RELATIVISTIC CONFIGURATION INTERACTION CALCULATIONS OF THE LOW-LYING STATES OF BiH

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Relativistic configuration interaction calculations of the low-lying states \(0^+(I), 1, 2, 0^+(II)\) arising from \(\sigma^2\pi^2\) configuration of BiH and the corresponding \(\lambda-s\) states \((3\Sigma^-, 1\Delta, 1\Sigma^+)\) are carried out. These states are found to be bound and the calculated spectroscopic properties are compared with the available experimental results for the \(X(0^+), \Lambda(1)\) and \(B(0^+)\) states. The dissociation energy of the ground state \(X(0^+)\) is calculated to be 2.17 eV. The ground state \(0^+(I)\) is found to be a mixture of \(3\Sigma^-_\pi\) (76%) and \(1\Sigma^+_\pi\) (16.3%). The \(0^+(II)\) and 2 states show avoided crossings at long distances.

1. Introduction

The bismuth hydride molecule has been of considerable spectroscopic interest as a result of large spin–orbit interaction. The ground state of BiH would be \(3\Sigma^-\) if there were no spin–orbit interaction but the spin–orbit interaction splits this into \(0^+\) and \(1\) states. Consequently, the hyperfine structure of the \(\Lambda(1)\) state has been of considerable experimental interest \([1,2]\). The first spectrum of BiH was recorded in the early thirties \([3,4]\). Heimer \([3,4]\) observed 3 systems of bands of BiH attributed to the emissions \(B(0^+) \rightarrow X(0^+), B(0^+) \rightarrow \Lambda(1)\) and \(D \rightarrow C\). The \(X\) and \(\Lambda\) states are assigned by Huber and Herzberg \([5]\) to \(0^+\) and \(1\) states arising from \(3\Sigma^-\), respectively. Khan and Khan \([6]\) have carried out the rotational analysis of a new absorption band system which they assign to \(X(0^+) \rightarrow E(0^+)\) absorption system. Lindgren and Nilsson \([7]\) have also recorded the \(X(0^+) \rightarrow E(0^+)\) absorption spectral systems of BiH to obtain the spectroscopic properties of low-lying states of BiH. The spectra of isoelectronic SbH and AsH are also of considerable interest \([8]\).

The BiH molecule is of considerable theoretical interest since its ground-state electronic configuration \(\sigma^2\pi^2\) is an open-shell configuration. Further, 3 \(\lambda-s\) states arise from \(\sigma^2\pi^2\) \((3\Sigma^-, 1\Sigma^+, 1\Delta)\) among which

\[\text{the interaction between } 3\Sigma^-_\lambda, 1\Sigma^+_\lambda \text{ is expected to be large. Thus BiH is an interesting candidate for relativistic calculations as a result of large spin–orbit interaction. Theoretical study of relativistic effects on the spectroscopic properties of molecules containing very heavy atoms is a topic of considerable activity \([9-21]\). Section 2 describes the method of our calculations and section 3 discusses our results and comparisons with experimental spectra.}

2. Methodology

The general method of relativistic configuration interaction calculations for molecules containing very heavy atoms is outlined in ref. \([16]\). In this method the relativistic effective potentials are averaged with respect to spin at the SCF (self-consistent field) stage and differentiated for the spin–orbit operator. The spin–orbit operator thus obtained is used to compute one-electron spin–orbit integrals which are introduced at the CI stage. We employ relativistic effective potentials for the Bi atom. These potentials are the same as the ones used by Christiansen \([17]\) in his recent calculations of the ground state of Bi2. We included \(d^{10}s^2p^3\) as the valence shell of Bi atom.

A few low-lying configurations of the BiH molecule and the \(\lambda-s\) and \(\omega-\omega\) states arising from them
Table 1
A few low-lying MO configurations of BiH and the \( \lambda-s \) and \( \omega-\omega \) states arising from them (only the p electrons on Bi are shown)

<table>
<thead>
<tr>
<th>Configuration</th>
<th>( \lambda-s ) states</th>
<th>( \omega-\omega ) states</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \sigma^2 \pi^2 )</td>
<td>( 3\Sigma^- )</td>
<td>0(^+), 1</td>
</tr>
<tr>
<td>( \sigma^2 \sigma^* \pi )</td>
<td>( 3\Pi )</td>
<td>0(^+), 0(^-), 1, 2</td>
</tr>
<tr>
<td>( \sigma \sigma^* \pi^2 )</td>
<td>( 5\Sigma^- )</td>
<td>0(^+), 1, 2</td>
</tr>
<tr>
<td>( \sigma^* \pi )</td>
<td>( 3\Delta )</td>
<td>3, 2, 1</td>
</tr>
<tr>
<td>( \sigma \pi^3 )</td>
<td>( 3\Pi )</td>
<td>2, 1, 0(^-), 0(^+)</td>
</tr>
<tr>
<td>( \pi^4 )</td>
<td>( 1\Sigma^+ )</td>
<td>1</td>
</tr>
</tbody>
</table>

are shown in table 1. The dissociation limits of some of these states and the experimental atomic separations [22] are shown in table 2. As one can see from these tables there are quite a few low-lying states for BiH. In this investigation we carry out calculations of the \( \omega-\omega \) states and \( \lambda-s \) states arising from \( \sigma^2 \pi^2 \) configuration (0\(^+\), 1, 2, 0\(^+(II)\), 3\( \Sigma^- \), 1\( \Sigma^+ \), 1\( \Delta \)). Calculations of other states and the states of BiH\(^+\) are being carried out and will be reported in a future publication.

All low-lying \( \lambda-s \) states giving rise to \( \omega-\omega \) states of the same symmetry are included in our configuration interaction calculations. In particular the configurations shown in table 1 were included as reference configurations together with \( \sigma^* 2\pi^2 \) reference configurations. The d electrons of Bi were included at the SCF stage but were frozen at the CI stage of calculations. Single and double excitations from these reference configurations resulted in 3123 configurations for the 0\(^+\) states, 1565 configurations for the 1 state and 2695 configurations for the 2 state. A double-zeta Slater-type basis is employed for the Bi and H atoms. The optimized atomic exponents for Bi are reported in ref. [17]. The basis set for H used here is the same as the one Balasubramanian and Pitzer [14] used for SnH calculations.

3. Results and comparisons with spectra

The calculated spectroscopic properties of the low-lying states of BiH are shown in table 3. The experimental values are also quoted in table 3 for comparison. As one can see, the calculated values are in reasonable agreement with the experimental results. The splitting between the 0\(^+\) and 1 states arising from 3\( \Sigma^- \) state is calculated to be 5737 cm\(^{-1}\) which is in reasonable agreement with the experimental value of 4917 cm\(^{-1}\).

Our calculated bond distances for the 0\(^+\), 1, 2, and 0\(^+(II)\) states are \( \approx 0.1 \) A larger than the corresponding experimental values. This trend is similar to the earlier calculations on TIH [16], SnH [14] and other molecules. This can be attributed to a combination of several sources such as the lack of d correlation, the use of effective potentials, etc.

In table 3, we show the properties of 3\( \Sigma^- \), 1\( \Delta \) and 1\( \Sigma^+ \) states for comparisons. The 0\(^+\) and 1 states correspond to 3\( \Sigma^- \) and 3\( \Sigma^+ \) in type (c) coupling. As seen in table 3, spin–orbit interaction not only splits the 0\(^+\) and 1 components of 3\( \Sigma^- \) but also stabilizes these states. The significant mixing of 3\( \Sigma^- \) and 1\( \Sigma^+ \) lowers 0\(^+(I)\). Thus the 0\(^+(II)\) state goes up in energy with respect to 1\( \Sigma^+ \) as a result of this interaction. The

Table 2
Dissociation limits of the few low-lying states of BiH

<table>
<thead>
<tr>
<th>Molecular states</th>
<th>Dissociated atoms</th>
<th>Energy (cm(^{-1})) of the atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>2, 1, 1(II), 0(^-), 0(^+)</td>
<td>( ^4S_{3/2} + 2^2S_{1/2} )</td>
<td>0.0</td>
</tr>
<tr>
<td>2(II), 1(III), 1(IV), 0(^-(II)), 0(^+(II))</td>
<td>( ^2P_{3/2} + 2^2S_{1/2} )</td>
<td>11419</td>
</tr>
<tr>
<td>3, 2(III), 2(IV), 1(V), 1(IVD), 0(^-(III)), 0(^+(III))</td>
<td>( ^2P_{1/2} + 2^2S_{1/2} )</td>
<td>15437</td>
</tr>
<tr>
<td>1(VIII), 0(^+(IV)), 0(^-(IV))</td>
<td>( ^2P_{1/2} + 2^2S_{1/2} )</td>
<td>21661</td>
</tr>
</tbody>
</table>
vibrational frequencies of $0^+$, 1, 2 and $0^+$(II) states are also lowered as a result of spin–orbit interaction.

The experimental dissociation energy of BiH is calculated based on the extrapolation of $E(0^+)$ state assuming dissociation into Bi($2D_{3/2}$) + H($2S_{1/2}$) atoms [7]. The $E(0^+)$ state appears to be predissociated as a result of the crossing of the 1 state arising from $^5\Sigma^-$ state which dissociates into ground-state atoms (see tables 1 and 2). Consequently, there is some uncertainty in this experimental value. Huber and Herzberg [5] rightly indicate in their table on BiH that the $D_0^0$ reported there is an upper-bound value. This upper bound is 2.9 eV. Our calculated dissociation energy is based on the difference between the minimum of $0^+$ state and its energy at 9.0 bohr. This value is 2.17 eV. Since our calculated dissociation energies are usually in the range of 80–90% of the experimental values, this value should not be regarded as very accurate.

Our calculated potential-energy curves of the low-lying states of BiH are shown in fig. 1. As one can see from fig. 1, the 2 state has a barrier. This is attributable to an avoided crossing. At shorter distances and near equilibrium distances the 2 state is dominantly $^1\Delta_2$. However, at long distances the $^5\Sigma_2^-$ arising from $\sigma\sigma^*\pi^2$ dominates so that the 2(I) state would dissociate into Bi($4S_{3/2}$) + H($2S_{1/2}$) atoms.

The $0^+$(I) state is 76% $^3\Sigma_0^+$ and 16.3% $^1\Sigma_1^+$ at 3.5 bohr. The $^3\Pi_0^+$ states arising from $\sigma\pi^3$ and $\sigma^2\sigma^*\pi$ also make non-negligible contributions (1.6%) at 3.5 bohr. At 6.0 bohr, the $0^+$(I) state is 54% $^3\Sigma_0^+$, 12.2% $^1\Sigma_0^+$, 14% $^3\Sigma_0^+$ ($\sigma^2\pi^2$), 3% $^1\Sigma_0^+$ ($\sigma^2\pi^2$), 6.3% $^3\Pi_0^+$ ($\sigma^2\sigma^*\pi$), 5.4% ($\sigma\sigma^*\pi^2$), and the rest of the population is attributed to excitations from these references. Thus the $0^+$(I) state is contaminated quite heavily by spin–orbit interactions. The $0^+$(II) state is 70.4% $^1\Sigma_0^+$, 14.6% $^3\Sigma_0^+$, 8.2% $^3\Pi_0^+$ ($\sigma\pi^3$), and 1.3% $^3\Pi_0^+$ ($\sigma^2\sigma^*\pi$) at 3.5 bohr. At 6.0 bohr, the $0^+$(II) state is 39.4% ($\sigma\sigma^*\pi\pi^2\beta\beta$), 20% $^3\Pi_0^+$ ($\sigma^2\sigma^*\pi$), 10.4% $^1\Sigma_0^+$ ($\sigma^2\pi^2$), 8.4% $^3\Pi_0^+$ ($\sigma\pi^3$), 9.1% $^3\Pi_0^+$(o$^2\pi^2$), 1.7% ($^3\Sigma_0^-$), and the rest of the population attributed to single and double excitations.

The dissociation limit of $^3\Sigma^-$ in fig. 1 to Bi($4S_{3/2}$) + H($2S_{1/2}$)
H(2s) was calculated without spin–orbit integrals, while the 2, 1, and 0+ states were calculated at 9.0 Bohr with the spin–orbit integrals. The difference in this energy is thus attributable to spin–orbit interaction.

Acknowledgement

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References