High resolution infrared emission spectra of GaH and GaD

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The high resolution infrared emission spectra of gallium hydride and gallium deuteride have been recorded with a Fourier transform spectrometer. There were 1045 lines observed including those from the \(v = 1 \to 0\) to \(v = 7 \to 6\) bands for the \(^{69}\text{GaH}\) and \(^{71}\text{GaH}\) species and \(v = 1 \to 0\) to \(v = 4 \to 3\) bands for the \(^{69}\text{GaH}\) and \(^{71}\text{GaH}\) species. Dunham \(U_{ij}\)'s for each isotomer were obtained by fitting the data set of each isotopomer separately to the Dunham energy levels of the \(X' \Sigma^+\) electronic ground state. The mass-reduced Dunham \(U_{ij}\)'s were determined using two independent methods. In the first fit the \(U_{ij}\)'s constants were determined by the traditional method where all the constants were treated as adjustable parameters and determined statistically. In the second fit the \(U_{ij}\)'s which satisfied the condition \(j < 2\) were treated as adjustable parameters and the remaining constants were fixed by constraints imposed by the Dunham model. In order to predict the positions of transitions with \(\nu\)'s and \(J\)'s much higher than those observed the entire data set was fit directly to the eigenvalues of the Schrödinger equation containing a parameterized internuclear potential energy function.

I. INTRODUCTION

In contrast to isovalent aluminum hydride, \(^1\) relatively few spectroscopic studies have been reported for gallium hydride and deuteride. Garton ascribed bands observed in the 2160–2400 Å region of the spectrum to GaH.\(^2\) Since then there have been several classical spectroscopic studies that have focused mainly on the analysis of bands involving the nominally forbidden \(a^3\Pi-X' \Sigma^+\) intercombination transitions of GaH and GaD.

Neuhaus recorded and analyzed the 0–0 bands of the GaH \(a^3\Pi_{1,-3} \to X' \Sigma^+\) and \(a^3\Pi_0 \to X' \Sigma^+\) transitions and the GaD \(a^3\Pi_{1,-3} \to X' \Sigma^+\) transition.\(^3\) In a subsequent study he observed predissociation in the \(a^3\Pi-X' \Sigma^+\) transitions of GaH and GaD, but only the lines in the spectrum of GaD were sharp enough for rotational analysis.\(^4\) Ginter and Innes\(^5\) analyzed 16 bands of GaH including some bands of previously unobserved \(a^3\Pi_2-X' \Sigma^+\) and doubly forbidden \(a^3\Pi_0 \to X' \Sigma^+\) transitions.\(^6\) More recently, Lakshminarayana and Shetty formed GaD by exciting a mixture of gaseous gallium metal, iodine vapor, deuterium, and krypton in a microwave discharge and rotationally analyzed several emission bands of the GaD \(a^3\Pi_{1,-3} \to X' \Sigma^+\), \(a^3\Pi_0 \to X' \Sigma^+\), and \(a^3\Pi_0 \to X' \Sigma^+\) transitions.\(^8\)

Results from theoretical studies on GaH and GaD are also available. Ginter and Battino applied the Rydberg–Klein–Rees (RK) method to obtain potential energy curves for the \(a^3\Pi\) and \(X' \Sigma^+\) states of selected Group IIIa hydrides, including GaH.\(^9\) Pettersson and Langhoff have calculated the theoretical electric dipole moment and dissociation energy for the \(X' \Sigma^+\) electronic ground state of GaH.\(^10\) The multiconfiguration self-consistent field (MCSCF) [complete active space SCF (CASSCF)] calculation by Kim and Balasubramanian yielded potential energy curves, spectroscopic constants, and dipole-moment functions for 25 electronic states of GaH, of which 17 of these states have yet to be observed.\(^11\)

More recently, Jones and co-workers\(^12\) recorded high resolution vibrational-rotational spectra of the GaH and GaD \(X' \Sigma^+\) ground states using diode laser spectroscopy. GaH (GaD) was formed in a high temperature reaction involving molten gallium and hydrogen (deuterium). The recorded line positions were reduced to Dunham \(Y_{ij}\) constants and potential parameters. However, they were able to measure relatively few rovibrational transitions and they covered a narrow spectral range due to the limited tunability of diode lasers. They reported ~100 lines with a nominal accuracy of 0.001 cm\(^{-1}\).

As noted by Jones and co-workers, the simultaneous analysis of the rovibrational spectra of the Group IIIa diatomic hydrides and deuterides provides an excellent way of determining the extent of Born–Oppenheimer breakdown.\(^13\) Gallium has two naturally occurring isotopes, \(^{69}\text{Ga} (60.2\%)\) and \(^{71}\text{Ga} (39.2\%).\) The simultaneous analysis of GaH and GaD spectra yields data of comparable quality for the four different isotopomers, thus allowing the effects of Born–Oppenheimer breakdown to be examined for both nuclear centers.

In this paper we report on the analysis of the infrared (IR) emission spectra of GaH and GaD recorded with a Fourier transform spectrometer. Although this technique lacks the sensitivity of tunable diode laser spectroscopy, it does, however, provide wide spectral coverage and highly accurate rovibrational line positions. We observed over 1000 lines in the GaH and GaD spectra with the best lines being measured to a precision of ±0.0002 cm\(^{-1}\). The reduction of the data set to spectroscopic constants was accomplished by fitting the data separately to the energy levels of the Dunham model and a parameterized potential energy model.

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II. EXPERIMENT

All spectra were recorded on a Bruker IFS 120 HR spectrometer at the University of Waterloo. A total of three high resolution spectra were recorded, two for GaH and one for GaD. In order to record each spectrum, 12 g of gallium metal was placed in the center of a 1.2 m long mullite (3Al₂O₃·2SiO₂) tube with heat supplied by a tube furnace. The mullite cell was located external to the spectrometer and aligned to the emission port through the use of an external globar lamp. The apparatus is described in greater detail elsewhere. The Ga in the mullite tube was gradually heated to operating temperature at a rate of ~5 °C/min and when a temperature of 500 °C was achieved, the pumping port was closed, and 5 Torr of argon gas was added to the system to prevent the deposition of solid material on the cell windows. At 1200 °C hydrogen or deuterium was added to the cell. All high resolution spectra were recorded at 1400 °C.

A HgCdTe detector was used to record all spectra. Each high resolution spectrum involved the coaddition of 75 individual scans each recorded at a resolution of 0.007 cm⁻¹. The GaD spectrum and one of two GaH spectra were recorded using a KBr beamsplitter and KBr windows. In these spectra the lower wave-number limit of 800 cm⁻¹ was dictated by detector sensitivity while the 1700 cm⁻¹ upper limit was set by a short wavelength cutoff filter. As is evident in Fig. 1, the bandhead of the GaH fundamental band (υ=1→0) lies beyond the 1700 cm⁻¹ upper cutoff limit. In order to record the band head region of the GaH fundamental band the 1700 cm⁻¹ upper wave-number cutoff filter was replaced with a 2200 cm⁻¹ upper wave-number cutoff filter. In addition the KBr beamsplitter and KBr windows were replaced with a CaF₂ beamsplitter and CaF₂ windows; the CaF₂ transmission curve raises the lower wave-number limit to 1150 cm⁻¹.

III. RESULTS AND DISCUSSION

Data analysis was facilitated using the PC-DECOMP computer program of Brault which determines line positions by fitting measured line profiles to Voigt line shape functions. Absolute wave number calibration of the GaH line positions was achieved by utilizing impurity H₂O lines in the spectrum.

Portions of the two high resolution GaH spectra are displayed in Figs. 1 and 2. In the spectrum shown in Fig. 1, the bands υ=1→0 to υ=4→3 were observed and the sharp and unblended lines with a signal to noise (S/N) ratio greater than 100 were measured to a precision of ±0.0003 cm⁻¹. The lower S/N ratio in the spectrum of Fig. 2 degraded the precision of the measured line centers of the strong and unblended lines to ±0.0005 cm⁻¹. Initially, each of the GaH spectra was independently calibrated relative to the strongest and sharpest H₂O lines. However, calibrating the spectra in this manner introduced a systematic shift of 0.0002 cm⁻¹ between lines common to both spectra. In order to place the measured rotational lines from both spectra on the same absolute wave-number scale, thereby circumventing any systematic shift in the calibration between spectra, we were forced to adopt the following calibration procedure. The strongest GaH rotational lines from the first spectrum (the best of the two spectra in terms of S/N) were calibrated relative to H₂O lines and these GaH lines were used to calibrate the remaining lines in both spectra.
The quality of the GaD spectrum is illustrated in Figs. 3 and 4. The vibrational bands that were observed are \( v = 1 \rightarrow 0 \) to \( v = 7 \rightarrow 6 \). All rotational lines in the GaD spectrum were calibrated relative to \( \text{H}_2\text{O} \) lines. Rotational lines of GaH present in the GaD spectrum were then used to verify that the GaH and GaD spectra were in fact on the same wave number scale. Although the internal consistency between measured lines in both the GaH and GaD spectra is perhaps as good as \( \pm 0.0001 \text{ cm}^{-1} \), the error in the absolute calibration (with \( \text{H}_2\text{O} \) lines serving as the source of calibration) is difficult to ascertain without additional independent measurements.

The observed rotational lines for \( ^{69}\text{GaH}, ^{71}\text{GaH}, ^{69}\text{GaD}, \) and \( ^{71}\text{GaD} \) are available from PAPS, or from the authors on request. Each of the four isotopomer data sets was separately fit to the parameterized energy levels of the Dunham model

\[
E(v,J) = \sum_{i,j} Y_{ij} (v+\frac{1}{2})^i [J(J+1)]^j, \tag{1}
\]

where \( v \) and \( J \) are the vibrational and rotational quantum numbers. The Dunham \( Y_{ij} \) constants for each isotopomer are given in Table I. Since our IR data set was able to access vibrational-rotational levels almost up to 50% of the potential well depth the new Dunham constants \( Y_{41}, Y_{31}, Y_{32}, \) and \( Y_{04} \) for both GaH and GaD and \( Y_{00} \) and \( Y_{13} \) for GaD were determined. In addition, the high quality of our data set also lead to improving the precision of the Dunham constants quoted by Urban et al.\(^{12,13}\)

Explicitly factoring the reduced-mass dependence out of \( Y_{ij} \) gives the equation

\[
E(v,J) = \sum_{i,j} \mu^{-(i+2j)/2} U_{ij} (v+\frac{1}{2})^i [J(J+1)]^j. \tag{2}
\]

Equation (2) is strictly valid only within the Born–Oppenheimer approximation. In the case of Born–Oppenheimer breakdown, Eq. (2) is modified as\(^{20,21}\)

\[
E(v,J) = \sum_{i,j} \mu^{-(i+2j)/2} U_{ij} (v+\frac{1}{2})^i [J(J+1)]^j \times \left( 1 + \frac{m_e}{M_A} \Delta A_{ij} + \frac{m_e}{M_B} \Delta B_{ij} \right), \tag{3}
\]

where \( m_e \) is electron mass, \( M_A \) and \( M_B \) are atomic masses for centers \( A \) and \( B \), and \( \Delta A_{ij} \) are Born–Oppenheimer breakdown constants. Values of the \( U_{ij} \)'s and \( \Delta A_{ij} \)'s determined from a least-squares fit of all the isotopomer data to Eq. (3) are given in Table II under the column heading “unconstrained fit.” The standard deviation of the fit was 0.642.

A further refinement to the Dunham model entails the placement of constraints on the \( U_{ij} \)'s for \( j > 2 \). Dunham has shown that the potential parameters for a power series potential are all uniquely determined by the set of \( U_{00} \)'s and \( U_{11} \)'s. Consequently, the remaining \( U_{ij} \)'s with \( j > 2 \) are all expressible in terms of \( U_{00} \)'s and \( U_{11} \)'s. For the purpose of least-squares fitting, the \( U_{00} \)'s and \( U_{11} \)'s are treated as ad-

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|}
\hline
\( Y_{ij} \) & \( ^{69}\text{GaH} \) & \( ^{71}\text{GaH} \) & \( ^{69}\text{GaD} \) & \( ^{71}\text{GaD} \) \\
\hline
\( Y_{10} \) & 1.603 940 94(57) & 1.603 612 94(73) & 1.143 227 36(13) & 1.142 769 38(18) \\
\( Y_{30} \) & 0.324 166(182) & 0.323 468(227) & 0.116 383 1(315) & 0.116 163 6(454) \\
\hline
\( 10^3 Y_{40} \) & -6.654 5(216) & -6.600 4(264) & -1.583 91(446) & -1.573 18(661) \\
\( 10^3 Y_{50} \) & ... & ... & -7.156(231) & -7.338(353) \\
\hline
\( Y_{01} \) & 6.143 409 51(372) & 6.140 908 83(548) & 3.121 885 40(81) & 3.119 390 44(112) \\
\( Y_{11} \) & -0.190 637 61(523) & -0.190 507 11(717) & -0.068 997 84(470) & -0.068 914 16(576) \\
\hline
\( 10^3 Y_{21} \) & 2.730 17(435) & 2.737 83(586) & 0.709 005 15(88) & 0.707 051 227 \\
\( 10^3 Y_{31} \) & -4.264(147) & -4.054(195) & -0.808 68(279) & -0.828 38(440) \\
\( 10^4 Y_{41} \) & -1.640(173) & -1.730(224) & -0.184 47(176) & -0.198 00(301) \\
\( 10^4 Y_{51} \) & -3.596 96l(193) & -3.593 712(288) & -0.930 208 9(146) & -0.928 731 0(230) \\
\hline
\( 10^3 Y_{02} \) & 8.616 371(961) & 8.582 0(129) & 1.580 546(602) & 1.577 578(813) \\
\( 10^3 Y_{12} \) & -8.070(387) & -6.956(535) & -1.019 3(113) & -0.983 6(151) \\
\( 10^3 Y_{22} \) & -1.048 6(483) & -1.277 5(699) & -0.103 896 795(95) & -0.106 90(116) \\
\( 10^3 Y_{32} \) & 1.351 25(385) & 1.346 22(597) & 0.180 331 121(11) & 0.179 705(209) \\
\( 10^3 Y_{42} \) & -1.591 9(797) & -1.551 108 & -0.129 24(320) & -0.134 20(474) \\
\( 10^3 Y_{03} \) & 2.628 20(200) & 3.044 285 & -0.214 03(357) & 0.216 44(501) \\
\( 10^3 Y_{13} \) & -4.777 255 & -4.653 413 & -0.394 11(578) & -0.375 98(984) \\
\hline
\end{tabular}
\caption{Dunham \( Y_{ij} \) constants of \( ^{69}\text{GaH}, ^{71}\text{GaH}, ^{69}\text{GaD}, \) and \( ^{71}\text{GaD}. \)}
\end{table}
TABLE II. (a) Mass-reduced Dunham constants for GaH in cm$^{-1}$. See text for an explanation of constrained and unconstrained fits. (b) Born-Oppenheimer breakdown constants from constrained and unconstrained fits.

(a) | Parameterized potential model. Our technique is similar to the procedure developed by Coxon and Hajigeorgiou. Specifically, the method involves fitting spectral lines directly to the eigenvalues of the radial Schrödinger equation containing a parameterized potential function. With the effective radial Schrödinger equation for the $^1\Sigma^+$ state of a diatomic molecule written as

$$\frac{\hbar^2}{2\mu} \psi'' - U_{\text{eff}}(R) + E(v,J) - \frac{\hbar^2}{2\mu} \left[ 1 + q(R) \right] \frac{J(J+1)}{R^2}$$

the effective internuclear potential for vibrational motion is given by

$$U_{\text{eff}}(R) = U_{BO}(R) + \frac{\mu_A}{M_A} + \frac{\mu_B}{M_B},$$

and the form of the Born-Oppenheimer potential is chosen to be

$$U_{BO}(r) = D_0 \left[ 1 - \frac{r^2}{2} \right],$$

where

$$\beta(r) = -z \sum_{i=0}^{\infty} \beta_i R^i,$$

and

$$z = \frac{(R-R_e)}{(R+R_e)},$$

is one-half the Ogilvie–Tipping parameter.

The latter terms in Eq. (5) are corrections for atomic centers $A$ and $B$ which take into account Born-Oppenheimer breakdown and homogeneous nonadiabatic mixing from distant $\Sigma$ electronic states and are represented by the power series expansions

$$U_A(R) = \sum_{j=1}^{\infty} u_A^j (R-R_e)_j$$

and

$$U_B(R) = \sum_{i=1}^{\infty} u_B^i (R-R_e)_i.$$

Similar effects for rotational motion, namely $J$-dependent Born-Oppenheimer breakdown and heterogeneous nonadiabatic mixing from distant $\Pi$ states, are accounted for through the inclusion of the $q(R)$ term in Eq. (4) where

$$q(R) = M_A^{-1} \sum_{i=1}^{\infty} q_A^i (R-R_e)_i + M_B^{-1} \sum_{i=1}^{\infty} q_B^i (R-R_e)_i.$$
TABLE III. Internuclear potential parameters. Values of $u_i^j$ given are in cm$^{-1}$ Å$^{-1}$ and values of $q_i^j$ are given in Å$^{-1}$.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-4} D_e$ (cm$^{-1}$)</td>
<td>2.29</td>
<td></td>
</tr>
<tr>
<td>$R_e$ (Å)</td>
<td>1.660 130 365 553 748</td>
<td>4.75 × 10$^{-7}$</td>
</tr>
<tr>
<td>$\beta_0$</td>
<td>4.275 027 073 887 386</td>
<td>1.80 × 10$^{-6}$</td>
</tr>
<tr>
<td>$\beta_1$</td>
<td>3.376 962 034 094 6903</td>
<td>2.27 × 10$^{-5}$</td>
</tr>
<tr>
<td>$\beta_2$</td>
<td>6.417 723 606 340 8252</td>
<td>2.55 × 10$^{-4}$</td>
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<tr>
<td>$\beta_3$</td>
<td>13.879 380 707 128 897</td>
<td>3.05 × 10$^{-3}$</td>
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<tr>
<td>$\beta_4$</td>
<td>25.819 625 651 843 3906</td>
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<td>$\beta_5$</td>
<td>53.791 352 147 482 6917</td>
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<td>$\beta_6$</td>
<td>84.889 069 770 902 5848</td>
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<td>$\beta_7$</td>
<td>-435.807 384 478 5366</td>
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<tr>
<td>$\beta_8$</td>
<td>673.234 544 141 024 7204</td>
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<td>$\beta_9$</td>
<td>7 916.002 626 552 2011</td>
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<td>$u_{ij}^{Ga}$</td>
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<td>$u_{ij}^{H}$</td>
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<td>$M_{Ga}$ (71Ga)</td>
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<tr>
<td>$M_{H}$ (2H)</td>
<td>2.014 101 779</td>
<td></td>
</tr>
</tbody>
</table>

Technically determined are listed along with their uncertainties quoted to one standard deviation. The thermochemical value for the dissociation energy $D_e$ was taken from Ref. 26 and quoted atomic masses from Ref. 27.

The constrained and unconstrained Dunham $U_{ij}$ constants in Table II are for the most part in agreement to within three standard deviations. This indicates that effects ascribed to perturbations with higher lying electronic states are essentially insignificant. It is worth noting that $\Delta_{01}^e$ and $\Delta_{01}^H$ from the unconstrained and constrained fits are just barely determined to three standard deviations. On the other hand, a disproportionate number of $\Delta's$ are well determined from both fits for the hydrogen center; this is consistent with the atomic mass of the gallium atom contributing only 1.4% (2.8%) to the reduced mass of the diatomic hydride (deuteride) molecule. Therefore, the immediate conclusion that one can draw from these results is that the contribution of Born–Oppenheimer breakdown by the gallium metal center is essentially insignificant.

Results from the parameterized potential model fit serve as a cross check on the conventional treatment of Born–Oppenheimer breakdown given by Eq. (3). According to Coxon and Hajigeorgiou,\textsuperscript{24}

$$\Delta_{01}^i \approx 2(m_e \beta_i^B) R_e^B \left[ \frac{dU(R)}{dR} \right]_{R=R_e^B},$$

where $i$ is $A$ or $B$ and

$$\beta^B = \left[ \frac{d^2 U^B(R)}{dR^2} \right]_{R=R_e^B}$$

is the harmonic force constant for the Born–Oppenheimer potential. [Strict equality applies only if a small Dunham correction is added to the right-hand side of Eq. (13).] Substituting Eq. (10) [or Eq. (11)] into Eq. (13) and Eq. (6) into Eq. (14) gives

$$\Delta_{01}^i \approx \frac{4m_e \beta_i^B}{M_{Ga} \Delta_{01}^B} \left[ 1 - e^{-B_i} \right]^2 - u_i^j.$$  

Using the parameter values in Table III yield the values, $\Delta_{01}^Ga = -6.077(69)$ and $\Delta_{01}^H = -4.233 75(62)$. Adding the small Dunham correction to these values give $\Delta_{01}^Ga = -6.059(69)$ and $\Delta_{01}^H = -4.215 95(62)$. By comparing these values to the ones listed in Table II shows that only the $\Delta_{01}^e$'s are in good agreement whereas the value of $\Delta_{01}^Ga$ from the constrained Dunham fit is almost a factor of 6 smaller than the value derived from the analysis presented here.

The discrepancy in the $\Delta_{01}^Ga$'s can be explained as follows. With the Eq. (3) multiplicative factor

$$\left[ 1 + \frac{m_e}{M_{Ga}} \Delta_{01}^Ga + \frac{m_e}{M_{H}} \Delta_{01}^H \right],$$

that corrects for Born–Oppenheimer breakdown and the corrected values of $\Delta_{01}^Ga$ and $\Delta_{01}^H$ quoted above yield the values

$$\frac{m_e}{M_{Ga}} \Delta_{01}^Ga = -0.000 048 2,$$

$$\frac{m_e}{M_{H}} \Delta_{01}^H = -0.000 046 8,$$

$$\frac{m_e}{M_{Ga}} \Delta_{01}^H = -0.002 294 8.$$
for the terms in Eq. (16). One can immediately see that the $\Delta_{01}^{Ga}$ term is fairly insensitive to change in isotopic mass and is almost two orders of magnitude smaller than the $\Delta_{01}^{H}$ term. These two properties in combination with high correlation between $\Delta_{01}^{Ga}$ and $U_{ij}$ in a least-squares fit hinder the determination of $\Delta_{01}^{Ga}$ to a much greater extent than for $\Delta_{01}^{H}$. Therefore, the form of the Born–Oppenheimer correction given by Eq. (16) is an insensitive way of determining metal-centered $\Delta$'s from a least-squares fit when the diatomic molecule is a heavy-metal hydride.

IV. CONCLUSION

Fourier transform emission spectroscopy is an excellent technique for recording high resolution vibrational-rotational spectra of high temperature molecules in the infrared region. As is evident in this work presented on GaH and GaD, this technique gives broad spectral coverage and an excellent S/N ratio thus making it possible to record a significant number of line positions with high precision. The high quality of line positions makes the data set particularly useful in the determination of spectroscopic constants and internuclear potentials.

The four isotopomer data sets, $^{69}$GaH, $^{71}$GaH, $^{69}$GaD, and $^{71}$GaD, were fit individually to the energy levels of the Dunham model to determine Dunham $Y_{ij}$'s and combined together in a fit to determine the mass-independent Dunham $U_{ij}$'s. A second set of $U_{ij}$'s was determined from a fit where the $U_{ij}$'s were fixed to the Dunham model as adjustable parameters and the remaining $U_{ij}$'s were fixed to constraints imposed by the Dunham model. The Dunham constants allow for the prediction of line positions with high $J$. In order to predict the line positions of GaH and GaD with high $\nu$ an internuclear potential energy function was determined. This was achieved by a direct fit of the spectral data to the eigenvalues of an effective radial Schrödinger equation containing a parameterized internuclear potential energy function.

ACKNOWLEDGMENTS

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18 See AIP document no. PAPS JCPSA-99-8379-12 for the 12 pages of tables. Order by PAPS number and journal reference from American Institute of Physics, Physics Auxiliary Publication Service, 500 Sunny Side Boulevard, Woodbury, New York 11797-2999. The price is $1.50 for each microfiche (60 pages) or $5.00 for photocopies of up to 30 pages, and $0.15 for each additional page over 30 pages. Airmail additional. Make checks payable to the American Institute of Physics.