Noble Gas−Metal Chemical Bonds. Microwave Spectra, Geometries, and Nuclear Quadrupole Coupling Constants of Ar−AuCl and Kr−AuCl

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Abstract: The pure rotational spectra of Ar−AuCl and Kr−AuCl have been measured using a pulsed-jet cavity Fourier transform microwave spectrometer. Both complexes have been found to be linear and are relatively rigid in their ground vibrational states. The noble gas−gold stretching frequencies have been estimated to be 198 and 161 cm^{-1} for Ar−AuCl and Kr−AuCl, respectively. From the isotopic data obtained, r_0 structures have been calculated for both Ar−AuCl and Kr−AuCl, while a partial substitution (r_s) structure has been obtained for Kr−AuCl. The Ar−Au distance has been found to be 2.47 Å, while the Kr−Au distance is 2.52 Å. Ab initio calculations have been performed at the MP2 level of theory on both complexes to obtain geometries, vibrational frequencies, and dissociation energies. The dissociation energies for Ar−AuCl and Kr−AuCl have been estimated to be 47 and 71 kJ mol^{-1}, respectively. The nuclear quadrupole coupling constant of Au has been found to change significantly on complex formation (to −259.8 MHz in Ar−AuCl, and −349.9 MHz in Kr−AuCl) from its value in the monomer unit (+9.6 MHz in AuCl), which is consistent with extensive charge rearrangement on formation of the complexes. This, in conjunction with the sizable dissociation energies, indicates that the Ar−Au and Kr−Au bonds are weakly covalent.

I. Introduction

Although the great majority of substances studied using cavity pulsed-jet Fourier transform microwave (FMTW) spectrometers have been van der Waals complexes, very few have contained metals or metal compounds. Prior to 1999 the spectra of only Ar−Hg[1] and Ar−NaCl[2] had been reported. Both have been found to be true van der Waals complexes, loosely bound, with long Ar−metal bonds and low Ar−metal stretching frequencies and dissociation energies (∼8 kJ mol^{-1} for Ar−NaCl).

Very recently we have reported the spectra of three new metal-containing complexes: Ar−AgF, Ar−AgCl, and Ar−AgBr.[3] They had been prepared by irradiating silver metal near the orifice of a pulsed nozzle using a Nd:YAG laser, and reacting the resulting plasma with SF$_6$, Cl$_2$, or Br$_2$, respectively, contained in the Ar backing gas of the jet. All three complexes were found to be linear and rather rigid (from their centrifugal distortion constants) with short Ar−Ag bonds (∼2.6 Å) and high Ar−Ag stretching frequencies (∼140 cm^{-1}). Ab initio calculations estimated a dissociation energy of ∼21 kJ mol^{-1} for Ar−AgF. Clearly these are considerably more strongly bound than most van der Waals complexes.

It was noted that Ar−AgCl is isoelectronic with the well-known ion [Cl−Ag−Cl]$^-$, so that the Ar−AgX complexes might show evidence of weak chemical bonding. This would be indicated by significant rearrangement of electron distribution

of Ar and AgX on complex formation, which would correspond to variations of the nuclear quadrupole hyperfine structure. Although such variations were found for Cl and Br, the changes could plausibly be accounted for by a large amplitude bending vibration typical of weakly bound van der Waals complexes. Changes at Ar and Ag could not be probed because none of their isotopes has a quadrupole moment.

The other coinage metal analogues of AgCl$_2$$^-$, namely [Cl−Cu−Cl]$^-$ and [Cl−Au−Cl]$^-$, are rather more stable. While AgCl$_2$$^-$ has been observed only in solution,[4] the latter two have been isolated in the solid phase.[5−7] It would thus seem not unreasonable that stable complexes of the type Ar−CuX and Ar−AuX might also be found, and that they would be even more strongly bound than Ar−AgX. They would have the added advantage that all isotopes of both Cu and Au have $I = {}^3/_2$ and a quadrupole moment, so changes in electronic structure at the metal on complex formation could easily be probed.

In a subsequent study we have measured and analyzed the spectra of the Cu analogues, Ar−CuF, Ar−CuCl, and Ar−CuBr.[8] The experiments were analogous to those on Ar−AgX, with Cu replacing Ag. All anticipated features were found: the complexes are linear, and from their centrifugal distortion constants, rather more rigid than their Ag analogues. The Ar−Cu bond lengths are ∼2.25 Å, much less than the Ar−Ag lengths. An ab initio calculation of the Ar−Cu bond energy in

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Ar−CuF gave $D_e = 47$ kJ mol^{-1}. The Cu quadrupole coupling constants almost double on complex formation, with the differences going about one-third of the way to the value in $CuCl_2^-$ (ref 5). The changes in the halogen coupling constants, though smaller than those of the metal, cannot be accounted for reasonably in terms of large-amplitude bending. The ab initio calculation indicated a net charge transfer of $\sim$0.1 electron from Ar to CuF, as well as valence molecular orbitals with fully shared electron density between Ar and Cu. There is thus strong evidence of Ar−metal chemical bonding in these complexes.

The present paper reports an extension of the work to complexes of gold. This time two complexes have been studied, namely Ar−AuCl and Kr−AuCl. The former was chosen to provide comparison with analogous Cu and Ag complexes. The latter is the first Kr complex of this type to be studied. It was chosen because Kr complexes in general tend to be more tightly bound than Ar complexes.[9] Kr is known to undergo real chemical bonding (e.g., in KrF_2), so it was hoped that even stronger evidence of rare gas−metal bonding could be found. Spectra of several isotopomers of both complexes have been measured; bond lengths, vibration frequencies, and nuclear quadrupole coupling constants for both Au and Cl have been obtained, among other things. The results, along with those from ab initio calculations, give further, even stronger, evidence of noble gas−metal chemical bonding.

II. Experimental Section

The spectra were observed with the cavity pulsed-jet FTMW spectrometer and associated laser ablation system which have been described in detail earlier.[10,11] Briefly, the spectrometer cell consists of a Fabry−Perot cavity containing two spherical mirrors 28.5 cm in diameter, radius of curvature 38 cm, held approximately 30 cm apart. One mirror is fixed, while the other can be moved to tune the cavity. The pulsed supersonic sample jets are injected into the cavity from a nozzle (General Valve, series 9) mounted in the fixed mirror. Though this arrangement optimizes both the sensitivity and resolution of the spectrometer, it also causes all lines to be doubled by the Doppler effect because the direction of the jet is parallel to that of the microwave propagation.

The frequency range of the present experiment was 6−20 GHz. Frequency measurements were referenced to a Loran frequency standard accurate to 1 part in 10^{10}. Observed line widths were $\sim$7−10 kHz fwhm. For isolated lines frequencies were obtained from the power spectrum and are estimated to be accurate to $\pm$1 kHz. Frequencies of closely spaced lines were obtained by fitting directly to the time-domain decay spectra,[12] and their estimated accuracies are somewhat less.

The ablation system has been designed so that a rod of metal is mounted immediately in front of the nozzle.[11] Metal plasma is produced by irradiation with the second harmonic (532 nm) of a pulsed Nd: YAG laser. The metal plasma reacts with an appropriate precursor contained in the backing gas, and the resulting mixture is injected immediately as a pulsed supersonic jet into the cavity. The sample molecules are stabilized in the essentially collision-free environment of the jet. In the present experiments the rod was replaced by a small piece of gold foil wrapped around a glass rod. The precursor gas was Cl_2 (0.1%) in the backing gas at 6 bar. The backing gases were pure Ar and pure Kr for Ar−AuCl and Kr−AuCl, respectively. The strongest lines were easily seen with 100 pulses. For some isotopomers with low abundance (Kr-containing isotopomers) $\sim$5000 pulses were needed to produce a usable signal-to-noise ratio.

III. Quantum Chemical Calculations

The geometries of Ar−AuCl and Kr−AuCl were optimized at the second-order Møller−Plesset (MP2)[13] level of theory using the GAUSSIAN 98 suite of programs.[14] For Au a relativistic core potential (RECP) was used.[15] The basis set used for gold was a (9s/7p/6d/3f) Gaussian basis set contracted to (8s/4p/5d/3f).[15,16] For Cl we used the (631111s/52111p) McLean-Chandler basis set[17] augmented with one d-polarization function ($\alpha_d = 0.75$).[18] For Ar and Kr we used the cc-pVTZ basis set.[19] All structures were constrained to a linear geometry.

IV. Experimental Results and Analysis

Prior to a search for the spectrum of Ar−AuCl ab initio calculations were carried out at the MP2 level of theory. This level was used because optimized geometries had been found earlier for both Ar−CuCl and Ar−AgCl to agree quite well with experiment. The main uncertainty was in the Ar−Au bond length, which was estimated to be $\sim$2.45−2.55 Å. The AuCl length was predicted to be near that of the AuCl monomer (similar to the situation for the Cu and Ag complexes). For the $J = 4-3$ transition the predicted search range was 600 MHz. Lines were found near 9590 MHz, and at increments of $\sim$2400 MHz to both high and low frequency, consistent with the spectrum of a linear complex.

With the assumption that the lines arose from Ar−AuCl a detailed assignment was made; this was not a straightforward process. A similar trend was expected for Ar−AuCl as had been found for Ar−CuCl, where the Cu nuclear quadrupole coupling constant (NQCC) of the complex was roughly double that of the CuCl monomer.[8,20] This was not the case here, however. In Ar−AuCl the Au NQCC is radically different from that in the monomer. An initial fit gave for the complex $eQq(Au) \approx -260$ MHz, as opposed to +9.6 MHz in the monomer.[21] It was only from the Cl NQCC, which is $\sim$85% of that of the monomer, that the assignment could be confirmed.

From the Cl NQCC and the intensities of the transitions, the lines initially observed were assigned to Ar−Au^{37}Cl. With the assumption that the monomer and complex have the same Au−Cl bond length, the Ar−Au length was estimated as $\sim$2.47 Å, and line frequencies for Ar−Au^{35}Cl were predicted. Those of the $J = 4-3$ transition were found within 2 MHz of the prediction; a portion of the hyperfine structure of this transition is shown in Figure 1. In all, lines of five transitions, $J = 3-2$ to 7−6, were measured and assigned for both isotopomers of Ar−AuCl. The observed frequencies and their quantum number

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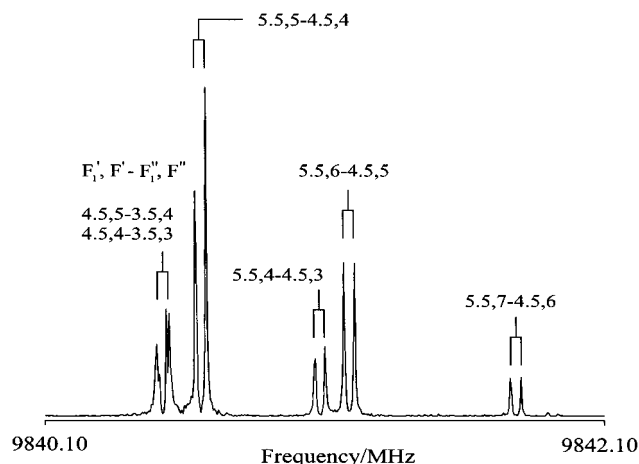(17) McLean, A.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639.

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Figure 1. A portion of the hyperfine structure of the $J = 4-3$ transition of $^{40}Ar-Au^{35}Cl$. Experimental conditions: 0.2 μs microwave pulse width, 0.1% Cl_2 in Ar at 7−5 bar backing pressure, 200 averaging cycles, 8k transform.

**Table 1.** Molecular Constants Calculated for $Ar-Au^{35}Cl$ and $Ar-Au^{37}Cl$ in MHz[a]

parameters	$Ar-Au^{35}Cl$	$Ar-Au^{37}Cl$
B_0	1229.927926(29)	1199.882035(34)
$D_J \times 10^4$	2.1178(40)	1.9668(46)
eQq(Au)	−259.8352(21)	−259.8816(84)
eQq(Cl)	−54.0502(31)	−42.6105(57)
C_I(Au) $\times 10^4$	4.52(79)	4.52[b]
no. of lines	83	69
RMS error (kHz)	0.97	0.90

[a] Numbers in parentheses are one standard deviation in units of the last significant figure. [b] Fixed to $Ar-Au^{35}Cl$ value.

assignments (using the coupling scheme $\mathbf{I}_{Au} + \mathbf{J} = \mathbf{F}_1$; $\mathbf{I}_{Cl} + \mathbf{F}_1 = \mathbf{F}$) are listed in the Supporting Information. The frequencies were fitted to spectroscopic constants using Pickett's global fitting program SPFIT;[22] the resulting constants are given in Table 1. Because of their low natural abundances, no lines were observed for isotopomers containing ^{36}Ar or ^{38}Ar.

For Kr−AuCl the Kr−Au bond length was first estimated by adding 0.1 Å (the difference between the Kr and Ar van der Waals radii) to the Ar−Au length to give a Kr−Au length of 2.57 Å, and the spectrum of Kr−AuCl was predicted. The spectrum is complicated by the large number of Kr isotopes. A group of weak lines was found near 9242 MHz, which from the Cl NQCC and line intensities was tentatively assigned to $^{86}Kr-Au^{35}Cl$ (13.1% abundant). The Au NQCC had changed appreciably again, this time to $\approx$−350 MHz. This assignment gave a Kr−Au bond length of ∼2.52 Å, from which were predicted transitions of other isotopomers. Lines of the most abundant species $^{84}Kr-Au^{35}Cl$ (43.2% abundant) were found within 5 MHz of the predicted frequency; they were considerably stronger than those of $^{86}Kr-Au^{35}Cl$, with the strongest lines requiring only 400−500 averaging cycles to obtain a satisfactory signal-to-noise ratio. A portion of the hyperfine structure of the $J = 7-6$ transition is shown in Figure 2. Altogether spectra of four isotopomers were assigned and measured: $^{82}Kr-Au^{35}Cl$ ($J = 5-4$ to 8−7, 9% abundance), $^{84}Kr-Au^{35}Cl$ ($J = 5-4$ to 9−8, 43%), $^{84}Kr-Au^{37}Cl$ ($J = 5-4$ to 9−8, 14%), and $^{86}Kr-Au^{35}Cl$ ($J = 5-4$ to 9−8, 13%). Their measured frequencies and assignments are listed in the Supporting Information; again the coupling scheme is $\mathbf{I}_{Au} + \mathbf{J} = \mathbf{F}_1$; $\mathbf{I}_{Cl} + \mathbf{F}_1 = \mathbf{F}$. The spectroscopic constants derived using SPFIT are given in Table

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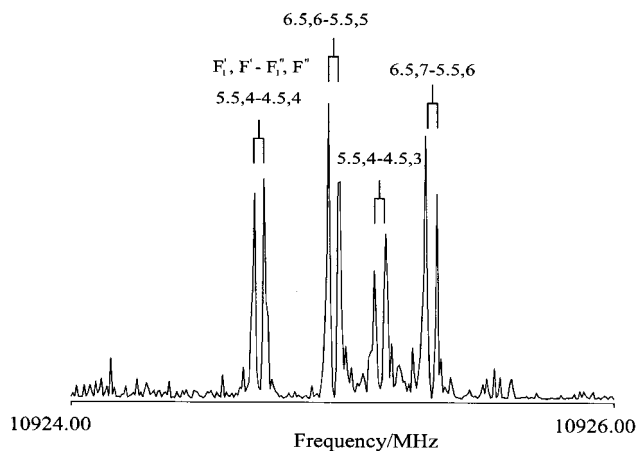
Figure 2. A portion of the hyperfine structure of the $J = 7-6$ transition of $^{84}Kr-Au^{35}Cl$. Experimental conditions: 0.2 μs microwave pulse width, ∼0.1% Cl_2 in Kr at 7−5 bar backing pressure, 500 averaging cycles, 4k transform.

2. Transitions of $^{83}Kr-Au^{35}Cl$ (9% abundant), which would have been of interest because ^{83}Kr has $I = 9/2$ and should produce quadrupole splitting, were not found. Presumably the hyperfine splittings reduced the line intensities to below the detection limit of the spectrometer.

Similarly to $Ar-CuX^8$ and $Ar-AgX^3$ (where X = F, Cl, Br), no lines from either complex in excited vibrational states were observed.

V. Structures of the Complexes

A. Geometries. The rotational constants in Tables 1 and 2, all of which are well determined, have been used to obtain geometrical information for the two complexes. Unfortunately it has not been possible to obtain such precise and reliable values for geometries, for two basic reasons: (i) in both complexes, but especially in Ar−AuCl, the Au atom is very near the center of mass, where vibration−rotation effects cause the greatest uncertainties in its determined position; and (ii) ^{40}Ar and ^{197}Au are 99.6% and 100% abundant, respectively, and information from isotopic substitution, which would be especially valuable in these complexes, again especially for Ar−AuCl, is sparse. Nonetheless, bond lengths have been obtained which provide interesting insights into the complexes, particularly when they are compared with results from ab initio calculations, which have also been carried out.

To start with, ground-state effective (r_0) geometries have been obtained directly from the rotational constants. Since there are two bond lengths, isotopic pairs of rotational constants were needed for each determination. The results are given in Table 3. For Ar−AuCl, with only one pair available, only one set of bond lengths has been obtained. The values are reasonable, however, and compare well with the equilibrium (r_e) values calculated at the MP2 level of theory. The r_0 (AuCl) value is very close to r_e in the AuCl monomer;[21] this is similar to the situation in Ar−CuCl[8] but not Ar−AgCl.[3] The agreement should be viewed skeptically, given the nearness of the Au atom to the center of mass (∼0.08 Å), which could in turn mean uncertainties in the bond lengths as much as ±0.02 Å.

For Kr−AuCl there are several possible isotopic pairs, and r_0 geometries from four pairs are also given in Table 3. The bond length variations illustrate the well-known uncertainties inherent in such structures.[23] Again, however, the values are close to the ab initio values and the r_e value for AuCl monomer.

Table 2. Molecular Constants Calculated for Four Isotopomers of Kr—AuCl in MHz[a]

parameters	^{82}Kr—Au^{35}Cl	^{84}Kr—Au^{35}Cl	^{84}Kr—Au^{37}Cl	^{86}Kr—Au^{35}Cl
B_0	791.325477(67)	780.525187(28)	764.319789(47)	770.140718(36)
$D_J \times 10^5$	8.464(63)	8.217(23)	7.714(46)	8.016(31)
eQq(Au)	−349.707(47)	−349.857(23)	−349.886(27)	−349.828(27)
eQq(Cl)	−51.954(37)	−52.012(21)	−40.930(24)	−51.992(26)
no. of lines	31	62	41	44
RMS error (kHz)	1.20	1.12	1.09	1.07

[a] Numbers in parentheses are one standard deviation in units of the last significant figure.

Table 3. Geometries of the Complexes[a]

Ar—AuCl	r(Ar—Au)	r(Au—Cl)
r_0(^{40}Ar/^{35}Cl,^{40}Ar/^{37}Cl)	2.4693	2.1983
r_e(ab initio)	2.4620	2.2177
r_e(AuCl monomer)[b]		2.19903

Kr—AuCl	r(Kr—Au)	r(Au—Cl)
r_0(^{82}Kr/^{35}Cl,^{84}Kr/^{35}Cl)	2.5214	2.2118
r_0(^{84}Kr/^{35}Cl,^{84}Kr/^{37}Cl)	2.5257	2.2034
r_0(^{82}Kr/^{35}Cl,^{86}Kr/^{35}Cl)	2.5214	2.2118
r_0(^{84}Kr/^{35}Cl,^{86}Kr/^{35}Cl)	2.5214	2.2118
average	2.5224(18)	2.2097(36)
r_s(^{84}Kr/^{35}Cl→^{82}Kr/^{35}Cl,^{84}Kr/^{37}Cl)	2.52251	2.20442
r_s(^{84}Kr/^{35}Cl→^{86}Kr/^{35}Cl,^{84}Kr/^{37}Cl)	2.52248	2.20443
r_e(ab initio)	2.5073	2.2234
r_e(AuCl monomer)[b]		2.19903

[a] Numbers in parentheses are one standard deviation in units of the last significant figure. [b] Reference 21.

For Kr—AuCl there are enough isotopic data to evaluate a substitution (r_s) structure.[24] This method attempts to reduce effects of zero-point vibration by determining atomic positions from isotopic differences. The most abundant isotopomer, ^{84}Kr—Au^{35}Cl, was chosen as a basis, and the positions of the Kr and Cl atoms were determined from the changes in moments of inertia on isotopic substitution. For Kr two values were obtained, using substitution of both ^{82}Kr and ^{86}Kr. Au was located using the first moment equation. The two resulting geometries, which are very close, are also given in Table 3. Because of the reduction in vibrational contributions, they should be considered our preferred geometries, with bond length uncertainties ∼±0.003 Å or better. They too are in good agreement with the ab initio and monomer structures.

It is interesting to compare the derived bond lengths with the sums of van der Waals and ionic radii. Appropriate values are found in the textbook by Huheey.[25] Sums of the van der Waals radii of Ar, Kr, and Au atoms give r(Ar—Au) = 3.60 Å and r(Kr—Au) = 3.70 Å, roughly 1.25 Å longer than the bond lengths found here. Huheey gives the ionic radius of Au$^+$ as 1.51 Å, only 0.2 Å shorter than its van der Waals radius. However, this is for coordination number 6; from a comparison with Ag$^+$ and Cu$^+$, this radius might reduce to 1.0 Å for coordination number 2. Even then, when this is added to the noble gas van der Waals radii values of r(Ar—Au) = 2.9 Å and r(Kr—Au) = 3.0 Å are obtained, still significantly greater (by 0.4−0.5 Å) than the measured values. The Au—X bonds in AuX are only ∼40% ionic[21] so it is likely that r(Au$^+$) is >1.0 Å here. Thus the unusually short Ng—Au bonds found in the present work strongly suggest some degree of chemical bonding between the noble gas and gold.

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Table 4. Ab Initio Determined Properties of Ar—AuCl and Kr—AuCl[a]

property	Ar—AuCl	Kr—AuCl
bond lengths (Å)		
r_e(Au—Cl)	2.2177	2.2234
exptl	2.1983[b]	2.2044[c]
r_e(Ng—Au)	2.4620	2.5073
exptl	2.4693[b]	2.5225[c]
wavenumbers (cm^{-1})		
Au—Cl stretch	413	409
Ng—Au stretch	184	163
exptl	198[d]	161[d]
Ng—Au—Cl bend	80	76
dissociation energy (kJ mol^{-1})		
D_e (Ng—Au bond)	46.9	71.3

[a] Ng ≡ noble gas. [b] r_0 structure. [c] r_s structure. [d] From $\omega_e = (4B_0^3/D_J)^{1/2}$.

B. Vibrational Wavenumbers and Dissociation Energies. The centrifugal distortion constants are remarkably small, with values considerably smaller than those usually found for van der Waals complexes (for Ar—NaCl, for example, $D_J \approx 9$ kHz). These can be converted to noble gas—Au stretching frequencies using a diatomic approximation:

$$\omega_e \approx \left(\frac{4B_0^3}{D_J}\right)^{1/2} \tag{1}$$

The values obtained are 198 and 161 cm^{-1} for Ar—Au^{35}Cl and ^{84}Kr—Au^{35}Cl, respectively. These values are much closer to those of chemical bonds than to those of van der Waals bonds. (The same procedure for Ar—NaCl gives 21 cm^{-1} (ref 2); however, the authors consider this to be artificially small.) They compare well with those from the ab initio calculations discussed earlier, as shown in Table 4; this is especially the case for Kr—AuCl. Table 4 also contains ab initio values for the Au—Cl stretch and for the bend. The relatively high values of the former justify the use of the diatomic approximation to get the experimental value.

Dissociation energies calculated ab initio are also given for the two complexes in Table 4. These, too, are relatively large, especially for Kr—AuCl, and approach those of conventional chemical bonds. The value for Ar—AuCl is very similar to that calculated earlier for Ar—CuF (47.3 kJ mol^{-1} (ref 8)) and about double a comparable value for Ar—AgF (23.2 kJ mol^{-1} (ref 3)).

It is possible also to calculate the noble gas—Au stretching force constants using the diatomic approximation. The values for the gold complexes are compared with those of analogous Cu and Ag complexes in Table 5. There is a rough correlation of the force constants with the ab initio dissociation energies, which are also in Table 5. A similar rough correlation was found in the ab initio calculations of the properties of OC—MX (M = Cu, Ag, Au) by Antes et al.[18] In both sets of complexes the results indicate that the Ag derivatives are considerably more weakly bound than the Cu or Au derivatives, with the bond

Table 5. Stretching Wavenumbers and Force Constants, Bond Lengths, and Calculated Dissociation Energies of Noble Gas−Coinage Metal Halides

	$\omega(MX)$ (cm^{-1})		$\omega(Ng-M)^{a,b}$	$r(Ng-M)$	$k(Ng-M)^{a,c}$	D_e^d
complex	monomer	complex^d	(cm^{-1})	(Å)	(mdyn Å^{-1})	(kJ mol^{-1})
Ar−CuF	621^e	674	224	2.22	0.794	47
Ar−CuCl	418^f	456	197	2.27	0.648	
Ar−CuBr	313^g	350	170	2.30	0.534	
Ar−AgF	513^h	541	141	2.56	0.356	23
Ar−AgCl	344^i	357	135	2.61	0.335	
Ar−AgBr	247^i		124	2.64	0.298	
Ar−AuCl	383^j	413	198	2.47	0.785	47
Kr−AuCl	383^j	409	161	2.52	0.936	71
ArAuAr^{+k}			201^l	2.54		44^k
KrAuKr^{+k}			186^l	2.57		69^k

^{a} Ng ≡ noble gas. ^{b} Evaluated from centrifugal distortion constants in a diatomic approximation from $\omega_e = (4B_0^3/D_J)^{1/2}$. ^{c} Evaluated from $\omega_e(Ng-M)$ using a diatomic approximation. ^{d} Ab initio values. Ng−CuF from ref 8. Ng−AgF from ref 3. Ng−AuCl from present work. ^{e} Reference 26. ^{f} Reference 27. ^{g} Reference 28. ^{h} Reference 29. ^{i} Reference 30. ^{j} Reference 21. ^{k} Reference 31; values of D_e are one-half the heats of atomization given. ^{l} Asymmetric stretch $\nu(\sigma_u)$.

Table 6. Comparison of Nuclear Quadrupole Coupling Constants (MHz) of Au(I), Cu(I), and Ag(I) Chlorides and Their Complexes

	Au(I)		Cu(I)		Ag(I)
	$eQq(Au)$	$eQq(Cl)$	$eQq(Cu)$	$eQq(Cl)$	$eQq(Cl)$
MCl	9.63^a	−62.0^a	16.2^b	−32.0^b	−36.5^c
Ar−MCl	−259.8	−54.0	33.2^d	−28.0^d	−34.5^e
Kr−MCl	−349.8	−52.0			
[Cl−M−Cl]$^-$	(−)765^f	(−)35^f	(+)61.4^g	(−)19^g	(−)16.7^e
	(−)802^f				

^{a} Reference 21. ^{b} Reference 20. ^{c} Reference 32. ^{d} Reference 8. ^{e} Reference 3; from an ab initio calculation. ^{f} References 6 and 7. ^{g} Reference 5.

strengths of the latter being comparable. The calculated dissociation energies of the carbonyl derivatives suggest they are rather more stable than the noble gas complexes. Analogous experiments on these complexes are clearly in order.

Ng−AuCl, where Ng is a noble gas, are isoelectronic with the species NgAuNg$^+$. The properties of the NgAuNg$^+$ species have been calculated by Pyykkö and are also listed in Table 5.[31] The Au−Ng bond lengths in these species are very comparable to those found in this work; the Ar−Au and Kr−Au bond dissociation energies are also very comparable to those calculated for Ar−AuCl and Kr−AuCl.

C. Nuclear Quadrupole Coupling and ab Initio Results. The noble gas−Au bond lengths, vibrational wavenumbers, and dissociation energies all suggest that the noble gas−Au bonds are approaching chemical bonds. In this case there should be very significant rearrangement of the electron densities of both the constituents on complex formation. The most direct evidence of this should be found in the nuclear quadrupole coupling constants (NQCC), which depend on the electric field gradients at the nuclei.

Table 6 gives a comparison of the NQCC from the present work with those of monomeric Au(I) chloride, of the isoelectronic ion [Cl−Au−Cl]$^-$, and of the corresponding Cu(I) and Ag(I) derivatives. It is clear that the anticipated large NQCC

changes have been found. Though this is particularly so for Au and Cu, the changes in the NQCC of Cl are also of interest.

For linear, weakly bonded van der Waals complexes the changes in coupling constants on complex formation are usually interpreted in terms of large amplitude bending vibrations using the following equation:[33]

$$eQq = [eQq_0 + \Delta(eQq)]\left\langle\frac{3\cos^2\beta - 1}{2}\right\rangle \quad (2)$$

where eQq and eQq_0 are the NQCC of the complex and monomer, respectively; $\Delta(eQq)$ is the coupling constant change caused by electron rearrangement on complex formation; β is the Eckart angle between the AuCl unit and the a-inertial axis; and the averaging is over the ground vibrational wave function. The Eckart angle β is related to θ, the angle of bend of the complex, by

$$\langle\sin^2\theta\rangle \sim (1 + \delta^2)\langle\sin^2\beta\rangle \quad (3)$$

where $\delta = I_{AuCl}/I_{Ng-AuCl}$. If $\Delta(eQq)$ is assumed to be zero, as is usually the case for van der Waals complexes, then the Cl coupling constants give a value of θ in the range of 18−19°, which seems somewhat excessive given the apparent rigidity of the complexes described above. The idea that $\Delta(eQq) = 0$ is probably incorrect.

If the simple Townes−Dailey theory is applied to the Cl coupling constants one gets:

$$eQq = \left(n_\sigma - \frac{n_\pi}{2}\right)eQq(Cl) \quad (4)$$

where $eQq(Cl)$ is the coupling constant of a singly occupied 3pσ orbital on Cl (=+109.7 MHz (ref 23)); n_σ and n_π are the 3pσ and 3pπ orbital populations on Cl. This equation is evidently valid for NQCC of Cl in all situations.[23,34,37] Values for n_σ and n_π have been obtained from the Mulliken orbital populations given in Table 7. For AuCl, Ar−AuCl, and Kr−AuCl they lead to eQq values of −52.6, −52.6, and −51.6 MHz, respectively. Although the absolute values are in fair agreement with experiment, the changes in the Cl NQCC are not well

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Rotational Spectra of Ar—AuCl and Kr—AuCl

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Table 7. Mulliken Orbital Populations n for AuCl and Ng−AuCl Complexes

|	ClAu + Ar	ClAu−Ar	ClAu + Kr	ClAu−Kr
n_s^{Cl}	1.99	1.98	1.99	1.98
$n_{p\sigma}^{Cl}$	1.50	1.49	1.50	1.50
$n_{p\pi}^{Cl}$	3.96	3.94	3.96	3.94
n_s^{Au}	0.58	0.71	0.58	0.75
$n_{p\sigma}^{Au}$	0.13	0.17	0.13	0.20
$n_{p\pi}^{Au}$	0.11	0.12	0.11	0.12
$n_{d\sigma}^{Au}$	1.88	1.83	1.88	1.82
$n_{d\pi}^{Au}$	4.00	4.00	4.00	3.97
$n_{d\delta}^{Au}$	4.00	4.00	4.00	4.00
n_s^{Ng}	2.00	1.98	2.00	1.97
$n_{p\sigma}^{Ng}$	2.00	1.88	2.00	1.83
$n_{p\pi}^{Ng}$	4.00	3.99	4.00	3.98

reproduced. This is similar to the results found for the Cu derivatives (−31.8 to −30.7 MHz from the calculations in ref 8).

The changes in the NQCC of Au (and of Cu (ref 8)) can in no way be interpreted with eq 2; not only are the changes too large but they are also of the wrong sign, for they show an increase in magnitude. For AuCl there is also a sign change. Whether the latter is very significant in a discussion of electronic rearrangement on complex formation is unclear: there is also a sign change, as well as a significant variation in eQq values, between the different Au(I) halides.[21,35,36] What would seem more significant is the very large change toward the values for the [Cl−Au−Cl]⁻ ion, roughly paralleling the corresponding changes for the Cu analogues. There is no doubt that the [Cl−M−Cl]⁻ ions are chemically bonded, and the implication that the complexes go significantly toward this is certainly there. It is notable too that the coupling constant change for the Kr derivative is rather greater than that with the Ar derivative, consistent with the greater bond energy discussed above.

It might seem on the surface that the Townes−Dailey theory, along with the ab initio results, might also be applicable to the Au coupling constants. However, we have recently found that using it for transition metals is unreliable at best,[37] and so have made no attempt to do this. Furthermore, serious difficulties have been encountered in predicting NQCC of Au in the AuX monomers, even with sophisticated ab initio theory including relativistic effects.[38] However, the ab initio results do show one interesting trend: there is a donation of ∼0.14 and ∼0.20 electron to AuCl from Ar and Kr, respectively. It is interesting that Pyykkö predicted substantial charge transfer from the noble gas to the metal cation: ∼0.2 for ArAuAr⁺ and ∼0.35 for KrAuKr⁺.

What would be very helpful would be some indication of charge redistribution on the noble gas. This could be shown using ⁸³Kr quadrupole coupling, and it is a pity that the spectra of complexes containing this isotope could not be seen. Experiments with halides such as AuF or AgF, where there are fewer isotopes and/or less hyperfine splitting, are being undertaken to try to obtain this information.

If there is to be noble gas−metal bonding then the ab initio calculations should show molecular orbitals with significant overlap. Figure 3 shows two such orbitals, one σ and one π, for each of the complexes, formed from the valence atomic orbitals of the elements.[39] Both are doubly occupied; none are the HOMO. They provide further evidence of chemical bonding in the complexes.
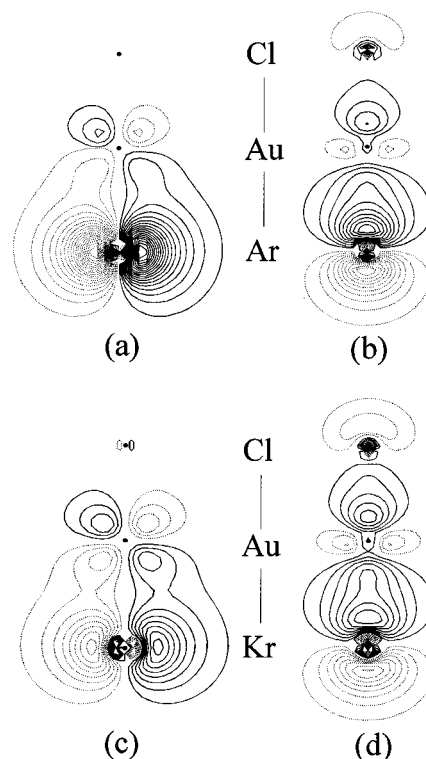
Figure 3. Contours of electron density: (a) 8π orbital of Ar−AuCl (values of contours: 0.015n where $n = 1−15$); (b) 11σ orbital of Ar−AuCl (values of contours: 0.025n where $n = 1−12$); (c) 11π orbital of Kr−AuCl (values of contours: 0.025n where $n = 1−9$); and (d) 14σ orbital of Kr−AuCl (values of contours: 0.025n where $n = 1−15$). The dotted lines indicate a negative value of the wave function.

VI. Conclusions

The microwave spectra of the linear complexes Ar−AuCl and Kr−AuCl have been measured. The small centrifugal distortion constants indicate the complexes are relatively rigid. The Ar−Au bond distance was found to be 2.47 Å while for Kr−Au it is 2.52 Å. Ab initio calculations at the MP2 level of theory have modeled the complexes well, particularly the bond lengths and vibration frequencies, and have estimated the dissociation energy to increase from 47 kJ mol⁻¹ for Ar−AuCl to 71 kJ mol⁻¹ for Kr−AuCl. The large variations observed for the Au nuclear quadrupole coupling constant show that there are substantial charge rearrangement effects on formation of the complexes. From a Mulliken population analysis it was found that there is a donation of ∼0.14 and 0.20 electron from Ar and Kr, respectively, to Au on complex formation. The large changes in the nuclear quadrupole coupling constants, in conjunction with the sizable dissociation energies, indicate the Ar−Au, and more so the Kr−Au, bonds are weakly covalent in character.

Supporting Information Available: Tables of observed transition frequencies of Ar−Au³⁵Cl, Ar−Au³⁷Cl, and four isotopomers of Kr−AuCl (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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