Excited Electronic States of AuF†

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We have recorded laser excitation spectra of transitions from the ground X1Σ+ state of gaseous gold fluoride (AuF) into three excited electronic states in the visible region. We prepared the sample in a dc electric discharge by flowing a dilute mixture of SF6 in argon through a hollow gold cathode. Two of these electronic states give rise to the previously reported yellow bands of the molecule, for which a rotational analysis is given here for the first time. We have analyzed the (0,0), (1,1), (0,1), and (1,2) bands of these two transitions, which we identify as [17.8]0+→X1Σ+ and [17.7]1-X1Σ+. Their red-degraded (0,0) band heads lie at 563.0 and 566.2 nm, respectively. The (0,0) band of a new, red-degraded [14.0]1-X1Σ+ transition at 715.1 nm has also been recorded and analyzed. An accurate set of molecular constants of the three excited states as well as the ground state has been determined by least-squares fitting all of the optical data together with measurements made by other workers of the pure rotational spectrum of AuF in its ground state. These constants include the electronic term energies, vibrational frequencies, rotational constants, and Ω-doubling constants. We discuss the nature of these three excited electronic states in terms of the ionic Au+F− electronic configurations from which they are derived.

Introduction

Gold monofluoride (AuF) has been the subject of several spectroscopic studies. The first report of its spectrum was by Saenger and Sun,1 who recorded low-resolution emission bands in the yellow region. They identified vibrational bands with ν′ − ν″ = 0 and −1 of an electronic system tentatively assigned as 1Π-1Σ. Andreev and BelBruno2 recorded several ν′ − ν″ = 0 and ±1 vibrational bands of the same system and found that they corresponded to two closely spaced electronic transitions. They assigned these two transitions as Σ−X1Σ+ and 1Π-1Σ+, guided in part by calculations they performed using density functional theory. The resolution of both of these studies was too low to provide for a rotational analysis.

The ground electronic state of the molecule has been the subject of two high-resolution studies. Evans and Gerry3 recorded the J = 1 ← 0 rotational transition within the ν = 0 and 1 levels by Fourier transform microwave spectroscopy, thereby determining values for the rotational constant, the 197Au quadrupole coupling constant, and the 197Au and 19F nuclear spin-rotation constants. Okabayashi et al.4 measured the pure rotational spectrum within the ν = 0 to 13 levels and up to J = 27 using a source-modulated microwave spectrometer at a resolution that did not resolve the hyperfine structure. They performed a least-squares fit to all measured transitions using a Dunham-type expansion, determining rotational and vibrational constants for the ground state. Ten different computational studies of the AuF molecule have been reported,5–13 two of which included calculations on excited electronic states.6,12

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5 Experimental Methods

We chose to study the electronic spectrum of gold fluoride to perform a rotational analysis of the previously reported yellow bands as well as to search for other electronic bands in the visible region. We have now searched over the region extending from 553 to 800 nm. We have succeeded in rotationally analyzing the (0,0), (1,1), (0,1), and (1,2) bands of the two states in the yellow region, assigning the transitions as [17.8]0+→X1Σ+ and [17.7]1-X1Σ+. We label the upper states using the Hund’s case (c) notation [To]Ω, where To is the energy of the state in 10^3 cm^{-1}, relative to X1Σ+ (ν = 0). We have also rotationally analyzed a new electronic transition, identified as the [14.0]1-X1Σ+ (0,0) band, which lies at 715 nm.

The [17.7]1-X1Σ+ bands showed partially resolved hyperfine structure at low J, and in an earlier report in this journal, we described an analysis of this hyperfine structure in the [17.7]1-X1Σ+ (0,0) band.14 Here we showed that the value of the upper state’s magnetic hyperfine constant, h_1 = -543 (4) MHz, implies that the state has significant 1A_g character. The purpose of the present article is to report the vibrational, rotational, and fine structures of the three excited electronic states of the AuF molecule and to describe the character of the states in terms of the electronic configurations from which they are derived.

We recorded the electronic spectrum of gold fluoride (AuF) in the visible region by laser excitation spectroscopy. The gaseous sample was generated using a hollow cathode sputtering source in which a dilute mixture of sulfur hexafluoride (SF6) in argon was flowed through a 3 mm diameter hole in a 6 mm diameter, 10 mm long solid gold cathode. A 7 mA dc electric discharge was run via a wire anode located 10 mm from the cathode. The discharge plasma was expanded through a 3 mm wide slit into a vacuum chamber pumped to 1.6 Torr. The excitation laser beam crossed the molecular flow 10 mm below the slit. Laser-induced fluorescence was collected at f/2 by a 50 mm diameter lens and passed through a red-pass filter that...
Electronic states as isolated Hund’s case (c) states because, given the presence or absence, respectively, of a P(1) line. Furthermore, an example of such a band is shown in Figure 1, which displays Rhodamine 6G dye as the lasing medium, whereas for the V-10 laser). For the yellow bands, the ring laser operated with a Ti:sapphire crystal pumped by a Coherent Verdi V-10 laser. Following this work, high-resolution averaging 10 shots of the dye laser with a digital oscilloscope (Stanford SR510). We observed molecular line widths of 1.7 MHz (fwhm), which are consistent with Doppler broadening at a translational temperature of 300 K. The ring laser is equipped with a wavemeter, which was calibrated by detecting argon fluorescence signal was demodulated with a lock-in amplifier (Hamamatsu R928). From the discharge. The collected light was then focused onto a side-on photomultiplier tube. Blocked light to the blue of the laser, including argon emission from the discharge. The collected light was then focused onto a side-on photomultiplier tube (Hamamatsu R928).

Electronic spectra were initially recorded using a pulsed dye laser with a resolution of ~0.1 cm⁻¹. With this laser, we were not able to resolve fully the rotational structure of the R branches, but we could rapidly scan wide spectral regions to locate electronic bands. The spectra were recorded by signal averaging 10 shots of the dye laser with a digital oscilloscope (Tektronix TDS-420A). Following this work, high-resolution spectra were then recorded using a single-mode, continuous-wave ring laser (Coherent 899-29 pumped by a Coherent Verdi V-10 laser). For the yellow bands, the ring laser operated with Rhodamine 6G dye as the lasing medium, whereas for the [14.0]1-XΣ⁺(0,0) band at 715 nm, a Ti:sapphire crystal was used. The laser beam was mechanically chopped, and the fluorescence signal was demodulated with a lock-in amplifier (Stanford SR510). We observed molecular line widths of ~450 MHz (fwhm), which are consistent with Doppler broadening at a translational temperature of 300 K. The ring laser is equipped with a wavemeter, which was calibrated by detecting argon transitions optogalvanically in a niobium hollow cathode lamp filled with argon.

Results

Because the ground state of AuF has been well characterized via its pure rotational spectrum, the assignment of the rotational structure of all of our bands was straightforward. An example of such a band is shown in Figure 1, which displays the AuF yellow bands. The assignment of the value of Ω as 0 or 1 to each upper state was unambiguously provided by the presence or absence, respectively, of a P(1) line. Furthermore, the [17.7]1-XΣ⁺(0,0) band and [17.8]0-XΣ⁺(0,0) bands do not have a Q branch, whereas the [17.7]1-XΣ⁺ and [14.0]1-XΣ⁺ perpendicular bands showed strong Q branches. The vibrational assignments of the three upper states were secured by searching one upper state vibrational interval to the red of the (0,0) bands and finding no bands in those regions.

The two upper states of the yellow bands are separated by only 102 cm⁻¹. They could potentially be assigned as Σ⁺ and Π states, as was previously proposed, or as components of a Σ state. Steimle et al. have shown that the Σ⁺/Π and Σ models are isomorph and will equivalently describe the rotational, fine, and hyperfine structures. However, as we described in our earlier report, the hyperfine structure in the Ω = 1 state is not consistent with it being assigned as either a pure Π or Σ state. Therefore, we chose to fit these two excited electronic states as isolated Hund’s case (c) states because, given the large off-diagonal spin–orbit interactions expected in a 5d transition-metal compound, the states will be mixtures of multiple Hund’s case (a) states.

We performed a single global fit to all of our observed transitions. The rotational energies were fitted to a Hund’s case (c) energy level expression that did not include terms in Ω:  

\[
\langle J\Omega|H_{\text{hyd}}|J\Omega\rangle = B_J(J+1) - D_J \frac{J(J+1)^2}{2} + H_J \frac{J(J+1)^3}{4} 
\]

(1)

Because we recorded spectroscopic transitions involving multiple vibrational levels of the [17.7]1, [17.8]0, and XΣ⁺ states, we used standard expressions for the vibrational dependence of the rotational and centrifugal distortion constants, namely

\[
\begin{align*}
B_v &= B_e - \alpha_e (v + 1/2) + \gamma_e (v + 1/2)^2 \\
D_v &= D_e + \beta_e (v + 1/2) 
\end{align*}
\]

(2, 3)

In addition, the [17.7]1 and [14.0]1 states displayed significant Ω-doubling, with splittings that increased as J², as expected for an Ω = 1 state. To treat this Ω-doubling, we added terms to the Hamiltonian that were written as

\[
\langle J\Omega_e|H_{\text{QD}}|J\Omega_f\rangle = \pm \frac{1}{2} \left[ q_J(J+1) - q_{QD} \frac{J(J+1)^2}{2} + q_{QD} \frac{J(J+1)^3}{4} \right] 
\]

(4)

For the [17.7]1 state, where we have accurate information on the v = 0 and 1 levels, we expressed the vibrational dependence of the first two Ω-doubling parameters as follows

\[
\begin{align*}
q_v &= q_e + \alpha_v (v + 1/2) \\
q_{QD} &= q_{QD} + \alpha_{QD} (v + 1/2) 
\end{align*}
\]

(5, 6)

We included in our data set several pure rotational transitions of AuF that have been measured within the first three vibrational levels of the ground electronic state. In ref 3, the hyperfine-resolved J = 1 ← 0 transition was measured in the v = 0 and 1 levels. Because our Hamiltonian does not include hyperfine interactions, we calculated the hyperfine-free frequencies as ν_f=1=0 = 2B_e, where B_e is the rotational constant reported in ref 3. Each datum in the least-squares fit was weighted by the inverse square of its estimated uncertainty. For the microwave transitions, the uncertainties were taken to be 10 kHz, whereas for the optical transitions, the uncertainties of all but a few weak or blended lines were taken to be 0.0010 cm⁻¹. Most of the rotational branches were measured and fitted out to J'' > 50. The first few lines of each rotational branch in the [14.0]1-XΣ⁺ and [17.7]1-XΣ⁺ transitions showed partially resolved hyperfine structure, so these lines were not included in the fit.

Because all microwave and optical transitions involve the ground electronic state, the entire data set was treated in a single global fit. The variance of this least-squares fit relative to the experimental uncertainties is 0.79, which indicates that the effective Hamiltonian fits the data to within its estimated experimental uncertainty. The results of the least-squares fit are
Excited Electronic States of AuF

TABLE 1: Molecular Constants for the Ground and Excited Electronic States of AuF∗

<table>
<thead>
<tr>
<th>constant</th>
<th>X′Σ+</th>
<th>[14.0]1b</th>
<th>[17.7]</th>
<th>[17.8]0∗</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ω</td>
<td>0.0</td>
<td>14 260.0927(24)</td>
<td>17 681.72542(22)</td>
<td>17 776.44163(23)</td>
</tr>
<tr>
<td>ωxΩ</td>
<td>563.60904(19)</td>
<td>512.37330(19)</td>
<td>520.52278(19)</td>
<td></td>
</tr>
<tr>
<td>ωzΩ</td>
<td>2.896924(63)</td>
<td>0.25043160(42)</td>
<td>0.25456371(43)</td>
<td></td>
</tr>
<tr>
<td>r(Å)</td>
<td>2.0985(40) × 10^-6</td>
<td>0.25120809(91)</td>
<td>0.00195021(38)</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>2.32477(25) × 10^-7</td>
<td>2.3497(78) × 10^-7</td>
<td>9.93(17) × 10^-9</td>
<td></td>
</tr>
<tr>
<td>β</td>
<td>3.669(64) × 10^-10</td>
<td>-1.23(16) × 10^-12</td>
<td>-1.427(33) × 10^-12</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>-1.37(17) × 10^-13</td>
<td>0.00288023(94)</td>
<td>0.00324233(54)</td>
<td></td>
</tr>
<tr>
<td>qe</td>
<td>0.001873054(13)</td>
<td>-2.9605(48) × 10^-4</td>
<td>-8.225(34) × 10^-4</td>
<td></td>
</tr>
<tr>
<td>qd</td>
<td>0.00195021(38)</td>
<td>1.407(26) × 10^-3</td>
<td>2.478(46) × 10^-12</td>
<td></td>
</tr>
<tr>
<td>qin</td>
<td>2.32477(25) × 10^-10</td>
<td>-4.499(82) × 10^-8</td>
<td>1.971078(17)</td>
<td></td>
</tr>
<tr>
<td>r(Å)</td>
<td>1.918442482(49)</td>
<td>1.9679693(36)</td>
<td>1.9557239(17)</td>
<td></td>
</tr>
</tbody>
</table>

* All values are in inverse centimeters, except for the derived bond length. Values in parentheses represent one standard deviation in units of the last quoted digit. b For the [14.0]1 state, all values shown are for the ν = 0 level (not equilibrium values). c The value reported is that of ΔGΩ=2.

displayed in Table 1. A list of the observed and calculated wavenumbers of the optical transitions is provided in the Supporting Information.

Discussion

To understand the electronic structure of gold monofluoride, we will consider the low-lying electronic states as being predominantly described by a Au+ - F- ionic configuration. The ground X′Σ+ state in this model is derived from the separated ion limit of Au+ (5d96s, 3D) + F- (2p6, 1S). Excitation into the low-lying electronic states then corresponds to a 5d → 6s promotion on the Au+ ion. The manifold of molecular states created by this electronic excitation arise from either the separated ions Au+ (5d66s, 1D) + F- (2p6, 1S) to give 1Δ, 1Π, and 1Σ or Au+ (5d66s, 3D) + F- (2p6, 1S) to give 1Δ, 1Π, and 1Σ in the Hund’s case (a) limit. Large gold-centered spin–orbit interactions will severely mix these states in a transition to Hund’s case (c) coupling. In the free Au+ ion, the 5d9 (2D5/2)6s and 5d9 (2D3/2)6s singly excited configurations lie 2.0 and 3.6 eV, respectively, above the Au+ (5d66s, 1S) ground state in the Au+ ion.18

The ab initio calculation of Guichemerre et al. provides a similar description of the ground and lowest excited electronic states of AuF. These authors employed multireference configuration interaction (MRCI) and coupled-cluster (CC) methods with scalar-relativistic energy-consistent pseudopotentials. They found that the ground and lowest excited electronic states of AuF can be described by the electronic configurations

$$X′Σ^+:(1σ)^4(1π)^4(1δ)^4(2π)^4(2σ)^2$$ (7)

$$1^3Σ^+:(1σ)^4(1π)^4(1δ)^4(2π)^4(2σ)^2(3σ)^4$$ (8)

$$1^3Π:(1σ)^4(1π)^4(1δ)^4(2π)^4(2σ)^2(3σ)^4$$ (9)

$$1^3Δ:(1σ)^4(1π)^4(1δ)^4(2π)^4(2σ)^2(3σ)^4$$ (10)

where the 1σ and 1π orbitals are derived mostly from F 2p atomic orbitals (AOs), the 1δ orbitals are Au 5d5 AOs, the 2σ orbitals are antibonding combinations of Au 5dσ and F 2pσ AOs, the 2π orbital is an Au 5δ σ AO, and the 3σ orbital is an Au 6s AO.

We have identified one Ω = 0+ and two Ω = 1 excited electronic states of AuF by laser excitation spectroscopy from the ground state. In the ab initio work, eight Ω = 0 or 1 states from configurations 8–10 given above were identified: under the selection rule ΔΩ = 0 or ±1, these are the only states that are accessible from the ground 1Σ+ state via a one-photon transition. The effects of the gold spin–orbit interactions were included in calculating the properties of these excited states. These properties are given in Table 2 together with values determined from our experimental work. Hund’s case (a) labels are shown for the calculated states, but the large spin–orbit mixing of states of a given Ω, but different S and Λ, will leave Ω as the only good quantum number label.

The [17.8]0+ state (T = 2.20 eV) can be identified by its term energy of the 1Π0+ state (calculated to lie at 2.40 eV) rather than the 2Σ+ state, which is calculated to lie much higher at 3.58 eV. The nearby [17.7]1 state is associated with the calculated 1Π1 state, although the hyperfine structure of this state points to it having significant Λ character.14 The second Ω = 1 state we have identified, [14.0]11 (T = 1.77 eV), is close in energy to the 1Σ+ state calculated to lie at 1.79 eV. Although the low intensity of the [14.0]1-X′Σ+ (00) transition did not permit us to record its spectrum at sub-Doppler resolution, partially resolved hyperfine splittings were observed for the first few lines of each rotational branch. From the observed structure in the Q branch, it is clear that the 107Au hyperfine splitting forms a “regular” Landé pattern, with levels of higher F lying

<table>
<thead>
<tr>
<th>type</th>
<th>state</th>
<th>Ω</th>
<th>T in eV</th>
<th>r(Å)</th>
<th>ω(cm^-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>calculated</td>
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<td>0</td>
<td>1.76</td>
<td>1.98</td>
<td>540.6</td>
</tr>
<tr>
<td>calculated</td>
<td>1′Σ+</td>
<td>1</td>
<td>1.79</td>
<td>1.98</td>
<td>538.5</td>
</tr>
<tr>
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<td>2.34</td>
<td>1.98</td>
<td>508.5</td>
</tr>
<tr>
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<td>526.1</td>
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<td>496.4</td>
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<td>3.58</td>
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</tr>
<tr>
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<td>4.24</td>
<td>2.03</td>
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<td>1.98</td>
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<td>observed</td>
<td>[17.7]1</td>
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<td>2.19</td>
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<td>0</td>
<td>2.20</td>
<td>1.95</td>
<td>520.523</td>
</tr>
</tbody>
</table>

* Calculated states from ref.12. b Observed states from this work. c Term energy of ν = 0 level. d Bond length of ν = 0 level. e Value of ΔGΩ=2 determined by the position of the (1,0) band R head recorded using a lower resolution pulsed laser.
to higher energy. This pattern is opposite of that found for the [17.7]1 state,\textsuperscript{14} and it implies that the Hund’s case (c) magnetic hyperfine parameter is positive, $h_1 > 0$. The sign of this quantity is consistent with an assignment of the state as $^{3}\Sigma^+_1$\textsuperscript{14} but where the Hund’s case (a) label has limited meaning.

Conclusions

We have characterized three excited electronic states of AuF by recording electronic transitions from the ground $^{1}\Sigma^+$ state by laser excitation spectroscopy. The two upper states of the yellow bands had been previously observed,\textsuperscript{1,2} but we have now analyzed their rotational structure. The [14.0]1 state has been identified and analyzed in this work for the first time. By least-squares fitting an effective Hamiltonian to the observed transitions, we have determined accurate values for the vibrational, rotational, and $\Omega$-doubling constants. The electronic configurations from which these excited states are derived have been described.

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Supporting Information Available: Observed and calculated wavenumbers and assignments for all measured bands. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes


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