin-orbit term. The effect of the spin-orbit term on the energy is small in all cases; hence we report only the results without the spin-orbit term. The spin-orbit term does cause significant mixing of states, most notably ${}^1\Pi_1$ with ${}^3\Pi_1$, and this has a major effect on transition probabilities, but the effect on the energy was small.

For the more highly excited states, our calculations are considerably less accurate than for the ${}^1\Sigma^+$, ${}^3\Sigma^+$, and ${}^3\Delta$ states. For our program using Cartesian orbitals, different $C_{\infty v}$ symmetries involve the same Cartesian orbitals but with different sign relationships among the coefficients. While the program in principle maintains the starting symmetry, in practice any asymmetry from the SCF orbitals or from round-off effects can cause a collapse from a high-energy root of the desired $C_{\infty v}$ symmetry to a lower energy root of the same C_{2v} symmetry but a different $C_{\infty v}$ symmetry. Thus the more highly excited states were calculated using only those reference configurations primarily involved and the results should be regarded as relatively rough estimates of the properties of these states.

3. Results and Comparison with Experiments

The results are summarized in Table 5 as the derived spectroscopic properties T_e , R_e , and ω_e for the seven Λ -S states without the spin-orbit

interaction. As noted above, the effect of the spin-orbit term on these values is small for SnO. The original calculated energies at a sequence of interatomic distances are given in Table 6; a few of the potential curves are shown in Fig. 1.

The emission bands from the $^3\Pi(0^+)$ and $^3\Pi(1)$ states to the 0^+ ground state were measured in detail by Deutsch and Barrow.¹ The general magnitude of the T_e values agrees very well.

Capelle and Linton³ obtained additional bands for the system near $20,000\text{ cm}^{-1}$ first reported by Joshi and Yamdagni² at $19,000\text{ cm}^{-1}$. While Capelle and Linton assign this system as $^3\Sigma^+(1) \rightarrow ^1\Sigma^+$, their T_e of $20,622\text{ cm}^{-1}$ is considerably higher than our calculated value of $17,650\text{ cm}^{-1}$. Also it seems as if the transition from either the 0^+ or the 1 component of $^3\Sigma^-$ should be as strong as that from $^3\Sigma^+(1)$. Thus the possibility should be considered that the $20,622\text{ cm}^{-1}$ state is either $^3\Sigma^-(0^+)$ or $^3\Sigma^-(1)$.

The assignment⁴ of the system with $T_e = 29,624\text{ cm}^{-1}$ to $^1\Pi(1)$ [$1(V)$] seems reasonable, but our calculated T_e of $26,700\text{ cm}^{-1}$ is considerably lower. Since this is a fourth excited one state, our calculated value cannot be regarded as very reliable. There may be substantial mixing of one states by the spin-orbit interaction which we were unable to include in our calculations.

The calculated characteristics R_e and ω_e of the ground state agree reasonably well with experiment. Our dissociation energy, based on the calculation at 8 bohr, of 3.70 eV is considerably smaller than the experimental value⁴ of 5.49 eV. This probably arises from inadequacies in our CI which is extensive but far from complete.

The calculated vibration frequencies agree very well with experiment for the ground state and the $\sigma^2\pi^3\pi^*$ excited configuration in either the

3_{Σ}^{+} or 3_{Σ}^{-} states. The agreement for the $\sigma\pi 4^{*}$ states is not very good, but our calculations are less reliable for these more highly excited states.

4. Discussion

Although the effect of the spin-orbit term on energies is not very large for SnO it can cause large mixing of states of nearly equal energy. It is apparent from Fig. 1 and Table 6 that there will be extensive mixing for 1 states between 3.25 and 3.6 Bohr. States of this symmetry arise from 3_{Σ}^{+} , 3_{Δ} , 3_{Σ}^{-} , and 3_{Π} with the first lowest at longer distances and the last lowest in energy at distances less than 3.25 Bohr. Less extensive mixing occurs for 0^{+} and 0^{-} symmetries in this same region. These avoided crossings occur far enough up the repulsive part of the potential curve that the resulting curves appear to be normal in shape. However, striking effects might arise in collisions or other phenomena.

These results predict the approximate energies for several unobserved states. The $3_{\Sigma}^{+}(1)$, $3_{\Sigma}^{-}(0^{+})$, and $3_{\Sigma}^{-}(1)$ states should all be observable in transition to or from the ground state, but only a single transition has been reported in this range. Thus there are interesting opportunities for further investigation.

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

<u>Configuration</u>	<u>Λ-S State</u>	<u>ω-ω State</u>
$\sigma^2 \pi^4$	1_{Σ}^{+}	0^{+}
$\sigma \pi^4 \pi^{*}$	3_{Π}	$0^{+}, 0^{-}, 1, 2$
	1_{Π}	1
$\sigma^2 \pi^3 \pi^{*}$	3_{Σ}^{+}	$0^{-}, 1$
	3_{Δ}	1, 2, 3
	3_{Σ}^{-}	$0^{+}, 1$
	1_{Σ}^{+}	0^{+}
	1_{Δ}	2
	1_{Σ}^{-}	0^{-}

Table 2. Molecular States of SnO Related to Atoms

Molecular States	Dissociation Limit	Atomic Energies in cm^{-1}
$0^+, 1, 2$	O/Sn $^3P_2 + ^3P_0$	Sn + 0 0.0
$0^-, 1$	$^3P_1 + ^3P_0$	158.5
0^+	$^3P_0 + ^3P_0$	385
$0^+, 0^-(2), 1(3), 2(2), 3$	$^3P_2 + ^3P_1$	1691.8
$0^+(2), 0^-, 1(2), 2$	$^3P_1 + ^3P_1$	1850
$0^-, 1$	$^3P_0 + ^3P_1$	2077

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

<u>State</u>	<u>RC^a</u>	<u>Total</u>
$1_{\Sigma}^{+}(0^{+})$	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. Optimized Orbital Exponents in Slater Type Basis Functions. The Principal Quantum Numbers are Shown in Parentheses

	Sn	O
		9.6982(1)
s	2.6829(5)	6.9562(1)
	1.6074(5)	2.6786(2)
		1.6927(2)
p	2.3775(5)	3.7183(2)
	1.3523(5)	1.6671(2)
d	3.9532(4)	-
	1.5175(4)	

Table 5. Spectroscopic Properties of SnO. Experimental Values in Parentheses Below

State	T_e / cm^{-1}	$R_e / \text{\AA}$	$\omega_e / \text{cm}^{-1}$
$1_{\Sigma}^{+}(0^{+})$	0	1.94 (1.83)	800 (823)
$3_{\Sigma}^{+}(0^{-}, 1)$	18606 (20622?)	2.13	542 (554?)
$3_{\Delta}(1, 2, 3)$	20561	2.16	493
$3_{\Sigma}^{-}(0^{+}, 1)$	22750 (20622?)	2.15	530 (554?)
$1_{\Sigma}^{-}(0^{-})$	22890	2.14	540
$3_{\Pi}(0^{+}, 0^{-}, 1, 2)$	24100 (24333, 0 ⁺) (24890, 1)	2.06 (2.01, 0 ⁺) (1.99, 1)	770 (555.0 ⁺) (560, 1)
$1_{\Pi}(1)$	26700 (29624)	2.06 (1.95)	710 (574)

Table 6. Potential Energy Curves of SnO (R in Bohr, E in Hartree)^a

R	1_{Σ}^{+}	3_{Σ}^{+}	3_{Δ}	3_{Σ}^{-}	1_{Σ}^{-}	3_{Π}	1_{Π}	$1_{\Sigma}^{+}(\text{II})$
3.0	-.0219	.1657	-	.1929	-	.1243	.1533	.2803
3.25	-.1018	.0348	.0572	.0705	-	.0341	-	.1694
3.5	-.1296	-.0168	-	.0081	.0086	-.0062	-	.1088
3.65	-.1358	-	-	-	-	-	-	-
3.75	-.1349	-.0441	-.0338	-.0231	-.0225	-	-	.0696
3.82	-	-	-	-	-	-.0254	-.0136	-
3.85	-.1318	-.0487	-.0389	-.0284	-.0279	-.0260	-.0142	.0627
4.0	-.1240	-.0511	-.0420	-.0320	-.0314	-.0247	-.0134	.0567
4.1	-	-.0506	-.0423	-	-	-.0218	-.0110	-
4.5	-.0863	-.0384	-.0320	-.0236	-.0232	-.0028	.0063	.0604

^a The zero of energy is that for 1_{Σ}^{+} at 8.0 Bohr.

Figure 1. Potential curves for several states for SnO .

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