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Confirmation of the Existence of Gold(I) Fluoride, AuF: Microwave Spectrum and Structure

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This communication reports the microwave spectrum of gold(I) fluoride, AuF, prepared by laser ablation of Au metal in the presence of an F precursor, and observed using a cavity pulsed jet Fourier transform microwave spectrometer. The $J = 1-0$ transition has been measured for molecules in the ground and first excited vibrational states; its assignment was confirmed from the Au and F hyperfine structure, and by using different F precursors. The equilibrium bond length r_e has been determined.

Historically AuF has been one of the most elusive of all metal halides. At one time it was believed impossible to prepare,[1] and theoretical papers speculating on how it might be observed have been published until quite recently.[2,3] Many theoretical papers have appeared which predict spectroscopic and structural properties.[2−8] These calculations are complicated by the need to include relativistic effects.

Experimental evidence is very sparse and largely unconfirmed. Rice and Beattie suggested they had observed AuF emission when Au wire was exploded in F_2.[9] Saenger and Sun vibrationally resolved yellow emission bands while etching gold films in the presence of O_2/SF_6 or O_2/CF_4 mixtures; they attributed these to AuF, and evaluated from them a vibrational frequency, among other constants.[10] They were unable to rule out AuF^+ and AuO^+ as the cause of the bands; however, subsequent theoretical work has suggested that AuF is indeed the source.[5] This work also prompted speculation that AuF could be prepared in a thermal plasma torch using Au, CF_4, and O_2 in an Ar or He diluent.[3] Finally, Schröder et al. found a signal due to AuF^+ in a neutralization−reionization mass spectrometric experiment, which they attributed to ionization of AuF. They estimated a lifetime >25 μs for AuF and indirectly estimated a bond dissociation energy of ∼290 kJ mol^{-1}.[11] There has been no prior confirmed direct observation of AuF itself or direct measurement of its structural properties.

The present experiments were carried out with a Balle-Flygare type[12] cavity pulsed jet Fourier transform microwave spectrometer, which has been described in detail elsewhere.[13] Samples entrained in pulsed jets of noble gas are injected from a pulsed nozzle mounted in one of the mirrors of a Fabry−Perot cavity cell. Since the directions of the jet and of microwave propagation are parallel, all lines are doubled by the Doppler effect. Line widths for AuF were ∼7−10 kHz. Line frequencies were obtained from the average of the two Doppler components, and are estimated to be accurate to better than ±1 kHz. The microwave synthesizer is referenced to a Loran C frequency standard and is accurate to 1 part in 10^{10}.

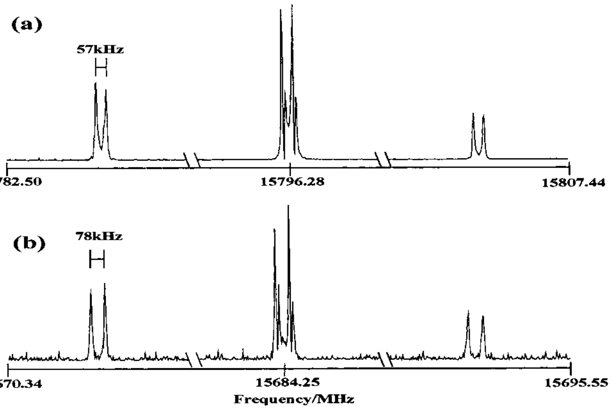

Figure 1. (a) A composite of the hyperfine structure of the $J = 1-0$ transition of AuF in the $v = 0$ vibrational state. Experimental conditions: 0.1% SF_6 in argon; backing pressure 5−7 bar; microwave pulse width 0.8 μs; average number of pulses 250. (b) A composite of the hyperfine structure of the $J = 1-0$ transition of AuF in the $v = 1$ vibrational state. Experimental conditions: 0.1% SF_6 in neon; backing pressure 5−7 bar; microwave pulse width 0.8 μs; average number of pulses 2500.

A piece of gold foil wrapped round a glass rod, and held at the nozzle outlet, was irradiated with a frequency-doubled Nd:YAG laser (532 nm, ∼5−10 mJ/pulse) in the presence of 0.1% of an F precursor in a noble gas (stagnation pressure 5−7 bar). Both SF_6 and CF_3I were used as the F precursor; SF_6 gave the stronger signal. The noble gas used was Ar or Ne for the ground or first excited vibrational state, respectively. Strong AuF lines were easily seen with 50 pulses.

Only the $J = 1-0$ transition was available in the frequency range of the spectrometer. Its frequency was initially predicted from the ab initio bond lengths and vibration frequencies in ref 2, scaled by comparison with the differences between predicted and experimental values for AuCl and AuBr.[14] Ground-state lines were found within 30 MHz of the prediction. A value for α_e was initially estimated from the trends between the Au and Ag halides.

The observed transitions are depicted in Figure 1, for both the ground and first excited vibrational states. They show ^{197}Au hyperfine structure with ^{19}F structure superimposed. Their assignment to AuF was confirmed by the use of two different precursors, and by the disappearance of the signal when the laser was turned off and/or the precursor was absent. The line frequencies and derived constants are listed in Table 1; in the fit the line frequencies were weighted according to the inverse squares of their predicted relative intensities. The constants include rotational constants, ^{197}Au quadrupole coupling constants, and both ^{197}Au and ^{19}F nuclear spin-rotation coupling constants for each vibrational state. Since only the $J = 1-0$ transition was obtainable, the rotational constants will be systematically too small because of neglect of centrifugal distortion (up to ∼0.014 MHz, from ab initio estimates[5]). Table 1 also contains the equilibrium rotational constant, B_e, and the vibration−rotation constant, α_e, derived from the observed constants using the equation $B_v = B_e - \alpha_e(v + {}^1/_2)$.

The equilibrium AuF bond length, r_e, has been obtained from the rotational constants. Its value is also in Table 1. The

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Table 1. Observed Frequencies and Molecular Constants for AuF in the $v = 0$ and 1 Vibrational States (in MHz[a])

$J'-J''$	$F_1'-F_1''$ [b]	$F'-F''$	$v = 0$	obs − calc	$v = 1$	obs − calc
1−0	$^3/_2-^3/_2$	2−2	15783.0035	3.4[c]	15670.8423	3.5[c]
	$^3/_2-^3/_2$	2−1	15783.0035	3.4	15670.8423	3.5
	$^3/_2-^3/_2$	1−1	15783.0035	−5.4	15670.8423	−5.6
	$^3/_2-^3/_2$	1−2	15783.0035	−5.4	15670.8423	−5.6
	$^5/_2-^3/_2$	3−2	15796.2828	0.0	15684.2549	0.0
	$^5/_2-^3/_2$	2−1	15796.3026	0.0	15684.2753	0.0
	$^5/_2-^3/_2$	2−2	15796.3026	0.0	15684.2753	0.0
	$^1/_2-^3/_2$	1−2	15806.9715	−2.8	15695.0528	−2.8
	$^1/_2-^3/_2$	1−1	15806.9715	−2.8	15695.0528	−2.8
	$^1/_2-^3/_2$	0−1	15806.9715	8.3	15695.0528	8.5

parameters	AuF ($v = 0$)	AuF ($v = 1$)
B_v	7896.81976(47)	7840.79272(47)
eQq(Au)	−53.2344(67)	−53.7722(67)
C_I(Au) × 10^3	−7.85(52)	−8.19(52)
C_I(F) × 10^3	−16.5(17)	−17.0(17)

	equilibrium constants
B_e	7924.83328(57)
α_e	56.02704(66)
r_e/Å	1.918449(5)[d]

[a] Numbers in parentheses are one standard deviation in units of the last significant figure. [b] Coupling scheme: $\mathbf{F_1 = J + I_{Au}}$, $\mathbf{F = F_1 + I_F}$. [c] Residuals in kHz. [d] This r_e value is taken from the B_e given, and the uncertainty given reflects those of the fundamental constants, atomic masses, and rotational constants. Inclusion of γ_e and centrifugal distortion could decrease its value by as much as 0.000015 Å.

uncertainty given is estimated from those in the atomic masses, fundamental constants, and rotational constants. Inclusion of effects of centrifugal distortion and of the higher order vibration−rotation constant γ_e could decrease its value by up to 1.5×10^{-5} Å. Our r_e value is close to, but smaller than, almost all published ab initio predictions; the closest predictions have been relativistic MP2 calculations (1.922 Å,[5] 1.90 Å,[8] and 1.899 Å[6]).

Perhaps the most remarkable feature of the spectrum is its regularity. It is strong and easy to generate, and the line widths do not indicate a particularly short-lived species. Evidently ideal conditions for the preparation have been found: a plasma of Au with SF_6 (or CF_3I) precursor in a large quantity of noble gas. This is very similar to what was predicted in ref 3, though without O_2. Similarly, the supersonic jet, in which the samples are in a collision-free environment, seems the perfect way to stabilize it. The mass spectrometric experiments of ref 11 suggested a lifetime of at least 25 μs; our line widths extend this to over 100 μs.

The regularity extends to the rotational constants and structure. Correct rotational constants were obtained by adjusting ab initio values using comparisons with other coinage metal halides. The value of α_e was well predicted by comparison with other molecules; its ab initio value is within 2 MHz of the experimental value.[5] The relative intensities of the two vibrational states are consistent with $\omega_e \sim 500$ cm^{-1}.[3,10] On the other hand, the hyperfine constants show unusual features. The ^{197}Au quadrupole coupling constant is negative, in contrast to the values for AuCl and AuBr,[14] and could not be reproduced with a preliminary ab initio calculation. The spin-rotation constants are both negative, again an unusual feature. Though negative ^{19}F constants are not unknown,[15] spin-rotation constants are difficult to account for quantitatively. These results present a new challenge for further ab initio calculations.

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