Spectroscopic constants and potential energy curves of Bi$_2$ and Bi$_3^-$

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We compute the spectroscopic constants of 26 electronic states of Bi$_2$ and six electronic states of Bi$_3^-$. In addition, the potential energy curves of electronic states of Bi$_2$ dissociating into Bi($^4S$) + Bi($^4S$), Bi($^4S$) + Bi($^2D$), Bi($^4S$) + Bi($^2P$), Bi($^2D$) + Bi($^2D$), and Bi($^4S$) + Bi($^4P$) limits are computed. We use a complete active space multiconfiguration self-consistent field (CAS-MCSCF) followed by first-order configuration interaction (FOCI) and second-order configuration interaction (SOCI) methods. In addition, the spin–orbit effects are included through the relativistic configuration interaction (RCI) method. Our computed spectroscopic properties facilitate the assignment of recently observed negative ion photodetachment spectra as well as the electronic spectra accumulated up to now. The observed lifetime and transition moment dependence on internuclear distance are also explained based on computed potential energy curves.

I. INTRODUCTION

The spectroscopy of very heavy dimers and trimers of the sixth row atoms in general and Bi$_2$ in particular has been the topic of several studies. The recent review by one of the authors summarizes the developments on spectroscopic constants and potential energy curves of heavy dimers and trimers.

The bismuth clusters, especially Bi$_2$ and Bi$_3$, have been studied by several experimental techniques. The Bi$_2$ molecule appears to be the experimentally most studied among the sixth row dimers. The $A-X$ system of Bi$_2$ has been studied by several authors.

The most comprehensive earlier study of Bi$_2$ is due to Gerber et al. who have obtained the potential energy curves of several electronic states of Bi$_2$ using the Rydberg–Klein–Rees (RKR) method from the experimentally derived molecular constants. Gerber et al. studied the Bi vapor excitation spectra in a cw Ar ion laser. They made a suggestion that there exists a new state $X'$ ($\omega_2 = 154$ cm$^{-1}$) which lies 1500 cm$^{-1}$ below the $X$ state, previously thought to be the ground state. However, in a subsequent study, Bondybey and English showed that the $X'$ state observed by Gerber et al. is actually due to Bi$_4$ and the $X(0^+_g)$ state is unambiguously the ground state of Bi$_2$. This was further substantiated by the studies of Fabre et al. and Effantin. Gerber et al. observed five electronic transitions in the infrared–visible region.

The most studied system of Bi$_2$ is the $A(0^+_u) - X(0^+_g)$ system. The $A$ state is most probably the $0^+_u$ component of the $3\Sigma^+_u$ excited state of Bi$_2$. Bondybey and English observed a laser-induced-fluorescence system with $T_\sigma = 17859$ cm$^{-1}$ and $\omega_2 = 132$ cm$^{-1}$ in Ne and Ar matrices. These authors have also studied the spectra of Bi$_4$. A striking feature of the Bi$_4$ spectra is that they show no evidence of Jahn–Teller distortion in the excited states. The matrix spectra of Bi$_2$ have also been studied by Teichman and Nixon.

Drosch and Gerber have studied Bi$_2$ using optically pumped cw laser. The $A-X$ system was studied extensively leading to 150 line transitions attributed to the $A-X$ system. Ehret and Gerber have obtained the lifetimes and transition moments of the $A-X$ system. A particularly striking feature of the $A-X$ system is that the transition moments do not appear to change at all for internuclear distances between 2.6 and 3.3 Å. The lifetimes of the vibrational levels ($v' = 1-34$) ranged between 50 to 600 ns.

Recently, Polak et al. have studied the negative ion photodetachment spectra of Bi$_2^-$, Bi$_3^-$, and Bi$_4^-$. A unique feature of the photodetachment technique is that it facilitates observation of dipole and other forbidden transitions. They find four excited electronic states of Bi$_2$ lying above the $X(0^+_g)$ state. In addition, more than one electronic state of Bi$_3$ is observed in the 13 500 cm$^{-1}$ region, but this was considered mere tentative. They also observed the $A(0^+_u)$ electronic state studied before by the other authors. The theoretical calculation in this study was stimulated by the work of Lineberger and co-workers.

Fink et al. have observed the band spectra for Bi$_2$ in the near infrared region. The observed weak band sequences in the spectra between 7620 and 7800 cm$^{-1}$ were attributed to new states of Bi$_2$, but no definitive assignments could be made from the observed spectral features.

The first objective of this study is to compute the spectroscopic constants of all electronic states of Bi$_2$ below 14 000 cm$^{-1}$ of the ground state to aid in the interpretation of the photodetachment spectra. In addition, we compute several electronic states above the 14 000 cm$^{-1}$ region with the objective of aiding assignment of other observed spectra and possibly predicting electronic states which are yet to be observed. We also compute the electronic states of Bi$_2^-$. Section II outlines our method of theoretical calculations. Section III consists of results and discussion. Section IV describes the nature of low-lying electronic states of Bi$_2$.

II. METHOD OF CALCULATION

Table I shows the possible electronic states of Bi$_2$ arising from $^4S + ^4S$, $^4S + ^2D$, $^4S + ^2P$, $^2D + ^2D$, $^4S + ^4P$ atoms in
the absence of spin–orbit coupling. The spin–orbit coupling would of course be very large for the Bi atom and split various states in Table I into several spin–orbit states. The spin–orbit coupling would also mix two states with the same Ω quantum number. It is evident from Table I that Bi₂ is the most complex main group dimer in having numerous electronic states resulting from different spin multiplets and spin–orbit coupling.

We compute the spectroscopic constants and potential energy curves using a complete active space MCSCF (CASSCF) followed by configuration interaction (CI) methods. We employed relativistic effective core potentials (RECPs) for the Bi atom which retained the outer 6s⁶p³ shells in the valence space. The remaining electrons were replaced by RECPs. Hay and Wadt have also generated RECPs for Bi which give equally good results in the absence of spin–orbit coupling, but the RECPs generated by Ross et al. include the important spin–orbit effects for Bi.

We employed a (3s3p) valence Gaussian basis set augmented by a set of six–component d polarization functions with αₚ = 0.06. Thus our basis set is of triple zeta + polarization quality.

Both CASSCF and CI calculations were made in the D₂h point group. We retained the valence 6s and 6p orbitals of the Bi atoms in the active space. This led to an active space consisting of two a₂, two b₂u, one b₂u, one b₂g, one b₁u, and one a₁u orbitals in the D₂h group. Ten outermost electrons of Bi₂ were kept as active electrons. In the CASSCF, all these electrons are distributed in all possible ways among the active space of orbitals. Separate CASSCF calculations were made for each electronic state of Bi₂ with different spin multiplicity and spatial symmetry.

The potential energy curves for all internuclear distances were computed using the first-order CI (FOCI) method. The FOCI method included all configurations in the CASSCF plus those configurations generated by distributing nine electrons in the internal space and one electron in the orthogonal external space in all possible ways. The FOCI method was used to generate the natural orbitals for the relativistic CI (RCI) calculations to be discussed later. The FOCI method was also used to compute the spectroscopic constants of the excited states of Bi₂.

The negative ion of Bi₂ was treated on an equal footing with the neutral Bi₂. However, it is well established that electron affinities are very sensitive to higher-order correlation effects. Hence we employed a more accurate second-order CI (SOCI) method to compute the ground state of Bi₂⁺ and the same SOCI method applied to the ground state of Bi₂. The SOCI method included all configurations in the FOCI and those configurations obtained by distributing nine electrons in the internal and two electrons in the external space in all possible ways for Bi₂⁻. The SOCI calculations of the neutral Bi₂ included all configurations in the FOCI plus configurations generated by distributing eight electrons in the internal and two electrons in the external space in all possible ways.

The effect of spin–orbit coupling was introduced using the relativistic configuration interaction (RCI) method following the FOCI. The FOCI natural orbitals were used in the RCI. In the RCI, we included all low-lying electronic states which yield an Ω state of the desired symmetry as reference configurations. Subsequently, single and double excitations were allowed from these reference configurations. The introduction of spin–orbit coupling into the Hamiltonian would mix all Ω states which give a Ω state of the desired symmetry. Table II shows the list of reference configurations included in the RCI.

As seen from Table II, the 0⁺ state calculations included reference configurations which constitute the ¹Σ⁺ ground state, ³Πₑ, ³Sigma⁺ (0⁺), and excited ³Πₑ, ⁴Sigma⁺ + and excited ³Sigma⁺ + states. The 1⁺ state included ⁴Sigma⁺ + (1⁺), ³Πₑ (1⁺), ³Σ⁺⁻ (1⁺), ³Σ⁺⁻ (1⁺), and ³Sigma⁻⁻ (1⁺) states. The 1⁺ state included ⁴Sigma⁺ + (1⁺), ³Πₑ (1⁺), ³Σ⁺⁻ (1⁺), and ³Σ⁺⁻ (1⁺) states. The 1⁺
state included $^1 \Sigma_u^+ (1_u)$, $^1 \Delta_u (1_u)$, and $^3 \Sigma_u^- (1_u)$ states, while the $2_u$ state included $^3 \Delta_u (2_u)$ and $^1 \Sigma_u^- (2_u)$. The $0_u^+$ state included $^3 \Sigma_u^- (0_u^+)$ and $^1 \Sigma_u^- (0_u^+)$, while $3_u$ included $^1 \Delta_u (3_u)$. Hence our RCI included all important $\Omega$ states that will mix near $r_e$. All our preliminary calculations indicated that this array of reference configurations is completely adequate for the $0_u^+$ state at all distances. For other states, the list is complete for properties near $r_e$. For example, highly excited $^3 \Pi_u (1_u)$ could make a more important contribution at longer internuclear distances to the $^3 \Sigma_u^- (1_u)$ state, but makes no significant contribution near the $r_e$. Hence $^3 \Pi_u (1_u)$ was not included in the $^3 \Sigma_u^- (1_u)$.

The RCI calculations of Bi$_2^+$ 1/2g state included two reference configurations from $1\sigma^2_1 2\sigma^2_2 1\pi^4_1 \pi^4_2$ and five reference configurations arising from $1\sigma^2_1 1\sigma^2_2 2\sigma^2_0 1\pi^4_1 \pi^4_2$ which constitute $^6 \Sigma^+(1/2g)$ and $^2 \Sigma^+_u (1/2g)$. The $5(3/2)_g$ state included two reference configurations from $1\sigma^2_1 2\sigma^2_2 1\pi^4_1 \pi^4_2$ and five reference configurations from $1\sigma^2_1 1\sigma^2_2 2\sigma^2_0 1\pi^4_1 \sigma^4_0$ which in turn constitute the $^6 \Sigma^- (3/2)$ and $^4 \Delta (3/2)$ states.

All CASSCF/FOCI/SCI calculations were done using one of the author’s (K.B.)$^{33}$ modified versions of ALCHEMY II codes$^{34}$ to include RECPs. The spin–orbit integrals for the RCI were obtained using Pitzer’s ARGOS codes.$^{35,36}$ The RCI calculations were made using the codes based on the general polyatomic RCI described in Ref. 37. Our SOCI calculations included up to 304 000 configuration spin functions (CSFs) in the $D_{2h}$ group.

### III. RESULTS AND DISCUSSIONS

#### A. Theoretical spectroscopic constants and potential energy curves of Bi$_2$

Table III shows our computed spectroscopic constants for Bi$_2$. The spectroscopic constants of the $X 0_u^+$ were obtained using the CASSCF/ROCI/RGI method, while the constants of the excited states were obtained using the CASSCF/FOCI/RGI method. The $T_v$ values were obtained using the FOCI/RGI method in all cases to maintain consistency. The properties of states containing no $\Omega$ designation in parentheses were obtained without the inclusion of the spin–orbit term. However, all states lying below the 21 000 cm$^{-1}$ region were treated with somewhat greater accuracy including spin–orbit effects.

Figure 1 shows our computed potential energy curves of electronic states of Bi$_2$ in the absence of spin–orbit coupling. Figure 2 shows the potential energy curves of Bi$_2$ including spin–orbit effects. As mentioned in Sec. II, our treatment of spin–orbit coupling is more accurate near $r_e$ than at long distances, especially for the excited electronic states. Hence, we show potential energy curves for $\Omega$ states near the potential well.

As seen from Fig. 1, we computed all of the potential energy curves dissociating into 4$S$ + 4$S$ ground state atoms ($^1 \Sigma^+_u$, $^3 \Sigma^+_u$, $^3 \Sigma^-_u$, $^3 \Sigma^+_u$). Since there are numerous electronic states dissociating into 4$S + 2D$, 4$S + 2P$, 2$D + 2D$, and 4$S + 2P$, it was not possible to study exhaustively all these states. However, we chose selected states of importance in either assigning the existing spectra or in the prediction of electronic transitions in Bi$_2$. To this end, we show potential energy curves for Bi$_2$ and Bi$_4$ with spin–orbit effects.

![FIG. 1. Potential energy curves of Bi$_2$ in the absence of spin–orbit coupling.](image-url)
tion of new spectra. Consequently, we believe that this theoretical study should shed significant light on the possible low-lying states of Bi₂.

The ground state of Bi₂ is now experimentally established as the X' \( \Sigma^+ \) (0\(^+\)) state. Even though this state is predominantly \( \Sigma^+ \) even near its \( r_e \), mixing with \( \Pi^+ \) as a result of spin–orbit coupling is very significant.

The electron correlation effects were found to be very significant similar to the lighter group V trimers. This is because in the molecular region of the well, the ground electronic state has a closed-shell \( \Sigma^+ \) symmetry, while at the dissociation limit, it forms two open shell \( \Sigma^+ \) atoms. The full second-order CI (SOCl) correlating all 10 valence electrons yielded \( r_e = 2.76 \) Å, \( \omega_v = 151 \) cm\(^{-1}\), and \( D_e = 1.88 \) eV. The previous MRSDCI\(^{27}\) together with 15 electron potentials and a (4s4p4d) basis yielded improved \( \omega_v \) of 171 cm\(^{-1}\), but failed to yield a better \( r_e \). The experimental \( r_e \) of the \( X \) \( 0^+ \) is well established as 2.6596 Å. Hence even the SOCl method correlating 10 electrons overestimates the \( r_e \) by almost 0.1 Å. We believe that there are two sources of discrepancies. One has to do with the basis set especially in regards to the \( d \) polarization functions. An additional set of \( d \) polarization functions is quite likely to decrease \( r_e \) and increase \( \omega_v \). The other factor has to do with \( d \)-correlation effects, although it is believed that \( d \)-electron correlation effects arising from the \( 5d \) shells would be much smaller for Bi₂ compared to other early sixth row dimers such as Tl₂.\(^{29}\) The previous studies\(^{26,28}\) included 5d shells in the ECPs, but did not correlate the \( d \) shells. Considering this, the most probable source of errors in theoretical results is the basis set and the use of RECPs.

Although an accuracy of \( \pm 0.02 \) Å in \( r_e \) of \( \pm 10 \) cm\(^{-1}\) cannot be achieved with the treatment employed here for such a heavy dimer as Bi₂, the theoretical results give adequate information on the relative trends. This is extremely useful as the computed results aid in the assignment of the observed spectra and provide important insight into the nature of the low-lying electronic states in the observed systems and possible candidates perturbing or predissociating the observed bands. We estimate that the \( r_e \)'s of most of the electronic states in Table III have less than 5% error and in most of the cases the computed \( r_e \)'s are expected to be longer than experiment. The expected error in vibrational frequencies of electronic states of Bi₂ is 10%–15%. The computed \( T_e \) values for electronic states with \( T_e < 18 \) 000 cm\(^{-1}\) are expected to be accurate to \( \pm 3000 \) cm\(^{-1}\). For electronic states with \( T_e > 20 \) 000 cm\(^{-1}\), we expect a larger error of up to 20% mainly because spin–orbit effects could not be included for these states. However, based on the symmetry, and spectral properties of the observed states, we were able to assign almost all observed systems.

**B. Assignment of the observed spectra**

1. **Electronic states below 11 000 cm\(^{-1}\)**

A comprehensive summary of the observed states and our suggested assignment can be found in Table IV. Gerber and Broida\(^8\) have proposed the existence of a state that they labeled \( B(0) \) with \( T_e = 6500 \pm 1000 \) cm\(^{-1}\). Polak et al.\(^{28}\) have observed an electronic state in this region in their negative ion photodetachment spectra with a \( T_e \) value of 5460 cm\(^{-1}\). Our calculations reveal that the first excited state of Bi₂ is the \( 3\Sigma_u^+ (1_u) \) state with a theoretical \( T_e \) of 6651 cm\(^{-1}\) rather close to the experimentally observed \( B \) state with \( T_e = 5460 \) cm\(^{-1}\) (previous value 6500 \( \pm 1000 \) cm\(^{-1}\)). Our computations support the assignment of the observed \( B \) state to the \( 1_u \) component rather than \( 0^- \) suggested by Gerber and Broida.\(^8\)

Bondybey and English\(^{12}\) as well as Effantin et al.\(^{18}\) argued correctly that the state labeled \( X' \) (below the \( X \) state of Bi₂) first thought to be attributed to Bi₂ by Gerber and Broida\(^8\) is actually due to Bi₁. As seen from our computations, there is no electronic state below the \( X(0^-) \) state of Bi₁. Therefore the previous assignment of \( X \) to \( O_f \) and the \( X' \) to \( O_f \) \( \Sigma^- \) is fully supported by our calculations and all works subsequent to Bondybey and English.\(^{12}\)

An electronic state labeled \( A' (0) \) was observed by Gerber and Broida\(^8\) with \( T_e = 9500 \pm 2000 \) cm\(^{-1}\) and \( \omega_v = 141 \) cm\(^{-1}\). The most recent negative ion photodetachment spectra by Polak et al.\(^{28}\) place this state somewhat lower at \( T_e = 8220 \) cm\(^{-1}\) with \( \omega_v = 132 \) cm\(^{-1}\) (listed in Table IV). As seen from Table IV, the \( 3\Sigma_u^+ (0_u^-) \) component with a theoretical \( T_e = 10 \) 013 cm\(^{-1}\) is the most consistent state, although the nearby \( \Delta_u (2_u) \) cannot be completely ruled out. Hence, we tentatively assign the \( A' \) state to \( 3\Sigma_u^+ (0_u^-) \). It is interesting to note that our computed \( 3\Sigma_u^+ (1_u) - 3\Sigma_u^+ (0_u^-) \) splitting of 5100 cm\(^{-1}\) is somewhat
TABLE IV. Assignment of experimentally observed systems consistent with theoretical constants.

<table>
<thead>
<tr>
<th>State</th>
<th>$T_c (\text{cm}^{-1})$</th>
<th>$\omega_c (\text{cm}^{-1})$</th>
<th>Expt.</th>
<th>Theory</th>
<th>Expt.</th>
<th>Theory</th>
<th>Footnote</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X^+_0$</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td>173</td>
<td>151 (171)</td>
</tr>
<tr>
<td>$B^+ \Sigma^+_0(1_u)$</td>
<td>5 460 (6 500)</td>
<td>6 651</td>
<td>134</td>
<td>114</td>
<td></td>
<td></td>
<td>a</td>
</tr>
<tr>
<td>$A^- \Sigma^+_0(0_u^-)$</td>
<td>8 225</td>
<td>11 780</td>
<td>132</td>
<td>112</td>
<td>a, g</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a^\pi \Delta_u(2_u)$</td>
<td>9 875</td>
<td>12 833</td>
<td>125</td>
<td>133</td>
<td>a, c</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(17 395)</td>
<td></td>
<td>123</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$B^+ \Sigma^+_0(0_u^+)$</td>
<td>10 826</td>
<td>13 700</td>
<td>91 (106)</td>
<td>111</td>
<td>a, b</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$b^\pi \Delta_u(3_u)$</td>
<td>15 246</td>
<td>18 905</td>
<td>132</td>
<td>138</td>
<td>c</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Pi_u(0_u^-)$</td>
<td>16 850</td>
<td>18 892</td>
<td>143</td>
<td>143</td>
<td>d</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$eB^+ \Delta_u(2_u)$</td>
<td>17 336</td>
<td>22 481</td>
<td>145</td>
<td>140</td>
<td>d</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$A^- \Sigma^+_0(0_u^-)$</td>
<td>17 739</td>
<td>22 300</td>
<td>132</td>
<td>140</td>
<td>e</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E^+ \Pi_u(0_u^-)$</td>
<td>(26 505)</td>
<td>31 815</td>
<td>64</td>
<td>75</td>
<td>e</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$G^+ \Sigma^+_0$</td>
<td>(29 609)</td>
<td>30 855</td>
<td>107</td>
<td>88</td>
<td>e</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$V^+ \Sigma^+_0(0_u^-)$</td>
<td>30 172</td>
<td>...</td>
<td>32</td>
<td>...</td>
<td>b</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$H^+ \Pi_u(1_u)$</td>
<td>(32 657)</td>
<td>37 931</td>
<td>92</td>
<td>92</td>
<td>e</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$I^+ \Pi_u(3_u)$</td>
<td>32 167</td>
<td>40 179</td>
<td>156</td>
<td>97</td>
<td>e</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C^- \Sigma^+_0$</td>
<td>36 456</td>
<td>36 208</td>
<td>155</td>
<td>119</td>
<td>e</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R^- \Sigma^+_0(2_u)$</td>
<td>53 200</td>
<td>51 657</td>
<td>140</td>
<td>105</td>
<td>f</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E^- \Pi_u(1_u)$</td>
<td>(32 657)</td>
<td>37 931</td>
<td>92</td>
<td>92</td>
<td>e</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$I^+ \Pi_u(3_u)$</td>
<td>32 167</td>
<td>40 179</td>
<td>156</td>
<td>97</td>
<td>e</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C^- \Sigma^+_0$</td>
<td>36 456</td>
<td>36 208</td>
<td>155</td>
<td>119</td>
<td>e</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R^- \Sigma^+_0(2_u)$</td>
<td>53 200</td>
<td>51 657</td>
<td>140</td>
<td>105</td>
<td>f</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a Experimental constants from Ref. 28.
b The experimental $\omega_c$ of 106 cm$^{-1}$ was obtained by Effantin et al. (Ref. 18) for this state.
c Experimental $T_c$ of 12 395 cm$^{-1}$ in the Ar matrix from Ref. 10.
d Experimental constants in the Ar matrix from Ref. 10.
e Experimental values from Ref. 44.
f Experimental constants from Ref. 15.
g An earlier experimental value of 6500 ± 1000 cm$^{-1}$ is reported in Ref. 8.
h The number in parentheses obtained using 15e RECP's and a (4s4p4d) basis set (Ref. 26).

Theoretical constants are likely to be in greater error as they are obtained using the FOCI/RCI (lower level) levels of theory. At present, there exists no rotational analyses of these systems to provide $r_c$ values for these states.

Polak et al.\textsuperscript{28} find an electronic state with a $T_c$ of 9870 cm$^{-1}$. As seen from Table IV, the most consistent state in this region with our computation is an electronic state which we label $3\Delta_u(2_u)$, but it is actually a mixture of $3\Delta_u(2_u)$ and $3\Delta_u(2_u)$. The spin–orbit coupling term introduces 3% $\Delta_u-\Delta_u$ mixing in this state and thus lowers this state in relationship to other spin–orbit components of $\Delta_u$. We believe that this state is the same as the state labeled $a$ by Teichman and Nixon.\textsuperscript{10} These authors recorded the absorption spectra of matrix-isolated Bi$_2$. The new system with origin $\nu_0 = 12 395$ cm$^{-1}$ resulting from the $X^0_g$ state was found to have an $\omega_c$ of 123 cm$^{-1}$ by Teichman and Nixon. We do not find any $u$ state other than $3\Delta_u(2_u)$ in this region and thus assign this to $3\Delta_u(2_u)$.

In an interesting laser-induced fluorescence study of Bi$_2$, Effantin et al.\textsuperscript{18} used the ultraviolet lines of both Ar$^+$ and Kr$^+$ lasers to observe a new system of Bi$_2$. They assign this to $V^0_u^-X^1\Sigma^+$. They found that the $V^0_u^+$ state radiates to yet another new state labeled $B^+0_g^+$. Effantin et al. assigned the $B^+0_g^+$ to the $0_g^+$ component of the $\Sigma_g^+$ state dissociating into $^4S + ^4S$ ground state Bi atoms (see Table I).

Effantin et al.\textsuperscript{18} placed the $B^+0_g^+$ state with an $\omega_c$ of 106 cm$^{-1}$ at 10 826 cm$^{-1}$ above the $X^0_g$ state. Polak et al.\textsuperscript{28} also find a system in their negative detachment spectra attributed to an electronic state with $T_c = 10 820$ cm$^{-1}$ and $\omega_c = 91$ cm$^{-1}$.

As seen from Table IV, our computation evidently supports the existence of $3\Sigma^+_g(0_g^+)$ with a theoretical $T_c = 13 700$ cm$^{-1}$ and $\omega_c = 111$ cm$^{-1}$. The smaller $\omega_c$ is consistent with the computed longer $r_c$ (see Table III). We will discuss the nature of the $V^0_u^-$ state subsequently, but although the $B^+0_g^+$ state is predominantly $3\Sigma^+_g(0_g^+)$, it is contaminated significantly by $3\Sigma^+_g(0_g^+)$.

2. Electronic states in the 15 000–30 000 cm$^{-1}$ region

Teichman and Nixon\textsuperscript{10} found in the Ar matrix an electronic state labeled $b$ with $\nu_0 = 15 246$ cm$^{-1}$ attributed to Bi$_2$ in absorption from the $X^0_g$ state. The most consistent electronic state with our computations is the $3\Delta_u(3_u)$ state which is computed theoretically to have a $T_c$ of 18 905 cm$^{-1}$. Considering that our computed $T_c$'s are consistently higher than experimental values, we are inclined to argue that this system is due to the forbidden $3\Delta_u(3_u)$–$X^0_g$ transition. Indeed, Teichman and Nixon find that the absorption systems resulting from the new states are all weak and have speculated that these are due to possibly forbidden electronic transitions. Polak et al.\textsuperscript{28} also appear to find some bands in this region, but no definitive analyses could be made as there appears to be more than one state in this region.

An electronic state with an approximate experimental
The rotational analysis of the $A-X$ system has now computed properties of this state. Nevertheless, our computed $\omega_e$ of the $^2\Sigma^+_{u}$ state, viz., 2.87 $\text{cm}^{-1}$, is in remarkable accord with the computed $\omega_e$. Gerber et al.$^8$ and Teichman and Nixon$^10$ find an electronic state which they label $c$. This state is attributed to the third absorption system below the well-characterized $A(X^1\Sigma^+)$ system. The origin band of this state in the Ar matrix appears to be at 17336 $\text{cm}^{-1}$ with an $\omega_e$ of 145 cm$^{-1}$. Effantin et al.$^{18}$ label the same state $R^*$ and speculate that this state should be of $u$ symmetry. As seen from Table IV, we indeed find $^1\Delta_u (2_u)$ with a theoretically computed $T_e$ of 22481 $\text{cm}^{-1}$. The observed state most consistent with this value is the $^1\Delta_u (2_u)$ state. It should be mentioned that $^1\Delta_u (1_u)$ is raised relative to $^1\Delta_u$ since the $^3\Sigma^+ (1_u)$ is lower relative to $^3\Sigma^+_{e}$ due to spin–orbit mixing of $^3\Sigma^+ (1_u)$ and $^3\Delta_u (1_u)$. This means that the $^1\Delta_u (1_u)$ component could be in this region, although we could not compute this state since it is a higher root. Consequently, the $B^+(c)$ state is either $^3\Delta_u (1_u)$ or $^1\Delta_u (2_u)$, although the forbidden nature of the $^1\Delta_u (2_u)$-$X^1\Sigma^+$ transition is consistent with the weak $c$-$X$ bands observed by Teichman and Nixon.

The experimentally most studied system of Bi$_2$ is the $A$-$X$ system. The rotational analysis of the $A$-$X$ system has now been made by Gerber et al.$^8,9$ All experimental studies assign the $A$ state to a $^3\Sigma^+ (0_u^+)$ state of Bi$_2$. As seen from Table IV, our computations reveal that the $A$ state is the $^3\Sigma^+_{e}$ component of $^3\Sigma^+_{u}$. Evidently, the theoretical $T_e$ is too high mainly because the spin–orbit coupling could not be included in the computed properties of this state. Nevertheless, our computed $r_e$ of the $^3\Sigma^+_{u}$ state, viz., 2.87 $\text{Å}$ is in remarkable accord with the experimental value of 2.863 $\text{Å}$ obtained from the rotational analysis. Our computed $\omega_e$ of 140 $\text{cm}^{-1}$ for the $^3\Sigma^+_{u}$ ($0_u^+$) state is also in reasonable agreement with the experimental value of 165 $\text{cm}^{-1}$. The $A$ state is unambiguously assigned to the $^3\Sigma^+_{u}$ ($0_u^+$) state.

Gerber and Broida$^8$ have observed a new doublet photoluminescence system labeled the $E-B$ system. The $B$ state is the $^3\Sigma^+ (1_u)$ component in Table IV. This means that the $E$ state is of $g$ symmetry. The experimental $\omega_e$ of the $E$ state is 63.5 $\text{cm}^{-1}$ and the deduced $T_e$ value is 26 505 $\text{cm}^{-1}$. As seen from Table IV, the most consistent state with the $E$ state is an excited $^3\Pi_g (0_u^+)$ state. We are not sure if it is $^3\Pi_g (0_u^+)$ or $^3\Pi_g (0_u^+)$, since both can radiate to the $^3\Sigma^+_{u}$ ($0_u^+$) state. Our computed $T_e$ of 31 815 $\text{cm}^{-1}$ in the absence of spin–orbit coupling could be lowered further when spin–orbit effects are included. The small theoretical $\omega_e$ of 75 cm$^{-1}$ supports the assignment of $E$ to this $^3\Pi_g$ state.

Gerber, Sakuri, and Broida$^9$ observed weak photoluminescence attributed to a $N-G$ system, wherein the lower $G$ state was believed by these authors to be the same as the one participating in the $G-A$ system observed by Reddy and Ali.$^4$ The constants of the $G$ state deduced by Gerber et al.$^9$ were similar to those of Reddy and Ali.$^4$ This suggests that the $G$ state should be of $g$ symmetry. An approximate $T_e$ value of 26 505 $\text{cm}^{-1}$ was deduced for the $G$ state.

As seen from Table IV, the most consistent state with the $G$ state is an excited $^1\Sigma^+_{g}$ state. Our computed $T_e$ (30 855 $\text{cm}^{-1}$) is only a bit larger than the experiment. Further, the theoretical $\omega_e$ also seems to support this assignment, although we consider this only a tentative assignment.

### 3. States with $T_e > 30 000 \text{cm}^{-1}$

Effantin et al.$^{18}$ observed a new electronic transition which they labeled $V^1\Pi^+ (0_u^+)-^3\Pi^+_u$ system. The $B^+$ state assigned to $^3\Sigma^+_{e}$ ($0_u^+$) was discussed before. The $V^1\Pi^+$ state needs to be assigned. We found a $^3\Sigma^+_{e}$ state dissociating into $^1\Sigma^+_g (0_u^+)$ near this state as well as $^3\Sigma^+_{e}$ ($0_u^+$). The fact that the $\omega_e$ deduced experimentally by Effantin et al.$^{18}$ is only 32 cm$^{-1}$ is consistent with the shallow nature of the $^3\Sigma^+_{e}$ state deduced from our computation. Furthermore, the $^3\Sigma^+_{e}$-$^3\Sigma^+_{g}$ transition is strongly allowed, which would explain the origin of the $V-B$ electronic system.

Reddy and Ali$^4$ have observed an emission system which they call the $H-A$ system. The $A$ state is the well-characterized $^3\Sigma^+_{e}$ ($0_u^+$) state. This suggests that the $H$ state should be of $g$ symmetry. We indeed find a $^1\Pi_g (II)$ state (i.e., the second excited state of $^1\Pi_g$ symmetry with a theoretical $T_e$ of 37 931 $\text{cm}^{-1}$). Reddy and Ali could observe only the $v=0$ state of the $H$ state and thus there exists no experimental $\omega_e$ for the $H$ state. We are tempted to assign the $H$ state to $^1\Pi_g (III)$, but our assignment will be more definitive if further experimental studies will yield the $r_e$ and $\omega_e$ of the $H$ state in question.

Reddy and Ali$^4$ also observe another emission system with the band origin $v_0 = 15 487$ $\text{cm}^{-1}$ terminating to the $A(0^+_u)$ state designated as the $I-A$ system. Experimental $T_e = 33 217$ $\text{cm}^{-1}$ and $\omega_e = 156.4$ $\text{cm}^{-1}$ have been deduced for the $I$ state. We find a $^3\Pi_g (III)$ state with a computed $T_e = 40 179$ $\text{cm}^{-1}$ most consistent with this state. Again, the theoretical constants do not include the spin–orbit effects for the $^1\Pi_g (II)$ state which could alter the $T_e$ by 7000 $\text{cm}^{-1}$. The theoretical $\omega_e$ is, however, too small compared to an experimental value of 156 $\text{cm}^{-1}$. While it is evident that the $I$ state must be a $g$ state, our assignment of $I$ to $^1\Pi_g (III)$ is very tentative. The $^3\Sigma^+_{u}$ or $^1g$ components arising from the $^3\Sigma^+_{u}$ state dissociating into Bi (2$D$) + Bi (2$D$) could certainly be more strongly bound and can be a potential candidate for the $I$ state.

Dammay et al.$^{15}$ observed five new systems in the 160–230 nm region. One of these corresponds to the same C–X absorption spectrum studied by Almy and Sparks$^1$ in the earlier part of this century. The C state has well-characterized spectroscopic constants of $T_e = 36 456$ $\text{cm}^{-1}$ and $\omega_e = 155$ $\text{cm}^{-1}$. We find a $^3\Sigma^+_{u}$ electronic state of Bi$_2$ with a theoretical $T_e$ of 36 208 $\text{cm}^{-1}$. We are not too surprised by the fortuitous agreement with the experimental $T_e$ since the spin–orbit effect on $T_e$ for this state appears to be similar to the ground state effectively canceling the effect on $T_e$. Our computed $\omega_e$ trend is also consistent with the trend for other...
electronic states. There exists a \( ^1\Pi_u \) (II) state with a computed \( T_e \) of 38 000 cm \(^{-1}\), but with a rather small \( \omega_e \) = 71 cm \(^{-1}\). Since the experimental C-state's \( \omega_e \) is almost twice this value, we argue that the C state should be assigned to the \( ^1\Sigma^+ \) state supporting strongly allowed \( ^C \Sigma^+_u - ^2\Sigma^+ \) emission. This appears to be akin to the A \(^1\Sigma^+_u - ^X^1\Sigma^+_g \) systems of As\(_2\), which occurs in the 40 350 cm \(^{-1}\) region.\(^{39}\)

Damany et al.\(^{15}\) have observed a number of electronic states of Bi\(_2\) in the 46 500–59 700 cm \(^{-1}\) region which they label \( F, Q, R, S, T \), respectively. All these states are attributed to the Rydberg states of Bi\(_2\) dissociating into Rydberg states of the Bi atom. Our FOCI method and basis sets are not expected to be completely adequate for the computation of Rydberg states. Yet we find a \(^1\Sigma_u^+ \) (II) state with \( r_e = 3.33 \text{ Å}, \omega_e = 140 \text{ cm}^{-1} \), and \( T_e = 51 657 \text{ cm}^{-1} \). This state appears to be consistent with the \( R \) state of Damany et al., although their \( r_e = 2.96 \text{ Å} \) is considerably shorter. However, we are not surprised by such a difference for a state with \( T_e \sim 52 000 \text{ cm}^{-1} \) since as mentioned before the basis set is not adequate for these states.

### C. Dissociation energy of Bi\(_2\)

Rovner et al.\(^{37}\) as well as Kohl et al.\(^2\) have deduced the \( D^+_{\Sigma} \) value of Bi\(_2\) as 2.03 eV from the mass spectrum assuming a \(^1\Sigma \) ground state. If this value is corrected for the zero-point energy, one gets a \( D_e \) of 2.05 eV.

Ehret and Gerber\(^{24}\) have employed double resonance polarization spectroscopy to investigate the excited electronic states of Bi\(_2\). One of the obtained spectral systems (with two-step excitation) converges to the dissociation limit of a new electronic state. From this, these authors deduced the ground state \( D_e \) of Bi\(_2\) to be 16 778 ± 5 cm \(^{-1}\) or 2.08 eV. This value is very close to the value deduced from the mass spectra.

Our CASSCF/SOCI/RCI \( D_e \) of Bi\(_2\) is 1.88 eV. This value is evidently lower than the established experimental results. It is clear that the addition of one more set of \( d \) polarization functions and further extension of the \( s \) and \( p \) basis sets could improve the \( D_e \). The present value of 1.88 eV is, however, improved considerably compared to a previous theoretical value\(^{26}\) of 1.38 eV mainly because the present calculation includes a full second-order configuration interaction of all 10 valence electrons.

### D. Predissociations

Ehret and Gerber\(^{20,21}\) have studied the \( A-X \) system extensively. They find that the lifetimes of the vibrational levels \( (v = 1-34) \) of the \( A \) state varied between 50 and 600 ns. The transition moment of the \( A-X \) system was obtained as 1.4 ± 0.4 D.

As seen from Fig. 1, the \( A \ ^1\Sigma^+ \) curve crosses the \( ^1\Sigma^+_u \) (II) curve dissociating to \( ^4\Pi + ^2\Sigma \). Likewise, the \( ^3\Sigma^+_u \) repulsive curve dissociating to the ground state \(^4\Sigma + ^4\Sigma \) atoms crosses the \( A \ ^1\Sigma^+ \). The crossing of \( ^1\Sigma^+_u \) (II) with \( A \ ^1\Sigma^+ \) at \( r_e = 3.75 \text{ Å} \), while the crossing of the \( ^1\Sigma^+_u \) state occurs at \( r_e = 3.35 \text{ Å} \). Consequently, the crossing of the repulsive \( ^1\Sigma^+_u \) curve occurs prior to \( ^1\Sigma^+_u \) (II) and would be a more decisive state in the predissociation to the ground state atoms.

According to Herzberg\(^{40}\) the selection rule for case (c) predissociation is \( g-u, u-u, \Delta \Omega = 0, \pm 1 \). Since the state in question is a \(^3\Sigma^+_u \) (0 \( \omega_u \)) state, only \( u \) states could predissociate this state. Consequently, the repulsive \( ^3\Sigma^+_u \) state is the most attractive candidate for the predissociation. This state yields \( 0 \omega_u, 1 \omega_u, 2 \omega_u \), and \( 3 \omega_u \) spin–orbit components. Among them the \( ^3\Sigma^+_u \) \( (1 \omega_u) \) state is the most consistent state for predissociation.

The crossing of \( ^3\Sigma^+_u \) (1 \( \omega_u \)) with \( A \ ^1\Sigma^+ \) is estimated to occur at \( r_e \sim 3.3 \text{ Å} \). Consequently, only those vibrational levels of the \( A \ ^1\Sigma^+ \) \( (0 \omega_u) \) with classical turning points below \( r_e \sim 3.3 \text{ Å} \) could be observed in the \( A-X \) system. Our predicted curve crossing of \( ^3\Sigma^+_u \) (1 \( \omega_u \)) with \( A \ ^1\Sigma^+ \) explains nicely why the observed transition moment of the \( A-X \) system does not change much for internuclear distances between 2.6 and 3.3 \( \text{Å} \) and then changes sharply. The crossing of \( ^3\Sigma^+_u \) (1 \( \omega_u \)) with \( A \ ^1\Sigma^+ \) at \( r_e \sim 3.3 \text{ Å} \) will cut off all vibrational levels above this curve crossing. Furthermore, the crossing of repulsive \( ^3\Sigma^+_u \) with \( ^3\Sigma^+_u \) and other states will induce an avoided crossing of the corresponding \( \omega_u \) spin–orbit components. As seen from Fig. 1, there is no repulsive curve crossing between 2.6 and 3.3 \( \text{Å} \) in the \( A \ ^3\Sigma^+ \) curve.

The \( ^3\Sigma^+_u \) state also crosses the \( ^3\Delta_u, ^3\Sigma_u, ^3\Delta_g, ^3\Sigma_g \), and a few other \( u \) states. Consequently, these states will also be predissociated. On the other hand, the crossing of the repulsive \( ^3\Sigma^+_u \) (II) state would have little impact on predissociation since it crosses most of these curves at longer internuclear distances. Thus we conclude that the observed predissociation in the \( A-X \) system is due to the predissociation of \( ^3\Sigma^+_u \) \( (0 \omega_u) \) by \( ^3\Sigma^+_u \) \( (1 \omega_u) \). This also explains the dependence of the lifetimes of the \( A \) state on the \( \nu \) quantum number and transition moment invariance between 2.6 and 3.3 \( \text{Å} \) observed by Ehret and Gerber.

### E. Spectroscopic properties of Bi\(_2^+\)

#### 1. Constants and potential energy curves

Figure 3 shows the potential energy curves of Bi\(_2^+\), while Table V shows the spectroscopic constants of Bi\(_2^+\). The most favored orbital for the attachment of an electron to Bi\(_2\) is the lowest unoccupied molecular orbital (LUMO) which is the \( \pi^* \) orbital of Bi\(_2\). Hence the ground state of Bi\(_2^+\) is predicted to be \( ^2\Pi_g \) state in the absence of spin–orbit coupling.

As evidenced from Table V and Fig. 3, the spin–orbit coupling is very significant for Bi\(_2\). It splits the \( ^2\Pi_g \) state into \( (1/2) \Pi \) and \( (3/2) \Pi \) spin–orbit components. The \( (1/2) \Pi - (3/2) \Pi \) splitting of Bi\(_2^+\) is 8500 cm \(^{-1}\) as seen from Table V. The mixing of \( ^2\Pi_g \) \( (1/2) \) with \( ^4\Sigma_g (1/2) \) and \( ^2\Sigma_g (1/2) \) was found to be significant. Likewise the \( ^2\Pi_g (3/2) \) mixes heavily with the \( ^4\Sigma_g (3/2) \) state.

The attachment of an electron to the unoccupied \( 2\pi^* \) antibonding orbital of neutral Bi\(_2\) results in the \( ^2\Sigma_u^+ \) state. As seen from Fig. 3 and Table V, this state forms only a shallow minimum. This state lies 19 700 cm \(^{-1}\) above the ground state 4S + 4S.

There are two excited \( ^2\Pi_g \) states of Bi\(_2^+\) as well as a
$^2\Sigma^+_{u} (\Pi)$ state with a $T_e = 34,300$ cm$^{-1}$. However, these states cannot be populated in the negative ion generation as they are well above the ground state. In any case, they are rather weakly bound and would undergo autodetachment.

### 2. Electron affinity of Bi$_2$

At the CASSCF and FOCI levels of theories, the $^2\Pi_g$ state of Bi$_2^-$ lies above the $^1\Sigma^+_g$ ground state. Only a full second-order CI (SOCI) theory stabilizes the $^2\Pi_g$ state of Bi$_2^-$ relative to Bi$_2$, indicating the significance of electron correlation effects in the computation of electron affinities of clusters.

The spin–orbit effect has an important role in the determination of the electron affinity. The $^2\Pi_g (1/2)$ state of Bi$_2^-$ is much more stabilized by spin–orbit coupling than the $X$ ground state of Bi$_2$ due to its open-shell character. While there is spin–orbit stabilization of the $^2\Sigma^+_u$ state of Bi$_2$ through the mixing of $^1\Sigma^+_g$ with $^3\Pi_g$, this stabilization is less than the $^2\Pi_g (1/2)$ lowering of Bi$_2^-$ due to spin–orbit coupling. Consequently, spin–orbit effects increase the electron affinity of Bi$_2$.

Our final computed electron affinity of Bi$_2$ is 5200 cm$^{-1}$. Polak et al. have recently measured the electron affinity of Bi$_2$ from their photodetachment spectra as 10,250 cm$^{-1}$. Consequently, our computation underestimates the electron affinity of Bi$_2$ too much, as we expected. The main source of error is the basis set limitation. It is necessary to have a much larger basis set augmented with at least two more sets of $d$ polarization functions for the accurate computation of electron affinity. Nevertheless, these computations shed significant light on the nature of the ground state of Bi$_2^-$ in relation to the neutral $X(0^+_g)$ state of Bi$_2$.

### IV. THE NATURE OF ELECTRONIC STATES OF Bi$_2$ AND Bi$_2^-$

Since spin–orbit coupling of the Bi atom is very large, it would be interesting to analyze the mixing of various states of Bi$_2$ which would otherwise not mix in the absence of spin–orbit coupling. Table VI shows the composition of the low-lying spin–orbit states of Bi$_2$ and Bi$_2^-$. As seen from Table VI, even the predominantly closed shell $^1\Sigma^+_g$ ground state of Bi$_2$ is contaminated heavily by $^2\Pi_g (0^+_g)$ (19%). In the $^1\sigma_u$ component of $^2\Sigma^+_g$, the mixing with $^3\Delta_u (\bar{1}\sigma_u)$ is quite significant. This has the effect of lowering the $^1\sigma_u$ component of $^2\Sigma^+_g$. The $^3\Sigma^-_u$ component of the $^2\Sigma^+_u$ state is relatively pure (mixing with $^1\Sigma^+_g$ is less than 1%).

The second $^0\Sigma^+_u$ state [$^0\Sigma^+ (\Pi)$] exhibits an interesting behavior as a function of internuclear distance. Near the $r_e$ of the $X 0^+_g$ state, the $^0\Sigma^+ (\Pi)$ state is predominantly $^2\Pi_g (0^+_g)$, although as seen from Table VI, mixing with the $^1\Sigma^+_g$ ground states $^2\Sigma^+_g (0^+_g)$ and $^1\Sigma^+_g (0^+_g)$ is significant. At 3.2 Å (near its $r_e$), the $^0\Sigma^+ (\Pi)$ state is almost purely $^2\Sigma^+_g (0^+_g)$. This suggests an avoided crossing of the $^2\Pi_g (0^+_g)$ and $^2\Sigma^+_g (0^+_g)$ components.

The $^0\Sigma^+ (\Pi)$ state is influenced considerably by the avoided crossing of $^2\Pi_g (0^+_g)$ with $^2\Sigma^+_g (0^+_g)$. At 2.6 Å, the $^0\Sigma^+ (\Pi)$ state is purely $^2\Sigma^+_g (0^+_g)$, while at 2.8 Å, it becomes 58% $^3\Pi_u$, 8% $^1\Sigma^+_g$, 6% $^3\Sigma^-_g$, and 5% $^1\Sigma^+_g$. At longer

### Table VI. The RCI compositions of $\Omega$ states of Bi$_2$ and Bi$_2^-$. *

<table>
<thead>
<tr>
<th>State</th>
<th>Compositions</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0^+_u$</td>
<td>65% $^1\Sigma^-_u$, 16.5% $^3\Pi_u$</td>
</tr>
<tr>
<td>$^2\Sigma^+_u (1\sigma_u)$</td>
<td>66% $^3\Sigma^+_u$, 20% $^3\Delta_u$</td>
</tr>
<tr>
<td>$^2\Sigma^+_g (0^+_g)$</td>
<td>80% $^3\Sigma^-_u$, 0.6% $^5\Sigma^-_u$</td>
</tr>
<tr>
<td>$^1\Delta_u (\bar{1}\sigma_u)$</td>
<td>81% $^1\Delta_u$, 5% $^3\Delta_u$</td>
</tr>
<tr>
<td>$0^+_u (\Pi)$ at its $r_e$</td>
<td>90% $^3\Sigma^+_g (0^+_g)$</td>
</tr>
<tr>
<td>$0^+_u (\Pi)$ at 2.6 Å</td>
<td>11% $^1\Sigma^+_g$, 69% $^3\Pi_u$, 10% $^3\Sigma^-_u$, 6% $^3\Sigma^-_g$</td>
</tr>
<tr>
<td>$0^+_u (\Pi)$ at 2.6 Å</td>
<td>88% $^2\Sigma^+_g (0^+_g)$</td>
</tr>
<tr>
<td>$0^+_u (\Pi)$ at 2.8 Å</td>
<td>58% $^3\Pi_u$, 8% $^1\Sigma^+_g$, 6% $^3\Sigma^-_g$, 6% $^5\Sigma^-_g$</td>
</tr>
<tr>
<td>$0^+_u (\Pi)$ at 3.0 Å</td>
<td>43% $^3\Pi_u$, 12% $^2\Sigma^+_g$, 11% $^3\Sigma^-_g$, 5% $^5\Sigma^-_g$</td>
</tr>
<tr>
<td>$0^+_u (\Pi)$ at 3.2 Å</td>
<td>76% $^3\Sigma^-_g$, 18% $^3\Sigma^-_g$, 0.5% $^3\Pi_u$</td>
</tr>
<tr>
<td>$2\Sigma^+_u (0^+_g)$</td>
<td>90% $^3\Sigma^-_g$</td>
</tr>
<tr>
<td>1/2$g$</td>
<td>76% $^3\Pi_u$, 7% $^3\Sigma^-_g$, 5% $^1\Sigma^-_g$</td>
</tr>
<tr>
<td>3/2$g$</td>
<td>65% $^3\Pi_u$, 14% $^3\Sigma^-_g$, 8% $^3\Delta_u$</td>
</tr>
</tbody>
</table>

*States with odd $\Omega$ quantum numbers correspond to Bi$_2^-$. 

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**K. Balasubramanian and D. Liao: Potential energy curves of Bi$_2$ and Bi$_2^-$.**

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K. Balasubramanian and D. Liao: Potential energy curves of Bi and Bi'.

Distances, the mixing of $^3\Sigma_g^+$ ($1_g^+$) with other states becomes significant.

The $^1\Pi_g$ (I) state is 76% $^1\Sigma_g^+$ ($1_g^+$), 18% $^3\Sigma_g^-$ ($1_g^-$) at its $r_e$. Contrary to the $^3\Pi_g$ (II) state, we do not find avoided crossing of $^3\Pi_g$ ($1_g^+$) with $^3\Sigma_g^+$ ($1_g^+$) mainly because $^3\Pi_g$ ($1_g^+$) is raised relatively to $^3\Sigma_g^+$. Similarly, $^3\Sigma_g^+$ ($2_g^-$) and $^3\Pi_g$ ($2_g^-$) mixing is not significant. The $^3\Sigma_g^-$ ($2_g^-$) state was found to be relatively pure near its $r_e$.

As seen from Table VI, the $1/2g$ ground state of Bi is $1/2g$ is 76% $^1\Sigma_g$ ($1/2$), 12% $^3\Sigma_g^+$ ($1/2$), and 11% $^2\Pi_g$ ($1/2$). The $3/2g$ state is 65% $^1\Sigma_g$ ($3/2$), 14% $^3\Sigma_g^+$ ($3/2$), and 8% $^3\Delta_g$ ($3/2$). Consequently, it is concluded that most of the electronic states of Bi and Bi' are contaminated heavily by spin–orbit coupling.

Table VII shows the composition of the electronic states of Bi and Bi in the absence of spin–orbit coupling. This table also contains useful information on several excited states of Bi for which spectroscopic constants are shown in the absence of spin–orbit coupling. As seen from Table VII, the $^1\Sigma_g^+$ state of Bi is 70% $1\sigma^2 2\sigma^2 1\pi^2 1\sigma^2 2\pi^2$, 19% $1\sigma^2 2\sigma^2 1\pi^2 1\sigma^2 1\pi^2$, and 9% $1\sigma^2 2\sigma^2 1\pi^2 1\sigma^2 1\pi^2$. Clearly, a double excitation from $\pi_u$ to $\pi_u$ is more important than a double excitation from $2\sigma_g$ to $2\sigma_u$ near $r_e$.

The $^3\Sigma_g^+$, $^3\Delta_u$, $^3\Sigma_u^-$, $^1\Delta_u$ states are relatively simpler in that leading configuration(s) make up more than 80% contribution. The upper roots of $^3\Pi_g$ symmetry as well as $^3\Pi_g$, $^3\Delta_u$ (II), and $^3\Delta_u$ (III) are significantly more complex as seen from Table VII.

Table VIII shows the leading configurations of the electronic states of Bi' in the absence of spin–orbit coupling. The $^3\Sigma_g^+$ ground state is a 76%–12% mixture of $1\sigma^2 2\sigma^2 1\pi^2 1\sigma^2 1\pi^2$ and $1\sigma^2 2\sigma^2 1\pi^2 1\pi^2$ at the FOCI level. This illustrates the significant of electron correlation effects from a multireference list of configurations. Likewise the excited states of Bi' are even more complex, although most of these states have only shallow minima.

It is interesting to compare Bi with its lighter analogs, namely Sb, and As. The previous study by Balasubramaninan and Li 41 on Sb reveals that the X $0^+$ ground state of Sb is composed of 82% $^1\Sigma_g^+$ ($2\sigma^2 1\pi^2$), 12% $^3\Sigma_g^+$ ($2\sigma^2 1\pi^2 1\pi^2$), and 2% $^3\Pi_g$ ($2\sigma^2 1\pi^2 1\pi^2$). This evidently demonstrates that spin–orbit coupling is dramatically larger for Bi compared to Sb. Likewise the contamination of $^3\Delta_u$ ($1_u$) in the $1_u$ state is only 3% for Sb compared to 20% for Bi.

A critical comparison of the Mulliken populations of the electronic states of Bi and Sb reveals that the $6s$ shell is nearly complete in Bi, while the $6s$ population is 1.87 for Sb. This is a consequence of the relativistic mass–velocity
stabilization of the 6s² shell which makes the 6s² shell "inert" for Bi₂. The 3Σ⁺ (1₁) - X(0⁺) separation is 8760 cm⁻¹ for Sb₂, while it is 6650 cm⁻¹ for Bi₂. The corresponding 3Σ⁺ - X(1Σ⁺) theoretical separation for As₂ is 14500 cm⁻¹, while the experimental 3Σ⁺ - X(1Σ⁺) separation is 11860 cm⁻¹. Hence this separation decreases as one goes down the group.

The 3Σ⁺ (1₁) - 3Σ⁺ (0⁻) separation of 5129 cm⁻¹ is dramatically larger than the corresponding separation of only 120 cm⁻¹ for Sb₂. Hence it is evident that relativistic effects are dramatically larger for Bi₂ compared to Sb₂. It is interesting to note the 3Σ⁺ (1₁) - 3Σ⁺ (0⁻) separation of Bi₂ (5129 cm⁻¹) is similar to the 3Σ⁺ (0⁻) - 3Σ⁺ (1₁) separation of 4150 cm⁻¹ for Pb₂. The corresponding experimental value is known to be <5500 cm⁻¹.

The 3Σ⁺ (0⁻) - X (0⁺) separations for As₂, Sb₂, and Bi₂ are 24 640, 19 068, and 17 739 cm⁻¹, respectively. This trend is consistent with the 3Σ⁺ - X (0⁺) energy separation. Hence we conclude that in general the energy separations of excited states of group V dimers decrease as one goes down the group in the absence of spin–orbit coupling.

V. CONCLUSION

In this study CASSCF/FOCI/SOCI/RCI calculations which included up to 304 000 configurations were made on Bi₂ and Bi₂⁺. We found 26 bound electronic states for Bi₂ with Tᵱ < 50 000 cm⁻¹. Our computations facilitated the assignment of some 16 observed spectroscopic systems of Bi₂ including the most recent photodetachment spectra. Our computations reveal the existence of at least six bound states for Bi₂ of which the 3Π₁ (1/2) state is the ground state. The computed potential energy curves of Bi₂ explained the previously observed predissociation of the well-studied A-X system of Bi₂. The crossing of the repulsive 3Σ⁺ state dissociating to the ground state atoms with the A' 3Σ⁺ (0⁺) curve explained the observed lifetimes and predissociations. Similar predissociations for other states were predicted.

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