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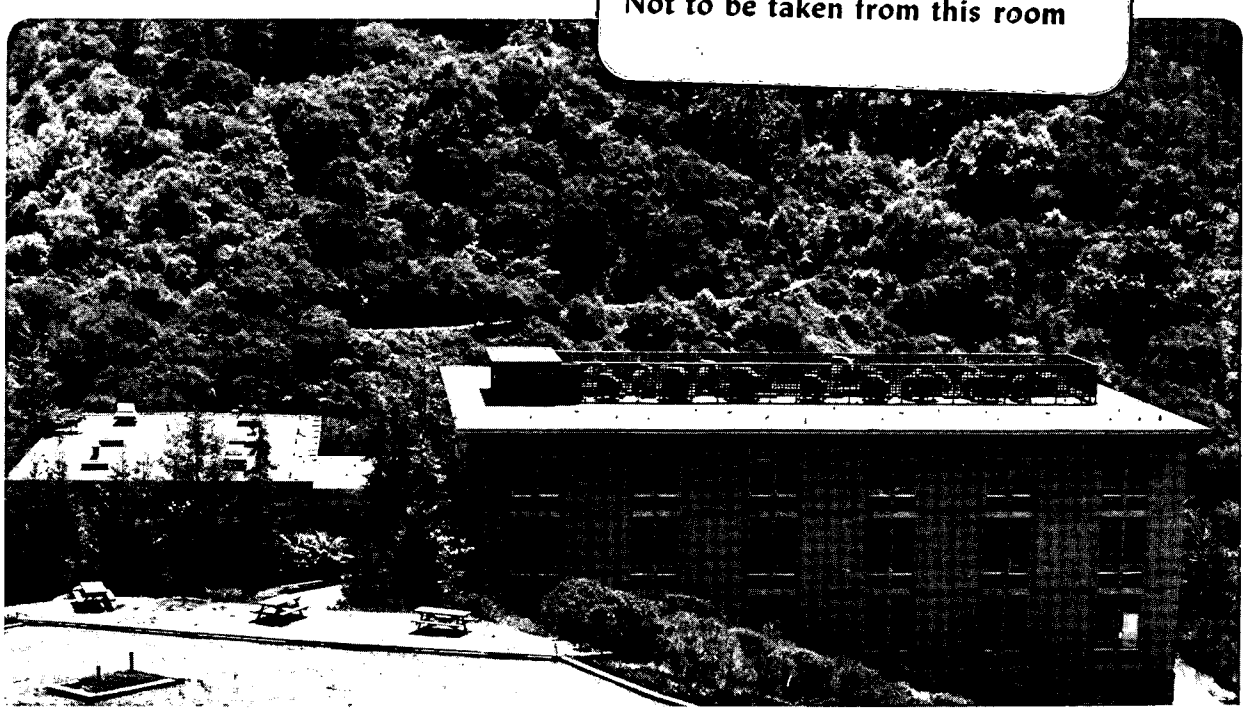

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Relativistic Quantum Calculations of Low-lying States of SnH: Comparisons with the Electronic Spectra of SnH and with the Properties of PbH

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Relativistic quantum calculations including spin-orbit interaction and configuration interaction are described for several low-lying states of SnH. The spectroscopic properties of these states are compared with the experimental electronic spectra. The properties of the $^2\Pi$, $^4\Sigma^-$, and $^2\Delta$ states are discussed in both Λ-S and ω-ω coupling schemes and compared with appropriate states of PbH. The dissociation energy is calculated to be 2.30 eV.

1. Introduction

The tin hydride molecule has been of considerable experimental and theoretical interest for several decades.[1-12] The first electronic spectra of SnH were recorded by Watson and Simon[1,2] in the high pressure arc. These spectra revealed the existence of bands in the red and two red-degrading bands in the violet. These authors attributed the red bands to $^2\Sigma - {}^2\Pi$ transitions and the violet bands were assigned to a $^2\Delta - {}^2\Pi$ transition with $^2\Pi$ as the ground state. Kleman[12] reinterpreted the red bands as due to $^4\Sigma^- - {}^2\Pi$ transitions by analogy to lighter group (IV) hydrides. Klynning and co-workers[4,5] have recorded the absorption spectra of SnH and SnD. Numerical energy expressions were fitted for these bands and the spectroscopic properties of the $^2\Pi$, $^4\Sigma^-$, and $^2\Delta$ states of SnH and SnD were calculated. There are remarkably few vibrational excitations observed - somewhat more for SnD than for SnH. Thus the vibrational frequency for SnH is sometimes calculated from a value for SnD.

The tin hydride molecule has been used by several authors as an interesting candidate for the rotational analysis of $^2\Pi$ and $^4\Sigma$ electronic states of a diatomic molecule.[6-9] Centrifugal distortion of the spin-orbit and spin-rotation interaction for several states of SnH have been considered. Theoretical analysis of the spin-orbit splitting of the $^2\Delta$ and $^4\Sigma^-$ states was considered by Veseth.[10,11]

The objective of this investigation is to study the properties of low-lying electronic states of SnH. In Section 2 we discuss the methodology of calculations. In Section 3 comparisons are made with experimental spectroscopic properties of SnH. In the last section we discuss the nature of CI wavefunctions of SnH and compare with earlier predictions and with PbH wavefunctions.

2. Method of Calculations

We use here the general method of relativistic effective potential calculations proposed by Christiansen, et al.[13] This method is discussed in detail in that paper and in a review paper by Pitzer.[14] In summary, relativistic effective potentials were obtained from numerical Dirac-Fock solutions of the tin atom. The SCF calculations used spin-averaged relativistic effective potentials with outer $d^{10}s^2p^2$ electrons as the valence electrons. Thus all other relativistic effects except the spin-orbit interaction were included at the SCF stage. The one-electron spin-orbit operator was obtained by differencing the relativistic effective potentials with respect to spin and was introduced for the configuration interaction calculations. This methodology was found to be quite successful in computing the spectroscopic properties of TℓH,[13] Pb_2,[15,16] Sn_2,[16] SnO,[17] PbO,[18] and PbH.[19]

A double zeta basis set was used for tin; it was optimized for the ^3P atom. The hydrogen basis set we employ here is the one used by Code and Huo[20] for SiH. These basis sets are shown in Table 1.

Table 2 shows a few MO configurations and the corresponding Λ-S and ω-ω states arising from them. In Table 3 the dissociation limits of these low-lying states and the energies of the dissociated atoms are shown.

Next we consider the selection of configurations for our CI calculations. Although the ground state ½(I) is primarily $^2\Pi_{\frac{1}{2}}$, various ½ states arising from the $\sigma\pi^2$, $\sigma^2\sigma'$, $\sigma\sigma'\pi$, and π^3 configurations should be included since these configurations can mix by correlation and spin-orbit interaction. These MO's must be expanded in Cartesians since our SCF program calls for Cartesian Slater functions. When the above configurations are expanded in Cartesians one obtains $\sigma^2\pi_x\beta$, $\sigma^2\pi_y\beta$, $\pi_x{}^2\sigma\alpha$, $\pi_y{}^2\sigma\alpha$, $\pi_x\alpha\pi_y\beta\sigma\alpha$, $\pi_x\beta\pi_y\alpha\sigma\alpha$, $\pi_x\alpha\pi_y\alpha\sigma\beta$, $\sigma^2\sigma'\alpha$, $\pi_x{}^2\pi_y\beta$, and $\pi_y{}^2\pi_x\beta$ as reference configurations.

Single and double excitations from these 10 reference configurations yield 1731 configurations for the ½ states. This includes excitations from the s but not the d orbitals on the tin atom. The 3/2 state included $\sigma^2\pi_x\alpha$, $\sigma^2\pi_y\alpha$, $\pi_x^2\sigma\beta$, $\pi_y^2\sigma\beta$, $\pi_x\alpha\pi_y\beta\sigma\beta$, $\pi_x\beta\pi_y\alpha\sigma\beta$, $\pi_x\alpha\pi_y\alpha\sigma\alpha$, $\pi_x^2\pi_y\alpha$ and $\pi_y^2\pi_x\alpha$, $\sigma\alpha\sigma'\alpha\pi_x\beta$, $\sigma\alpha\sigma'\alpha\pi_y\beta$ reference configurations. Single and double excitations from these reference configurations resulted in 1723 configurations for the 3/2 states. The 5/2 state included $\pi_x^2\sigma\alpha$, $\pi_y^2\sigma\alpha$, $\pi_x\alpha\pi_y\beta\sigma\alpha$, $\pi_x\beta\pi_y\alpha\sigma\alpha$, $\sigma\alpha\sigma'\alpha\pi_x\alpha$ and $\sigma\alpha\sigma'\alpha\pi_y\alpha$ reference configurations. Excitations from these reference configurations gave rise to 1044 configurations.

We also made calculations excluding the spin-orbit term. For the $^2\Pi$ state only the Cartesian reference configurations arising from $\sigma^2\pi$ were included. Similarly for $^4\Sigma^-$ and $^2\Delta$ only the reference configurations arising from $\sigma\pi^2$ were used. Single and double excitations were allowed. The exclusion of the reference configurations related to $\sigma\sigma'\pi$ and the excitations therefrom probably has only a small effect at bonding distances but will have increasing effect at longer distances.

3. Results and Comparisons with Experiments

The calculated spectroscopic properties of a few low-lying states of SnH and the corresponding experimental values[4,21] are shown in Table 4. The complete energy levels as a function of internuclear distance are given in Table 5 and the corresponding potential energy curves are shown in Figure 1.

$^2\Pi$ and $^4\Sigma^-$ Terms

Table 4 is organized in terms of the Λ-S coupling states with the spin-orbit splitting A or 6λ shown in the third column. The calculated bond distance is a little too large and the vibration frequency a little too small for the $^2\Pi$ state; both agree very well for the $^4\Sigma^-$ state. The

calculated values are averages for the 1/2 and 3/2 states in each case. The spin-orbit splittings are a little too large in each case, but the agreement seems quite satisfactory in view of the difficulty of the calculation. The calculated total excitation energy to the $^4\Sigma^-$ term is 85% of the observed value. Since the $^4\Sigma^-$ state energies were calculated as second roots of the 1/2 and 3/2 matrices, one might have thought that the error would more likely be in the direction of two large rather than too small an excitation energy. Possibly some higher-energy configurations that were omitted would have lowered the lower ($^2\Pi$) roots more than the second ($^4\Sigma^-$) roots.

The $^2\Delta$ Term, Predissociation and the Dissociation Energy

The $^2\Delta$ - $^2\Pi$ bands of SnH show[4] predissociation with line broadening beginning at an energy of 25,177 cm^{-1} in SnH, at about 25,777 cm^{-1} in SnD, and with the last rotational line at 26,092 cm^{-1}. Our calculations for the 5/2 state indicate that it is dominantly $^2\Delta_{5/2}$ at a bond distance (3.4 Bohr) but that it has a broad maximum, see figure 1, near 4.5 Bohr arising from an avoided crossing with the $^4\Pi_{5/2}$ state. Our calculations place this maximum at 26,500 cm^{-1} in remarkably good agreement with the experimental value.

While our results yield somewhat too shallow a potential well for the 5/2 state, the other characteristics are in excellent agreement. Some quantum tunneling is expected which yields line broadening to a lower energy for SnH than for SnD.

Huber and Herzberg[21] appropriately report for the dissociation energy $D_o^o \leq 2.73$ eV where the value 2.73 eV arises if dissociation is to the energy of $^3P_2 + {}^2S_{\frac{1}{2}}$ atoms. But our results clearly indicate a potential maximum substantially above that energy. Hence the dissociation energy

of SnH is well below the 2.73 eV value, and our best estimate is based on the energy difference for the $^2\Pi_{1/2}$ state from the minimum to 9 Bohr which yields 2.30 eV.

Our methods did not allow a reliable calculation for the $^2\Delta_{3/2}$ state which is the third 3/2 state, hence we have no value for the spin-orbit splitting in the $^2\Delta$ term. The experimental data indicate a small value which is surprisingly different for SnH and SnD.

4. Nature of CI Wavefunctions and Comparisons with the Corresponding States of PbH.

Table 6 shows the fractional Λ-S populations at two distances for the states of SnH considered in this paper. At 3.4 Bohr, which is close to the potential minimum for most of these states, there is only a little mixing among the Λ-S states. This is reflected both by the dominant population of a particular Λ-S state at this distance and the energies of these states in comparison to the corresponding ω-ω states (cf. Table 5). At 6.0 Bohr, however, the ω-ω states of SnH are mixtures of several Λ-S states. Thus the spin-orbit term causes greater mixing at long distances and near dissociation limits than at equilibrium bond distances for the SnH molecule.

In comparison with PbH,[19] the contaminating populations are usually much smaller for SnH, often about 10% or 20% of the corresponding values for PbH. This is expected in view of the much smaller spin-orbit effect for Sn as compared to Pb. But there are also some differences. The mixing of $\sigma\sigma'\pi$ with the lowest 1/2 and 3/2 states is no larger for PbH than for SnH at the bond distance, but it becomes much larger for PbH at larger R values. The 3/2(II) state retains primarily its $^4\Sigma^-$ character even at 6 Bohr for SnH, whereas for PbH that state has large populations from $\sigma^2\pi$, $\sigma\pi^2(^2\Delta)$, and $\sigma\sigma'\pi$ and little remaining from $^4\Sigma^-$.

In Table 6 the fourth column gives for 1/2 states the sum of the populations for $^4\Sigma^-_{1/2}$ and $^2\Sigma^-_{1/2}$ from the Λ-S configuration $\sigma\pi^2$. In most cases this is almost entirely $^4\Sigma^-$, but for the ground 1/2 state at 3.4 Bohr the 0.003 population can be divided approximately 2/3 or 0.002 $^4\Sigma^-$ and 1/3 or 0.001 $^2\Sigma^-$. This may be of interest for further study of the detailed structure of the rotational levels for the $^2\Pi_{1/2}$ state.

In some of the literature there is discussion about the mixing of states needed to give intensity to the $^4\Sigma^- \leftrightarrow {}^2\Pi$ transition and to explain various details of the energies of various states. From Table 6 it is evident that there is significant mixing of several contaminating states even at 3.4 Bohr and that this mixing increases rapidly with R. Thus there are several contributions to the $^4\Sigma^- \leftrightarrow {}^2\Pi$ intensity. Calculations of transition dipole integrals would be required to analyze this further; although such calculations are quite feasible, we have not undertaken them. Neither have we attempted to reconsider the analysis of the rotational fine structure in terms of these contaminating populations. We do note, however, that Kopp and Hougen's[6] concept of case (a') coupling for the $^4\Sigma^-$ state is supported by the mixing with $^2\Pi$ which is large enough to make $6\lambda = 270\ cm^{-1}$ exceed the rotational energy for low J values yet not so large as to make the designation $^4\Sigma^-$ inappropriate.

Veseth[11] attempted to explain certain features of the $^4\Sigma^-$ and $^2\Delta$ states by contamination by a single higher-energy state in each case. For $^2\Delta$ particularly this failed, and he concluded that a more general contamination was involved. Our calculations certainly support the idea that there are several higher energy states, especially those arising from $\sigma\sigma'\pi$ as well as $^2\Sigma^-$ and $^2\Sigma^+$ from $\sigma\pi^2$ (cf. Table 2), which are unobserved experimentally but which mix with the lower states under discussion.

Thus, with calculations only moderately more elaborate than those reported here, it would be possible to explore many fine details of the SnH spectrum that have attracted interest. Our results show no significant conflict with the experimental data and agree concerning several interesting features.

Acknowledgements

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Table I. Basis Set Employed in This Calculation[a]

	Sn Atom		H Atom
s	2.6828(5)	s	1.1264(1)
	1.6074(5)		1.4108(1)
p	2.3775(5)	p	1.4409(2)
	1.3523(5)		
d	3.9532(4)		
	1.5175(4)		

[a] Numbers in parentheses are principal quantum numbers.

Table II. A few MO Configurations and the Resulting Λ-S and ω-ω States. The MO's resulting from s and d orbitals on Sn are not shown.

MO Configuration	Λ-S State	ω-ω State
$\sigma^2\pi$	$^2\Pi$	1/2 3/2
$\sigma\ \pi^2$	$^4\Sigma^-$	1/2 3/2
	$^2\Sigma^-$	1/2
	$^2\Delta$	3/2 5/2
	$^2\Sigma^+$	1/2
$\sigma^2\sigma'$	$^2\Sigma^+$	1/2
$\sigma\sigma'\pi$	$^4\Pi$	1/2(4) 3/2(3) 5/2
	$^2\Pi(2)$	
π^3	$^2\Pi$	1/2 3/2

Table III. A Few Low-lying States and Their Dissociation Limits

ω-ω State	Dissociation Limit	Energy in cm^{-1}
1/2 (I)	$^3P_0 + {}^2S_{1/2}$	0.0
3/2 (I) 1/2(II), 1/2(III)	$^3P_1 + {}^2S_{1/2}$	1691.8
5/2 3/2(II), 3/2(III) 1/2(IV), 1/2(V)	$^3P_2 + {}^2S_{1/2}$	3427.7

Table IV. Spectroscopic Properties of SnH

		T_e / cm^{-1}	A or 6λ / cm^{-1}	R_e / Å	ω_e / cm^{-1}
$^2\Pi$	calc.	0	2376	1.83	1600
	exp.	0	2179	1.78	1715
$^4\Sigma^-$	calc.	13,265	328	1.78	1560
	exp.	15,580	270	1.77	1521
$^2\Delta$	calc.(5/2)	26,460	-	1.96	700
	exp.	23,790	(20)	1.85	1080

Table V. Potential Energy Curves of SnH

R	1/2(I)	3/2(I)	1/2(II)	3/2(II)	5/2	$^2\Pi$	$^4\Sigma^-$	$^2\Delta$
2.5	.0026	.0128	.0503	.0519	.1185	.0099	.0517	.1187
3.2	-.0805	-.0698	-.0177	-.0162	.0471	-.0782	-.0161	.0475
3.4	-.0839	-.0731	-.0189	-.0173	.0435	-.0768	-.0171	.0440
3.6	-.0831	-.0722	-.0172	-.0143	.0423	-0.749	-.0153	.0431
4.0	-.0741	-.0630	-.0104	-	.0425	-.0667	-.0082	.0439
4.5	-.0573	-.0460	-.0035	-	.0420	-.0493	-.0009	.0449
6.0	-.0151	-.0045	.0036	.0072	.0321			
9.0	0.0					-	-	-

Table VI. Fractional Populations of Various Λ-S Configurations for a Few Low-lying States of SnH

State	R/Bohr	$\sigma^2\pi(^2\Pi)$	$\sigma\pi^2(^4\Sigma^-)$*	$\sigma\pi^2(^2\Sigma^+)$	$\sigma\pi^2(^2\Delta)$	$\sigma\sigma'\pi$
1/2(I)	3.4	0.941	0.003	0.001	-	0.002
	6.0	0.683	0.040	0.003	-	0.070
3/2(I)	3.4	0.933	0.008	-	0.002	0.002
	6.0	0.614	0.111	-	0.008	0.060
1/2(II)	3.4	0.003	0.923	0.011	-	0.0
	6.0	0.025	0.682	0.014	-	0.039
3/2(II)	3.4	0.008	0.929	-	0.0	0.0005
	6.0	0.115	0.619	-	0.006	0.025
5/2	3.4	-	-	-	0.942	0.002
	6.0	-	-	-	0.209	0.691

* For 1/2 states this may include a contribution, usually small, from $\sigma\pi^2(^2\Sigma^-)$; see text.

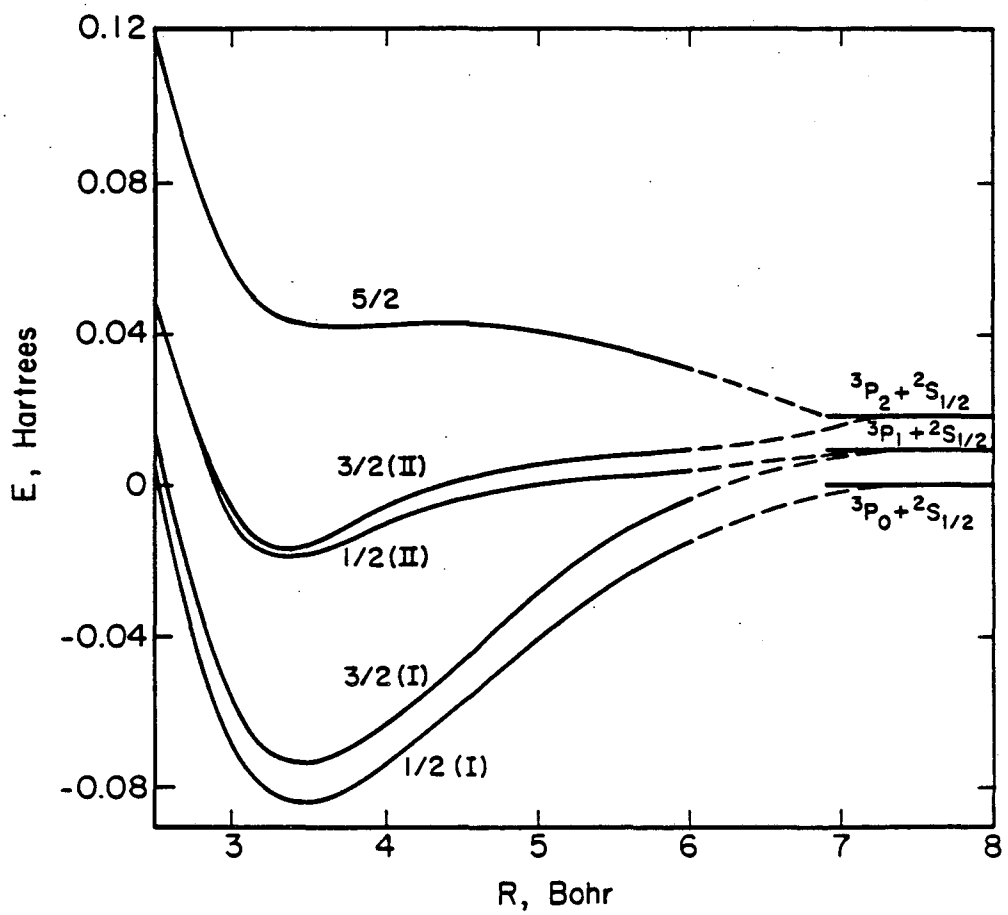

Figure 1. Potential energy curves of SnH.

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