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Chemistry in Laser-Induced Plasmas: Formation of M−C≡C−Cl (M = Ag or Cu) and their Characterization by Rotational Spectroscopy

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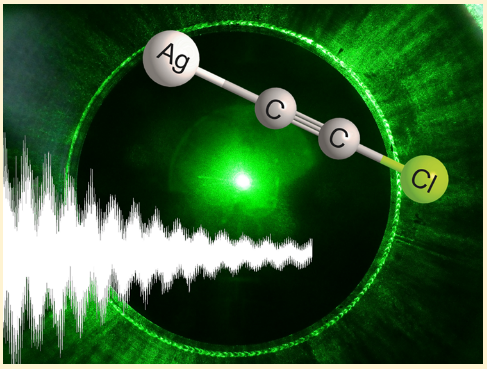
Supporting Information

ABSTRACT: The new linear molecule Ag−C≡C−Cl has been detected and fully characterized by means of rotational spectroscopy. It was synthesized by laser ablation of a silver rod in the presence of a gaseous sample containing a low concentration of CCl_4 in argon, cooled to a rotational temperature approaching ~1−3 K through supersonic expansion, and analyzed by chirped-pulse, Fourier transform microwave spectroscopy. Six isotopologues were investigated, and for each the spectroscopic constants B_0, D_J and χ_{aa}(Cl) were determined. The B_0 values were interpreted to give the following bond lengths: r(Ag−C) = 2.015(14) Å and r(C−Cl) = 1.635(6) Å, with r(C≡C) = 1.2219 Å assumed from an ab initio calculation at the CCSD(T)/aug-cc-pV5Z level of theory. The Cu analogue Cu−C≡C−Cl was similarly identified and characterized.



1. INTRODUCTION

Plasma is an important state of matter. It can be generated in various ways, for example, when a gas is heated to a very high temperature, or when an electric discharge passes through a gas or in the plume of vapor produced when a high-powered laser impinges on a solid. The composition of a plasma depends on its effective temperature. At the highest temperatures (as exist in the core of stars), it consists of fundamental particles and small monatomic ions. In regions cooler than found within stars, such as circumstellar shells[1] and the hotter parts of the interstellar medium, electrons and molecular-ion fragments can be present and provide the opportunity for molecule building on dust grains.[2] The chemistry that can occur in plasmas is therefore a matter of interest.

It is well-known that electric discharges in gases can produce small, highly stable molecules[3] and also hitherto unobserved species.[4] Laser ablation of solids is another convenient laboratory method of producing plasmas and has been employed in combination with microwave spectroscopy for a variety of purposes, including vaporization of refractory solids,[5] the production and characterization of free radicals,[6] and the synthesis of new species.[7,8] A Nd:YAG laser operating on its second harmonic at 532 nm, with a pulse duration of ca. 10 ns and an energy of ~10 mJ/pulse is sufficient to ablate metals (such as copper, silver, gold, and many others) to produce a small plume of plasma composed of metals ions, atoms, and electrons. If this plume immediately interacts with a gas of neutral molecules in its vicinity, fragmentation of the molecules can occur and the fragments can then undergo reactions. For example, interaction of a SF_6/Ar gas mixture with a plume of laser-ablated copper gives CuF and ArCuF, both of which were detected by their rotational spectra.[8] OCCuF was similarly detected by using a SF_6/CO/Ar mixture.[9] Sometimes small, thermodynamically stable, well-known species result. When a NH_3/ CCl_4/Ar gas mixture meets a plume of ablated copper, one product is cyanogen chloride ClCN (unpublished results). Another product is H_3N−Cu−Cl (unpublished results), previously unknown in the gas phase. Broadband rotational spectroscopy provides a powerful new method[10] by which to analyze gas-phase molecules generated within plasma and an opportunity to examine some exotic chemistry. In this article, we report the synthesis and identification by this means of two examples of a simple, interesting molecular type, namely M−C≡C−Cl (M = Ag or Cu).

2. EXPERIMENTAL AND THEORETICAL METHODS

The rotational spectra were observed by using the upgraded chirped-pulse, Fourier transform microwave (CP-FTMW) spectrometer at Newcastle University. The spectrometer and the experimental methodology have been described elsewhere.[10,11] Here the spectrometer was configured in the 7−18.5 GHz region with a pulsed nozzle perpendicular to the axis of microwave propagation. At a gas pulse repetition rate of 1.05 Hz, 8 free induction decay (FID) emissions per gas pulse were detected, each with 20 μs duration, and then digitized on an 8-bit 25 Gs/s oscilloscope after heterodyning. For observing Ag−C≡C−Cl and Cu−C≡C−Cl, a pulse of a gas mixture containing roughly 1% CCl_4 balanced in 6 bar of argon, was flowed over either a silver or copper target rod which was

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ablated with a Nd:YAG laser (Continuum Minilite, 532 nm, ~10 mJ/pulse of 10 ns duration, repetition rate is once per nozzle pulse) and subsequently expanded into the vacuum chamber. The final data sets represent a time-domain average of 2 M FIDs for Ag−C≡C−Cl and 3 M FIDs for Cu−C≡C−Cl, which were subsequently Fourier transformed with an applied high-resolution window function to improve resolving power. For Ag−^{13}C≡^{13}C−Cl and Cu−^{13}C≡^{13}C−Cl based isotopologues, an equivalent gas mixture was prepared with $^{13}CCl_4$ (Cambridge Isotopes). For the Ag−^{13}C≡^{13}C−Cl sample, a total of 660 k FIDs were collected, while for Cu−^{13}C≡^{13}C−Cl the total was 2.2 M. Both were Fourier transformed in identical fashion.

A geometry optimization for each molecule M−C≡C−Cl (M = Ag or Cu) was carried out by using quantum chemical calculations at the CCSD(T)/aug-cc-pV5Z level of theory with the MOLPRO package.[12] For Ag, the aug-cc-pV5Z-PP basis was employed, where PP indicates that a pseudopotential was used for the core electrons. All electrons were included in the correlation treatment for Cu, Cl, and C, however, using the basis functions aug-cc-pV5Z, aug-cc-pV(5+d), and aug-cc-pV5Z, respectively

3. RESULTS AND DISCUSSION

3.1. The Observed Spectra. We have recently been using the laser-ablation method to make a systematic investigation of the interactions of a range of simple Lewis bases B with either AgX or CuX, where X is a halogen atom.[13] In these experiments, in the case X = Cl, a pulse of argon containing approximately 1% of CCl_4 is expanded from a pressure of ca. 6 bar through a small hole into a vacuum. Before issuing into the vacuum chamber, the gas pulse passes over a silver rod. A suitably timed pulse from a Nd:YAG laser operating at 532 nm impinges on the metal rod to produce a plasma composed of metal ions, electrons, and (presumably) various fragments of the molecules contained in the gas pulse.

Figure 1 shows a photograph of the plasma plume produced with a silver rod. When the rotational spectra of substances in the gas pulse are detected (sufficiently far downstream from the point of ablation for the plasma to have decayed), it is possible to identify molecules such as AgCl and B···AgCl.

While attempting to observe the rotational spectrum of $^{14}N_2$···Ag−^{35}Cl by using a mixture containing $^{14}N_2$, CCl_4, and Ar in appropriate ratio, we detected a weak, simple spectrum composed of equally spaced groups of transitions (spacing ≈ 1500 MHz), each group apparently consisting of a doublet of spacing ≈ 50 MHz, but on closer examination each component of the doublet itself proved to be a doublet with individual components separated by only a few tens of kHz, as illustrated in Figure 2 (measured frequencies are available in the Supporting Information).

Neither the spacing between the groups nor the splitting internal to each doublet is consistent with $^{14}N_2$···Ag−^{35}Cl as the source of the observed spectrum, which is ca. 1000 times weaker than that observed for the AgCl precursor.

3.2. Identification of Ag−^{12}C≡^{12}C−^{35}Cl as the Carrier of the Observed Spectrum. Even when all nitrogen was removed from the gas mixture, the new spectrum persisted. Replacement of the Ag rod by one of Cu caused the observed spectrum to disappear, as did removal of CCl_4 from the gas mixture, thereby suggesting that the observed spectrum is associated with a molecule containing only Ag, C, and Cl atoms. The possibility that the spectral carrier is a complex involving argon with a (Ag,C,Cl) containing molecule will be ruled out later.

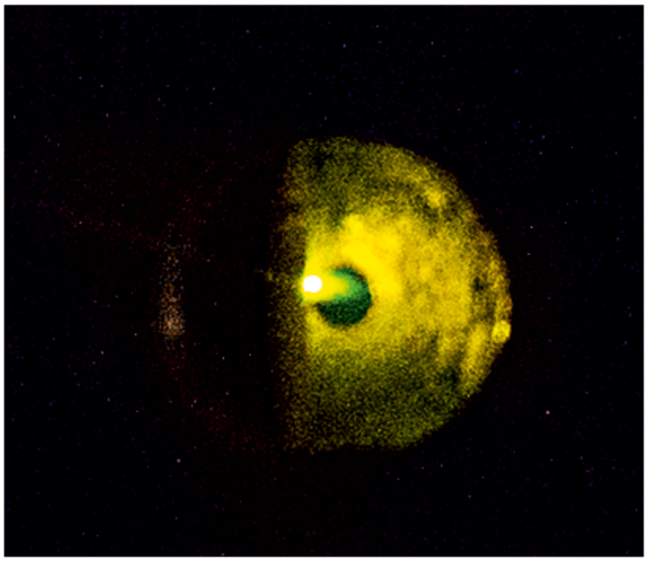

Figure 1. Photograph of the plasma plume generated by the focused laser pulse above the surface of the silver metal target, taken through a viewport centered on the axis of the expanding gas pulse (see Experimental and Theoretical Methods for description of spectrometer). The plume of vaporized material can be seen propagating from left to right at the center of the image. Recorded through a DBY39 filter (optical density of +7 at 532 nm) to protect photographic equipment from intense reflected laser light.

The nearly equal spacing of consecutive groups of transitions indicates that the source of the observed spectrum is a linear molecule or a symmetric-top molecule or a nearly prolate asymmetric-top molecule of effective rotational constant $B \approx$ 750 MHz. In the frequency range of our spectrometer (7−18.5 GHz), $J + 1 \rightarrow J$ transitions having $J = 3$ to 11 are observable. As indicated earlier, each $J + 1 \rightarrow J$ transition consists of a major doublet of spacing ≈ 50 MHz, with each component itself consisting of a minor doublet of separation only a few tens of kHz (Figure 2). The major doublet spacing increases linearly with J and is assumed to arise from two isotopologues associated with the two naturally occurring isotopes of silver, ^{107}Ag and ^{109}Ag (abundances 51.8% and 48.2%, respectively). The observation of only two Ag isotopologues rules out a molecule having two or more Ag atoms, as does a rotational constant $B \approx 750$ MHz. The minor doublet spacing, on the other hand, decreases with J. Such behavior is characteristic of nuclear quadrupole hyperfine structure. What is the origin of this hyperfine structure?

Of the three types of atoms, Ag, C, and Cl, we can assume that only the most abundant isotopes ^{107}Ag, ^{109}Ag, ^{12}C (abundance 98.9%) and ^{35}Cl (abundance 75.8%) occur in the isotopologue responsible for the initially observed spectrum. Of these, only ^{35}Cl ($I = 3/2$) has a nonzero nuclear electric quadrupole moment and can lead to the hyperfine structure. For the range of J observed and at our spectrometer resolution, hyperfine structure associated with a single ^{35}Cl nucleus is calculated to collapse to a doublet of small splitting. The presence of two ^{35}Cl atoms would lead to a more complicated hyperfine structure, and this possibility can be excluded. When the observed ^{35}Cl hyperfine doublet frequencies of several $J + 1 \rightarrow J$ transitions of either the ^{107}Ag or the ^{109}Ag isotopologue are fitted by using the familiar Hamiltonian for a linear molecule,

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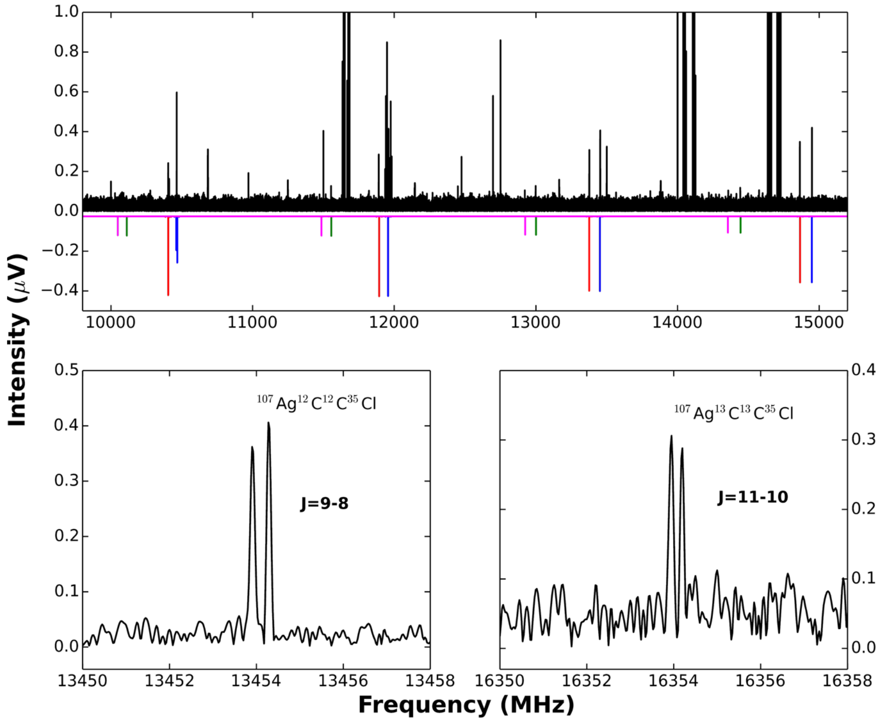

Figure 2. Upper panel shows (upward pointing) the rotational spectrum observed (2M FIDs) when pulses of supersonically expanded Ar/CCl_4 gas mixture interact with plasma produced by ablation of a silver rod with 532 nm radiation from a Nd:YAG laser. The downward-pointing spectrum is that simulated by using the spectroscopic constants given in Table 1. Transitions of $^{109}Ag-^{12}C\equiv^{12}C-^{35}Cl$ are in red, those of $^{107}Ag-^{12}C\equiv^{12}C-^{35}Cl$ are in blue, while transitions of $^{109}Ag-^{12}C\equiv^{12}C-^{37}Cl$ and $^{107}Ag-^{12}C\equiv^{12}C-^{37}Cl$ are in magenta and green, respectively. Measured transitions that do not assign to these species are attributable to other species present within the probed sample, including the diatomic molecule, AgCl. The left-hand lower panel shows an expansion of the doublet arising from ^{35}Cl hyperfine structure in the $J = 9 \rightarrow 8$ transition of $^{107}Ag-^{12}C\equiv^{12}C-^{35}Cl$. The corresponding doublet (obtained from 0.66M FIDs) in the $J = 11 \rightarrow 10$ transition of $^{107}Ag-^{13}C\equiv^{13}C-^{35}Cl$ is shown in the lower right-hand panel.

Table 1. Observed Ground-State Spectroscopic Constants of M−C≡C−Cl (M = Ag or Cu)

	spectroscopic constant			
isotopologue	B_0 (MHz)	10^2 D_J (kHz)	χ_{aa}(Cl) (MHz)	χ_{aa}(Cu) (MHz)
$^{107}Ag-^{12}C\equiv^{12}C-^{35}Cl$	747.45619(16)	2.567(82)	−76.93(26)	
$^{109}Ag-^{12}C\equiv^{12}C-^{35}Cl$	743.16060(19)	2.387(87)	−77.35(62)	
$^{107}Ag-^{12}C\equiv^{12}C-^{37}Cl$	722.13078(21)	2.549(97)	−61.08(53)	
$^{109}Ag-^{12}C\equiv^{12}C-^{37}Cl$	717.88218(28)	2.08(12)	−61.39(62)	
$^{107}Ag-^{13}C\equiv^{13}C-^{35}Cl$	743.37328(30)	2.33(14)	−77.8(11)	
$^{109}Ag-^{13}C\equiv^{13}C-^{35}Cl$	739.036371(95)	(2.33)[a]	−80.68(73)	
$^{63}Cu-^{12}C\equiv^{12}C-^{35}Cl$	989.14990(73)	17.89(64)	−84.78(49)	18.79(24)
$^{63}Cu-^{12}C\equiv^{12}C-^{37}Cl$	959.04302(38)	(17.89)[b]	−68.1(16)	19.09(62)
$^{65}Cu-^{12}C\equiv^{12}C-^{35}Cl$	976.73927(82)	17.64(73)	−84.4(15)	17.88(50)
$^{63}Cu-^{13}C\equiv^{13}C-^{35}Cl$	986.25614(29)	(17.89)[b]	−83.22(49)	17.81(26)

[a] Assumed from $^{107}Ag-^{13}C\equiv^{13}C-^{35}Cl$. [b] Assumed from $^{63}Cu-^{12}C\equiv^{12}C-^{35}Cl$.

the resulting ^{35}Cl nuclear quadrupole coupling constant is $\chi_{aa}(^{35}Cl) \approx -77$ MHz in each case. A survey of Cl nuclear quadrupole coupling constants in the literature reveals that $\chi_{aa}(^{35}Cl)$ values of the sign and magnitude observed here are commonly found in molecules in which a single terminal Cl atom is attached to carbon,[14] but only if the C−Cl bond either coincides with the principal inertia axis a of the molecule or makes a very small angle θ with it. An example of the former case is $H-C\equiv C-^{35}Cl$, for which $\chi_{aa}(^{35}Cl) = -79.7(1)$ MHz.[15] When the angle θ is not zero, $\chi_{aa}(^{35}Cl)$ is given by the usual projection formula $\chi_{aa}(^{35}Cl) = (1/2)\chi_0(^{35}Cl)\ (3\cos^2\theta - 1)$, where $\chi_0(^{35}Cl)$ is the value of the coupling constant along C−Cl bond direction. If θ is not very small, a significant reduction in the magnitude of $\chi_{aa}(^{35}Cl)$ results. For example, the carbene $Ag-C-^{35}Cl$ would have a large angle θ, therefore a $\chi_{aa}(^{35}Cl)$ much reduced in magnitude and consequently can be ruled out as the spectral source. A weakly bound complex involving Ar and a molecule containing Ag, C, and Cl atoms is unlikely to be a linear or a nearly linear molecule. A weak and long Ar to (Ag, C, Cl molecule) intermolecular bond would lead to smaller rotational constants than observed and a Cl nuclear quadrupole coupling constant much reduced in magnitude because of a projection of the above type and the effects of large amplitude zero-point averaging.

The only simple molecule containing Ag, C, and ^{35}Cl consistent with all of the arguments rehearsed above is the linear species $Ag-^{12}C\equiv^{12}C-^{35}Cl$. A fit of observed frequencies using the program PGOPHER[16] with a Hamiltonian

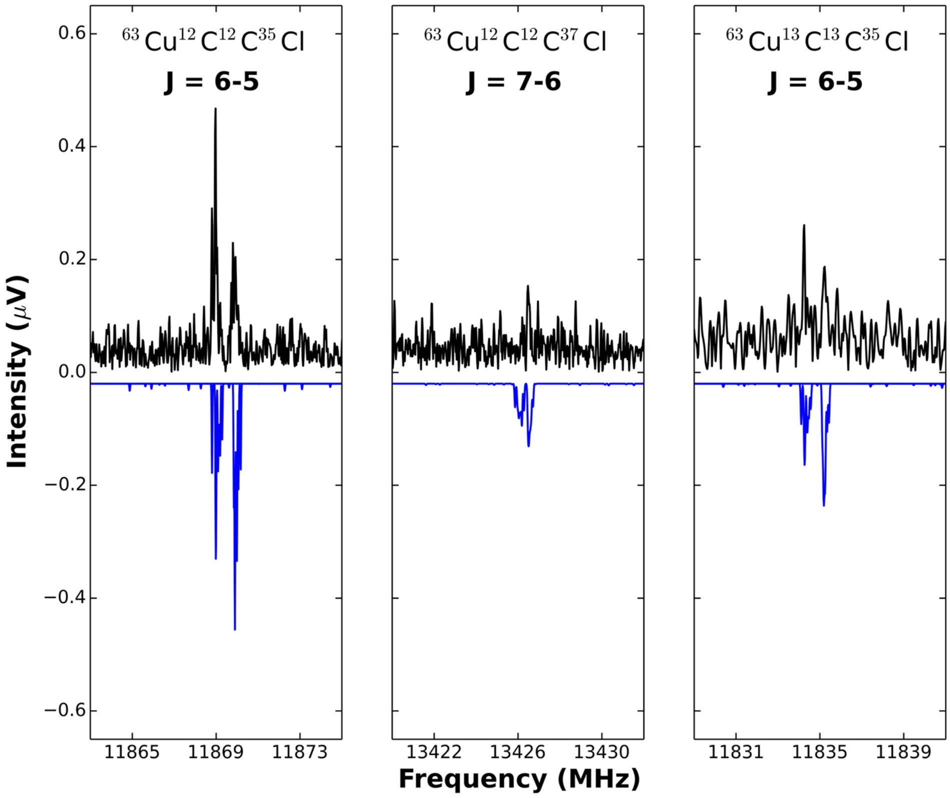

Figure 3. Observed and simulated transitions of various isotopologues of Cu−C≡C−Cl. The simulations are in color and downward pointing. The "noise" in the simulations is in fact unresolved hyperfine structure arising from Cu and Cl nuclear quadrupole coupling. The observed transitions resulted from the collection of 3 M FIDs in the left-hand and center panels and 2.2 M FIDs for the right-hand panel.

appropriate to the ground state of a semirigid, linear molecule, including Cl nuclear quadrupole coupling, leads to the spectroscopic constants B_0, D_J, and $\chi_{aa}(^{35}\mathrm{Cl})$ given in Table 1. The details of the fit are in the Supporting Information. If the observed rotational spectrum arises from Ag−^{12}C≡^{12}C−^{35}Cl, the corresponding spectra of the isotopologues ^{107}Ag−^{12}C≡^{12}C−^{37}Cl and ^{109}Ag−^{12}C≡^{12}C−^{37}Cl should be detectable with the same sample, given the natural abundance (24.2%) of ^{37}Cl ($I = 3/2$). Spectra of both isotopologues were indeed observed with the predicted Cl nuclear quadrupole hyperfine structure. The fitted spectroscopic constants for both are included in Table 1, while details of the fits are available as Supporting Information.

By using a sample of ^{13}CCl$_4$ (Cambridge Isotopes, 99 atoms % ^{13}C) in place of isotopically normal CCl$_4$, the rotational spectra of ^{107}Ag−^{13}C≡^{13}C−^{35}Cl and ^{109}Ag−^{13}C≡^{13}C−^{35}Cl were also observed (see Figure 2) and analyzed to give spectroscopic constants (also given in Table 1). Note that the ratio $\chi_{aa}(^{35}\mathrm{Cl})/\chi_{aa}(^{37}\mathrm{Cl})$ agrees with the ratio $Q(^{35}\mathrm{Cl})/Q(^{37}\mathrm{Cl}) = 1.2688$ of the chlorine nuclear electric quadrupole moments,[17] within the quite large experimental errors of the former, as required, and that $\chi_{aa}(^{35}\mathrm{Cl})$ is unchanged within the experimental error on substitution of ^{13}C at both ^{12}C atoms. The changes in the rotational constant B_0 accompanying the various isotopic substitutions are also consistent with bond lengths predicted for the linear molecule Ag−C≡C−Cl (see section 3.4).

3.3. Observation of the Rotational Spectrum of Cu−C≡C−Cl. If the conclusions from the two preceding sections are valid, it should also be possible to generate Cu−C≡C−Cl by an experimental approach similar to that used for Ag−C≡C−Cl but with a copper rod substituted for the silver rod. The rotational spectra of the three isotopologues ^{63}Cu−^{12}C≡^{12}C−^{35}Cl, ^{65}Cu−^{12}C≡^{12}C−^{35}Cl, and ^{63}Cu−^{12}C≡^{12}C−^{37}Cl were indeed observed when isotopically normal CCl$_4$ was employed. The spectra of all three isotopologues were weaker than those of the Ag analogues, as can be seen by comparing the Ag−C≡C−Cl transitions shown in Figure 2 with those of Cu−C≡C−Cl displayed in Figure 3. In fact, it is clear from examining Figure 3 that the transitions displayed for ^{63}Cu−^{12}C≡^{12}C−^{37}Cl are very near the limit of detection. As a result, only two different $J + 1 \rightarrow J$ transitions were detected and it was necessary to assume D_J unchanged from the parent isotopologue in order to obtain both the ^{63}Cu and ^{37}Cl nuclear quadrupole coupling constants. Consequently, the coupling constants have relatively large errors. The rotational spectrum of the isotopologue ^{63}Cu−^{13}C≡^{13}C−^{35}Cl was observed by using the ^{13}CCl$_4$ sample. The weakness of the Cu−C≡C−Cl transitions arises in part from the additional nuclear quadrupole hyperfine structure that results because both ^{63}Cu (abundance 69.2%) and ^{65}Cu (abundance 30.8%) have nuclei of spin $I = 3/2$ and significant electric quadrupole moments. Nevertheless, these more complicated spectra could be fitted by using PGOPHER,[16] with the choice of a standard Hamiltonian appropriate to the ground state of a semirigid linear molecule containing two quadrupolar nuclei to give the spectroscopic constants B_0, D_J, $\chi_{aa}(^{35}\mathrm{Cl})$, $\chi_{aa}(^{37}\mathrm{Cl})$, $\chi_{aa}(^{63}\mathrm{Cu})$ and $\chi_{aa}(^{65}\mathrm{Cu})$ included in Table 1. Detailed fits are available in the Supporting Information.

3.4. Geometry of Ag−C≡C−Cl and Cu−C≡C−Cl. Ab initio calculations confirm the experimental conclusion that the detected molecules are indeed Ag−C≡C−Cl and Cu−C≡C−

Table 2. Comparison of Properties of M−C≡C−Cl (M = Ag or Cu) Observed and Calculated at the CCSD(T)/aug-cc-pV5Z Level

	M = Ag		M = Cu	
spectroscopic property	ab initio	observed	ab initio	observed
$B(^{n}M^{12}C\equiv^{12}C^{35}Cl)$ (MHz)	742.6 (n = 107)	747.45619(16)	974.0 (n = 63)	989.14990(73)
$B(^{n}M^{12}C\equiv^{12}C^{35}Cl)$ (MHz)	738.3 (n = 109)	743.16060(19)	961.7 (n = 65)	976.72539(78)
$B(^{n}M^{12}C\equiv^{12}C^{37}Cl)$ (MHz)	717.4 (n = 107)	722.13078(21)	944.4 (n = 63)	959.04302(38)
$B(^{n}M^{12}C\equiv^{12}C^{37}Cl)$ (MHz)	713.2 (n = 109)	717.88218(28)	932.3 (n = 65)	
$B(^{n}M^{13}C\equiv^{13}C^{35}Cl)$ (MHz)	738.6 (n = 107)	743.37328(30)	971.2 (n = 63)	986.25614(29)
$B(^{n}M^{13}C\equiv^{13}C^{35}Cl)$ (MHz)	734.3 (n = 109)	739.03637(10)	958.9 (n = 65)	
molecular property	ab initio r_e values	observed r_0 values[a]	ab initio r_e values	observed r_0 values[a]
r(M−C) (Å)	2.0187	2.015(14)	1.8383	1.812(16)
r(C≡C) (Å)	1.2219	[1.2219]	1.2233	[1.2233]
r(C−Cl) (Å)	1.6491	1.635(6)	1.6479	1.639(6)
r(M···Cl) (Å)	4.8897	4.8722(2)	4.7095	4.6736(6)
	ab initio r_e values	observed r_s values	ab initio r_e values	observed r_s values
a_M (Å)	1.4113	1.4064(11)	1.8333	1.81718(83)
a_{Cl} (Å)	−3.4783	−3.46645(43)	−2.8761	−2.85710(53)
r(M···Cl) (Å)	4.8897	4.8729(12)	4.7095	4.6743(10)

[a] Calculated by fitting all available moments of inertia with r(C≡C) fixed at the ab initio value. The quoted errors are those generated by assuming a range of ±0.02 Å about the assumed r(C≡C) value.

Cl. The equilibrium bond lengths of Ag−C≡C−Cl and Cu−C≡C−Cl so determined are recorded in Table 2, together with the rotational constants they imply for the various isotopologues investigated. For comparison, the observed rotational constants are also included in Table 2. The small systematic differences of ca. 4.8 MHz for Ag−C≡C−Cl isotopologues and ca. 15.1 MHz for Cu−C≡C−Cl isotopologues between observed and calculated values no doubt arise because the observed rotational constants are zero-point quantities while those calculated refer to the hypothetical equilibrium geometry.

Although correlation problems prevent fitting of zero-point principal moments of inertia to determine independently all three distances r(M−C), r(C≡C), and r(C−Cl) necessary to define the r_0 geometry of the linear molecules M−C≡C−Cl (M = Ag or Cu), some progress is possible as follows. We assume that, for Ag−C≡C−Cl, r(C≡C) lies within 0.02 Å of the equilibrium value 1.2219 Å calculated at the CCSD(T)/aug-cc-pV5Z level of theory (a reasonable assumption given the high level of theory and the fact that the difference[18,19] between r_0 and r_e for the short, stiff triple bond in acetylene is 0.003 Å). The values that result from fitting the other two distances to all six observed zero-point principal moments of inertia (using the program STRFIT of Kisiel[20]) are then r(Ag−C) = 2.015(14) Å and r(C−Cl) = 1.635(6) Å, where the errors quoted reflect the range of values implied by the assumed range ±0.02 Å in r(C≡C). These results are included in Table 2 together with the corresponding r_0 quantities, similarly determined, for Cu−C≡C−Cl.

While the individual r_0 bond distances r(M−C) and r(C−Cl) are not well determined by this approach, the overall length of the molecule is. The distance r(M···Cl) between the two outer atoms turns out to be very insensitive to the assumed value of r(C≡C). For example, if we assign the large error of ±0.02 Å to the assumed distance r(C≡C) = 1.2219 Å in Ag−C≡C−Cl, r(Ag···Cl) takes the value 4.8722(2) Å. Similar conclusions follow for Cu−C≡C−Cl, as recorded in Table 2.

A better approach to the determination of the full geometry of each molecule M−C≡C−Cl (M = Ag or Cu) would be to obtain the r_s coordinate of every atom of the parent isotopologue by making isotopic substitutions at each atom in turn. Kraitchman[21] provided a simple equation relating the change ΔB_e in the *equilibrium* rotational constant accompanying isotopic substitution at an atom i in a linear molecule and the *equilibrium* coordinate z_i^e of the substituted atom i, namely

$$|z_i^e| = \left\{\left(\frac{h}{8\pi^2\mu}\right)\frac{\Delta B_e}{B_e B_e'}\right\}^{1/2} \tag{1}$$

where $\Delta B_e = B_e - B_e'$ is the change in the rotational constant accompanying the isotopic substitution, $\mu = M\Delta m/(M + \Delta m)$ is the reduced mass of the substitution, and M and Δm are the mass of the parent molecule and the mass change, respectively. Except for the simplest of linear molecules, equilibrium rotational constants are unavailable, however. Much used alternatives to equilibrium coordinates of atoms are the so-called r_s quantities. The r_s coordinate of an atom i is defined by using zero-point rotational constants in Kraitchman's equations in place of equilibrium values.[22] The r_s geometry has the advantage that it is closer to its r_e counterpart than the r_0 variety; for example, it is readily shown that $r_s = (r_0 + r_e)/2$ for a diatomic molecule. Moreover, r_s geometries show greater internal consistency when overdetermined than do the r_0 variety. The rotational spectra of the two ^{13}C singly substituted isotopologues M−^{13}C≡^{12}C−^{35}Cl and M−^{12}C≡^{13}C−^{35}Cl were not observed for either M = Ag or Cu in the present investigation, so a full r_s geometry is unfortunately not available for either molecule.

Nevertheless, some measure of the agreement between the partial r_s geometry and the r_e (ab initio calculated) version is available for each M−C≡C−Cl from a comparison of the principal axis coordinates a_M and a_{Cl} and, thereby, the distances between the outer atoms M and Cl obtained by the two methods. The results from ^{109}Ag and ^{37}Cl single substitutions made in the parent molecule ^{107}Ag−^{12}C≡^{12}C−^{35}Cl are $|a_{Ag}|$ = 1.4064(11) Å, $|a_{Cl}|$ = 3.46645(43) Å, respectively, and thence r(Ag···Cl) = 4.8729(12) Å, all of which are in good agreement with their equilibrium counterparts obtained ab initio at the CCSD(T)/aug-cc-pV5Z level of theory and with the r_0 versions

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(see Table 2). The corresponding r_s quantities for the Cu analogue are $|a_{Cu}|$ = 1.8172(8) Å, $|a_{Cl}|$ = 2.8571(5) Å, and r(Cu···Cl) = 4.6753(10)Å based on the $^{63}Cu-^{12}C\equiv^{12}C-^{35}Cl$ isotopologue as parent, and these too are in good agreement with the ab initio and r_0 values (see Table 2).

4. CONCLUSION

New tetra-atomic linear molecules Ag−C≡C−Cl and Cu−C≡C−Cl have been synthesized by a laser-ablation method and were unambiguously characterized by means of their rotational spectra. It is difficult to discuss the precise mechanism by which Ag−C≡C−Cl and Cu−C≡C−Cl are formed, but it is well-known that CCl, CCCl, and CCl_2 are among the products when a thermal plasma is sustained in CCl_4/Ar mixtures.[23] The microwave rotational spectra of CCCl and CCl_2 are known,[24,25] and thereby we were able to establish the presence of both species in the laser-ablated, supersonically expanded gas pulses in the experiments described here. The approximate ratio of the amounts of AgCCCl, CCl_2, and CCCl determined from their detected signals was 1.0:1.0:0.1, with a similar ratio appropriate for CuCCCl. The geometry of the $^2\Sigma$ ground state of the CCCl radical has r(C−C) = 1.267 Å, r(C−Cl) =1.634 Å, and ∠CCCl = 156.9°. The first and third of these lie midway between the corresponding values in ethyne and ethene (see ref 18 for the r_0 geometries of HC≡CH and $CH_2{=}CH_2$), while r(C−Cl) = 1.634 Å is very similar to the corresponding distance determined here for both Ag−C≡C−Cl and Cu−C≡C−Cl. This suggests a structure for CCCl with 2.5 C−C bonds. Given that the CCCl radical is present together with Ag/Cu atoms (and/or ions), the formation of Ag−C≡C−Cl and Cu−C≡C−Cl from CCCl by picking up a Ag or Cu atom is one possible mechanism. The method described here promises a route to the synthesis of other new, simple molecules.

■ ASSOCIATED CONTENT

S Supporting Information

Fits of the ground-state rotational spectra of six isotopologues of Ag−C≡C−Cl and four isotopologues of Cu−C≡C−Cl using the program PGOPHER. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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