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Nicholas R Walker, Simon G Francis, Steven L Matthews, Joshua J Rowlands, Anthony C Legon. Microwave Spectrum and Structure of Carbonyl Gold Iodide, OCAuI.. *Molecular Physics*, 2007, 104 (20-21), pp.3329-3337. 10.1080/00268970601110332 . hal-00513062

HAL Id: hal-00513062

<https://hal.science/hal-00513062>

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Journal:	<i>Molecular Physics</i>
Manuscript ID:	TMPH-2006-0049.R1
Manuscript Type:	Full Paper
Date Submitted by the Author:	26-Oct-2006
Complete List of Authors:	Walker, Nicholas; University of Bristol, School of Chemistry Francis, Simon; University of Bristol, School of Chemistry Matthews, Steven; University of York, Department of Chemistry Rowlands, Joshua; University of Bristol, School of Chemistry Legon, Anthony; University of Bristol, School of Chemistry
Keywords:	gold iodide, metal carbonyl , metal halide , laser ablation, microwave spectrum

Molecular Physics

Microwave Spectrum and Structure of Carbonyl Gold Iodide, OCAuI.

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Abstract

Carbonyl gold iodide, OCAuI, is generated in the gas phase through synchronising the laser ablation of a gold [sample](#) with the pulsed, supersonic expansion of gas containing carbon monoxide and an iodine precursor. Fourier Transform microwave (FT-MW) spectroscopy has been used to detect and assign lines in the pure rotational spectrum of the molecule. The frequencies of lines in the spectra of three isotopomers are presented and used to determine rotational, centrifugal distortion and hyperfine coupling constants through iterative least-squares fitting. Rotational constants, B_0 , of the three isotopomers allow a determination of the r_0 molecular geometry. The structure is linear. The bond lengths are consistent with previous studies of OCMX [complexes](#) (M=Cu, Ag, Au; X=F, Cl, Br, I). The frequency of the lowest energy vibrational stretching mode is estimated from the centrifugal distortion constant of the $^{16}\text{O}^{12}\text{CAuI}$ isotopomer. The nuclear quadrupole coupling constants of both iodine, χ_{aa}^{I} , and gold, χ_{aa}^{Au} , have been determined. The ionic character of the Au-I bond is calculated using χ_{aa}^{I} . Nuclear shielding parameters for OCAuI and other OCAuX species are determined from the measured nuclear spin-rotation constants, C_{bb}^{M} and C_{bb}^{X} .

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1. Introduction

The structural changes that occur when a metal atom binds to carbon monoxide provide insight into the nature of the bonding between the two species. Studies describe the production of salts containing $\text{Au}(\text{CO})^+$ and $\text{Au}(\text{CO})_2^+$ in the presence of a weakly-coordinating anion [1,2,3]. The latter complex is notable for a C-O stretching frequency of 2231 cm^{-1} which is the average of observations in different solvation environments [2]. This is greater than the value obtained from free CO (2143 cm^{-1}) suggesting a comparatively short C-O bond with only a very small contribution from $\sigma \rightarrow \pi^*$ back donation in this complex. Although synthesis of OCAuCl was reported in 1930 [4], very few other complexes containing a gold-carbonyl bond have been isolated in the condensed phase. Gerry and co-workers measured and assigned the spectra of gas phase OCCuX [5], OCAgX [6] and OCAuX [7] (where $X=\text{F}$, Cl and Br) obtaining rotational and hyperfine coupling constants for the molecules in each case. It was shown that these complexes typically have C-O bonds shorter and M-C bonds (where M is a metal atom) longer than those in other metal carbonyl complexes [2]. The recent study by Legon and co-workers [8] provided details of OCCuI and established the trend with respect to the heavier halogen atoms. This study presents a further opportunity to examine bonding between a carbonyl group and a metal atom in a compound not previously characterised in either condensed or gas phases.

The microwave spectrum of carbonyl gold iodide, OCAuI , is presented herein. The molecular geometry is determined by assigning rotational transitions in the microwave spectra of three isotopomers of the molecule. The centrifugal distortion constant, D_J , nuclear quadrupole coupling constants, χ_{aa}^{Au} and χ_{aa}^{I} and nuclear spin-rotation constant of iodine, C_{bb}^{I} have all been determined. The structural trends

identified in previous studies of OCMX [5,6,7,8] (where X now includes I in addition to F, Cl and Br) are re-examined with reference to data from the OCAuI molecule. A further motivation is provided by the opportunity to measure the large hyperfine splittings and coupling constants expected in this molecule. It has previously been shown that the nuclear quadrupole coupling constant of gold, χ_{aa}^{Au} , changes substantially on attaching carbon monoxide to the gold halide unit [7]. It is shown that both χ_{aa}^{Au} and χ_{aa}^{I} in OCAuI are significantly greater in magnitude than B_0 so treatment of these nuclear quadrupole coupling constants using perturbation theory would definitely not yield accurate predictions. It is shown here that the greatest fractional change in χ_{aa}^{Au} occurs where the halogen atom in the molecule is iodine.

2. Experimental

The experimental apparatus comprises a laser-vaporisation and supersonic-nozzle source coupled to a Balle-Flygare, Fourier-transform microwave spectrometer. The microwave spectrometer is described in several previous papers [8-10]; therefore only a brief description will be provided here. The cavity consists of two spherical aluminium mirrors (diameter = 35 cm; radius of curvature = 84 cm) separated by approximately 70 cm. A gold target was prepared by wrapping gold foil around a glass rod. The gas sample was passed over the surface of the target while material was ablated using the second harmonic of a pulsed Nd:YAG laser operating at 2 Hz. The target was continuously rotated and translated in order to expose a fresh gold surface to every laser pulse. The composition of the gas sample was optimised to ensure the greatest signal intensities for spectral lines of OCAuI. These were achieved in a sample of ~0.5% CH₃I and 2% CO in argon. The sources of CH₃I and CO used were each 99% pure. Isotopically-enriched samples of ¹⁶O¹³C (MSD Isotopes, Inc.) and

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$^{18}\text{O}^{12}\text{C}$ ([Cambridge Isotopes, Inc.](#)) were used to permit the study of different isotopomers. Subsequent to the plasma generation by laser ablation, the gas sample undergoes supersonic expansion into the Fabry-Perot cavity through an orifice in the centre of the stationary mirror.

The parallel propagation of the gas and microwave pulses enhances the resolution and sensitivity of the instrument but also increases the well-known Doppler splitting of each hyperfine component so that two peaks are observed for each spectral transition. The line frequency was determined by finding the average of the frequencies of the two Doppler components. Molecules are excited to higher rotational states by the microwave pulse if the transition from the lower state is resonant or nearly resonant with the radiation and subsequently undergo relaxation by spontaneous coherent emission at the transition frequency. The free induction decay is detected and Fourier-transformed to yield a plot of emission intensity against frequency. The experimental cycle described above was repeated and averaged as necessary to obtain a satisfactory signal-to-noise ratio for measured lines. All frequency measurements were referenced to an external source ([Symmetricom 58533A, GPS time and frequency reference receiver](#)) that is accurate to 1 part in 10^{12} . Individual hyperfine components have a full width at half height of 5 kHz and their frequencies were consequently measured with an estimated accuracy of ± 0.5 kHz.

3. Results and Discussion

3.1 Spectroscopic Analysis

The nuclear spin quantum numbers (I) of ^{197}Au and ^{127}I are $3/2$ and $5/2$, respectively, yielding extensive hyperfine structure in the rotational spectrum of

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OCAuI. Pickett's program SPFIT [11] was used to fit the measured line frequencies to the model rotational Hamiltonian shown below using iterative least-squares analysis;

$$H = H_R - \frac{1}{6} \mathbf{Q}(\text{I}) : \nabla \mathbf{E}(\text{I}) - \frac{1}{6} \mathbf{Q}(\text{Au}) : \nabla \mathbf{E}(\text{Au}) + \mathbf{I}_I \cdot \mathbf{C}^I \cdot \mathbf{J} \quad (1)$$

H_R is the Hamiltonian appropriate to the semi-rigid linear rotor. The next term describes the coupling of the iodine nucleus to the framework angular momentum, $\mathbf{J}$, through interaction of the nuclear electric quadrupole moment, $\mathbf{Q}(\text{I})$, with the electric field gradient at the iodine nucleus, $\nabla \mathbf{E}(\text{I})$. A similar term describes the equivalent interaction with respect to the gold nucleus. The magnetic (spin-rotation) coupling of $\mathbf{I}_I$ to $\mathbf{J}$ for the iodine nucleus yields a small frequency shift in existing components but no additional hyperfine structure. The contribution of the spin-rotation term for iodine, $\mathbf{I}_I \cdot \mathbf{C}^I \cdot \mathbf{J}$, to transition frequencies was accurately determined in fits to data acquired from every isotopomer. Fitting a Hamiltonian containing the spin-rotation constant of the gold nucleus yielded an uncertainty larger than the evaluated parameter. This effect was therefore excluded from the analysis.

The coupling scheme $\mathbf{J} + \mathbf{I}_I = \mathbf{F}_I$; $\mathbf{F}_I + \mathbf{I}_{\text{Au}} = \mathbf{F}$ was used to construct the matrices of H in the symmetric rotor basis and this is reflected in the assignment of quantum numbers to rotational transitions for each isotopomer studied. The frequencies of assigned transitions were fitted to the model Hamiltonian yielding values for rotational constants, B_0 and D_J , nuclear quadrupole coupling constants, χ_{aa}^{Au} and χ_{aa}^{I} , and the nuclear spin-rotation constant of the iodine nucleus, C_{bb}^{I} , for each isotopomer. The evaluated parameters are shown in Table 1. A full list of the measured line frequencies (ν_{obs}), assignments, and residuals ($\nu_{\text{obs}} - \nu_{\text{calc.}}$) are provided in appendix 1. The $\sigma_{\text{r.m.s}}$ of ~0.5 kHz obtained for each fit is of the same order of magnitude as the

estimated uncertainty in line measurements, indicating that the Hamiltonian given above is sufficient to describe the molecule given the experimental precision. Gold and iodine each possess only one stable isotope while carbon monoxide is available commercially in several isotopic combinations. Fits were therefore performed to data acquired from three isotopomers, each distinguished by the mass of either the carbon or oxygen atom; $^{16}\text{O}^{12}\text{CAuI}$, $^{18}\text{O}^{12}\text{CAuI}$ and $^{16}\text{O}^{13}\text{CAuI}$.

3.2 Interpretation of rotational and centrifugal distortion constants

No previous reports describe the experimental generation of OCAuI nor predict its molecular geometry. The structure initially assumed for the $^{16}\text{O}^{12}\text{CAuI}$ isotopomer was predicted from trends identified in earlier experiments on OCAuX (X=F, Cl, Br) [7]. These allowed an estimate of the rotational constant of the molecule, B_0 . A search for lines in the rotational spectrum of the molecule was performed. The first lines assigned to OCAuI were identified ~70 MHz from the starting point of the search. These required both the laser ablation plasma and carbon monoxide in the gas sample for signals to be observed. An example of the line intensity and resolution obtained during the experiments is shown in Figure 1. Hyperfine components were identified and assigned for several different $J'-J''$ transitions.

A preliminary determination of the molecular structure allowed lines in the spectra of two isotopically substituted species, $^{16}\text{O}^{13}\text{CAuI}$ and $^{18}\text{O}^{12}\text{CAuI}$, to be identified and assigned. The corresponding moments of inertia were used to calculate r_0 bond lengths using the STRFIT program [12]. These r_0 bond distances are defined with respect to $v=0$ moments of inertia in the same way that r_e data are obtained from equilibrium moments of inertia. Given that three data (each rotational constant) are

used to determine three parameters (each bond length), the result is actually a calculation rather than a fit so no standard deviation can be associated with the result. Data were acquired from only the ground vibrational state of each isotopomer thus precluding determination of the r_e structure in each case. Other methods of structural determination are not available owing to the absence of data from other isotopomers and vibrational states. The results of the structural calculations are shown in Table 2 and compared with data from the other carbonyl gold halides studied previously. The rotational constants obtained by fitting the spectra of the three isotopomers examined during this study are consistent with a linear geometry. However, a quasi-linear geometry with a low barrier to the linear form cannot be excluded from possibility. The trend in rotational constants confirms that the only physically reasonable order of atoms is OCAuI, consistent with the structures of all other OCMX species studied by microwave spectroscopy.

The r_0 distance between the gold and iodine atoms in OCAuI is calculated to be very similar to the r_e bond distance in the free diatomic molecule, AuI [13]. A similar trend has been identified in the OCMX molecules studied previously [5,8]. The M-C distance in OCAuI is ~ 0.02 Å longer than the same quantity in OCAuBr. This is consistent with a similar increment observed in the equivalent parameter between OCCuI and OCCuBr. As with the copper- and silver-containing analogues, the C-O distance in the complexes is seen to decrease incrementally with increasing mass of the halogen atom on descending Group 17. The change observed in the C-O distance between OCAuBr and OCAuI is similar to that seen in the equivalent complexes containing copper. As a consequence of relativistic effects [14], the M-C distance in all the various complexes containing gold is shorter than the M-C distance in each of the corresponding complexes of silver.

An earlier report on OCAuF, OCAuCl and OCAuBr used experimentally-measured rotational and centrifugal distortion constants to predict the frequencies of vibrational stretching modes [7]. The results of these predictions were then compared with those yielded by *ab initio* calculations using an MP2 method. The frequency predicted using experimental data obtained from OCAuF was found to be in very good agreement with that calculated theoretically for the Σ^+ CAu stretching mode. In contrast, data obtained from both OCAuCl and OCAuBr gave very poor agreement with the frequency of the Σ^+ CAu mode but much better agreement with the frequency of the Σ^+ AuX stretching mode. This difference in behaviour can be rationalised by examining the diatomic approximation used to estimate the vibrational stretching frequency from the experimental data.

The diatomic approximation assumes that a given molecular unit consists of two distinct, rigid units connected by a bond. The following expression can be used to calculate the frequency of the vibrational stretching mode of the unit [15];

$$\omega \approx \left(\frac{4B_0}{D_J} \right)^{\frac{1}{2}} \quad (2)$$

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The approximation is most appropriate and useful where a molecule (for example, Ar-HF) is known to contain one bond that is considerably weaker than all others. This is not necessarily true of the OCAuX species examined here and previously. It is informative to compare the magnitudes of the frequencies calculated *ab initio* for the Σ^+ AuX and Σ^+ CAu stretching motions in OCAuF, OCAuCl and OCAuBr [7]. While the frequency of the Σ^+ CAu stretch is lower than that of the Σ^+ AuX stretch in OCAuF, this order is reversed in OCAuCl and OCAuBr. Good agreement between the *ab initio* calculation and the result using the diatomic approximation can be seen for the Σ^+ CAu stretch in OCAuF. Agreement with the Σ^+ AuX stretch is achieved for the

chloride and the bromide. The lowest frequency stretching vibration of OCAuI is estimated to be 228 cm^{-1} during this work. Consistent with the earlier work on OCAuX, this is assumed to arise from the Σ^+ AuI stretching motion. The result is presented in Table 2 for comparison with those provided in earlier works.

Deleted: The lowest frequency stretching vibration is estimated to be 228 cm^{-1} for OCAuI where it is assumed to arise from the Σ^+ AuI stretching motion. This result is presented in Table 2 for comparison with those provided in earlier works. A high degree of accuracy is not expected because the centrifugal distortion constant in Eqn. 2 does not unambiguously distinguish the contributions of different bonds within the molecule to the overall vibrational motion. The approximated stretching frequencies for the OCAuX species are observed to decrease on descending Group 17 in agreement with the increasing mass of the halogen atom, X. ¶

3.3 Nuclear quadrupole coupling constants

The nuclear quadrupole coupling constants of the gold and iodine atoms, χ_{aa}^{Au} and χ_{aa}^{I} , are 78.3 and -1707.9 MHz respectively in diatomic AuI [13]. A significant change in both the sign and magnitude of χ_{aa}^{Au} occurs when CO attaches to AuI yielding a value of -981.038 MHz for this parameter [7]. Although the change in the quantity is greater than those in the OCAuX complexes containing the other halogen atoms, the absolute value of χ_{aa}^{Au} is actually smaller than the equivalent parameter for OCAuF, OCAuCl and OCAuBr. The value of χ_{aa}^{I} on addition of CO to AuI is -961.273 MHz, comparable in magnitude to χ_{aa}^{Au} for OCAuI. As a consequence of the substantial nuclear quadrupole coupling constants for both the gold and iodine atoms, the spectrum contains hyperfine structure in which each $J'-J''$ transition is spread over a very broad frequency range. Hyperfine components in the $J=7-6$ transition are of sufficient intensity to be measured and assigned over a 50 MHz frequency interval. Changes in χ_{aa}^{Au} and χ_{aa}^{X} on attachment of CO to AuX occur in all the other carbonyl gold halide complexes studied previously but are greatest in OCAuI. The values of χ_{aa}^{M} and χ_{aa}^{X} are also changed by attaching CO to the various CuX and AgX species studied [5,6,8] but the fractional changes are small in comparison with those seen in the corresponding gold-containing analogues.

The nuclear quadrupole coupling constants can be used to estimate the ionic character (i_c) of the Au-X bond [16] through Eqn. (3);

$$i_c = 1 + \left\{ \frac{\chi_{aa}^X}{eQq_{n,l,0}(X)} \right\} \quad (3)$$

where $\chi_{aa}^X = eQq_{aa}(X)$ is the experimentally-measured nuclear quadrupole coupling constant of a given molecule and $eQq_{n,l,0}(X)$ is the coupling constant that would result from a single np_z electron in the isolated halogen atom. Values [17] for $eQq_{n,l,0}(X)$ of 109.74 MHz, -769.62 MHz and 2292.44 MHz for $X = {}^{35}\text{Cl}$, ${}^{79}\text{Br}$ and ${}^{127}\text{I}$ respectively were used with the experimental measurements of χ_{aa}^X to calculate the results presented in table 3. The attachment of CO to AuX is found to increase the ionic character of the AuX bond by 0.23, 0.26 and 0.32 where $X = \text{Cl}$, Br and I respectively. This trend corresponds with another that defines the change in Au-X bond length on attachment of AuX to CO. The Au-X internuclear distance increases by 0.0182 Å, 0.0197 Å and 0.030 Å where $X = \text{Cl}$, Br or I respectively. The data of Evans *et al.* show that attaching CO to AuF results in a shorter bond between the gold and halogen atoms [7]. As reported in another earlier work, the Cu-F distance is also observed to decrease on attaching CO to CuF [5]. Based on this evidence and the above trends in ionic character and bond length it has been suggested that CuF might have higher ionic character than OCCuF [8]. It is possible to extend this hypothesis from the data presented here to suggest that AuF has higher ionic character than OCAuF. The consistency of the trends in bond length and ionic character for the various OCMX species is very satisfying.

3.4 Nuclear spin-rotation constants

Table 4 compares all nuclear spin-rotation constants evaluated during studies of OCAuX where X=F, Cl, Br or I. Earlier experiments on the fluoride and chloride yielded precise values for C_{bb}^{Au} but only a value for C_{bb}^{Br} was obtained from experiments on the bromide [7]. This is consistent with the results obtained from OCAuI during this work. The nuclear spin-rotation constant of iodine is precisely determined in the present fits but the equivalent parameter for gold could not be obtained.

Nuclear spin-rotation constants determined during the earlier study of OCCuX were used to provide nuclear shielding parameters for the Cu nucleus in each molecule [5]. The data presented here and data provided earlier by Evans *et al.* [7] permit the same information to be presented for all OCAuX species. For OCAuF and OCAuCl, the values determined for C_{bb}^{Au} are used to establish the properties of the gold nucleus in each molecule. No data are available for the gold nucleus in both OCAuBr and OCAuI. For this reason, the nuclear spin-rotation constants of the halogen atom are used to evaluate nuclear shielding parameters in the bromide and the iodide. The experimentally determined C_{bb} values are comprised of contributions from electronic and nuclear components [18];

$$C_{bb} = C_{bb}(\text{elec.}) + C_{bb}(\text{nucl.}) \quad (4)$$

and $C_I(\text{nucl.})$ can be calculated from the molecular geometry by

$$C_{bb}(\text{nucl.}) = -\left(\frac{2e\mu_N g_I B}{hc}\right) \sum_{i \neq A} \left(\frac{Z_i}{r_{Ai}}\right) \quad (5)$$

where e is the proton charge, μ_N is the nuclear magneton, g_I is the g factor for nucleus

A. The rotational constant is B while Z_i is the atomic number of nucleus i , located a

distance r_{Ai} from nucleus A. The value of $C_{bb}(\text{elec.})$ can be obtained by subtracting the result for $C_{bb}(\text{nucl.})$ given by eqn. 3 from the experimentally determined value for C_{bb} . All of these results are presented in Table 4.

The average shielding is the sum of contributions from paramagnetic, σ_p , and diamagnetic, σ_d , components;

$$\sigma = \sigma_p + \sigma_d \quad (6)$$

$C_{bb}(\text{elec.})$ is related to σ_p by Eqn. (7);

$$\sigma_p = -\left(\frac{m_p}{3mg_I B}\right) C_{bb}(\text{elec.}) \quad (7)$$

where m_p and m are the masses of the proton and electron respectively. A similar expression is used to determine σ_d ;

$$\sigma_d = -\left(\frac{m_p}{3mg_I B}\right) C_{bb}(\text{nucl.}) + \sigma_d(\text{atom}) \quad (8)$$

where $\sigma_d(\text{atom})$ is the free atom diamagnetic shielding available in tables [19] as 9533 ppm for Au, 3091 ppm for Br and 5488 ppm for I. The span, Ω , of the components of the shielding tensor parallel, $\sigma_{\parallel}$, and perpendicular, $\sigma_{\perp}$, to the molecular axis can also be determined [20]. The span is defined by $\Omega = \sigma_{\parallel} - \sigma_{\perp}$ and can be obtained from the experimental spin-rotation constants as follows;

$$\Omega = \left(\frac{m_p}{2mg_I B} \right) C_{bb} \quad (9)$$

The results for C_{bb} (nucl.), C_{bb} (elec.), σ_p , σ_d , σ and Ω are shown in Table 4 for the gold atom in OCAuF and OCAuCl, the bromine atom in OCAuBr and the iodine atom in OCAuI. [The \$\Omega\$ and \$\sigma\$ parameters evaluated for the halogen nuclei in OCAuBr and OCAuI are both significantly lower than those determined for the gold nuclei in OCAuF and OCAuCl, respectively. This trend is consistent with the greater number of electrons available to shield the nucleus in the gold atom.](#)

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5. Conclusions

Carbonyl gold iodide has been generated by laser ablation in conjunction with supersonic expansion and identified through assignment of its rotational spectrum. Data acquired from three isotopomers has been used to determine rotational, centrifugal distortion and nuclear hyperfine coupling constants. The rotational constants have permitted a determination of the r_0 molecular structure. The geometry is linear and the order of atoms is O-C-Au-I. The C-O distance is observed to be shorter than in complexes containing the lighter halogen atoms while the M-C distance is longer. An estimate of the lowest frequency vibrational stretch of the molecule has been made using the centrifugal distortion constant measured experimentally. Analysis of the nuclear quadrupole coupling constants has shown that the complex has more ionic character than the AuX monomer. Calculation from the experimentally-determined nuclear spin-rotation coupling constants has allowed

nuclear shielding parameters to be provided for various nuclei in all OCAuX species
(X=F, Cl, Br, I).

Acknowledgments

The authors thank the Engineering and Physical Sciences Research Council
for supporting this work. NRW thanks the Royal Society for the award of a Royal
Society University Research Fellowship.

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Figure Caption**Figure 1**

A hyperfine component in the $J'-J''=7-6$ rotational transition after 1300 averaging cycles. The quantum number assignment is $F_1'-F_1''$, $F'-F''$.

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Figure 1

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Table 1

	$^{16}\text{O}^{12}\text{CAuI}$	$^{16}\text{O}^{13}\text{CAuI}$	$^{18}\text{O}^{12}\text{CAuI}$
B_0 / MHz	621.434676(115) ^a	616.282355(84)	600.859744(65)
$D_J \times 10^5 / \text{MHz}$	2.051(130)	1.977(74)	1.845(58)
χ_{aa}^I / MHz	-961.273(50)	-961.031(26)	-961.065(24)
$\chi_{aa}^{\text{Au}} / \text{MHz}$	-981.038(47)	-981.570(23)	-981.317(33)
$C_{bb}^I \times 10^3 / \text{MHz}$	0.73(16)	0.58(11)	0.51(10)
N	24	37	48
$\sigma_{\text{r.m.s}} / \text{kHz}$	0.66	0.47	0.57

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[figure.](#)

Table 2

	OCAuX				AuX
	$r_{\text{O-C}} / \text{\AA}$	$r_{\text{C-Au}} / \text{\AA}$	$r_{\text{Au-X}} / \text{\AA}$	ν / cm^{-1}	$r_{\text{Au-X}}^{\text{a}}$
OCAuF ^{b,c}	1.134	1.847	1.909	516	1.918
OCAuCl ^b	1.132(2)	1.884(2)	2.2172(6)	406	2.199
OCAuBr ^b	1.132(1)	1.892(2)	2.3377(5)	292	2.318
OCAuI ^c	1.131	1.908	2.501	228	2.471 ^d

^a $r_{\text{O-C}}$, $r_{\text{C-Au}}$ and $r_{\text{Au-X}}$ distances in OCAuX are r_0 . The $r_{\text{Au-X}}$ distance in AuX is r_e .

^b Values given in ref. [7].

^c Isotopic substitutions for fluorine and iodine are not available so determination of bond distances in OCAuF and OCAuI involves exact calculation rather than fitting.

^d Value given in ref. [13].

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Table 3

X	χ_{aa}^M / MHz		χ_{aa}^X / MHz		Ionicity ^a , i_c		Δr / Å
	AuX	OCAuX	AuX	OCAuX	AuX	OCAuX	
F ^b	-53.31	-1006.3	-	-	-	-	-0.009
Cl ^b	9.633	-1026.0	-61.99	-36.39	0.44	0.67	+0.0182
Br ^b	37.26	-999.1	492.3	285.09	0.38	0.64	+0.0197
I	78.27 ^d	-981.0 ^c	-1707.9 ^d	-961.3 ^c	0.26	0.58	+0.030

^a Calculated from Eqn. 3 using values for $eQq_{n,l,o}(X)$ provided in ref. [17].

^b Values given in ref. [7].

^c This work.

^d Value given in ref. [13].

Table 4

	OCAuF (Au)	OCAuCl (Au)	OCAuBr (Br)	OCAuI (I)
C_{bb} / kHz	1.07(16) ^a	0.86(13) ^a	0.77(16) ^a	0.73(16) ^b
C_{bb} (nuc.) / kHz	-0.033	-0.029	-0.69	-0.369
C_{bb} (elec.) / kHz	1.100	0.884	1.46	1.099
σ_p / ppm	-3344(500)	-3899(590)	-730(152)	-962(211)
σ_d / ppm	9633	9660	3436	5811
σ / ppm	6289	5761	2706	4849
Ω / ppm	4866(728)	5658(855)	577(120)	958(210)

^a Values given in ref. [7].

^b This work.

MEASURED TRANSITIONS FOR $^{16}\text{O}^{12}\text{CaI}$, $^{16}\text{O}^{13}\text{CaI}$ AND $^{18}\text{O}^{12}\text{CaI}$

$J_u \rightarrow J_l$	$F_u \rightarrow F_l$	$F_u \rightarrow F_l$	Frequency / MHz $^{16}\text{O}^{12}\text{CAuI}$	o-c / kHz	Frequency / MHz $^{16}\text{O}^{13}\text{CAuI}$	o-c / kHz	Frequency / MHz $^{18}\text{O}^{12}\text{CAuI}$	o-c / kHz
$6 \rightarrow 5$	$\frac{15}{2} \rightarrow \frac{13}{2}$	$7 \rightarrow 6$	7453.6649	0.0				
	$\frac{17}{2} \rightarrow \frac{15}{2}$	$8 \rightarrow 7$	7453.8432	0.4				
	$\frac{11}{2} \rightarrow \frac{9}{2}$	$7 \rightarrow 6$	7454.4637	0.3				
	$\frac{17}{2} \rightarrow \frac{15}{2}$	$7 \rightarrow 6$	7456.2864	-0.5				
	$\frac{13}{2} \rightarrow \frac{11}{2}$	$7 \rightarrow 6$	7456.4297	-0.6				
	$\frac{15}{2} \rightarrow \frac{13}{2}$	$6 \rightarrow 5$	7456.4384	0.2				
	$\frac{13}{2} \rightarrow \frac{11}{2}$	$6 \rightarrow 5$	7456.48084	0.0				
	$\frac{7}{2} \rightarrow \frac{5}{2}$	$5 \rightarrow 4$	7457.8487	0.5				
	$\frac{13}{2} \rightarrow \frac{11}{2}$	$8 \rightarrow 7$	7461.1834	0.2			7214.2956	-0.2
	$\frac{15}{2} \rightarrow \frac{13}{2}$	$9 \rightarrow 8$	7461.5891	0.1			7214.7098	-0.7
	$\frac{17}{2} \rightarrow \frac{15}{2}$	$10 \rightarrow 9$	7465.3942	0.3			7218.5223	0.6
	$\frac{15}{2} \rightarrow \frac{13}{2}$	$8 \rightarrow 7$	7465.8895	-0.2			7218.9901	0.6
	$\frac{17}{2} \rightarrow \frac{15}{2}$	$9 \rightarrow 8$					7224.9469	-0.2

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7→6	$\frac{11}{2} \rightarrow \frac{9}{2}$	4→3			8606.8308	-0.2	8390.9085	0.1
	$\frac{13}{2} \rightarrow \frac{11}{2}$	5→4			8607.0403	-0.2	8391.1190	-0.3
	$\frac{11}{2} \rightarrow \frac{9}{2}$	6→5			8615.8634	0.1	8399.9381	0.7
	$\frac{13}{2} \rightarrow \frac{11}{2}$	7→6	8688.1748	0.5	8616.0382	0.1	8400.1104	0.8
	$\frac{15}{2} \rightarrow \frac{13}{2}$	6→5			8617.4835	-1.2	8401.5591	0.3
	$\frac{9}{2} \rightarrow \frac{7}{2}$	4→3	8695.4368	0.9	8623.2924	-0.3	8407.3545	0.1
	$\frac{11}{2} \rightarrow \frac{9}{2}$	5→4	8695.7933	-1.6	8623.6617	-0.7	8407.7365	-0.9
	$\frac{9}{2} \rightarrow \frac{7}{2}$	5→4	8696.3291	0.7	8624.1884	1.1	8408.2670	1.0
	$\frac{13}{2} \rightarrow \frac{11}{2}$	6→5	8696.5166	-0.3	8624.3863	-0.9	8408.4660	-0.4
	$\frac{11}{2} \rightarrow \frac{9}{2}$	7→6	8696.7060	-0.8	8624.5817	-0.2	8408.6708	-0.1
	$\frac{19}{2} \rightarrow \frac{17}{2}$	9→8	8697.9810	0.5	8625.8479	0.2	8409.9156	0.4
	$\frac{13}{2} \rightarrow \frac{11}{2}$	8→7	8698.3823	-0.6	8626.2552	-1.0	8410.3418	-0.1
	$\frac{17}{2} \rightarrow \frac{15}{2}$	8→7	8698.5322	0.3	8626.3912	-0.2	8410.4648	-0.2
	$\frac{19}{2} \rightarrow \frac{17}{2}$	8→7			8627.3370	-0.5	8411.4194	0.1
	$\frac{15}{2} \rightarrow \frac{13}{2}$	7→6			8627.4570	-0.2	8411.5375	-0.4
	$\frac{17}{2} \rightarrow \frac{15}{2}$	7→6					8412.3957	-1.5
	$\frac{19}{2} \rightarrow \frac{17}{2}$	7→6			8628.3122	-1.8		
	$\frac{15}{2} \rightarrow \frac{13}{2}$	8→7			8628.3166	-0.4	8412.4012	0.5

	$\frac{9}{2} \rightarrow \frac{7}{2}$	6→5			8628.3655	-0.4	8412.4580	-0.6
	$\frac{15}{2} \rightarrow \frac{13}{2}$	9→8	8703.1584	-0.2	8631.0253	-0.7	8415.1215	0.2
	$\frac{17}{2} \rightarrow \frac{15}{2}$	10→9	8703.8041	1.2	8631.6793	-0.3	8415.7718	0.1
	$\frac{17}{2} \rightarrow \frac{15}{2}$	9→8			8635.3278	-1.0	8419.4150	-0.1
	$\frac{19}{2} \rightarrow \frac{17}{2}$	10→9	8710.8599	0.5	8638.7290	-0.1	8422.8268	0.2
8→7	$\frac{13}{2} \rightarrow \frac{11}{2}$	5→4			9845.2653	0.4	9598.4993	-0.1
	$\frac{15}{2} \rightarrow \frac{13}{2}$	6→5			9846.2235	-0.7	9599.4569	-0.3
	$\frac{13}{2} \rightarrow \frac{11}{2}$	7→6					9605.1684	0.5
	$\frac{15}{2} \rightarrow \frac{13}{2}$	8→7			9852.4116	0.3	9605.6424	0.4
	$\frac{11}{2} \rightarrow \frac{9}{2}$	4→3					9605.8935	-1.3
	$\frac{17}{2} \rightarrow \frac{15}{2}$	7→6			9854.0656	-0.9	9607.2990	-0.2
	$\frac{13}{2} \rightarrow \frac{11}{2}$	6→5			9856.2528	-0.7	9609.4854	-0.3
	$\frac{11}{2} \rightarrow \frac{9}{2}$	5→4			9856.8348	0.1	9610.0598	-0.1
	$\frac{15}{2} \rightarrow \frac{13}{2}$	7→6			9857.0909	-0.6	9610.3278	-0.1
	$\frac{13}{2} \rightarrow \frac{11}{2}$	8→7			9857.9676	0.2	9611.2115	0.1
	$\frac{11}{2} \rightarrow \frac{9}{2}$	6→5			9858.0809	0.5	9611.3183	0.4
	$\frac{21}{2} \rightarrow \frac{19}{2}$	10→9			9859.2026	0.4	9612.4270	0.8
	$\frac{15}{2} \rightarrow \frac{13}{2}$	9→8					9612.6372	-0.5

$\frac{19}{2} \rightarrow \frac{17}{2}$	9→8					9613.0435	-0.9
$\frac{21}{2} \rightarrow \frac{19}{2}$	9→8			9860.0681	0.3	9613.3064	0.2
$\frac{17}{2} \rightarrow \frac{15}{2}$	8→7			9860.1600	0.6	9613.3970	-0.8
$\frac{11}{2} \rightarrow \frac{9}{2}$	7→6					9614.0393	1.3
$\frac{19}{2} \rightarrow \frac{17}{2}$	8→7					9614.4249	1.1
$\frac{17}{2} \rightarrow \frac{15}{2}$	9→8			9861.4070	0.0	9614.6475	-0.1
$\frac{17}{2} \rightarrow \frac{15}{2}$	10→9			9862.8815	0.2	9616.1351	-0.3
$\frac{19}{2} \rightarrow \frac{17}{2}$	10→9			9866.6906	-0.3	9616.9348	0.2
number of lines measured =		24		37		48	