Theoretical study of electric dipole and transition moments of GeH, SnH, and PbH

Douglas A. Chapman, Junqing Li, a) K. Balasubramanian, b) and S. H. Lin
Department of Chemistry, Arizona State University, Tempe, Arizona 85287-1604
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Electric dipole and transition moments are calculated in the relativistic CI formalism for five low-lying states of GeH, SnH, and PbH. In addition, results of complete active space MCSCF/CI calculations of the ground state dipole moments of these molecules are described. The ground state dipole moments (μr) of GeH, SnH, and PbH are calculated to be 0.09, 0.39, and 0.94 D, respectively, with polarity (M+H-) in all cases. Transition moments for the ω-ω components of the 3Π→4Σ- and 3Π→2Δ transitions in these molecules are calculated and compared with available experimental findings. The spin-orbit interaction is found to make a significant contribution to the dipole and transition moments of PbH.

I. INTRODUCTION

The electric dipole moments of the heavier Group IV diatomic hydrides in their ground X 2Π states are currently a topic of considerable interest. 1-5 An experimental determination 1 of the dipole moment of the X 2Π state of GeH is presently the only such data available for the series SiH, GeH, SnH, and PbH. Theoretical dipole moment values have been presented for SiH,2-5 SnH3; recently, such work has called the experimental value for the dipole moment of GeH into question. 6-8 To date, no theoretical dipole moment data are available for PbH in its X 2Π1/2 ground state or in its excited states. Further, previous theoretical studies on the GeH2 and SnH2 molecules have not explicitly addressed the effects of spin-orbit interaction on the ground state dipole moment. While these effects may be neglected, at least to the first order for the GeH and SnH molecules, such is not the case for PbH. Indeed, for lead hydride, the ground electronic state is more correctly described by the ω-ω designation as a 1/2 state due to the very large spin-orbit interaction present in the Pb atom.

The spectroscopic nature of the low-lying electronic states of SnH and PbH molecules are well characterized 9-12; the observed electronic spectra of these molecules, as well as GeH, are summarized in Ref. 26. Among the more interesting features present in the spectra of GeH and SnH is the presence of the “forbidden” 3Π→4Σ- transition which has been discussed by Veseth 13 in terms of Hund’s coupling cases (a) and (c). The mixing of Λ-S states necessary to give intensity to this transition in the tin hydride molecule has been briefly discussed by Balasubramanian and Pitzer. 11 In contrast to the low-lying electronic states of GeH and SnH, which may be adequately described by the so-called “intermediate” coupling case, the low-lying electronic states of PbH are mixed much more heavily by spin-orbit interaction. As a result, the electronic states of lead hydride cannot be properly addressed in terms of any single Λ-S configuration. Thus, it seemed of interest to calculate and compare electronic transition moments for spectral bands of these molecules from relativistic CI wave functions constructed in the ω-ω coupling scheme. In this way, the effects of mixing of different Λ-S states induced by spin-orbit contamination on the intensities of spectral bands in GeH, SnH, and PbH could be investigated.

The purpose of the present work is to apply the relativistic configuration interaction (RCI) technique and the complete active space MCSCF (CASSCF)/CI method to the calculation of electric dipole and transition moments for five low-lying states of GeH, SnH, and PbH. In Sec. II, the methods employed to obtain the wave functions, dipole moments, and transition probabilities are discussed. Section III contains results of RCI calculations on the 1/2(I), 1/2(II), 3/2(1), 3/2(II), and 5/2(1) states of GeH, SnH, and PbH, as well as results of calculations of the ground state electric dipole moments of these molecules using the complete active space MCSCF/CI method.

II. METHOD OF CALCULATION

The relativistic configuration interaction (RCI) calculations utilized triple zeta basis sets of Slater-type functions optimized for the 3P ground states of the Ge, Sn, and Pb atoms with the d 10s2p6 outer shell explicitly retained in the calculations. The hydrogen basis is that used by Cadé and Huo 14 in a calculation on SiH. These basis sets are shown in Table I.

Table I. Slater-type basis sets used in calculations on GeH, SnH, and PbH. Principal quantum numbers are shown in parentheses.

<table>
<thead>
<tr>
<th></th>
<th>Ge</th>
<th>Sn</th>
<th>Pb</th>
<th>H*</th>
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<td>2.2708(4)</td>
<td>2.5603(5)</td>
<td>3.3226(6)</td>
<td>1.1264(1)</td>
</tr>
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<tr>
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<td>0.5350(6)</td>
</tr>
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<tr>
<td>p</td>
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<tr>
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<td>0.7540(6)</td>
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</tr>
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<td>s</td>
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<td>4.9688(5)</td>
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</tr>
<tr>
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<td>2.5499(4)</td>
<td>2.7823(5)</td>
<td>9.540(6)</td>
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<td>1.0000(5)</td>
<td>1.0714(5)</td>
<td>9.540(6)</td>
</tr>
</tbody>
</table>

a) Permanent address: Department of Modern Chemistry, University of Science and Technology of China.

b) Alfred P. Sloan Fellow; Camille and Henry Dreyfus Teacher-Scholar.

* From Ref. 14.
The RCI calculations were carried out following a single configuration SCF. The SCF calculations included relativistic effective potentials (REPs) for the Ge, Sn, and Pb atoms. LaJohn et al., Hurley et al., and Ermier and Christiansen have generated Gaussian fits for averaged REPs and spin-orbit operators for a number of atoms based upon numerical potentials. The single-configuration SCF orbital space was generated for the \( X^2\Pi \) ground state of each molecule at internuclear distances 2.50–9.00 bohr.

The relativistic configuration interaction (RCI) technique used in this study is a multireference singles and doubles CI (MRSDCI) method including spin-orbit interaction based on the relativistic CI formalism of Christiansen, Balasubramanian, and Pitzer. This scheme has been very successful in investigations of electronic and spectroscopic properties of molecules which contain heavy atoms; work of this type has been reviewed recently.

The RCI technique has been applied previously to the calculation of spectroscopic properties of SnH and PbH by Balasubramanian and Pitzer. The reference configurations for the 1/2, 3/2, and 5/2 states tabulated in Ref. 11 were included as reference configurations in this investigation. In addition, the \( 1\sigma^2\pi^1 \) configurations were added as reference configurations for the SnH and PbH calculations. These configurations were found to be relatively more important at longer distances for these molecules than for GeH. Limited d-electron correlation was also included in the SnH and PbH calculations by keeping only the tin and lead \( \sigma_d \) electrons in the occupied CI space; promotion of these electrons was then allowed from all references. Single and double excitation of seven electrons from the above references generated CI spaces of 10 620 configurations for the 1/2 states, 9014 configurations for the 3/2 states, and 4926 configurations for the 5/2 states of SnH and PbH. The Ge \( \sigma_d \) electrons were kept frozen in the CI calculations. Slightly more extensive correlation of the five valence electrons of GeH from the smaller set of 1/2 state references produced 8913 configurations for these states, while the 3/2 and 5/2 spaces of GeH, which were generated from the same reference lists as were the 3/2 and 5/2 states of SnH and PbH, consisted of 9748 and 5277 configurations, respectively.

The electric dipole and transition moments were evaluated as expectation values over the RCI wave functions using a procedure developed recently. At the SCF stage of the calculation, the dipole and transition matrices were constructed from a single set of orthonormal orbitals of the \( X^2\Pi \) state of each molecule. The use of one set of orbitals to construct the transition matrices greatly facilitated the final evaluation of the transition moments over the CI wave functions, especially in the case of large configuration spaces. Electric dipole and transition moments calculated from highly correlated RCI wave functions have been shown to be reliable in comparison to nonrelativistic, all-electron results for lighter molecules; further, this method permits a rigorous determination of the spin-orbit contribution to the electric dipole moment, and, at present, is the only \textit{ab initio} method available which can be applied to calculation of transition probabilities between electronic states whose wave functions are constructed in the \( \omega-\omega \) coupling scheme.

The electric dipole moments of the \( X^2\Pi \) states of GeH, SnH, and PbH were also obtained from complete active space MCSCF (CASSCF)/CI calculations which utilized one of the present authors' (K.B.) modified version of the ALCHEMY II codes which was adapted to include relativistic ECPs. The \( d^{10}s^2p^2 \) configuration was explicitly included as the valence shell for the metal atoms, and REPs were employed for germanium, tin, and lead. A \( (3s3p4d) \) Gaussian basis was optimized in Ref. 16 for the ground state of the Ge atom; this basis was augmented by adding a set of \( s(0.03), p(0.02), \) and \( d(0.30,0.10) \) type functions. The \( (4s4p5d) \) basis was contracted to a \( (4s4p4d) \) type basis by contracting the three large exponent \( d \) type functions. The \( (3s3p4d) \) basis, optimized in Ref. 15 for the \( 3P \) ground state of the Sn atom, was extended with one set of \( s(0.02), p(0.02), \) and \( d \) type (0.09) functions. The resulting \( (4s4p5d) \) valence-level basis was then contracted to a \( (4s4p4d) \) type basis by contracting the two largest exponent \( d \) type functions in the Sn basis. The \( (3s3p4d) \) basis for Pb was taken from Ref. 17, and was extended with \( s(0.02), p(0.02), \) and \( d(0.08) \) type functions. This resulted in a \( (4s4p4d) \) basis comparable in size to the Ge and Sn basis sets. Van Duijneveldt's \( (5s3s) \) basis augmented by a set of \( p \) type polarization functions was employed for the hydrogen atom.

The orbitals for the first- and second-order configuration interaction calculations were generated by a complete active space MCSCF (CASSCF) calculation. In this method the five outer electrons \( [s^2p^3(M) + s^1(H)] \) were distributed in all possible ways among a chosen set of orbitals which constituted the active space. The molecule was oriented along the \( z \) axis. In the \( C_{2z} \) group, the active space consisted of three \( a_l \), one \( b_2 \), and one \( b_l \) orbitals which correlated into the outer \( s \) and \( p \) orbitals of the metal and the 1s hydrogen orbital at infinite separation.

CI calculations were carried out on the \( X^2\Pi \) states of SnH and PbH using the first-order CI (FOCI) method. The FOCI calculations included all configurations in the zero order CASSCF and the configurations generated by distributing four electrons in the internal space and one electron in the external space in all possible ways. The configuration count in \( C_{2z} \) symmetry for the ground states of SnH and PbH was 867.

Configuration interaction calculations were also performed in a second-order CI (SOCl) expansion for the \( X^2\Pi \) state of GeH with the objective of checking the accuracy of the FOCI results. The SOCI space included the configurations generated in the FOCI calculations discussed above, as well as the second-order space (three electrons distributed in the internal space, and two electrons in the MCSCF external space in all possible ways). The dimension of the SOCI space for GeH in the \( C_{2z} \) group generated in this way was 15 409 CSFs.

### III. RESULTS AND DISCUSSION

Figures 1–3 show the RCI dipole moment curves for low-lying electronic states of GeH, SnH, and PbH; spin-orbit corrected CASSCF/CI values for the ground states of
these molecules are summarized in Table II. Figures 4 and 5 show the RCI transition moment curves for the $\omega \omega$ components of the $^2\Pi \to ^4\Sigma^-$ and $^2\Pi \to ^2\Delta$ bands of GeH, SnH, and PbH. In subsequent sections these data are discussed, and the effects of spin-orbit interaction on the electric dipole and transition moments of these molecules are examined.

A. Spectroscopic constants and electric dipole moment functions for low-lying electronic states of GeH, SnH, and PbH

Balasubramanian and Pitzer have studied the low-lying electronic states of SnH$^{11}$ and PbH$^{12}$; the potential energy curves and dissociation relationships for the 1/2(II), 1/2(III), 3/2(II), 3/2(III), and 5/2(I) states of these molecules are shown in the earlier works. The previous studies utilized double zeta STO basis sets for the tin and lead atoms; the treatment in the present work is thus more extensive for both molecules in terms of basis set size and extent of correlation. For the ground states of these molecules, the RCI vibrational frequencies were slightly improved; the theoretical frequencies ($\omega_v$) for SnH (1689 cm$^{-1}$) and PbH (1501 cm$^{-1}$) are in good agreement with the experimental values$^{26}$ of 1715 cm$^{-1}$ (SnH) and 1564 cm$^{-1}$ (PbH). The dissociation energies obtained here are somewhat smaller than those listed in the previous work. These energies (2.03 eV, SnH; 1.52 eV, PbH) agree well with the experimental values$^{26}$ of <2.73 eV (SnH) and 1.59 eV (PbH). The limited $d$ correlation introduced into the RCI calculations was found to increase the dissociation energy of SnH by about 0.05 eV; this effect, along with inclusion of references important at longer distances in the 1/2 state CI, are probably responsible for the dissociation energies in the present work being a bit lower than those given in Refs. 11 and 12.

The RCI vibrational frequencies calculated for the 3/2(II), 3/2(III), and 5/2(I) states of both molecules did not
differ significantly from the earlier results. The calculated frequencies for the $1/2(\Pi)$ states of both molecules were improved somewhat (1530 cm$^{-1}$ for SnH; 432 cm$^{-1}$ for PbH), again due to correlation and larger basis sets. The transition energies and equilibrium geometries calculated using the current basis sets also are not substantially different from the previous works.

Spectroscopic constants were calculated from the RCI results for the ground state of the GeH molecule. The RCI vibrational frequency for the $X^2\Pi_{1/2}$ state (1862 cm$^{-1}$) is in good agreement with the experimental value (1833 cm$^{-1}$); as in the cases of SnH and PbH, the calculated $r_e$ for the ground state of GeH (3.13 bohr) is about 5% larger than the experimental value (3.00 bohr). The calculated dissociation energy (2.49 eV) is also in reasonable agreement with the experimental value, which is listed as <3.30 eV.

Vibrational frequencies and equilibrium geometries for the $X^2\Pi$ states of SnH and PbH were also calculated from FOCI wave functions. The FOCI $\omega_e$ and $r_e$ values for SnH (1682 cm$^{-1}$; 3.43 bohr) agree well with experimental results, as do the FOCI data for PbH ($\omega_e = 1464$ cm$^{-1}$; $r_e = 3.67$ bohr). Spectroscopic constants calculated from SOCI wave functions for the $X^2\Pi$ state of GeH ($\omega_e = 1898$ cm$^{-1}$; $r_e = 3.00$ bohr) were found to be in excellent agreement with experiment. It is noted that the SOCI $r_e$ value for GeH was found to be about 2% shorter than the corresponding FOCI $X^2\Pi r_e$ (3.06 bohr); this effect is presumably due to the more thorough treatment of correlation in the second-order wave function.

Table II shows the SOCI $\mu_e$ value for GeH, as well as the FOCI $\mu_e$ results for SnH and PbH and the CEPA $\mu_e$ value for SiH. Dipole moments for the $X^2\Pi_{1/2}$ states of GeH, SnH, and PbH were obtained from the CASSCF/CI results by applying the spin-orbit correction $\Delta \mu_e = \mu_e (\Sigma^+ - \mu_e [1/2(\Pi)])$, which was calculated from the RCI results. The effects of spin-orbit interaction on the ground state dipole moment of GeH were found to be slight; hence, only the GeH $X^2\Pi_{1/2} \mu_e$ value is listed in Table II. However, the difference between the $X^2\Pi_{1/2}$ and $\Sigma^+_{1/2} \mu_e$ values for the SnH and PbH molecules were found to be substantial; therefore, data for both states of these molecules

FIG. 4. Electronic transition moments between low-lying states of GeH.
are tabulated in Table II. Dipole moments for the $^2\Pi_{3/2}$ states of SnH and PbH were obtained by correcting the FOCI $\mu_\sigma$ values by the RCI result $\Delta \mu_\sigma^0 = \mu_\sigma (^2\Pi) - \mu_\sigma (^3/2(1))$. The CASSCF/Cl $X^2\Pi$ $r_e$ values were corrected in a similar manner to yield the equilibrium geometries for the $X^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ states shown in Table II.

Figure 1 shows the theoretical electric dipole moment functions near $r_e$ for the ground states of SiH, GeH, SnH, and PbH. The CEPA results for the $X^2\Pi$ state of SiH were taken from Ref. 5 and were included for completeness. As Fig. 1 shows, the RCI dipole moment curve for the $X^2\Pi$ state of GeH is in very good overall agreement with the "uncorrected" CEPA-1 curve of Werner and Buckingham. The RCI $\mu_\sigma$ value, 0.276 D ($Ge^+\cdot H^-$), is somewhat larger than the CEPA $\mu_\sigma$ value (0.093 D, $Ge^+\cdot H^-$). In light of the close agreement between the CEPA and RCI curves near $r_e$, the discrepancies between the $\mu_\sigma$ values may be attributed to differences in calculated $r_e$ values (3.00 bohr, CEPA vs 3.13 bohr, RCI), as well as to the steep slope of the $\mu$ vs $r$ curve in this region. The difference between the calculated $r_e$ values arises primarily from the use of singe-configuration SCF orbitals in the relativistic CI expansion, as well as from differences between the RCI and CEPA treatments in the extent of electron correlation. However, more accurate CASSCF/SOCI calculations, which employed the (4s4p4d) basis, gave a $\mu_\sigma$ value of 0.0976 D ($Ge^+\cdot H^-$) at $r_e = 3.00$ bohr. Thus, the agreement between the SOCI and CEPA results are very good. The corresponding CASSCF/FOCI $\mu_\sigma$ value was found to be about 6% larger than the SOCI $\mu_\sigma$ value. The effect of spin-orbit terms on the GeH dipole moment amounts to about a 0.5% decrease of the 1/2(1) state dipole moment relative to the $^2\Pi$ value. The SOCI $\mu_\sigma$ value is thus lowered to 0.0971 D when corrected for spin-orbit interaction. This value is in excellent agreement with the CEPA-1 value, as well as the coupled-pair functional (CPF) data of Pettersson and Langhoff, who obtained a value of 0.085 D ($Ge^+\cdot H^-$).

At present, the only available ground state dipole moment calculation on the SnH molecule is that of Pettersson and Langhoff, who obtained a value of 0.357 D (Sn$^+\cdot H^-$) at $r_e = 3.36$ bohr. The CASSCF/FOCI dipole moment of the $X^2\Pi$ ground state of SnH was found to be 0.405 D (Sn$^+\cdot H^-$) at the RCI $r_e$ (3.43 bohr). The RCI $\mu_\sigma$ value of 0.499 D (Sn$^+\cdot H^-$), calculated at the RCI $r_e$ (3.47 bohr) of the 1/2(1) state, is larger than both the CPF and FOCI results. Some of the difference between the RCI, FOCI, and CPF results could originate from neglect of spin-orbit effects in the CPF calculation, although again, differences in $r_e$ values, coupled with the steep slope of the SnH dipole curve (Fig. 1), could influence the RCI $\mu_\sigma$ value. Near $r_e$ of the 1/2(1) state, the inclusion of spin-orbit terms was found to

![Diagram of electronic transition moments between low-lying states of SnH and PbH.](image)

**FIG. 5.** Electronic transition moments between low-lying states of SnH and PbH.

### Table II. Theoretical electric dipole moments ($\mu_\sigma$) for SiH, GeH, SnH, and PbH.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>State</th>
<th>$r_e$ (bohr)</th>
<th>$\mu_\sigma$ (D)</th>
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<td>SiH</td>
<td>$^2\Pi$</td>
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<td>PbH</td>
<td>$^2\Pi_{3/2}$</td>
<td>3.57</td>
<td>+0.673</td>
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lower the SnH 1/2(I) dipole moment relative to the 2Π value by about 1.5%. When corrected for spin-orbit terms the FOCI μe value is lowered to 0.398 D. The CPF dipole moment, which does not include spin-orbit corrections, can similarly be corrected to 0.35 D.

To date, no theoretical or experimental data appear to be available for the dipole moment of the PbH molecule in its ground 1/2(1) state. The RCI calculations yielded a dipole moment of 1.052 D (Pb⁺H⁻) at the theoretical rse (3.70 bohr) of the 1/2(1) state. The dipole moment of the 1/2(1) state was found to be lowered relative to the corresponding 3Π state by 4%. This value may again be used to correct somewhat better CASSCF/FOCI results for spin-orbit effects. Thus, the calculated FOCI dipole moment (0.981 D, Pb⁺H⁻ at rse = 3.67 bohr) for the X 3Π state is lowered to 0.937 D by inclusion of spin-orbit terms.

As can be seen from Table II, the calculated dipole moment of the 3Π3/2 state of PbH is substantially smaller than the 3Π1/2 component. Note that the rse value of the 3Π3/2 state is 0.06 bohr shorter than the corresponding value for the 3Π1/2 state. Thus, the shortening of the bond is consistent with the small dipole moment since the dipole moment depends on the charge separation.

Figures 2 and 3 show the RCI dipole moment curves for five low-lying ωω states of GeH, SnH, and PbH, as well as the 2Π, 3Σ⁻, and 3Δ Λ-S states from which they arise. The RCI results indicate that the ground 1/2(1) state dipole moments of each of the three molecules are polarized M⁻H⁺ for r < 2.75-3.00 bohr, change polarity to M⁺H⁻ near 3.0-3.25 bohr, reach a maximum near 5.00 bohr, and change polarity once again at long distance. The behavior of the GeH and SnH curves in the region 2.75-4.00 bohr supports the findings of Petterson and Langhoff on the large dipole derivatives near rse for these molecules. As Fig. 3 shows, the dipole moment function for the 1/2(1) state of PbH is also nearly a linear function of r near rse (2.75-4.00 bohr).

The effect of the spin-orbit interaction on the electric dipole moments of these molecules becomes readily apparent from Figs. 2 and 3. In the region 2.75-4.00 bohr, the Ω = 1/2 and [3/2] components of the GeH and SnH 2Π states are predominantly (93%) of 2Π (σπ⁻) character; in this region, the 1/2(1) state dipole moments of GeH and SnH are lowered by spin-orbit interaction by 0.5% and 1.5%, respectively, relative to the 2Π states. Near rse of the lead hydride 1/2(1) state, however, the wave function is a mixture of 87% 3Π1/2 (σπ⁻) and 13% 3Σ₁/₂ (σπ⁺); correspondingly, the dipole moment of the PbH 1/2(1) state is lowered by 4% relative to the 3Π state. At longer distances, the 3/2(1) (3Π3/2) states of all three molecules interact with the 3Σ₁/₂ [3/2(II)] state from the σπ⁻ configuration. Spin-orbit contamination of this type was found to be much stronger in SnH and PbH than in GeH; in the latter molecule, mixing of the 3Π3/2 state from the excited σπ⁻ configuration into the 3/2(1) wave function was found to be relatively more important at longer distances than contamination from the 3Σ₁/₂ (σπ⁺) state. Nonetheless, these interactions appear to cause the 3/2(1) curves of these molecules to fall off more rapidly than the 1/2(1) curves.

Spin-orbit mixing of the Ω components of the same symmetry of the 2Π and 4Σ⁻ states in GeH, SnH, and PbH imparts interesting behavior to the 3/2(II) and 1/2(II) dipole moment curves in Figs. 2 and 3. In the region 2.75-4.00 bohr, the GeH 3/2(II) state is predominantly (90%) of 4Σ₁/₂ (σπ⁻) character; 3Π3/2 (σπ⁻) contamination is almost negligible in this region. The tin hydride 3/2(II) state shows a slight (0.5%) 3Π3/2 contamination in this region, and the analogous 3/2(II) state of PbH is strongly influenced by the 3Π3/2 state (4% weight). This spin-orbit mixing is manifest in Figs. 2 and 3 by the increased splitting between the 4Σ⁻ and 3/2(II) dipole curves from GeH to PbH. This effect becomes more pronounced at longer distances; while the 3Π3/2 contamination into the 4Σ₁/₂ wave functions of SnH and PbH was found to be more significant than for GeH (3Π3/2 weight at 6.0 bohr = 3%), the overall result of the spin-orbit contamination into the 3/2(II) states was a progressively larger divergence of the 3/2(II) - 4Σ⁻ curves from GeH to PbH.

As shown in Figs. 2 and 3, the 1/2(II) (4Σ₁/₂) dipole curves of GeH and SnH exhibit similar behavior over a wide range of internuclear distances. These states interact only slightly with the 3Π1/2 (σπ⁻) state at longer distances. However, the 1/2(II) states of GeH and SnH interact strongly with the 3Σ₁/₂ state from the excited σπ⁺ configuration, and the 1/2(II) dipole moment curves of these molecules remain polarized M⁺H⁻ near 7.00 bohr. In contrast, the 1/2(II) wave function of PbH consists of 21% 3Π1/2 (σπ⁻) character at long distance, causing the 1/2(II) curve of PbH to change polarity near 5.00 bohr, as shown in Fig. 3.

The 5/2(1) states of all three molecules, which arise principally from the 3Δ3/2 state from the σπ⁻ configuration, undergo avoided crossings near 5.00 bohr with the 3Π5/2 state arising from the σπ⁺ configuration. This avoided crossing is primarily responsible for the rapid fall-off of the 5/2(1) curves relative to the 3Δ curves for GeH, SnH, and PbH. The σ⁺ orbital was found to be antibonding in character, with strong p₀ contribution from the metal atoms, which would imply that excitation into this orbital leads to charge transfer states with net charge polarization oriented towards the metal. The 5/2(1) and 1/2(1) curves shown in Figs. 2 and 3 seem to bear this out, for as the σπ⁺ or σπ⁻ (for 1/2 states) weights increase, these states become further polarized as M⁺H⁻.

It is noted that the electronic states under consideration in this work correlate, at long distances, into the neutral-atom dissociation limits [3P(J = 0,1,2) + 3Σ₁/₂]. The electric dipole moment functions of these states must, therefore, asymptotically approach zero at infinite internuclear separation. The RCI dipole moment curves for GeH, SnH, and PbH in Figs. 2 and 3 are shown to 6.0 bohr and thus the internuclear distances are not large enough to reflect this behavior.

### B. Electronic transition moments for the 2Π to 4Σ⁻ and 3Π to 3Δ systems of GeH, SnH, and PbH

Figures 4 and 5 show the electronic transition moments calculated from the RCI wave functions for the 2Π to 3Δ, 1/2(1) → 1/2(II), 3/2(1) → 3/2(II), 1/2(1) → 3/2(II), and 3/2(1) → 5/2(1) transitions of GeH, SnH, and PbH. Of par-
ticular interest in Fig. 4 and the SnH portion of Fig. 5 are the transition moments $W[1/2(1) \rightarrow 1/2(2)]$, $W[1/2(2) \rightarrow 3/2(2)]$, and $W[3/2(1) \rightarrow 3/2(2)]$, which correspond to transitions between the $\Omega = 1/2$ and $3/2$ components of the $2\Pi$ and $4\Sigma^-$ states of GeH and SnH. The electronic spectra of GeH and SnH are similar in that two main features have been reported, namely, red bands which have been attributed in GeH$^{30}$ and SnH$^4$ to $2\Pi \rightarrow 4\Sigma^-$ transitions, and blue bands due to $2\Pi \rightarrow 2\Delta$ transitions.$^{6,31}$ Klynnning et al.$^6$ have resolved the red bands of SnH into two components: the first, appearing towards the red end, was identified with the (0-0) band of a $1\Pi_{1/2} \rightarrow 2\Sigma_{3/2}^-$ transition, while the second feature, occurring at shorter wavelengths, was interpreted as the (0-0) and (1-1) bands of a $1\Pi_{1/2} \rightarrow 2\Sigma_{1/2}^-$ transition. Further, some less intense branches interconnecting the $\Omega = 1/2$ and $3/2$ components were found. Similarly, Klem and Werhagen$^{30}$ have identified two bands with origins near 15 370 and 16 245 cm$^{-1}$ in the GeH spectra. As Figs. 4 and 5 show, the parallel transition moments $W[1/2(1) \rightarrow 1/2(2)]$ and $W[3/2(1) \rightarrow 3/2(2)]$, which correlate into the $1\Pi_{1/2} \rightarrow 4\Sigma_{3/2}^-$ and $1\Pi_{1/2} \rightarrow 4\Sigma_{1/2}^-$ transitions, respectively, are much larger than the perpendicular probabilities $W[1/2(1) \rightarrow 3/2(2)]$ from 3.0 to 7.0 bohr. The calculated transition energies for the $1/2(1) \rightarrow 1/2(2)$ transitions in GeH and SnH are 13 030 and 14 122 cm$^{-1}$, respectively, while the calculated adiabatic transition energies of the $3/2(1) \rightarrow 3/2(2)$ transitions are 12 692 cm$^{-1}$ (GeH) and 12 479 cm$^{-1}$ (SnH). The approximate placement of the bands calculated here thus agrees reasonably well with the interpretations of Klynnning et al.$^6$ and Klem and Werhagen$^{30}$ as to the nature of the $2\Pi \rightarrow 4\Sigma^-$ transitions in GeH and SnH. Further, approximate intensity ratios may be extracted from the RCI results for these bands. Near the theoretical $r_e$ for the GeH 1/2(1) state, the intensity ratio 3/2(1) $\rightarrow$ 3/2(2):1/2(1) $\rightarrow$ 1/2(2):1/2(1) $\rightarrow$ 3/2(2) was found to be 1:0.4:0.01; the corresponding ratio for SnH was 1:0.5:0.01. These approximate intensity ratios are for (0-0) bands without rotational line strength factors.

The mixing of states necessary to give intensity to the $2\Pi \rightarrow 4\Sigma^-$ transitions in GeH and SnH may be examined in terms of the $\Lambda-S$ populations in the RCI wave functions. These data have been tabulated in the earlier work on SnH.$^{11}$ The contaminating $2\Pi(\sigma^\pi)$ populations in the upper 3/2(II) states of GeH and SnH are seen to increase with distance. The 2II populations are found to be much more substantial for SnH; for example, at 4.0 bohr, the GeH 3/2(II) state consists of 85% $2\Sigma_{3/2}^-$ ($\sigma^\pi$) and 0.09% $1\Pi_{1/2}^\text{II}$ ($\sigma^\pi$), while at the same distance, the $1\Pi_{1/2}^\text{II}$ contribution into the SnH 3/2(II) state is 0.5%. Near 6.0 bohr, however, the GeH 3/2(II) state consists of 3% $1\Pi_{1/2}^\text{II}$ character, while the corresponding weight in SnH is nearly 12%. Likewise the contaminating $4\Sigma^-$ ($\sigma^\pi$) populations are seen to increase in the lower 1/2(1), 3/2(II) states at longer distances. At 4.0 bohr, the GeH 3/2(II) state is 90% $1\Pi_{3/2}^\text{II}$ ($\sigma^\pi$) and 0.07% $2\Sigma_{3/2}^-$ ($\sigma^\pi$). At 6.0 bohr, however, the contaminating $2\Sigma_{3/2}^-$ population increases to 4%. Thus, mixing of $1\Pi_{3/2}^\text{II}$ ($\sigma^\pi$) and $2\Sigma_{3/2}^-$ ($\sigma^\pi$) states seems to be largely responsible for the intensities of the 3/2(1) $\rightarrow$ 3/2(II) components of the $2\Pi \rightarrow 4\Sigma^-$ transitions in GeH and SnH. Similarly, mixing of $2\Pi_{1/2}^\text{II}$ and $4\Sigma_{1/2}^-$ populations also occurs, but to a lesser extent, thus giving intensity to the 1/2(1) $\rightarrow$ 1/2(II) component of the $2\Pi \rightarrow 4\Sigma^-$ transition. Further, the $4\Sigma_{1/2}^-$ state from the $\sigma^\pi$ configuration is found to make a slight contribution to the 1/2(1) and 1/2(II) states of GeH and SnH. This contamination, while small, could nonetheless contribute to the A doubling observed in the ground states of GeH and SnH.$^{13}$

Figures 4 and 5 also show the calculated transition moments for the GeH and SnH $2\Pi \rightarrow 2\Delta$ bands, as well as the $\Omega = 3/2 \rightarrow 5/2$ component of these transitions. As can be seen from these figures, the effect of spin-orbit interaction (which may be interpreted as the deviation between the $W(2\Pi \rightarrow 2\Delta)$ and $W(3/2(1) \rightarrow 5/2(1))$ curves), becomes appreciable near 5.0 bohr. This effect is due to the avoided crossing between the $2\Delta(\sigma^\pi)$ and $4\Pi(\sigma^\sigma\pi)$ states at this distance. This avoided crossing is also thought to be responsible for the predissociations observed in the GeH and SnH $2\Delta$ states.$^{11}$

The RCI transition moments for the PbH molecule, also shown in Fig. 5, demonstrate the large spin-orbit mixing in PbH in comparison to GeH and SnH. The contaminating $\Lambda-S$ populations in both the upper and lower wave functions of PbH are much larger in comparison to GeH and SnH; these data are tabulated in the earlier work.$^{12}$ Of the three observed spectral features in PbH, only two bands have been tentatively assigned.$^{26}$ The transition moment data of Fig. 5 indicate that the parallel components 1/2(1) $\rightarrow$ 1/2(II) and 3/2(1) $\rightarrow$ 3/2(II) of the PbH $2\Pi \rightarrow 4\Sigma^-$ system should be much more intense than the perpendicular 1/2(1) $\rightarrow$ 3/2(II) component. The transition moment data would indicate that the 3/2(1) $\rightarrow$ 3/2(II) transition should be nearly as intense as the 1/2(1) $\rightarrow$ 1/2(II) band, at least for (0-0) and (1-1) bands. The intensity ratio 1/2(1) $\rightarrow$ 1/2(II):3/2(1) $\rightarrow$ 3/2(II):1/2(1) $\rightarrow$ 3/2(II) for the $\omega-\omega$ components of the $2\Pi \rightarrow 4\Sigma^-$ transitions, calculated near $r_e$ of the PbH 1/2(1) state, was found to be 1:0.88:0.3. The RCI transition moment data thus seem to support the suggestion$^8$ (as quoted in Ref. 11) that the red and the infrared systems of the PbH molecule originate principally from $2\Pi \rightarrow 4\Sigma^-$ transitions.

IV. CONCLUSION

Relativistic configuration interaction calculations of electric dipole and transition moments have been described for five low-lying states of GeH, SnH, and PbH. Electric dipole moments calculated from RCI and CASSCF/FOCI and SOCI wave functions were found to agree well with previous theoretical values for the $X'2\Pi$ states of GeH and SnH. Electronic transition moments for five bands in GeH, SnH, and PbH were calculated and compared with experimental findings; the mixing of $\Lambda-S$ states needed to give intensity to the $2\Pi \rightarrow 4\Sigma^-$ transition in these molecules was examined, and the approximate band positions for this transition were found to agree with experiment.

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17 W. Ermllr and P. A. Christiansen (private communication).
27 The major authors of ALCHEMY II codes are B. Liu, B. H. Lengsfield, and M. Yoshimine.
30 B. Kleeman and E. Werhagen, Ark. Fys. 6, 399 (1953).
31 B. Kleeman and E. Werhagen, Ark. Fys. 6, 359 (1953).