Spectroscopic constants and potential energy curves of 47 electronic states of InSb, InSb+, and InSb−

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Spectroscopic constants and potential energy curves of 26 electronic states of InSb, 12 electronic states of InSb+, and 9 electronic states of InSb− are obtained using complete active space self-consistent field, first-order configuration interaction, second-order configuration interaction, and relativistic configuration interaction methods (CASSCF/FOCI/SOCI/RCI), including spin–orbit interaction. The SOCI calculations included up to 700,000 configurations. Spectroscopic constants obtained predict several allowed electronic transitions for InSb, InSb+, and InSb− which are yet to be observed. The ground states of InSb, InSb+, and InSb− are found to be \( X^2\Sigma^{-}_{0^+} \), \( X^2\Sigma^{-}_{1/2} \), and \( X^2\Sigma^{-}_{1/2} \) with the constants \( \text{InSb}\ X^2\Sigma^{-}_{0^+} = R_e = 3.02 \, \text{Å} \), \( \omega_e = 121 \, \text{cm}^{-1} \), \( D_e = 1.35 \, \text{eV} \); \( \text{InSb}^+ \ X^2\Sigma^{-}_{1/2} = R_e = 3.03 \, \text{Å} \), \( \omega_e = 136 \, \text{cm}^{-1} \), \( T_e = 494 \, \text{cm}^{-1} \); \( \text{InSb}^- \ X^2\Sigma^{-}_{1/2} = R_e = 2.695 \, \text{Å} \), \( \omega_e = 191 \, \text{cm}^{-1} \), \( D_e = 2.5 \, \text{eV} \). The adiabatic ionization potential and electron affinity of InSb are calculated as 6.33 and 1.41 eV, respectively. Analogous to the recently observed \( \Delta^3\Pi \rightarrow X^3\Sigma^{-} \) system of GaAs, spectral bands in the 20–200 cm\(^{-1}\) region are predicted for InSb. Another \( \Sigma^3\Pi(\Pi) \rightarrow X^3\Sigma^{-} \) system is predicted at 15,830 cm\(^{-1}\). Both the \( \Sigma^3\Pi \) states in these systems are found to be predissociated through crossing of a repulsive \( ^5\Sigma^{-} \) curve. The two low-lying electronic states of InSb− \( (^2\Sigma^{-}_{1/2}, ^2\Pi_{1/2}) \) undergo relativistic avoided crossing.

I. INTRODUCTION

Generation and spectroscopic studies of Group III–Group V semiconductor clusters and their ions have received considerable attention in recent years.\(^{1-29}\) The electronic properties of related \( \text{Si}_n \), \( \text{Ge}_n \) clusters and their ions have also been the topic of several studies.\(^{30-37}\) The study of mixed Group III–Group V clusters such as \( \text{In}_n\text{Sb}_m \), \( \text{Ga}_n\text{As}_m \), and \( \text{In}_n\text{P}_m \) are especially of great importance since Group III–Group V compounds are used in fast semiconductor devices. Mixed III–V clusters are especially intriguing due to their substantial difference in the fragmentation patterns and ionization behavior from the corresponding Group IV clusters. In addition the possibility of isomers even for small III–IV clusters\(^{25}\) makes these species very interesting. Mixed clusters offer additional challenge to theoretical calculations as competing electronic states of the III and V atoms form an interesting array of electronic states.

The present author\(^{10}\) carried out theoretical calculations on the electronic states of GaAs and GaAs+. Theoretical prediction of a \( ^2\Sigma^{-} \) ground state for GaAs+ was subsequently verified by an ESR spectrum of matrix-trapped GaAs+ by Knight and Petty.\(^{9}\) Theoretical prediction of an \( X^3\Sigma^{-} \) ground state for the diatomic GaAs was recently verified by Lemire et al.\(^{15}\) Meier et al.\(^{16}\) made a SCF/MRDCI study on electronic states of GaAs and GaAs+. More recently, an ambitious CASSCF/FOCI/RCI study which included up to 700,000 configurations on GaAs, GaAs+, and GaAs− was made.\(^{21}\)

Lemire et al.\(^{19}\) have carried out a spectroscopic study of the diatomic GaAs using the supersonic jet expansion method. They found electronic bands attributed to the \( ^3\Pi(\Pi) \rightarrow X^3\Sigma^{-} \) system. The bands in this system were found to be predissociated due to crossing of a repulsive \( ^5\Sigma^{-} \) curve and the two excited \( ^3\Pi \) curves. With the exception of the \( ^3\Pi \) system all other systems are predissociated. The results of theoretical calculations in Ref. 21 are in full accord with the experimental spectroscopic constants for GaAs obtained for \( X^3\Sigma^{-} \) and \( ^3\Pi \) states.

O'Brien et al.\(^{1}\) have studied Ga\(_n\)As\(_n\) clusters generated by laser vaporization of GaAs crystal. Mass analysis of these clusters revealed considerable deviation from a binomial distribution for smaller clusters while large clusters followed the expected binomial distribution. Photofragmentation studies of Ga\(_n\)As\(_n\)−, Si\(_n\)−, and Ge\(_n\)− have also been made.\(^{2,27}\) Ionization potentials of Ga\(_n\)As\(_n\) clusters exhibited even-odd alternations. Kolenbrander and Mandich have recently studied In\(_n\)P\(_n\) clusters.\(^{22}\)

There are no detailed spectroscopic studies on the diatomic InSb, InSb+, and InSb− at present. In view of the considerable interest on Group III–V diatomics and clusters, the authors anticipate that such experimental studies are likely to be made in the near future. Duncan and co-workers are studying such mixed main group clusters. Knight and co-workers have communicated that they are investigating ESR spectra of a matrix isolated InSb+ ion analogous to their earlier study on GaAs+.\(^{9}\) Due to significant experimental interest and since there are no experimental or theoretical studies on the diatomic InSb, InSb+, and InSb− species, it was decided to carry out high-level \textit{ab initio} calculations on potential energy curves of several electronic states of these species. We include both relativistic and ele-
tron correlation effects to a high order through CASSCF/FOCI/ESOI/RCI methods which included up to 700 000 configurations on InSb, InSb+, and InSb−. We compute potential energy curves of 26 electronic states of InSb, 12 electronic states of InSb+, and 9 electronic states of InSb−. Section II describes our method of theoretical calculations. Section III consists of results and discussions. Section IV comprises analyses of the nature of various electronic states, discussions on dipole moments, and Mulliken populations. Section V compares the computed properties of InSb with GaAs.

II. METHOD OF THEORETICAL CALCULATIONS

A complete active space MCSCF (CASSCF) method followed by first-order configuration interaction (FOCI) and second-order configuration interaction (SOCl) calculations are employed. Spin–orbit effects were also included for the lowest-lying electronic states using the relativistic CI (RCI) method. All calculations carried out here were made with relativistic effective core potentials (RECPs) which included the outer 5s25p1 shells for In and the outer 5s25p1 shells for Sb in the valence space, respectively.

Valence Gaussian basis sets of (4s4p1d) types shown in Table I for In and Sb were employed in the present study on InSb. The (3s3p) valence Gaussian basis set for In and Sb atoms optimized by LaJohn et al.38 was used as the starting point. To this a set of s, a set of three p functions and one set of six-component d functions with the exponents shown in Table I were added. We used the RECPs generated by LaJohn et al.38 for In and Sb atoms.

CASSCF calculations included all eight outer (valence) electrons of InSb in the active space. All calculations were actually made in the C2v point group orienting the diatomic InSb along the z axis. In this orientation, we included all those orbitals which correlated into the 5s and 5p orbitals of the separated atoms at infinite separation. Hence the active space for CASSCF included four a1 orbitals, two b1 orbitals, and two b2 orbitals. The calculations of InSb+, and InSb− included seven and nine active electrons, respectively. At the CASSCF level, seven, eight, and nine active electrons were distributed in all possible ways among the eight active orbitals for InSb+, InSb, and InSb−.

CI calculations were made using both first-order CI (FOCI) and full second-order CI (SOCl) methods. The FOCI calculations included (i) all configurations in the CASSCF and (ii) those configurations generated by distributing N − 1 electrons in the active space and 1 electron in the orthogonal external space in all possible ways, where N is the number of active electrons for various species (N = 7 for InSb+, N = 8 for InSb, and N = 9 for InSb−). The second-order CI (SOCl) calculations included all configurations in the FOCI and those configurations generated by distributing N − 2 electrons in the active space and two electrons in the external space in all possible ways. The FOCI calculations in the (4s4p1d) basis set included up to 38 000 configurations for those species. The SOCl calculations included up to 700 000 configurations.

Since both In and Sb are heavy atoms spin–orbit effects could be important for InSb. The spin–orbit coupling was introduced variationally allowing for mixing of different electronic states through the relativistic CI (RCI) method described by the author39 in a previous study.

Spin–orbit integrals in Gaussian basis sets were obtained using Pitzer’s modified version of ARGOS codes.40 The integrals thus obtained were transformed in the CI natural orbitals. The transformed spin–orbit matrix elements were added to the CI Hamiltonian matrix in the RCI procedure.

RCI calculations of the X0+ state of InSb included 3Σ−, (σ2π), 3Σ−, (π2σ), 3Π−, (σ3π), 3Π−, (π3σ), and 3Σ+ (πσ) reference configurations. Similarly RCI calculations of the 1 state included 2Σ−, 2Π+, 1Π, and other lower-lying states which give rise to Ω = 1.

RCI calculations of the X 4Σ−, state of InSb+ included 4Σ−, (σ4π), 2Σ−, (σ2π), 2Σ−, (π2σ), and a few other states which give Ω = 1/2 states. Similarly the 4Σ−, state included 4Σ−, (σ4π), 2Δ−, etc. RCI calculations of InSb− were also carried out in a similar manner. Spin–orbit splittings of low-lying electronic states were found to be at most 500 cm−1 for InSb and InSb+. For InSb−, the contribution is found to be larger due to relativistic 2Π+, 2Σ−, and 2Σ− avoided crossing.

All CASSCF/FOCI/ESOI calculations were made using the author’s42 modified version of ALCHEMY II codes43 to include relativistic ECPs (RECPs) as described in Ref. 42. RCI calculations were carried out using the method described in Ref. 40.

III. RESULTS AND DISCUSSION

A. InSb

1. Potential energy curves

Table II shows the possible low-lying electronic states of InSb and their ions together with their dissociation limits. For the neutral InSb potential energy curves of most of the electronic states shown in Table I (with the exception of probably repulsive 3Φ, 5Φ states and some upper repulsive roots) were calculated. The potential energy curves were calculated using the CASSCF/FOCI methods described in Sec. II.

Figure 1 shows the potential energy curves of InSb arising from In(2P) + Sb(4S) and In(2P) + Sb(2D) dissociation limits while Fig. 2 shows some states dissociating into In(2P) + Sb(2D) and electronic states dissociating into

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**Table I.** Valence Gaussian basis sets for In and Sb.

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<tr>
<th>Type</th>
<th>In exponent</th>
<th>Sb exponent</th>
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TABLE II. Dissociation relationship for low-lying electronic states of InSb, InSb+, and InSb-.

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<tr>
<th>Species</th>
<th>States</th>
<th>Dissociation limit</th>
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<td>InSb</td>
<td>$^3\Sigma^-$, $^3\Pi$, $^5\Sigma^- + ^5\Pi$</td>
<td>$\text{In}(2P) + \text{Sb}(4S)$</td>
</tr>
<tr>
<td>InSb</td>
<td>$^1\Sigma^+$, $^1\Sigma^-(2), ^3\Pi(3), ^3\Delta(2), ^1\Phi$</td>
<td>$\text{In}(2P) + \text{Sb}(2D)$</td>
</tr>
<tr>
<td>InSb</td>
<td>$^3\Sigma^- + ^3\Pi(2), ^5\Pi(2), ^5\Delta(2), ^1\Phi$</td>
<td>$\text{In}(2P) + \text{Sb}(2P)$</td>
</tr>
<tr>
<td>InSb</td>
<td>$^3\Sigma^- + ^3\Pi(2), ^1\Sigma^-$</td>
<td>$\text{In}(6P^2P) + \text{Sb}(4S)$</td>
</tr>
<tr>
<td>InSb</td>
<td>$^3\Sigma^-(2), ^3\Xi^-(2), ^1\Pi(2), ^3\Lambda$</td>
<td>$\text{In}(2P) + \text{Sb}(2P)$</td>
</tr>
<tr>
<td>InSb+</td>
<td>$^3\Sigma^+$</td>
<td>$\text{In}^+(4S) + \text{Sb}(4S)$</td>
</tr>
<tr>
<td>InSb+</td>
<td>$^3\Delta, ^3\Pi, ^3\Sigma^-$</td>
<td>$\text{In}^+(4S) + \text{Sb}(2D)$</td>
</tr>
<tr>
<td>InSb+</td>
<td>$^3\Pi, ^3\Delta$</td>
<td>$\text{In}^+(4S) + \text{Sb}(2P)$</td>
</tr>
<tr>
<td>InSb+</td>
<td>$^3\Sigma^-, ^3\Sigma^-, ^3\Xi^-, ^1\Pi(2), ^3\Lambda$</td>
<td>$\text{In}(2P) + \text{Sb}^+(4P)$</td>
</tr>
<tr>
<td>InSb+</td>
<td>$^3\Xi^-, ^3\Xi^-, ^3\Delta(2), ^3\Pi(2), ^3\Lambda$</td>
<td>$\text{In}(2P) + \text{Sb}^+(4P)$</td>
</tr>
<tr>
<td>InSb+</td>
<td>$^3\Delta, ^3\Pi, ^3\Sigma^-$</td>
<td>$\text{In}^+(4S) + \text{Sb}(4S)$</td>
</tr>
<tr>
<td>InSb-</td>
<td>$^3\Sigma^- + ^3\Pi, ^3\Delta, ^3\Sigma^+, ^3\Pi, ^3\Lambda$</td>
<td>$\text{In}(2P) + \text{Sb}^+(4S)$</td>
</tr>
<tr>
<td>InSb-</td>
<td>$^3\Sigma^- + ^3\Pi, ^3\Sigma^+, ^3\Pi, ^3\Xi^-, ^1\Pi$</td>
<td>$\text{In}(2P) + \text{Sb}(4S)$</td>
</tr>
</tbody>
</table>

In$(2P) + \text{Sb}(2P) + \text{In}(6P^2P) + \text{Sb}(4S)$, and In$(4P) + \text{Sb}(2P)$ dissociation limits.

As seen from Fig. 1, the ground state of InSb is a $^3\Sigma^-$ state. A very low-lying excited $^3\Pi$ state crosses the $^3\Sigma^-$ curve since the $R_c$ of the $^3\Pi$ state is shorter than the $R_c$ of the $^3\Sigma^-$ state. There are $^3\Delta$, $^3\Sigma^+$, and $^3\Pi$ very low-lying excited states for InSb. For the $^1\Sigma^+$ state there is an avoided crossing between the $\pi^e$ electronic configuration with the $\sigma^2\pi^2$ configuration. Thus the short-$R_c$ minimum in the $^1\Sigma^+$ curve is due to the $\pi^2\pi^2$ electronic configuration. The different shape of the $^1\Sigma^+$ curve compared to the $^1\Delta$ curve is due to the avoided crossing of the $\pi^2$ with $\sigma^2\pi^2$. The same way the spectroscopic constants of the $^1\Sigma^+$ and $^3\Sigma^+ + ^3\Pi$ states differ from the $^1\Delta$ state. The second $^1\Sigma^+$ state, namely $^1\Sigma^+ + ^3\Pi$, has an opposite behavior. It is predominantly $\sigma^2\pi^2$ at short distances and changes to $\pi^2\pi^2$ and other configurations as the internuclear distance increases.

The quintet states dissociating to the ground state In$(2P) + \text{Sb}(4S)$ atoms ($^3\Pi, ^3\Sigma^-$) exhibit interesting behavior. The $^3\Pi$ state is slightly bound while the $^3\Sigma^-$ state is repulsive and crosses the bound $^3\Pi(III)$, $^3\Pi(II)$, $^3\Sigma^+$, and $^3\Delta$ states (Fig. 1). This would result in the predissociation of the appropriate $\Omega$ components. We discuss this in Sec. III A 3.

Among the electronic states dissociating into In$(2P) + \text{Sb}(2D)$, the $^3\Sigma^+$, $^3\Delta$, $^3\Sigma^+$, $^3\Pi(II)$, and $^3\Pi(III)$ states are bound while the $^3\Sigma^-(II)$, $^3\Sigma^-(III)$, and $^3\Delta(II)$ states are repulsive. The $^3\Delta$ state is somewhat weakly bound.

The $^3\Pi(II)$ curve dissociating into In$(2P) + \text{Sb}(2D)$ has a broader potential well and a larger $R_c$. The $^3\Pi(III)$ dissociating to the same limit, to the contrary, has a shorter $R_c$ and a bit narrower potential well. But the $^3\Pi(II)$ state is more bound since the two $^3\Pi$ states dissociate into the same limit (see Fig. 1).

As seen from Fig. 2, the $^1\Sigma^+ + ^3\Pi$ curve dissociating into In$(2P) + \text{Sb}(2P)$ has a deeper and narrower well due to an avoided crossing of $\sigma^2\pi^2$ and $\pi^4$ configurations. This curve crosses several curves dissociating into the lower In$(2P) + \text{Sb}(2D)$ atoms (Fig. 2). In particular the crossing of a repulsive $^3\Pi$ state and subsequently at a longer distance, the crossing of $^3\Sigma^-(II)$ are worth noting. Since the $^3\Pi(IV)$ curve crosses at a shorter $r_c$ and gives rise to $\Omega = 0^+$ component, the interaction between $^1\Sigma^+(II)_{0^+}$ and $^3\Pi(IV)_{0^+}$ at the curve-crossing region would be strong. This will predissociate the $^3\Sigma^+(II)$ state into In$(2P) + \text{Sb}(2D)$ atoms since InSb is a heavy molecule.

Among those electronic states dissociating into In$(2P) + \text{Sb}(2P)$, the $^1\Sigma^+ (II)$ and $^3\Sigma^+ (II)$ curves are

![Fig. 1. Potential energy curves of InSb arising from In$(2P) + \text{Sb}(4S)$ and In$(2P) + \text{Sb}(2D)$ limits.](image1)

![Fig. 2. Potential energy curves of InSb arising from In$(2P) + \text{Sb}(2D)$, In$(2P) + \text{Sb}(2P)$, In$(6P^2P) + \text{Sb}(4S)$, and In$(4P) + \text{Sb}(2P)$ limits.](image2)
bound. The $^3\Sigma^+ (II)$ curve crosses the $^3\Sigma^- (II)$ repulsive curve near the well and a $^1\Pi(IV)$ curve at a shorter $r_c$. This means that the $^3\Sigma^- (II)_1$ component will be predissociated. The $^1\Sigma^-_0^-$ component should survive predissociation since both the curves crossing with $^3\Sigma^+ (II)$ do not give rise to $\Omega = 0$ states.

We also studied the potential energy curves dissociating into the In($6p^2P$) + Sb($4S$) Rydberg limit. Since our basis set of In is of $4s4p1d$ quality, the results obtained for Rydberg states may not be of the same accuracy as the ground state but sufficiently satisfactory. This is further evidenced by a CASSCF/FOCI In($^3P$)–In($6p^2P$) energy separation of 31 300 cm$^{-1}$ compared to an experimental value of 32000 cm$^{-1}$. Thus the accuracy of even electronic states dissociating into Rydberg atoms is quite good. The $^3\Pi(III)$ state dissociates into In($^4P$) + Sb($^2P$).

### 2. Spectroscopic constants

Table III shows the spin–orbit corrected spectroscopic constants for the bound electronic states of InSb. As seen from Table III, the ground state of InSb is a $^1\Sigma_0^+$ state with $r_c = 3.02$ Å and $\omega_c = 121$ cm$^{-1}$ at the spin–orbit corrected SOCl level of theory. The FOCI results are also quite satisfactory. The ground state $^1\Sigma_0^-$, $^3\Sigma^-_1$ spin–orbit splitting is calculated as 492 cm$^{-1}$ using the RCI method. The spin–orbit splitting of the isoelectronic Sb$_2$ dimer was calculated by the author and Pitzer before as 342 cm$^{-1}$. (See Ref. 45 for a comparative review of main group dimers and trimers.) The larger spin–orbit splitting of InSb is because Sb makes larger spin–orbit contribution. The $r_c$ and $\omega_c$ values for the Sn$_2$ $^1\Sigma^- (0^+_g)$ ground state are 2.76 Å and 197 cm$^{-1}$, respectively. Thus Sn$_2$ has a deeper well compared to InSb.

The $^1\Pi$ state of InSb has a slightly longer bond length compared to the $^1\Sigma^-_1$ state. This is primarily because of spin–orbit contamination of $^1\Sigma^- (\sigma^2\pi^2)$ with $^1\Sigma^+ (\sigma^2\pi^2)$ in the $^3\Sigma_0^+$ state of InSb. The trend found for InSb is also akin to the corresponding trend for Sn$_2$. For Sn$_2$, $\Delta r_c$ and $\Delta \omega_c$ values for the $0^+$ and $1$ states are +0.01 Å and −8 cm$^{-1}$. The larger changes in the $r_c$ and $\omega_c$ of InSb are consistent with the larger spin–orbit splitting.

The lowest $^1\Pi$ state of InSb has a shorter $r_c$ of 2.769 Å compared to the ground state. The $\omega_c$ is correspondingly larger compared to the ground state. This is consistent with the potential energy curves in Fig. 1. The $^1\Pi$ state of InSb also behaves similar to the $^3\Pi$ state.

The $^1\Delta$ state arising from the $\sigma^2\pi^2$ configuration has spectroscopic properties similar to the $^1\Sigma^-_1$ state since the latter state also arises predominantly from the $\sigma^2\pi^2$ electronic configuration. It is worth noting that if the properties of the $^1\Delta$ state are computed using the $^1A_1$ orbitals, they are somewhat different, since the $^1A_1$ state undergoes an avoided crossing of $\pi^4$ and $\sigma^2\pi^2$. As a result, the properties of $^1\Delta$ obtained as the second root of $^1A_1$ differ from the properties obtained from the $^1A_1$, first root orbitals. This is an artifact of the change in the $^1A_1$, orbital composition in this region.

The $^3\Pi$ state has a much longer bond length as seen from Table III and Fig. 1. This state is only weakly bound with respect to the ground state atoms.

The $^1\Sigma^+_0^-$ state arising predominantly from $\pi^4$ at its $r_c$ has a shorter bond length of 2.56 Å as expected for this state. The $\omega_c$ is increased for this state due to spin–orbit contamination with $^3\Sigma^-$ by 20 cm$^{-1}$. The $^1\Sigma^+ (II)$ state has a longer bond length of 2.81 Å. The relatively small energy separation between the two $^1\Sigma^+$ states is a result of the avoided crossing of $\pi^4$ with $\sigma^2\pi^2$ configurations.

The $^3\Pi(II)$ and $^3\Pi(III)$ states should be of interest to experimentalists since the corresponding $^3\Pi(III)$ state of GaAs has been observed by Lemire et al. recently. For InSb at the FOCI level these states lie 15 800 and 20 200 cm$^{-1}$, respectively, above the ground state. At the more accurate SOCl level of theory, the $^3\Pi(II)$ state is 15 930 cm$^{-1}$ above the ground state.

The $^3\Pi(IV)$ state lying 22 300 cm$^{-1}$ with a long $r_c$ (3.36 Å) may also be an interesting candidate for experimental studies although this state has a considerably longer bond and is only weakly bound. This state could be observed in absorption.

The $^1\Sigma^+$ state has a shorter $r_c$ (2.80 Å) compared to the $^1\Sigma^+_0^-$ ground state but has comparable properties to the $^1\Pi$ state of InSb. Other electronic states of InSb such as $^3\Pi(II)$, $^3\Pi(III)$, $^3\Delta(II)$, etc., have only long range minima and are weakly bound.

Table III compares the SOCl/RCI spectroscopic constants for 11 bound electronic states of InSb with the corresponding FOCI results. SOCl calculations, in general, tend to stabilize the molecular regions of the potential well compared to the dissociation limit thereby enhancing the $D_v$. For example, the potential well of the $^3\Pi(II)$ state is considerably stabilized at the SOCl level.

Table III reveals that the $r_c$ and $\omega_c$ values of the low-lying electronic states of InSb are not altered substantially by the higher 

### Table III. Spectroscopic constants of InSb.

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<th>State</th>
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<th>$T_c$ (cm$^{-1}$)</th>
<th>$\omega_c$ (cm$^{-1}$)</th>
<th>$\mu_r$ (D)</th>
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<td>$^1\Pi(II)$</td>
<td>3.20</td>
<td>3.20</td>
<td>35716</td>
<td>35716</td>
</tr>
<tr>
<td>$^3\Pi(III)$</td>
<td>3.13</td>
<td>3.13</td>
<td>44565</td>
<td>44565</td>
</tr>
</tbody>
</table>

*Positive polarity means In $^+$ Sb $^-$ polarity.*
order electron correlations. The $T_e$ values of the excited electronic states, however, alter due to higher-order correlation effects. The SOCI $T_e$ values should be considered more definitive compared to the FOCI values.

3. Predicted electronic transitions of InSb

There are a number of possible dipole allowed electronic transitions for InSb. From the $X^3\Sigma_g^-$ ground state electronic transitions to the $1\Pi_1$, $3\Sigma^+ (III)_{1o}$, $1\Sigma^+ (II)_{0s}$, $3\Pi(II)_{0s}$, $3\Pi(III)_{0o}$, $3\Pi(III)_{1o}$, $3\Pi(IV)_{0o}$, and $3\Pi(IV)$, transitions are allowed. Among these, the transitions to the $1\Pi(II)_{0o}$ and $3\Pi(III)_{0o}$ system would be particularly strong. We discuss these first.

The $3\Pi(II)_{0o}$, $X^3\Sigma_g^-$ and $3\Pi(III)_{0o}$, $X^3\Sigma_g^-$ transitions occur in the region of 15 800 and 20 200 cm$^{-1}$ at the FOCI level. More accurate $T_e$ of 15 540 cm$^{-1}$ was obtained at the SOCI level for the $1\Pi$ (II) state. Hence the predicted FOCI $3\Pi(III)_{1o}$, $X^3\Sigma_g^-$ transition energy should be about 1200 cm$^{-1}$ in error but in the opposite direction. The spin-orbit splitting is estimated to be less than 1000 cm$^{-1}$ for the two $3\Pi$ states. Hence the predicted transition energies for the $3\Pi(II)_{0o}$, $X^3\Sigma_g^-$ and $3\Pi(III)_{0o}$, $X^3\Sigma_g^-$ transitions are 15 500 ± 500 and 21 700 ± 1000 cm$^{-1}$, respectively.

The $3\Pi(III)_{1o}$, $X^3\Sigma_g^-$ transition of GaAs was recently observed by Lennie et al.13 The experimental $T_e$ value for this transition was calculated as 23 800 cm$^{-1}$ by these authors. This value was in excellent agreement with a CASCF/FOCI value of 24 600 cm$^{-1}$ obtained by the author for GaAs before.21 The theoretical $T_e$ value for the $3\Pi(III)$ state was calculated as 2.68 Å in good agreement with an experimental value of 2.60 Å. The experimental and theoretical $\omega_e$ values of the $3\Pi(III)$ state are 160 and 152 cm$^{-1}$, respectively. These results provide considerable confidence in our present CASCF/FOCI/RCI calculations.

The $X^3\Pi_{1o}$, $X^3\Sigma_g^-$ and $1\Sigma^+_{1o}$, $X^3\Sigma_g^-$ transitions become allowed for InSb due to spin–orbit contamination of $3\Sigma^-$ and $1\Sigma^+$. The transition energies of the former and latter transitions are 14 000 and 8100 cm$^{-1}$, respectively.

The $3\Sigma^+_{1o}$, $X^3\Sigma_g^-$ as well as $3\Sigma^+_{1o}$, $X^3\Sigma_g^-$ transitions are good candidates for theoretical investigations although in a pure $\lambda \rightarrow \delta$ coupling scheme, the $3\Sigma^+_{1o}$, $X^3\Sigma_g^-$ transition is forbidden. Since spin–orbit coupling for InSb is strong this transition would be somewhat probable. The $3\Sigma^+_{1o}$, $X^3\Sigma_g^-$ transition occurs in the 21 900 cm$^{-1}$ region.

4. Predissociations

As seen from Fig. 1, the repulsive $5\Sigma^-$ curve dissociating into the $In^2P + Sb^4S$ atoms crosses the $1\Delta$, $1\Sigma^+$, $3\Pi$, $3\Pi(II)$, $3\Pi(III)$, $2\Sigma^+$, and $3\Delta$ curves. In the presence of spin–orbit coupling the $5\Sigma^-$ state gives rise to $\Omega = 0^-$, 1, and 2 states. Since predissociation process is akin to perturbation, two states of the same $\Omega$ symmetry can interact through spin–orbit coupling. Depending on the magnitude of the spin–orbit coupling term, the interaction could be strong. Since InSb is a heavy molecule, we expect spin–orbit interaction in the curve crossing region to be large enough to induce predissociation.

The $5\Sigma^-$ and $5\Sigma^+$ components would predissociate the $1\Pi_{1o}$, $3\Pi(II)_{0o}$, $3\Pi(III)_{0o}$, $3\Sigma^+_{1o}$, $3\Sigma^+_1$, and $3\Delta$ components. Similarly, the $5\Sigma^-$ state would interact with the $1\Delta_{2o}$, $3\Pi(II)_{2o}$, $3\Pi(III)_{2o}$, and $3\Delta$ components. Hence the $\Sigma^+$ curve dissociating into In($^2P$) + Sb($^2D$) would survive predissociation by the $5\Sigma^-$ curve since the $5\Sigma^-$ state has no component with $0^+$ symmetry.

The $1\Pi(II)_{0o}$ and $3\Pi(III)_{0o}$ components will survive predissociation induced by the $5\Sigma^-$ curve crossing since $5\Sigma^-$ state does not give rise to a state of $0^+$ symmetry. Thus among various $3\Pi(II)_{1o}$, $X^3\Sigma_g^-$, $3\Pi(III)_{1o}$, $X^3\Sigma_g^-$ states, the $3\Pi_{0o}$, $X^3\Sigma_g^-$ and $3\Pi(III)_{0o}$, $X^3\Sigma_g^-$ systems would be intense and bands should be observable for several vibrational quantum numbers. For other electronic states in the $1\Pi$–$X^3\Sigma_g^-$ system only those vibrational levels with classical turning points below the curve crossing $r$ of $3\Pi(II)_{1o}$, $3\Sigma^+$, and $3\Pi(III)_{1o}$ could be observed.

The above predictions of predissociations for InSb are consistent with the recently observed predissociation pattern for the GaAs $1\Pi_{1o}$–$X^3\Sigma^-$ system.15 Experimentally Lemire et al.15 found no transitions which terminate on $\nu' > 1$ for $\Omega' = 2$ of the $1\Pi$ (III) state. Similarly no transitions could be found terminating on $\nu' > 0$ for $\Omega' = 1$ and $\Omega' = 0^-$ of $3\Pi$ (III) states. But transitions terminating on $\Omega = 0^+$ substrate were observed. These observations are consistent with earlier comparable calculations on GaAs.10 In view of the similar predicted predissociation patterns it would be interesting to record the spectrum of InSb in the predicted region.

5. Partition function and dissociation energy of InSb

Theoretical dissociation energy $D_e$ is calculated at various levels of theory through the difference of energy at $r_e$ and long distance (8.0 Å). At the CASCF/FOCI level, the value obtained this way for $D_e$ (InSb) is 1.1 eV. At a full SOCI level this value improves to 1.35 eV. The zero-point energy obtained from the $\omega_e$ of the $X^3\Sigma_g^-$ state is 0.01 eV. Thus the difference between $D_e$ and $D_0$ for InSb should be approximately 0.01 eV.

Even a full SOCI level of theory ignores the effect of $d$ correlation effects on $D_e$. In an earlier investigation on GaAs the author estimated the effect of $d$ correlation as an increase in $D_e$ by 0.2 eV. We expect comparable improvement in the $D_e$ of InSb due to $d$ correlation effects. However, spin–orbit effects tend to destabilize the InSb bond by the same factor. Hence $D_e$ (InSb) is predicted as 1.4 ± 0.1 eV.

De Maria et al.46 have made a thermodynamic study of InSb using a mass spectrometer. The gaseous molecules in equilibrium with solutions of indium and antimony were determined. From the measured partial pressures, partial molar-free energies, the heats of enthalpies in solutions were calculated. These values in turn facilitated the computation of thermodynamic dissociation energies for Sb$_2$, In$_2$, InSb, and Sb$_2$. The $\omega_e$ of InSb was estimated from the Debye temperature of InSb to be 260 cm$^{-1}$. The $r_e$ was taken to be 3.15 Å. The ground state of InSb was assumed correctly as $5\Sigma^-$ in analogy to the well-known ground state of Sn$_2$. The
InSb₂ molecule was assumed to be linear by DeMaria et al. The interatomic distance of InSb₂ were taken to be \( r(\text{Sb-Sb}) = 2.82 \ \text Å \) and \( r(\text{In-Sb}) = 3.15 \ \text Å \). Based on these assumptions, average dissociation energies of Sb₂, In₂, InSb, and \( D_0^0 (\text{InSb-Sb}) \) were calculated as 71.2, 22.4, 35.4, and 66.7 kcal/mol.\(^\text{46}\)

Although the assumed \( \omega_\text{e} \) of InSb (260 cm⁻¹) is certainly too high compared to a value of 115–130 cm⁻¹ obtained from our calculations, the assumed \( r_e \) value (3.15 Å) of InSb is quite reasonable. Thus only the vibrational partition function needs correction.

The \( D_0^0 \) obtained by DeMaria et al.\(^\text{46}\) can be corrected using the formula

\[
\delta D_0^0 = RT \ln(q'/q^*),
\]

where \( q' \) is the assumed partition function while \( q^* \) is the corrected partition function. Since the main difference between the assumption made by DeMaria et al. and our theoretical constants is in the \( \omega_\text{e} \) of InSb, the vibrational partition function was corrected. The \( \delta D_0^0 \) obtained this way for the correction in the vibrational partition function is \(-1.6 \) to \(-1.7 \) kcal/mol depending on the temperature used (1000–1500 K). Consequently the \( D_0^0 \) of InSb should be corrected to 33.4 kcal/mol or 1.45 eV. Note that our direct SOCI \( D_e \) of InSb is 1.35. Since the \( \omega_\text{e} \) of InSb in the absence of spin–orbit coupling is 130 cm⁻¹, the \( D_e \) value is obtained by correcting the \( D_e \) by zero-point energy as 1.34 eV. As indicated above the \( d \) correlation effects tend to increase \( D_e \) by 0.2 eV while spin–orbit effects destabilize by about the same factor. The theoretical \( D_0^0 \) (InSb) = 1.35 eV obtained this way is in very good agreement with the corrected thermodynamic value of 1.45 eV. Hence \( D_0^0 \) (InSb) is predicted as \( 1.40 \pm 0.1 \) eV.

The assumption of a linear ground state for InSb₂ by DeMaria et al.\(^\text{46}\) is not entirely consistent with the author's earlier calculations on GaAs₂ which have revealed GaAs₂ to be bent in a \( X^2B_2 \) ground state with a very acute triangular geometry. Furthermore, DeMaria et al. have assumed the multiplicity of the ground state to be 1 while it should be 2 for InSb₂. In view of these assumptions, the bond energy of \( D_0 \) (InSb₂–Sb) could be off to a larger extent compared to \( D_0^0 \) (InSb). Theoretical study of InSb₂ would thus be quite interesting. Such studies on trimers of In and Sb will be the topic of future investigations.

The present author and Pitzer\(^\text{44}\) calculated the \( D_e \) value of the isoelectronic Sn₂ using a SCF/RCI method. The \( D_e \) value calculated this was 1.86 eV. They also corrected the thermodynamic \( D_e \) value by recalculating the partition functions with theoretical spectroscopic constants for several excited states as \( D_0^0 = 44.7 \) kcal/mol or 1.94 eV. The corrected \( D_0^0 (\text{Sn₂}) \) was found to be in excellent agreement with the experimental value. The \( D_0^0 \) (InSb) should be smaller than \( D_0^0 \) (Sn₂) and since \( D_0^0 \) (Sn₂) is fairly well established as 1.9 eV, the deduced \( D_0^0 \) (InSb) = 1.40 ± 0.1 eV is very consistent with the \( D_0^0 \) (Sn₂).

B. InSb⁺

1. Potential energy curves and spectroscopic constants

Table IV shows the spectroscopic constants for InSb⁺ arising from both In⁺ + Sb limits and In⁺ + Sb⁺ limits. Figure 3 shows the actual potential energy curves of InSb⁺. As seen from Table IV and Fig. 3, the ground state of InSb⁺ is unambiguously a \( X^4Σ_{1/2}^+ \) state dissociating into \( \text{In}^+(1S) + \text{Sb}(4S) \). Since the first ionization potential of the In atom is smaller than the antimony atom, the \( \text{In}^+(1S) + \text{Sb}(4S) \) dissociation limit is considerably lower than the \( \text{In}^2(2P) + \text{Sb}^+(3P) \) limit.

The \( ^4Σ_{3/2}^+ - ^4Σ_{1/2}^+ \) spin–spin splitting is calculated as 327 cm⁻¹ comparable to the neutral \( ^2Σ^0 - ^2Σ^- \) separation of 492 cm⁻¹. The spin–orbit contamination of the \( ^4Σ_{1/2}^+ \) state with a low-lying \( ^2Σ_{1/2}^+ \) state arising from the same configuration was found to be significant. This result is an increase in the \( X^4Σ_{1/2}^+ r_e \) by 0.003 Å. The \( \omega_\text{e} \) corresponding decreases by 1 cm⁻¹.

The ground state InSb⁺ is analogous to the \( X^4Σ^- \) ground state for GaAs⁺ predicted by the author\(^\text{10}\) before using comparable level of theory. Knight and Petty\(^\text{9} \) subsequently recorded the ESR spectra of matrix-isolated GaAs⁺ which exhibited a quart structure confirming the previous theoretical prediction.\(^\text{10}\)

An excited electronic state of \( ^2Σ^- \) symmetry arising from the same \( σσ^* \) configuration is found for InSb⁺. This state lies 8755 cm⁻¹ above the ground state. The \( ^2Π \) and \( ^2Δ \) electronic states dissociating into \( \text{In}^+(1S) + \text{Sb}(2D) \) are immediately above the \( ^2Σ^- \) state.

The next duo of electronic states dissociating into \( \text{In}^+(1S) + \text{Sb}(2P) \) of \( ^4Σ^+ \) and \( ^2Π(II) \) symmetries are found in the 18 000 cm⁻¹ region. Since these two states are close to each other, the spin–orbit contamination of the \( Ω = 1/2 \) components of \( ^4Σ^+ \) and \( ^2Π(II) \) states is expected to be significant.

There are many electronic states for InSb⁺ dissociating into \( \text{In}^2(2P) + \text{Sb}^+(3P) \). The \( ^4Π \) and \( ^2Π \) and \( ^2Π(III) \) states dissociating into this limit are bound. The \( ^2Δ(II) \) state is evidently repulsive (Fig. 3). The \( ^2Π(II) \) state exhibits dou-

**TABLE IV. Spectroscopic constants of InSb⁺**

<table>
<thead>
<tr>
<th>State ( )</th>
<th>( R_e (\text{Å}) )</th>
<th>( T_e (\text{cm}^{-1}) )</th>
<th>( \omega_\text{e} (\text{cm}^{-1}) )</th>
<th>( \mu_e (\text{D}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ^4Σ_{1/2}^+ )</td>
<td>3.351</td>
<td>3.203</td>
<td>63</td>
<td>4.3</td>
</tr>
<tr>
<td>( ^4Σ_{3/2}^+ )</td>
<td>3.348</td>
<td>3.200</td>
<td>327</td>
<td>64</td>
</tr>
<tr>
<td>( ^2Σ^- )</td>
<td>2.997</td>
<td>2.934</td>
<td>8 755</td>
<td>109</td>
</tr>
<tr>
<td>( ^2Π )</td>
<td>3.407</td>
<td>3.36</td>
<td>9 053</td>
<td>125</td>
</tr>
<tr>
<td>( ^2Δ )</td>
<td>3.129</td>
<td>3.04</td>
<td>11 155</td>
<td>75</td>
</tr>
<tr>
<td>( ^2Π(II) )</td>
<td>2.95</td>
<td>2.90</td>
<td>15 953</td>
<td>151</td>
</tr>
<tr>
<td>( ^2Σ^+ )</td>
<td>3.039</td>
<td>3.01</td>
<td>26 148</td>
<td>108</td>
</tr>
<tr>
<td>( ^2Π(III) )</td>
<td>2.998</td>
<td>2.939</td>
<td>29 704</td>
<td>68</td>
</tr>
<tr>
<td>( ^2Σ^- (II) )</td>
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<td>37 084</td>
<td>201</td>
<td>201</td>
</tr>
<tr>
<td>( ^2Π(III) )</td>
<td>3.21</td>
<td>40 907</td>
<td>267</td>
<td>267</td>
</tr>
</tbody>
</table>
The table and figure are described below.

**Fig. 3. Potential energy curves of InSb**

**Table IV**

<table>
<thead>
<tr>
<th>Transition</th>
<th>Description</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Sigma^- \rightarrow \Pi )</td>
<td>( 0.52 )</td>
<td>( 0.37 )</td>
</tr>
<tr>
<td>( \Pi \rightarrow \Pi )</td>
<td>( 1.1 )</td>
<td>( 0.58 )</td>
</tr>
<tr>
<td>( \Pi \rightarrow \Sigma^- )</td>
<td>( 5.33 )</td>
<td>( 4.85 )</td>
</tr>
</tbody>
</table>

The value obtained for \( D_e \) is 0.52 eV. This value is in remarkable agreement with the direct FOCl value of 0.52 eV. Thus, internal consistency in the calculations is established. Using the SOCI I.P.(InSb), SOCI \( D_e \) (InSb), and SOCI I.P.(In) we obtain \( D_e \) (InSb\(^+\)) to be 0.3 eV. Again, this value is in excellent agreement with the direct SOCl \( D_e \) (InSb\(^+\)) of 0.37 eV. Since the SOCI I.P. of the indium atom is closer to an experimental value of 5.79 eV, we believe that SOCl spectroscopic constants should be more accurate.

The accuracy of the present calculations on InSb\(^+\) can also be judged by comparable Group IV–VI calculations and experimental photoelectron spectrum of Wang *et al.* In this joint theoretical–experimental study electronic states of PbSe, PbTe, SnSe, SnTe, and their positive ions were studied. The theoretical I.P.s, \( r_e \), \( \omega_e \), and \( D_e \)s were in very good agreement with experimental values. For example, the calculated \( r_e \)s were found to be within 0.04–0.06 \( \text{Å} \) of the experimental values. The theoretical \( \omega_e \)s of the Group IV–VI ions were within 2%–6% of experimental values. The MRSDCI I.P.s came very close to experimental values deduced from the photoelectron spectra.

### 2. Ionization potential and the predicted features in the photoelectron spectrum of InSb

The CASSCF/FOCI adiabatic I.P. of InSb for the following process:

\[
\text{InSb}(^3\Sigma^-_0^-) \rightarrow \text{InSb}^+ (^4\Sigma^-_{3/2}) + e^-
\]

is calculated as 5.92 eV including spin–orbit effects. A more accurate SOCI/RCI level of theory this value is 6.27 eV. As seen from Table IV, the \( \Delta r_e \) difference in the ground state of InSb and InSb\(^+\) is +0.15 \( \text{Å} \). The increase in the bond length is anticipated since the highest occupied \( \sigma \) orbital of InSb is a bonding MO and hence removal of a bonding electron leads to elongation of the bond. Removal of a \( \pi \) electron then leads to a \( ^2\Pi \) electronic state for InSb\(^+\) which has an \( r_e = 3.36 \) \( \text{Å} \), approximately 0.3 \( \text{Å} \) larger than the neutral InSb \( X^3\Sigma^-_0^- \), state. This suggests considerable orbital relaxation effects.

The \( \Sigma^- \) and \( \Delta \) electronic states of InSb\(^+\) have bond lengths close to the \( X^3\Sigma^- \) ground state of InSb. This means transitions to these states would be sharp. Equivalently, the Franck–Condon factor would be large for this transition.

The electronic transition from the \( X^3\Sigma^- \) ground state of InSb to the \( X^3\Sigma^-_{3/2} \) ground state of InSb\(^+\) would involve considerable vibrational progression since \( \Delta r_e \) for this transition is +0.15 \( \text{Å} \). Thus the photoelectron spectrum from the ground state of InSb to the ground state of InSb\(^+\) should have a smaller Franck–Condon factor and thus the spectrum should show broader peaks exhibiting vibrational progressions.

The \( ^2\Pi \) (I) state of InSb\(^+\) is a mixture of \( 1\sigma^22\sigma^23\sigma^2\pi^2 \) (81%) and \( 1\sigma^22\sigma^2\pi^2 \) (7%) configurations near the \( r_e \) of InSb\(^+\). Similarly the \( ^2\Pi \) (II) state of InSb\(^+\) is \( 1\sigma^22\sigma^2\pi^2 \) (75%), \( 1\sigma^22\sigma^23\sigma^2\pi \) (6%), and other configurations. Note that at the \( R_e \) of the neutral InSb ground state (3.05 \( \text{Å} \)), the \( ^2\Pi \) state of InSb\(^+\) is composed of \( 1\sigma^22\sigma^23\sigma^2\pi \) (71%) and \( 1\sigma^22\sigma^2\pi^2 \) (16%). At 2.8 \( \text{Å} \), the \( ^2\Pi \) state of InSb\(^+\) is made of \( 1\sigma^22\sigma^23\sigma^2\pi \) (52%) and \( 1\sigma^22\sigma^2\pi^2 \) (33%). Thus the two configurations undergo an avoided crossing which would
result in a complex photoelectron spectra. However, the
$^4\Sigma^-$ ground state of InSb is somewhat purer. This situation
is analogous to GaAs$^+$. This means the InSb($X^3\Sigma^-$) → InSb$^+$ $[\Pi^2, \Pi^2(\Pi)]$ transitions would be comprised of
satellite peaks analogous to the predicted photoelectron spectrum for GaAs. The separation between $^2\Pi$ and $^2\Pi(\Pi)$ states of InSb$^+$ is only 6800 cm$^{-1}$ at the SOCl level of
theory. This is the primary reason for the strong interaction of $1\sigma^22\sigma^23\sigma^2\sigma^2$ and $1\sigma^22\sigma^2\sigma^3$ configurations of InSb$^+$.

C. InSb$^-$
1. Potential energy curves and spectroscopic constants

Figure 4 shows the potential energy curves of InSb$^-$ obtained using a full CASSCF/FOCI method. Although the
FOCI calculations included up to 38 000 configurations we
do not expect the FOCI calculations to be as accurate as the
SOCl calculations especially for InSb$^-$.

As seen from Fig. 4, there are virtually degenerate elec-
tronic states for InSb$^-$ of $\Sigma^+$ and $^2\Pi$ symmetries. The $^2\Pi$
state has a slightly longer bond length compared to the $^2\Sigma^+$
state ($\Delta R_e = 0.05$ Å). The $^2\Pi$-$^2\Sigma^+$ energy separation of
InSb$^-$ at the FOCI level is only 58 cm$^{-1}$. Hence the ground
state of InSb$^-$ cannot be established unambiguously at this
level of theory.

The existence of two nearly degenerate states for InSb$^-$ makes it more interesting since the $^2\Sigma^+$ state undergoes an
avoided crossing with the $^2\Pi_{1/2}$ state as a result of near-
degeneracy of these states and larger spin–orbit coupling for
InSb$^-$ compared to the lighter analogs in this group of com-

As seen from Table V, when spin–orbit effects are in-
cluded through the RCI method, the $X^2\Pi_{1/2}$ state is the
ground state of InSb$^-$. The $^2\Pi$ state arises from the
$1\sigma^22\sigma^23\sigma^2\sigma^3$ configuration and is thus an inverted $^2\Pi$. Consequently, the $^2\Pi_{1/2}$ component is lowered with respect to $^2\Pi$ by 1075 cm$^{-1}$.

The $^2\Sigma^+$ state undergoes considerable spin–orbit mix-
ing with the nearly degenerate $^2\Pi_{1/2}$ state. This increases the
$R_e$ of the $^2\Sigma^+$ state by 0.06 Å. The $\omega_e$ sharply drops due to
the strong contamination with $^2\Pi$. The $^2\Sigma^+$ state is effec-
tively lowered due to this spin–orbit contamination. Effect-
ively, it lies 484 cm$^{-1}$ above the $^2\Pi_{1/2}$ state. The designa-
tion $^2\Sigma^+$ is thus crude and the correct designation for this
state is $1/2(1)$.

The $1/2(1)$ state approximately exhibits an opposite beha-
\behavior compared to the $1/2$ state. Its $R_e$ decreases by the
same factor (0.06 Å) while the $\omega_e$ increases by the same
factor due to spin–orbit mixing. This state is raised with re-
spect to the $^2\Pi$ state as expected for an inverted $^2\Pi$ state.
Thus InSb$^-$ is quite interesting from the standpoint of rel-
ativistic effects.

The $^2\Pi$ excited state of InSb$^-$ has a long bond length
(3.4 Å) and a correspondingly smaller $\omega_e$. This is antici-
pated for a high spin state of a negative ion such as InSb$^-$. The $^4\Delta$ and $^4\Sigma^-$ states have relatively shorter bond
lengths compared to the $^2\Pi$ state. These states are approxi-
mately 12 000–13 500 cm$^{-1}$ above the ground state of
InSb$^-$. The crossing of many electronic states for $R = 2.8–3.0$
Å would make the spectrum very complex in this region (see
Fig. 4). The $^4\Pi(\Pi)$ state is predominantly repulsive.

The $^4\Pi(\Pi)$, $^2\Sigma^+$ (\Pi), and $^4\Delta$ excited states of InSb$^-$
are relatively more bound compared to the quartet states.
The existence of 9 or more low-lying bound electronic states
for InSb$^-$ below 15 000 cm$^{-1}$ is consistent with the cor-
responding states of GaAs$^-$.

TABLE V. Spectroscopic constants of InSb$^-$.  

<table>
<thead>
<tr>
<th>State \ method</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>SOCl</td>
<td>FOCI</td>
<td>SOCl</td>
</tr>
<tr>
<td>$X^2\Pi_{1/2}$</td>
<td>2.776</td>
<td>2.705</td>
<td>0</td>
</tr>
<tr>
<td>$^2\Sigma^+$</td>
<td>2.646</td>
<td>2.72</td>
<td>884</td>
</tr>
<tr>
<td>$^2\Pi_{1/2}$</td>
<td>2.721</td>
<td>2.65</td>
<td>2 615</td>
</tr>
<tr>
<td>$^4\Pi$</td>
<td>…</td>
<td>3.4</td>
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</tr>
<tr>
<td>$^4\Delta$</td>
<td>…</td>
<td>3.18</td>
<td>…</td>
</tr>
</tbody>
</table>

FIG. 4. Potential energy curves of InSb$^-$.  

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The predicted spectroscopic constants and potential energy curves of InSb$^-$ would be especially of interest to experimentalists pursuing negative photoelectron or photodetachment spectra of anions. For example, Lineberger and co-workers\textsuperscript{50-52} have carried out similar studies on many species to obtain electron affinities and to probe the electronic states of the neutral species. Since InSb$^-$ is well bound, the negative photoelectron spectrum of InSb$^-$ could be a possible method to study the predicted electronic states of neutral InSb.

2. Electron affinity and dissociation energy for InSb$^-$

The FOCI/RCI adiabatic electron affinity of InSb for the process

\[ \text{InSb}(\Sigma_{0}^{+}) + e^- \rightarrow \text{InSb}^- (\Pi_{3/2}) \]

is calculated as 1.0 eV. It is well known that electron correlation effects tend to have significant impact on electron affinities. A full SOCI/RCI adiabatic E.A. of InSb is 1.39 eV.

The electron affinity of the In atom as deduced from the long distance calculations at the SOCI/RCI level is 0.3 eV in excellent agreement with an experimental value of 0.32 eV obtained by Hotop and Lineberger.\textsuperscript{50} As listed by Hotop and Lineberger,\textsuperscript{50} the antimony atom has a larger electron affinity of 1 eV. This is manifested in the molecular region of the electronic states of InSb$^-$ as we discuss in a subsequent section on Mulliken populations. That the negative charge of InSb$^-$ resides more on the antimony atom than on the In atom as the E.A. of Sb is greater than the In atom.

The dissociation energy of InSb$^-$ was computed as the difference of its energy at \( r_e \) and at a long distance of 8.0 \AA. At the FOCI level of theory the value obtained this way is 2.1 eV. At the same level of theory the neutral InSb has a \( D_e \) of 1.1 eV (see Sec. III A 5). Thus at the FOCI level of theory InSb$^-$ is 1 eV more bound compared to the neutral InSb.

At the full SOCI level, the \( D_e \) (InSb$^-$) is calculated as 2.5 eV. Since SOCI calculations are more accurate than FOCI calculations, we predict that \( D_e \) (InSb$^-$) = 2.7 $\pm$ 0.2 eV.

It can be seen from the predicted \( D_e \) and E.A. of InSb$^-$ and InSb, respectively, that there is a difference of $\sim$ 1.3 eV between \( D_e \) (InSb$^-$) and E.A. (InSb). This means that those electronic states of the neutral InSb lying $< 1.3$ eV of the ground state of InSb could be probed using negative ion photoelectron spectroscopy of InSb$^-$. Thus $\Pi_I$, $\Pi_I$, $\Delta$, $\Pi_I$, and $\Sigma^+$ states of InSb should be accessible for experimental photodetachment studies.

IV. ANALYSES OF WAVE FUNCTIONS AND THE NATURE ON LOW-LYING ELECTRONIC STATES OF InSb, InSb$^+$, AND InSb$^-$

A. Dipole moments

Tables III and IV show the dipole moments of the low-lying electronic states of InSb and InSb$^+$, respectively, obtained at the SOCI level near the equilibrium geometries of the respective states. Note that dipole moments of charged species are gauge dependent. In all cases the dipole operator was placed on the In atom.

All low-lying electronic states of InSb ($\Sigma^-$, $\Pi_I$, $\Delta$, $\Sigma^+$, $\Sigma^-$) are very ionic with In$^+$ Sb$^-$ polarity. The $\Sigma^-$ ground state has a large dipole moment of 2.3 D in the absence of spin–orbit coupling. This value is much larger compared to the isoelectronic GaAs for which the $\Sigma^-$ ground state has a dipole moment of 1.34 D.

Since the spin–orbit coupling term mixes the $\Sigma_{0}^-$, ($\sigma^2\pi$) with $\Sigma_{1}^+$, ($\sigma^3\pi$), the \( \mu_p \) value of the $X^0^+ \text{ state of InSb is expected to be altered as the } r_e \text{ changes significantly due to the spin–orbit contamination. Hence relativistic density matrices and properties were obtained using the enhancement to our RCI codes described in Ref. 53. Table III also shows the dipole moments of the X$\Sigma^+$, $\Sigma^-$ states including the effects of spin–orbit coupling. The spin–orbit contamination of the $\Sigma^-$ state with the $\Sigma^+$ state increases the dipole moment by almost 0.32 D since the bond length of $\Sigma^-$ increases due to this contamination. Hence, spin–orbit mixing has a large contribution to the dipole moment of InSb. It would be quite interesting to measure the $\mu_p$ of InSb in the X$^0^+$ ground state.

The $\Sigma^-$ state to the contrary is not influenced much by spin–orbit coupling since contamination with the low-lying $\Pi_I$ and $\Pi_I$ states add up to only 0.2%. Thus $\Delta \mu_p$ for the X$\Sigma^-$ state is $\sim$ 0.034 D.

The dipole moment of the $\Pi_I$ state is a bit larger than the X$\Sigma^-$ state in the absence of spin–orbit coupling. Note that the \( \mu_p \) value of GaAs in the $\Pi_I$ state at the SOCI level is 1.61 D.\textsuperscript{21}

The dipole moments of the excited electronic states of InSb such as $\Pi_I$ and $\Pi_I$ have opposite polarity (In$^-$ Sb$^+$). This suggests that the $\Pi_I$($\Pi$)X$\Sigma^-$ and $\Pi_I$($\Pi$)X$\Sigma^-$ transitions of InSb involve considerable charge transfer. This trend for InSb is akin to the corresponding trend for GaAs.\textsuperscript{21}

The dipole moments of InSb$^+$ are large and negative. Since the dipole operator was placed on the In atom the negative value suggests that significant portion of the positive charge resides on the In atom. As we discuss later this is consistent with the Mulliken population charge distributions.

The dipole moments of the $\Sigma^+$ and $\Pi_I$ electronic states of InSb$^-$ are large and positive. The positive polarity suggests that significant portion of the negative charge is on the Sb atom in InSb$^-$. This is fully consistent with the experimental electron affinities of In (0.3 eV) and Sb (1 eV) listed by Ho and Lineberger.\textsuperscript{50} Thus Sb would preferably keep the electron compared to the indium atom.

B. Composition of the CI wave functions of InSb, InSb$^-$, and InSb$^+$

1. InSb

The compositions of the CI wave functions of electronic states of InSb are of interest. The ground state of InSb ($\Sigma^-$) is found to be predominantly composed of the $1s^2\sigma^2\pi^2\rho^2\tau^2$ configuration (87%) and configuration spin functions arising from the $1s^2\sigma^2\pi^2\rho^2\tau^2$ (3%). The 1s and 2s orbitals are predominantly Sb(5s) and In(5s), respectively. The 2p or-
bital is a mixture of Sb(5p) and In(5p) orbitals. The 1π orbital is found to be a predominantly Sb(5p) orbital. There is significantly smaller contribution by the In(5p) orbital to the 1π orbital. The 2π orbital to the contrary is composed predominantly of the In(5p) orbital. The occupancies of the 1π, and 1σπ orbitals add up to 1.979 while the occupancy of the 3σ orbital is 1.894. This makeup of orbitals is consistent with In⁺ - Sb⁻-ionic character of the bonds.

The 3Π and 1Π states are predominantly composed of the 1ο2σ2ζ3ο1π² (81%, 73%) configuration. The 1Δ state is composed mainly of the 1ο2σ2ζ3ο1π² configuration (88%).

The first two 1Σ⁺ states exhibit interesting trends as a function of internuclear distance. At small distances, the 1Σ⁺ (I) state is predominantly 1ο2σ2ζ1π⁴ (75%) although mixing with 1σ2ζ3ο1π² is significant near the short rο of this state (7%). At very short distance (R = 2.2 Å), the 1Σ⁺ state is 83% 1σ2ζ2σ1π⁴, 2.5% 1σ2ζ3ο1π², and only 2.5% 1σ2ζ3ο1π². At 2.90 Å, 1Σ⁺ (I) becomes 1σ2ζ2σ3ο² (40%), 1σ2ζ2σ3ο² (19%), and 1σ2ζ3ο² (14%). Thus the 1Σ⁺ state undergoes an avoided crossing of 1σ2ζ3ο² with 1σ2ζ2σ3ο² which is reminiscent of the corresponding state of GaAs.

The 1Σ⁺ (II) state exhibits approximately an opposite orthogonal behavior to the 1Σ⁺ (I) state. At 2.2 Å it is 74% 1σ2ζ3ο1π² and 3% 1σ2ζ2σ1π⁴. At 2.70 Å, it is 67% 1σ2ζ3ο1π² and 10% 1σ2ζ2σ1π⁴. At 2.90 Å, the 1Σ⁺ (II) state becomes 35% 1σ2ζ3ο1π², 20% 1σ2ζ2σ1π⁴, and 17% 1σ2ζ2σ1π⁴. Hence among various states of InSb, the 1Σ⁺ states exhibit the most interesting behavior as a function of internuclear distance.

The high-lying states of InSb such as 3Σ⁺ (II), 1Σ⁻, etc., are also complex mixtures of 1σ2ζ2σ1π² and 1σ2ζ3ο1π² configurations. The 3Π(II), and 3Π(III) states which are potential candidates for experimental studies are also mixtures of 1σ2ζ2σ3ο1π² and 1σ2ζ3ο1π², and other configurations.

2. InSb⁺

The ground state of InSb⁺ is predominantly made of the 1σ2ζ2σ3ο1π² configuration. The 2Σ⁻ and 2Δ states of InSb⁺ arise from the same configuration.

Among various electronic states of InSb⁺ the 2Π state and the 4Σ⁻ (II) state exhibit interesting compositions leading to avoided crossings and somewhat different shapes of potential energy curves for these states. At short distances (R < 3 Å) the 2Π state of InSb⁺ is a mixture of 1σ2ζ2σ1π² (53%) and 1σ2ζ3ο1π² (33%) although the former configuration dominates. At longer distances (R ~ 3.5 Å) this state becomes predominantly 1σ2ζ3ο1π². The 2Π(II) state exhibits an opposite behavior. Near 2.7 Å these two configurations make almost equal contributions to the two 2Π states. As discussed in Sec. III B 2, this would result in complex photoelectron spectral bands corresponding to transitions terminating into these states.

The 4Σ⁻ (II) state is a mixture of 1σ2ζ2σ3ο1π², 1σ2ζ2σ3ο1π², and 1σ2ζ3ο1π² configurations at shorter distances. The contributions from Rydberg configurations are also quite noticeable at these distances. At longer distances this state becomes significantly 1σ2ζ2σ3ο1π². Consequently, there is an avoided crossing in this state which leads to minima (second one relatively weak) separated by a barrier (see Fig. 3). Thus the photoelectron spectrum corresponding to InSb (X' Σ⁻) - InSb⁺ 4Σ⁻ (II) would be quite interesting in that it would exhibit features corresponding to quantum tunneling and predissociation. The crossing of the 2Δ(II) repulsive curve would predissociate the 4Σ⁻ (II) component but the 4Σ⁻ (II) should survive.

3. InSb⁻

The two low-lying electronic states of negative ion InSb are relatively simple in characters from the standpoint of CI composition in the absence of spin–orbit coupling. The 2Π and 2Σ⁺ states of InSb⁻ are predominantly composed of the 1σ2ζ2σ3ο1π² and 1σ2ζ3ο1π² configurations. The mixing of 1σ2ζ2σ3ο1π² configurations (3.4%) is quite noticeable in the 2Σ⁺ state.

C. Mulliken populations

Table VI shows Mulliken population analyses of the low-lying electronic states of InSb, InSb⁺, and InSb⁻. In that table, we have omitted the d and s populations. The s populations are between 1.4 and 1.7 for In and close to 2.0 for Sb in most of the states. The d populations add up to 0.20.

The Σ⁻ ground state of InSb is composed of In (5s0.69p0.75) and Sb (5s0.03p0.32). Note that the s population of Sb is almost 2.0, and this is also seen from the actual composition of the 3σ orbital of InSb. The larger Sb p population and an overall Sb population of 5.38 suggests an excess of 0.38 electrons on the antimony atom in the Σ⁻ state of InSb. This is fully consistent with the calculated dipole moment of InSb which suggests In⁻ Sb⁺ polarity of bonds.

The 2Π(II) and 3Π(III) states of InSb have substantially larger In populations compared to both the Σ⁻ ground state and 2Π state. These are consistent with the predicted

<table>
<thead>
<tr>
<th>TABLE VI. Mulliken population analyses of InSb, InSb⁺, and InSb⁻.</th>
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<td>Species</td>
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</tr>
<tr>
<td>InSb⁻</td>
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<td>InSb⁻</td>
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<td>InSb⁻</td>
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<tr>
<td>InSb⁻</td>
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<tr>
<td>InSb⁺</td>
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</tbody>
</table>
charge transfers in the $X^3\Sigma^- \rightarrow \Pi(\Pi)$ and $X^3\Sigma^- \rightarrow \Pi(\Pi)$ transitions. Similarly the $\Pi(\Pi)$ state has larger In population. The In $(5p)$ population is noticeably larger for the $\Pi(\Pi)$, $\Pi(\Pi)$, and $\Sigma^+$ states.

The total In and Sn Mulliken populations in the $\Sigma^-$, $\Pi$, and $\Pi$ states of In$^+$ are approximately 2.2–2.3 and 4.7–4.8, respectively. This suggests that $70\%–75\%$ of the positive charge resides on the indium atom In$^+$. The experimental I.P.s of In and Sn are 5.79 and 8.64 eV, respectively. $^{43}$ Thus the Mulliken populations and dipole moments of In$^+$ are fully consistent with the fact that the I.P. of Sn is substantially larger than that of In.

The total In and Sn population of the $\Sigma^+$ and $\Pi$ states of In$^+$ are 3.14–3.19 and 5.81–5.86, respectively. This suggests that nearly $81\%–85\%$ of the negative charge is on the antimony atom In$^+$ electronic states. Note that experimental electron affinities of In and Sn are 0.3 and 1 eV, respectively. $^{50}$ Hence since antimony has greater electron affinity, most of the negative charge shifts to the Sn atom in In$^+$.

The In–Sn overlap populations approximately depend on the $r_e$ values although for repulsive states the overlaps are negative. Thus the In–Sn overlap is larger for the neutral $\Pi$ state compared to the $X^3\Sigma^-$ state (Table VI). The overlap populations of the negative ionic states are larger than the neutral states, while the overlaps of the positive ionic states are reduced. This is consistent with the strengthening of the In–Sn bond in the former case while in the latter case In–Sn bond is weakened.

D. RCI wave functions and spin–orbit contamination

The compositions of the RCI wave function of the low-lying electronic states of In$^+$ are quite interesting. Spin–orbit mixings of electronic states of In$^+$ are small.

The 1/2(I) state of In$^+$ exhibits a very interesting trend as a function of internuclear distance. At 2.5 Å, the 1/2 state is composed of 86% $2\Sigma_{1/2}$ (1σ$^2$2σ$^2$3σ$^1$π$^4$) and 12% $2\Pi_{1/2}$ (1σ$^2$2σ$^2$3σ$^1$π$^4$). At 2.7 Å it becomes 56%–35% mixture of these two states. At 2.8 Å the composition reverses to 35% $2\Sigma_{1/2}$ and 65% $2\Pi_{1/2}$. Consequently, not only the spin–orbit contamination of $2\Sigma_{1/2}$ and $2\Pi_{1/2}$ is large in these states but they undergo avoided crossings. The 1/2(II) of In$^+$ state exhibits an opposite behavior.

The $X^3\Sigma^-$ ground state of In$^+$ is 92% $\Sigma^-$, 3% $\Pi^+$, and only 0.1% $\Pi^0$. Both $\Sigma^-$ and $\Sigma^+$ arise from the same 1σ$^2$2σ$^2$3σ$^1$π$^2$ configurations. This spin–orbit contamination is significant even in the ground state of In$^+$.

The In$^+$ is composed of 91% $4\Sigma_{1/2}$ and 14% $2\Sigma_{1/2}$ at 3.5 Å. Thus spin–orbit contamination is less in In$^+$ compared to the neutral In $X^3\Sigma^-$ state. Hence spin–orbit contamination is the largest for the In$^+$ and the smallest for In$^+$. The near-degeneracy of the $\Sigma^+$ and $\Pi$ states is the primary factor which is responsible for the significant spin–orbit mixing of $2\Sigma_{1/2}$ with $2\Pi_{1/2}$ in the case of In$^+$.

V. COMPARISON OF InSb AND GaAs

Table VII shows a comparison of selected spectroscopic constants of electronic states of GaAs with InSb and the corresponding ions. As evidenced from Table VII, the calculated $R_e$ of InSb are approximately 0.4 Å longer than the corresponding values for GaAs. The $\omega_e$ values are correspondingly smaller. This is anticipated for the heavier InSb.

The energy separations of valence electronic state of InSb in the absence of spin–orbit coupling are in general quite comparable although for the lowest-lying electronic states, $T_e$ of InSb states are larger than the corresponding values for GaAs.

The $T_e$ values of the $\Pi$ and $\Pi$ states of InSb are roughly 2300–3000 cm$^{-1}$ smaller than the corresponding values for GaAs. This is mainly due to the fact that the J-weighted $4S$–$2D$ separation for Sn is 9317 cm$^{-1}$ while the corresponding separation for As is 10786 cm$^{-1}$. Since both the $\Pi$ and $\Pi$ electronic states of InSb arise from $2\Pi(2P) + Sb(2D)$, the smaller $T_e$ values of the $\Pi$ and $\Pi$ states of InSb compared to GaAs is understandable.

The I.P., E.A., and $D_e$ of GaAs at the best level of theory are 6.9, 1.3, and 1.9 eV, respectively. The corresponding SOCI/RCI values for InSb are 6.33, 1.41, and 1.45 eV, respectively. The smaller $D_e$ for InSb is quite understandable for a heavier diatomic.

Since most of the positive charge of the In$^+$ ion resides on the indium atom, the I.P. relationship of GaAs to InSb should correspond to the I.P. relationship of Ga and In atoms. The I.P.s of Ga and In are 6.0 and 5.79 eV, respectively. $^{43}$ Hence the I.P. of InSb should be smaller than the I.P. of GaAs. This is in accord with our theoretical I.P.s of these species.

As discussed before, most of the negative charge of In$^+$ is localized on the antimony atom. The E.A. of As and Sn are 0.81 and 1.08 eV, respectively. $^{50}$ Thus the E.A. (In$^+$) should be larger than E.A. (GaAs). Note that this quantitative argument is consistent with the SOCI E.A.s of these two species.

<table>
<thead>
<tr>
<th>TABLE VII. Comparison of selected properties of GaAs, GaAs$^+$, and GaAs$^{-}$ with InSb$^+$, InSb$^-$, and InSb$^+$</th>
<th>$R_e$ (Å)</th>
<th>$\omega_e$ (cm$^{-1}$)</th>
<th>$T_e$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaAs</td>
<td>InSb</td>
<td>GaAs</td>
<td>InSb</td>
</tr>
<tr>
<td>$\Sigma^-$</td>
<td>2.55</td>
<td>3.0</td>
<td>214</td>
</tr>
<tr>
<td>$\Pi$</td>
<td>2.38</td>
<td>2.77</td>
<td>236</td>
</tr>
<tr>
<td>$\Sigma^+$</td>
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<tr>
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<td>3.37</td>
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<td>2.80</td>
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<tr>
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<td>3.20</td>
<td>160</td>
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<tr>
<td>$\Sigma^-$</td>
<td>2.94</td>
<td>3.35</td>
<td>89</td>
</tr>
<tr>
<td>$\Pi$</td>
<td>2.519</td>
<td>3.00</td>
<td>250</td>
</tr>
<tr>
<td>$\Pi$</td>
<td>3.06</td>
<td>3.36</td>
<td>120</td>
</tr>
</tbody>
</table>

$^{+}$ MG (V) stands for either GaAs or InSb.

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Based on the above comparison of the electronic properties of InSb and GaAs, we predict the electronic structure of InSb to be heavier species in this group, namely, TiBi. Since the I.P. of Ti is 6.1 eV, the I.P. of TiBi is expected to be larger than InSb. The change in the I.P. trend of Ti is primarily due to the larger spin-orbit effects which stabilize the $S_{1/2}$ ground state of Ti compared to the $S_{0}$ closed shell ground state of Ti$^+$. The I.P. of TiBi is expected to be substantially reduced compared to the I.P. of InSb mainly due to spin-orbit stabilization. We predict that $D_e$(TiBi) $<$ 0.7 eV. The bond lengths of the electronic states of TiBi would also be considerably longer.

The electron affinity of the Bi atom is 0.95 eV and hence is only a bit smaller than the Sb atom. Hence the E.A. of TiBi should be comparable.

$\text{InSb}$ $X^2\Sigma^{-}_0^+\!:\!R_e = 3.02 \, \text{Å}, \quad \omega_e = 121 \, \text{cm}^{-1}, \quad D_e = 1.35 \, \text{eV},$

$X^2\Sigma^{-}_1\!:\!R_e = 3.03 \, \text{Å}, \quad \omega_e = 136 \, \text{cm}^{-1}, \quad T_e = 494 \, \text{cm}^{-1};$

$\text{InSb}^+\!:\! \times \!X^2\Sigma^{-}_0^+\!:\! R_e = 3.35 \, \text{Å}, \quad \omega_e = 63 \, \text{cm}^{-1}, \quad D_e = 0.37 \, \text{eV};$

$\text{InSb}^-\!:\! \times \!3\Pi_{3/2}^-\!:\! R_e = 2.695 \, \text{Å}, \quad \omega_e = 191 \, \text{cm}^{-1}, \quad D_e = 2.5 \, \text{eV}.$

Since the $S_{3/2}^\text{2}$ separation for Bi is 11 400–15 400 cm$^{-1}$, we predict that the $3\Pi_{1/2}^-\!:\!X^2\Sigma^{-}_0^+$ transition energies of TiBi should be larger than the corresponding energies for InSb.

VI. CONCLUSION

In this investigation potential energy curves and spectroscopic constants of 26 electronic states of InSb, 12 electronic states of InSb$^+$, and 9 electronic states of InSb$^-$ were obtained using a complete active space SCF (CASSCF) followed by FOCI and SOCI calculations which included up to 700 000 configurations. The ground state properties of InSb, InSb$^+$, and InSb$^-$ were calculated as

Many spectroscopic transitions in the IR–UV regions are predicted for InSb. Specifically the $3\Pi_{1/2}^-\!:\!X^2\Sigma^{-}_0^+$ and $3\Pi_{3/2}^-\!:\!X^2\Sigma^{-}_0^+$ transitions are predicted at 15 900 and 20 200 cm$^{-1}$, respectively. Both the $3\Pi_{1/2}$ and $3\Pi_{3/2}$ states were found to be predissociated. Thermodynamic $D_0^\text{e}(\text{InSb})$ is corrected by reevaluating the partition function of InSb as 1.45 eV. The dipole moments of $X^2\Sigma^{-}_0^+$, $X^2\Sigma^{-}_1^+$, and $3\Pi_{3/2}^-$ states of InSb are calculated at the SOCI level of theory as 2.63, 2.27, and 2.3 D, respectively, with In $^+$ $\text{Sb}^-$ polarity.

The adiabatic I.P. and E.A. of InSb are calculated as 6.33 and 1.41 eV, respectively. The $X^2\Sigma^{-}_1^+$ and $3\Pi_{3/2}^-$ states of InSb$^-$ undergo avoided crossing due to the near-degeneracy of these states. Most of the positive charge resides on In in the $X^2\Sigma^{-}_1^+\!:\!$ ground state of InSb$^-$ while most of the negative charge resides on Sb in the $3\Pi_{3/2}^-\!:\!$ ground state of InSb$^-$. More bound electronic states below 15 000 cm$^{-1}$ are found for InSb$^-$ compared to the neutral InSb molecule.

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29M. A. Duncan (private communication).
30L. Knight, Jr. (private communication).
42The authors of ALCHEMY II are B. Liu, B. Lengsfeld, and M. Yoshimine.

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