Spectroscopic Constants and Potential Energy Curves of GaBr

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Spectroscopic constants and potential energy curves are computed for the low-lying states of GaBr using complete active space MCSCF (CASSCF) followed by configuration interaction (CI) calculations. Among the 15 electronic states of GaBr considered here, 11 states are bound, for which spectroscopic properties are calculated. The potential energy curves of 15 states are reported. Our calculations predict a number of excited states of GaBr which are yet to be observed. © 1992 Academic Press, Inc.

INTRODUCTION

Spectroscopic studies of group (III) halides have received considerable attention (1–8) in recent years. Such compounds are formed in chemical etching of GaAs with a hydrogen halide or halogen etchant gas (9). Group (III) halides are also intermediates in chemiluminescent reactions. Hence it would be of interest to comprehend the nature of bonding in these species and to compute their spectroscopic constants and potential energy curves.

The absorption spectrum of GaBr was studied by Miescher and Wehrli (1) in the 27 000–29 000 cm⁻¹ and near the 37 000 cm⁻¹ region. The two subsystems A and B were assigned to the first region (1) and their vibrational constants have been improved by Borkowska-Burnecka recently (8). However, a subsystem called C near 37 000 cm⁻¹ assigned by Miescher and Wehrli in 1933 has been barely investigated since the band was diffuse due to a shallow upper state potential curve (7), although Glenewinkel-Meyer et al. (10) indicated that a band in the 37 000–42 000 cm⁻¹ region of the chemiluminescence spectrum, from the reaction of Ga⁺ with Br₂, coincided with the C–X system of neutral GaBr.

Theoretical studies of the ground state of GaBr using a valence (3σ3p 1d) Gaussian basis set have been made for the model calculation of the GaAs + Br reaction (9). Their objective was to investigate the potential energy curves and spectroscopic properties of many excited states of GaBr. In this study we carried out relativistic complete active space MCSCF/first-order configuration interaction (FOCI) calculations on 15 electronic states of GaBr. After this, we made second-order CI (SOCl) calculations on some of the states of GaBr which included up to 1 191 520 configurations.

METHOD OF INVESTIGATION

The electronic states of GaBr were investigated using complete active space MCSCF (CASSCF) and first-order CI calculations. In addition second-order CI calculations were carried out on some electronic states of GaBr. All calculations employed relativistic effective core potentials (RECP) which included the outer 4s24p1 shells for the Ga

1 Camille and Henry Dreyfus Teacher-Scholar.
atom and the outer $4s^24p^5$ shells for the Br atom in the valence space, respectively. We employ the Gaussian RECPs generated by Hurley et al. (11) for each atom. These authors have also optimized $(3s3p)$ valence Gaussian basis sets for the $^2P$ ground electronic states of these atoms. Each set was augmented by one set of diffuse $s$, $p$, and one set of $d$-type polarization functions. The exponents of the additional functions are $\alpha_s = 0.02644$, $\alpha_p = 0.0164$, and $\alpha_d = 0.20$ for the Ga atom, and $\alpha_s = 0.05710$, $\alpha_p = 0.04334$, and $\alpha_d = 0.250$ for the Br atom.

The orbitals for the FOCI calculations were generated using the CASSCF method. The gallium valence $4s$ and $4p$ and chlorine $4s$ and $4p$ orbitals correlate into four $a_1$, two $b_2$, and two $b_1$ orbitals in the $C_{2v}$ symmetry group. Excitations from the $1a_1$ orbital which correlated into the $4s$ orbital of the Br atom were not allowed in the CASSCF but the seven remaining orbitals were included in the active space in the CASSCF step. The eight outer electrons of GaBr were distributed in all possible ways among these seven orbitals in the CASSCF method. Separate CASSCF calculations were carried out for states of different spatial and spin symmetries in the $C_{2v}$ group.

The first-order CI calculations were carried out following CASSCF calculations, which included excitations from the $1a_1$ orbital. All configurations in the CASSCF plus configurations generated by distributing nine electrons in the internal space and one electron in the external space in all possible ways were included in this step.

After the FOCI calculation, the SOCl method was used for some states. In these calculations, all configurations in the CASSCF and FOCI plus configurations generated by distributing eight electrons in the internal space and two electrons in the external space in all possible ways were included. The CASSCF and FOCI/SOCI calculations were carried out using Balasubramanian's (13) modified version of ALCHEMY II codes to include RECPs.

RESULTS AND DISCUSSION

Table I shows the dissociation relationships for the possible low-lying states and the energy separations obtained by the CASSCF/FOCI method at the dissociation limits for the molecular electronic states of GaBr. The experimental atomic energy separations were taken from Moore's table (12). The experimental values reported in Table I are $J$-averaged. For all of the electronic states of GaBr, the theoretical values are larger than the corresponding experimental values. The agreement of theoretical and exper-

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$^2$ The major authors of ALCHEMY II are B. Lengsfield, B. Liu, and M. Yoshimine.

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<table>
<thead>
<tr>
<th>Dissociation Relationships of Some Low-Lying States of GaBr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular States</td>
</tr>
<tr>
<td>$1\Sigma^+(2)$, $1\Sigma^-(2)$, $1\Xi^-(2)$, $1\Xi^+$, $1\Xi^-$</td>
</tr>
<tr>
<td>$1\Pi(2)$, $3\Pi(2)$, $1\Delta$, $2\Delta$</td>
</tr>
<tr>
<td>$1\Pi$, $3\Pi$, $1\Xi$, $2\Xi$</td>
</tr>
<tr>
<td>$1\Sigma^+(2)$, $1\Sigma^-(2)$, $1\Xi^-(2)$, $1\Xi^+$, $1\Xi^-$</td>
</tr>
<tr>
<td>$1\Pi(2)$, $3\Pi(2)$, $1\Delta$, $2\Delta$</td>
</tr>
</tbody>
</table>

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imental energies of the Rydberg \((4s^25p^1)^2P\) state of Ga in Table I is especially worth noting since the starting \((3s3p)\) basis set was optimized for the valence orbitals. The theoretical ordering of the valence and Rydberg states is in accord with the corresponding experimental ordering.

Figure 1 shows the potential energy curves calculated by the FOCI method while Table II shows the FOCI spectroscopic constants. The experimental spectroscopic constants are known for the \(X^1\Sigma^+\) state and the spin-orbit components for the \(3\Pi\) state. The experimental \(B^3\Pi_1\) and \(A^3\Pi_0^+\) states were found to be at 28 532 and 28 162 cm\(^{-1}\) (1). Borkowska-Blunscheim improved vibrational constants and gave new vibrational assignments for some of the vibrational bands of the \(A-X\) and \(B-X\) systems (7). They also reported vibrational isotopic shifts with respect to the \(^{69}\text{Ga}\)\(^{79}\text{Br}\) molecule. The \(T_h's\) of \(B^3\Pi_1\) and \(A^3\Pi_0^+\) have not changed since 1934 and we carried out calculations on the \(^{69}\text{Ga}\)\(^{81}\text{Br}\) molecule. The theoretical FOCI \(T_h\) of the \(3\Pi\) state in Table II is 24 231 cm\(^{-1}\) which shows only a fair agreement with the corresponding experimental value. The SOCl calculations improved this agreement. The FOCI \(R_e\) of the

![Potential energy curves for GaBr](image)

**FIG. 1.** Potential energy curves for GaBr.
ground state is 2.373 Å which is a little longer than the experimental value of 2.353 Å. However, the FOCI $\omega_e$ of the ground state is in good agreement with the experimental $\omega_e = 263$ cm$^{-1}$. The agreement in the $\omega_e$ of the first excited state of GaBr between theory (370 cm$^{-1}$) and experiment (372 cm$^{-1}$) is very good.

Table III shows the SOCI spectroscopic constants of GaBr. The SOCI calculations include electron correlation to a greater degree than FOCI calculations by including two-electron excitations into the external space of orbitals. A comparison of the FOCI and SOCI results in Tables II and III shows that the $R_e$ values predicted by the SOCI method are a little longer than those by the FOCI method but they are in reasonable agreement with each other. The $T_e$ values are all much improved at SOCI level. For example, the experimental $T_e$ of the $B^3\Pi_1$ and $A^3\Pi_0^*$ states are 28.532 cm$^{-1}$ and 28.162 cm$^{-1}$, respectively, while our SOCI $T_e$ of the $^3\Pi$ state in the absence of spin–orbit coupling is 27.994 cm$^{-1}$. The smaller theoretical $T_e$ is primarily because the electron correlation effects of the $X^1\Sigma^+$ are still not fully accounted for even at the SOCI level and partly because our (4s4p1d) basis set is somewhat less satisfactory for the excited states.

**Table II**
FOCI Spectroscopic Constants of GaBr

<table>
<thead>
<tr>
<th>State</th>
<th>$R_e$ (Å)</th>
<th>$T_e$ (cm$^{-1}$)</th>
<th>$\omega_e$ (cm$^{-1}$)</th>
<th>$\mu_e$ (D)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1\Sigma^+$</td>
<td>2.373</td>
<td>0.0</td>
<td>265</td>
<td>2.18</td>
</tr>
<tr>
<td>$^3\Sigma^+$</td>
<td>2.339</td>
<td>24.23</td>
<td>270</td>
<td>1.19</td>
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<tr>
<td>$^3\Sigma^*$</td>
<td>3.638</td>
<td>32.28</td>
<td>42</td>
<td>-0.51</td>
</tr>
<tr>
<td>$^1\Delta$</td>
<td>3.851</td>
<td>32.52</td>
<td>32</td>
<td>-0.54</td>
</tr>
<tr>
<td>$^3\Delta$</td>
<td>3.871</td>
<td>32.52</td>
<td>40</td>
<td>-0.36</td>
</tr>
<tr>
<td>$^3\Sigma^-$</td>
<td>3.485</td>
<td>32.96</td>
<td>100</td>
<td>-0.80</td>
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<tr>
<td>$^3\Sigma^*(II)$</td>
<td>3.608</td>
<td>34.06</td>
<td>62</td>
<td>-0.78</td>
</tr>
<tr>
<td>$^1\Pi$</td>
<td>—</td>
<td>36.28</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>$^1\Delta(II)$</td>
<td>2.374</td>
<td>41.53</td>
<td>245</td>
<td>-0.30</td>
</tr>
<tr>
<td>$^3\Pi(III)$</td>
<td>2.928</td>
<td>50.41</td>
<td>208</td>
<td>3.16</td>
</tr>
<tr>
<td>$^1\Sigma^*(II)$</td>
<td>2.488</td>
<td>64.38</td>
<td>179</td>
<td>-1.00</td>
</tr>
</tbody>
</table>

$^a$ Positive polarity means Ga$^+\cdot$Br$^-$. 

**Table III**
SOCI Spectroscopic Constants of GaBr

<table>
<thead>
<tr>
<th>State</th>
<th>$R_e$ (Å)</th>
<th>$T_e$ (cm$^{-1}$)</th>
<th>$\omega_e$ (cm$^{-1}$)</th>
<th>$\mu_e$ (D)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1\Sigma^+$</td>
<td>2.398</td>
<td>0.0</td>
<td>254</td>
<td>2.81</td>
</tr>
<tr>
<td>$^3\Pi$</td>
<td>2.347</td>
<td>27.25</td>
<td>262</td>
<td>1.46</td>
</tr>
<tr>
<td>$^3\Sigma^*$</td>
<td>3.722</td>
<td>33.23</td>
<td>35</td>
<td>-0.28</td>
</tr>
<tr>
<td>$^3\Delta$</td>
<td>3.962</td>
<td>33.41</td>
<td>28</td>
<td>-1.60</td>
</tr>
<tr>
<td>$^1\Delta$</td>
<td>3.957</td>
<td>33.42</td>
<td>30</td>
<td>-1.62</td>
</tr>
<tr>
<td>$^1\Pi$</td>
<td>—</td>
<td>38.24</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

$^a$ Positive polarity means Ga$^+\cdot$Br$^-$. 
The $D_e$ of the $X^1\Sigma^+$ ground state is 4.17 eV at the SOCl level and 4.06 eV at the FOCI level. The Davidson correction to the SOCl results did not change the $D_e$ at all, indicating the completeness of the SOCl method. For GaBr an experimental $D_0^\infty = 4.31$ eV was deduced from the analysis of the fluctuation bands and extrapolation of vibrational levels of $^3\Pi_{0^+}$ and $^3\Pi_{1^+}$ states (6). Since the experimental $\omega_c$ of the ground state is 263 cm$^{-1}$, we deduce the experimental $D_e$ of GaBr as 4.33 eV. From the flame photometry (14), a $D_0^\infty = 4.45$ eV is deduced which yields $D_e = 4.47$ eV. While this value is in very good agreement with our computed SOCI $D_e$ of 4.2 eV, we consider the agreement somewhat fortuitous since our computed value does not include the effect of spin–orbit coupling. The spin–orbit coupling on the Br atom will decrease the $D_e$ but further improvement of the basis set and electron correlation effects will increase the $D_e$. The two effects thus cancel out leading to an excellent agreement in our computed $D_e$.

Miescher and Wehrli (1) studied the absorption spectrum of GaBr, from which they deduced the existence of $B^3\Pi_1$, $A^3\Pi_{0^+}$, and $C^1\Pi$ electronic states for GaBr and suggested the bandheads of $A^3\Pi_{0^+}$ and $B^3\Pi_1$ to be at 28166 and 28536 cm$^{-1}$, respectively. They also observed a vertical transition for the $C-X$ system at 37 310 cm$^{-1}$. The theoretical FOCI and SOCl $T_e$'s of $C^1\Pi$ are 32 285 and 38 240 cm$^{-1}$, respectively. Both the FOCI and SOCl calculations indicated that $^1\Pi$ state is shallow. Consequently, our computed energy separations of the electronic states of GaBr support the previous assignments and observations.

Miescher and Wehrli (1) found that the $C^1\Pi-X^1\Sigma^+$ system was diffuse, and described those as fluctuation bands. As can be seen in Fig. 1, the potential energy curve of the $^1\Pi$ state barely has a minimum which could cause an absorption band to be diffuse. In addition the $^1\Pi$ state crosses many excited states with shallow minima close to each other as shown in Fig. 1. Therefore our calculations fully support the early experimental observations.

The second roots of II symmetry, $^1\Pi_{III}$ and $^3\Pi_{III}$, are found to be repulsive while the first and the third roots, $^1\Pi$, $^3\Pi$, and $^3\Pi_{III}$, have minima as can be seen in Fig. 1.

Tables II and III also show the dipole moments of electronic states of GaBr at the FOCI and SOCl levels of theory, respectively. The $\mu_e$ of the ground state increases by 0.63 D in going from the FOCI to the SOCl level of theory. As seen from Tables II and III, most of the excited states have polarity of $\mu_e$ (Ga–Br$^+$) opposite to the ground state, indicating charge transfer in the electronic transitions from the ground state to these excited states. Our SOCl constants for the ground state of GaBr are in good agreement with the previous MRSDCI values (9) ($R_e = 2.40$ Å, $\omega_c = 255$ cm$^{-1}$, $\mu_e = 2.6$ D and $D_e = 4.1$ eV).

Table IV shows the compositions of electronic states of GaBr as revealed by the contributions of various electronic configurations. The contributions of Rydberg electronic configurations in several excited states, which are mainly the second and third roots of corresponding symmetries, are rather large. The computed $T_e$ values of such states would not be very accurate since the basis set was optimized for the ground state atoms, although they are augmented with one set of diffuse s, p and one set of d-type polarization functions.

The ground state arises from the closed shell configuration $1\sigma^22\sigma^23\sigma^11\pi^4$ (91.5%) with appreciable contribution from the $1\sigma^22\sigma^21\pi^22\pi^2$ configuration (3.5%). The $3\sigma$ molecular orbital is predominantly Ga(4s) while the $1\pi$ and $2\sigma$ molecular orbitals are predominantly Br(4p). This analysis of the FOCI natural orbitals confirms the
Ga⁺-Br⁻ ionic character of the bond. The first excited state, ³II, has a predominant (93.9%) configuration of 1s²2s²3σ²1π⁴2π⁴ which results from an electron excitation from the 3σ MO to the 2π MO. The C⁴II state is predominantly 1σ²2σ²3σ²1π⁴2π⁴ near the equilibrium geometry but 1σ²2σ²3σ²1π⁴2π⁴ at a longer distance. Hence the C⁴II state is shallow. It should be noted that the ¹Σ⁺(II) state contains considerable amounts (10.0%) of Rydberg character and the Tₑ of ¹Σ⁺(II) is below that of the C⁴II state.

The electronic configurations contributing to ³Σ⁻(II) are 61.0% 1σ²2σ²3σ²1π⁴2π⁴ and 25.4% 1σ²2σ²1π⁴2π⁴ near the equilibrium geometry. This suggests that the ³Σ⁻(II) state undergoes an avoided crossing, which is responsible for the rather unusual shape of the potential energy curves seen in Fig. 1. The ³II(III) and ¹Δ(II) states are composed of a number of configurations which include some Rydberg configurations as seen from Table IV.

Table V shows the Mulliken population analyses of the low-lying electronic states of GaBr. The ground state has a strong ionic character with the polarity Ga⁺ Br⁻ since the total gross population of the gallium atom is much below 3.0. This is consistent in its dipole moment which shows rather large charge separation. The overlap populations of the three excited states have the sign opposite to the ground state which corroborates the smaller ω₂'s of the corresponding states. The ³Σ⁺, ¹Δ, and ¹Δ states have similar gross populations since their energy curves and spectroscopic properties

<table>
<thead>
<tr>
<th>State</th>
<th>Electronic Configurations</th>
</tr>
</thead>
<tbody>
<tr>
<td>¹Σ⁺</td>
<td>10²2σ²3σ²1π²(91.5%), 10²2σ²1π²2π² (3.5%)</td>
</tr>
<tr>
<td>³II</td>
<td>10²2σ²3σ²1π²2π²(93.9%)</td>
</tr>
<tr>
<td>³Σ⁻</td>
<td>10²2σ²3σ²1π²2π²(90.6%), 10²2σ²1π²2π² (1.6%), 10²2σ²3σ²1π³(1.5%), 10²2σ²1π²2π² (1.4%)</td>
</tr>
<tr>
<td>¹Δ</td>
<td>10²2σ²3σ²1π²2π² (93.3%), 10²2σ²1π²2π² (1.7%), 10²2σ²3σ²1π³ (1.5%), 10²2σ²3σ²1π²2π² (1.5%)</td>
</tr>
<tr>
<td>³Δ</td>
<td>10²2σ²3σ²1π²2π² (93.4%), 10²2σ²1π²2π² (1.7%), 10²2σ²3σ²1π³ (1.6%)</td>
</tr>
<tr>
<td>³Σ⁺(II)</td>
<td>10²2σ²3σ²1π²2π² (67.5%), 10²2σ²3σ²1π³ (10.0%), 10²2σ²3σ²1π²2π² (7.9%), 10²2σ²3σ²1π³ (2.8%), 10²2σ²3σ²1π³ (1.2%)</td>
</tr>
<tr>
<td>¹II</td>
<td>10²2σ²3σ²1π²2π² (91.7%), 10²2σ²3σ²1π³ (2.6%)</td>
</tr>
<tr>
<td>¹Δ(II)</td>
<td>10²2σ²3σ²1π²2π² (41.3%), 10²2σ²3σ²1π³ (30.6%), 10²2σ²3σ²1π²2π² (8.1%), 10²2σ²3σ²1π³ (2.5%), 10²2σ²3σ²1π³ (2.2%)</td>
</tr>
<tr>
<td>³II(III)</td>
<td>10²2σ²3σ²1π²2π² (76.4%), 10²2σ²3σ²1π²2π² (8.1%), 10²2σ²3σ²1π³ (2.7%), 10²2σ²3σ²1π²2π² (1.1%), 10²2σ²3σ²1π³ (0.9%), 10²2σ²3σ²1π³ (0.7%)</td>
</tr>
<tr>
<td>³Σ⁻(II)</td>
<td>10²2σ²3σ²1π²2π² (61.6%), 10²2σ²3σ²1π³ (25.4%), 10²2σ²3σ²1π²2π² (1.5%)</td>
</tr>
</tbody>
</table>
TABLE V

Mulliken Population Analysis near the Equilibrium Geometries of the Electronic States of GaBr

<table>
<thead>
<tr>
<th>States</th>
<th>Ga</th>
<th>Br</th>
<th>Ga(d)</th>
<th>Br(d)</th>
<th>Overlap</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ^3\Sigma^- )</td>
<td>2.57</td>
<td>7.43</td>
<td>1.81</td>
<td>0.65</td>
<td>0.32</td>
</tr>
<tr>
<td>( ^3\Pi )</td>
<td>2.80</td>
<td>7.20</td>
<td>1.25</td>
<td>1.44</td>
<td>0.15</td>
</tr>
<tr>
<td>( ^3\Sigma^+ )</td>
<td>3.02</td>
<td>6.98</td>
<td>1.89</td>
<td>1.08</td>
<td>0.07</td>
</tr>
<tr>
<td>( ^3\Delta )</td>
<td>3.15</td>
<td>6.85</td>
<td>1.96</td>
<td>1.13</td>
<td>0.07</td>
</tr>
<tr>
<td>( ^1\Delta )</td>
<td>3.16</td>
<td>6.84</td>
<td>1.96</td>
<td>1.13</td>
<td>0.07</td>
</tr>
<tr>
<td>( ^1\Pi )</td>
<td>2.97</td>
<td>7.03</td>
<td>1.56</td>
<td>1.32</td>
<td>0.07</td>
</tr>
</tbody>
</table>

are about the same. The contribution of the Ga(d) function in the ground state is appreciable (0.12) indicating that the polarization effects make a significant contribution to the ionic ground state. The overlap population of the \(^3\Pi\) state near the equilibrium geometry of the ground state is zero reflecting shallowness of the \(^3\Pi\) state.

CONCLUSION

In this investigation we computed the spectroscopic constants and potential energy curves of 15 electronic states of GaBr. Spectroscopic constants are computed for several excited electronic states of GaBr which are yet to be observed.

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