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Distortion of ethyne on coordination to silver acetylide, $C_2H_2 \cdots AgCCH$, characterised by broadband rotational spectroscopy and *ab initio* calculations

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The rotational spectra of six isotopologues of a complex of ethyne and silver acetylide, $C_2H_2 \cdots AgCCH$, are measured by both chirped-pulse and Fabry-Perot cavity versions of Fourier-transform microwave spectroscopy. The complex is generated through laser ablation of a silver target in the presence of a gas sample containing 1% C_2H_2 , 1% SF_6 , and 98% Ar undergoing supersonic expansion. Rotational, A_0 , B_0 , C_0 , and centrifugal distortion Δ_J and Δ_{JK} constants are determined for all isotopologues of $C_2H_2 \cdots AgCCH$ studied. The geometry is planar, C_{2v} and T-shaped in which the C_2H_2 sub-unit comprises the bar of the “T” and binds to the metal atom through its π electrons. In the r_0 geometry, the distance of the Ag atom from the centre of the triple bond in C_2H_2 is 2.2104(10) Å. The $r(HC\equiv CH)$ parameter representing the bond distance separating the two carbon atoms and the angle, $\angle(CCH)$, each defined within the C_2H_2 sub-unit, are determined to be 1.2200(24) Å and 186.0(5)°, respectively. This distortion of the linear geometry of C_2H_2 involves the hydrogen atoms moving away from the silver atom within the complex. The results thus reveal that the geometry of C_2H_2 changes measurably on coordination to $AgCCH$. A value of 59(4) Nm^{-1} is determined for the intermolecular force constant, k_σ , confirming that the complex is significantly more strongly bound than hydrogen and halogen-bonded analogues. *Ab initio* calculations of the r_e geometry at the CCSD(T)(F12*)/ACVTZ level of theory are consistent with the experimental results. The spectra of the $^{107}Ag^{13}C^{13}CH$ and $^{109}Ag^{13}C^{13}CH$ isotopologues of free silver acetylide are also measured for the first time allowing the geometry of the $AgCCH$ monomer to be examined in greater detail than previously. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4868035>]

I. INTRODUCTION

Experiments exploiting microwave spectroscopy are able to contribute highly precise and quantitative information about the geometry of complexes generated in the gaseous phase. The present work forms part of a wider effort that has recently applied microwave spectroscopy and *ab initio* calculations to characterise complexes that each consist of a coinage metal halide bound to simple Lewis bases such as CO, N_2 , H_2O , H_2S , NH_3 , and H_2 .^{1–8} This programme has recently focussed on complexes containing interactions between a metal atom and the π orbitals of either ethene⁹ or ethyne.¹⁰ According to the Dewar-Chart-Duncanson model, electron density is donated from π orbitals of the hydrocarbon to unfilled d -orbitals on the metal. This interaction is reinforced by a reciprocal transfer of electrons from d -orbitals of the metal into π^* antibonding orbitals of the hydrocarbon resulting in the formation of a strong bond. It is challenging to observe reactions on surfaces or in solution with the selectivity necessary to understand the interplay between many competing factors. Gas phase spectroscopy provides a powerful means of probing fundamental effects in isolation and

allows precise structural information to be obtained for complexes that contain only a single metal atom or ion.

The C_2H_4 molecule in $C_2H_4 \cdots AgCl$ coordinates with the metal atom through electrons in π orbitals resulting in a T-shaped (C_{2v}) geometry for the complex.⁵ It was shown that the $C=C$ double bond in the r_0 geometry for C_2H_4 lengthens by 0.0124 Å on attachment to the silver atom in $C_2H_4 \cdots AgCl$. The geometry of a complex containing ethyne, $C_2H_2 \cdots Ag-Cl$, was shown to be T-shaped, C_{2v} and planar.¹⁰ With respect to the geometry of the C_2H_2 monomer, the length of the $C\equiv C$ triple bond in $C_2H_2 \cdots Ag-Cl$ is greater by 0.017 Å. The angle $H-C\equiv^*$ is increased from 180° to 187.7(4)° in the r_0 geometry of the complex where $*$ indicates the midpoint of the $C\equiv C$ bond. It has been suggested that the geometries of $B \cdots Ag-X$ (where B is a simple Lewis base) complexes are generally consistent with empirical rules¹¹ originally developed to predict the geometries of hydrogen-bonded complexes. These rules would imply that where a bond is formed between either ethene or ethyne and a noble metal halide such as AgX (where X is a halogen atom), the complex will exist in a geometry where the axis of the AgX molecule intersects the internuclear axis of the atoms forming the π -bond and lies in the plane of symmetry of the π -orbital. This paper will explore the nature

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of the complex formed between C_2H_2 and the simple metal acetylide, AgCCH . The principal aims of this work are to probe the geometry of the complex formed between C_2H_2 and AgCCH and to test whether the empirical rules that accurately predict the geometries of similar hydrogen- and halogen-bonded complexes also apply to this example of a $\text{B} \cdots \text{AgCCH}$ complex. In addition, spectra have been measured and spectroscopic parameters determined for ^{13}C -containing isotopologues of AgCCH . The spectra measured for $^{107/109}\text{Ag}^{12}\text{C}^{12}\text{CH}$ and $^{107/109}\text{Ag}^{12}\text{C}^{12}\text{CD}$ are consistent with studies performed previously elsewhere.^{12,13}

II. EXPERIMENTAL

Two different spectrometers having different specifications were used to collect data during this work. Each of these is configured with a laser ablation source allowing the generation and study of metal-containing molecules. The initial experiment was conducted using a recently constructed CP-FTMW (chirped-pulse Fourier transform microwave) spectrometer. This instrument probes all transitions between 7 and 18.5 GHz simultaneously. The data permitted the identification of transitions and an initial assignment of the spectrum. A Fabry-Perot (FP) FTMW spectrometer was used in subsequent experiments. This device is tunable over the same range while having a bandwidth of 1 MHz for individual measurements. The FP-FTMW spectrometer has higher resolution than its CP counterpart and allowed more accurate determination of the spectroscopic parameters. Detailed descriptions of both microwave spectrometers^{14,15} and laser ablation sources^{16,17} used for this study have been given elsewhere and will not be repeated here.

In both instruments, a gas sample composed of $\sim 1\%$ SF_6 and $\sim 1\%$ C_2H_2 with a balance of argon is prepared at a stagnation pressure of 6 bars. This sample is pulsed from the 0.5 mm diameter circular orifice of a nozzle (Parker-Hannifin General Valve, Series 9) and passes over the surface of a silver rod from which material is ablated using 532 nm radiation from a Nd:YAG laser. Components in the resulting plasma react to yield $\text{C}_2\text{H}_2 \cdots \text{AgCCH}$. It was found to be possible to generate AgCCH from a sample that excludes SF_6 and contains $\sim 1\%$ C_2H_2 in 6 bars argon, consistent with work performed in other laboratories. However, the signal intensities of both AgCCH and $\text{C}_2\text{H}_2 \cdots \text{AgCCH}$ were found to be stronger when SF_6 was included in the gas sample. It was not possible to quantify the effect of SF_6 on these signal intensities to high precision given the challenges inherent in achieving shot-to-shot reproducibility from laser ablation events. However, an illustrative example can be provided. A signal/noise (S/N) ratio of 10:1 was achieved for the $4_{13} \leftarrow 5_{14}$ transition (observed at 15 620.2207 MHz) of $\text{C}_2\text{H}_2 \cdots \text{AgCCH}$ over 1200 averaging cycles when using the FP-FTMW spectrometer and a sample mixture consisting of 1% SF_6 , 1% C_2H_2 , and 98% argon. More than 2000 averaging cycles were found necessary to achieve a S/N ratio greater than 2:1 for the same transition in experiments performed under the same conditions while using a sample of 1% C_2H_2 and 99% argon (i.e., excluding SF_6). All the results presented herein were thus acquired while using gas samples contain-

ing SF_6 . A detailed mechanistic description of the process by which SF_6 or its fragmentation products might catalyse the production of AgCCH and $\text{C}_2\text{H}_2 \cdots \text{AgCCH}$ is unfortunately not available from these experiments.

Following supersonic expansion of the gas sample into either spectrometer, molecules and complexes in the sample are polarised by a pulse of microwave radiation. The delays between the opening of the solenoid valve and forming laser and microwave pulses are adjusted to optimise the intensities of observed rotational transitions. Each valve pulse is followed by a single microwave polarisation pulse and free induction decays (FID) measurement cycle in experiments performed using the FP-FTMW spectrometer. Each valve pulse performed using the CP-FTMW spectrometer is followed by a train of eight microwave polarisation pulses allowing the measurement of eight FID after every individual nozzle pulse. The averaged molecular FID is detected and Fourier transformed to yield the frequency domain spectrum. For the spectra acquired on the CP-FTMW spectrometer during this study, between 500 000 and 600 000 FIDs (acquired from between 62 500 and 75 000 valve pulses) were co-added in the time domain. The molecules travel perpendicular to the orientation of the detection horn antenna in the CP-FTMW spectrometer so that a single peak of FWHM $\cong 80$ kHz is observed for each transition. By choosing an instrumental geometry where propagation of the gas pulse is parallel to the axis of the FP cavity in the FP-FTMW spectrometer, an individual transition in the spectrum of $\text{C}_2\text{H}_2 \cdots \text{AgCCH}$ appears as a Doppler doublet with each component having full-width at half maximum ~ 5 kHz. Accurate frequency measurements are obtained on each instrument by locking to an external reference source accurate to 1 part in 10^{11} . Frequencies are measured with an estimated accuracy of $\sim \pm 0.5$ kHz using the FP-FTMW spectrometer.

Isotopically enriched samples of $^{12}\text{C}_2\text{D}_2$ and $^{13}\text{C}_2\text{H}_2$ were used to observe rotational transitions of $\text{Ag}^{12}\text{C}^{12}\text{CD}$, $\text{Ag}^{13}\text{C}^{13}\text{CH}$, $^{12}\text{C}_2\text{D}_2 \cdots \text{Ag}^{12}\text{C}^{12}\text{CD}$, and $^{13}\text{C}_2\text{H}_2 \cdots \text{Ag}^{13}\text{C}^{13}\text{CH}$. It will be shown that the silver atom in $\text{C}_2\text{H}_2 \cdots \text{AgCCH}$ is extremely close to the centre of mass in this complex. In order to unambiguously distinguish between the spectra of isotopologues containing ^{107}Ag and ^{109}Ag (which are present in naturally occurring silver in nearly equal abundance), experiments were performed using a sample of isotopically enriched ^{107}Ag (99.6% isotopically pure, CK Gas Products Ltd.) as a laser ablation target. This sample was available as a thin sheet of ^{107}Ag foil wrapped around a glass rod. The isotopic mass will be specified only where necessary in context of the discussion hereafter. Where the isotopic mass is not explicitly labelled, it can be assumed that the accompanying text is appropriate to the general case. It will sometimes be necessary to simultaneously refer to two isotopologues which differ in respect of the contained silver isotope. For example, “ $^{107/109}\text{Ag}^{12}\text{C}^{12}\text{CH}$ ” should be understood to indicate “ $^{107}\text{Ag}^{12}\text{C}^{12}\text{CH}$ and $^{109}\text{Ag}^{12}\text{C}^{12}\text{CH}$.”

III. AB INITIO CALCULATIONS

High level *ab initio* calculations are useful both to corroborate the interpretation of the spectra and to reduce the uncertainties on structural information deduced from the

spectra, particularly where insufficient data lead to highly correlated parameters in the spectral fit. We performed a series of high level calculations on the C_2H_2 , CuCCH , AgCCH , and AuCCH molecules, to compare to experimental structural information and to assign confidence intervals for the highest accessible level of theoretical prediction for the r_e values of the $\text{C}_2\text{H}_2 \cdots \text{AgCCH}$ complex. We report geometries optimised on a series of increasingly accurate potential energy surfaces, defined as

$$V_0 = E[\text{fc-CCSD(T)}(\text{F12}^*)/\text{ACVDZ}], \quad (1)$$

$$V_1 = E[\text{fc-CCSD(T)}(\text{F12}^*)/\text{ACVTZ}], \quad (2)$$

$$V_2 = V_1 + \Delta\text{CV with}$$

$$\Delta\text{CV} = E[\text{ae-CCSD(T)}(\text{F12}^*)/\text{ACVTZ}] - E[\text{fc-CCSD(T)}(\text{F12}^*)/\text{ACVTZ}], \quad (3)$$

$$V_3 = V_2 + \Delta\text{TQ with}$$

$$\Delta\text{TQ} = E[\text{fc-CCSDT(Q)}/\text{VDZ}] - E[\text{fc-CCSD(T)}/\text{VDZ}], \quad (4)$$

$$V_4 = V_3 + \Delta\text{DK with}$$

$$\Delta\text{DK} = E[\text{ae-CCSD(T)-DK}/\text{ACVTZ-DK}] - E[\text{ae-CCSD(T)}/\text{ACVTZ-DK}]. \quad (5)$$

The CCSD(T)(F12^{*}) method (explicitly correlated coupled cluster singles and doubles method with a perturbative treatment of triples^{18,19}) accounts for one-, two-, and three-body electron correlation effects, with very low basis set errors for the one- and two-body correlation contributions. Here, ae denotes that all electrons are included in the correlation treatment and fc denotes that only the valence electrons are included. The ΔCV , ΔTQ , and ΔDK correction energies improve the potentials by accounting, respectively, for core-valence electron correlation, a better treatment of three- and four-body electron correlation and a better treatment of special relativity. The technical details of our calculations are as follows: ACVDZ is short hand for the aug-cc-pwCVDZ basis set²⁰ for C, aug-cc-pVDZ for H,²¹ and the aug-cc-pwCVDZ-PP basis set for Cu, Ag, and Au.²² For Cu, Ag, and Au, a 10, 28, and 60 electron effective core potential²³ was used, respectively, to account for the effect of relativity. ACVTZ is short hand for the corresponding aug-cc-pwCVTZ basis combination, and VDZ denotes the cc-pVDZ combination. ACVTZ-DK denotes the aug-cc-pwCVTZ-DK basis sets^{24,25} for H, C, and Cu, where the contractions of the aug-cc-pwCVTZ basis sets have been reoptimised for use with the Douglas-Kroll method^{26,27} for treating all electron relativistic effects. The CCSD(T)(F12^{*}) calculations were performed with the Turbomole package^{28,29} using the def2-TZVP Coulomb fitting basis for the CABS approximation and the def2-QZVPP density fitting basis sets.³⁰ The geminal amplitudes were fixed according to the second-order coalescence conditions³¹ and a Slater-type correlation factor with exponent 1.0 a_0^{-1} was used.³² Second order DK-CCSD(T)

and CCSDT(Q) calculations were performed using the Molpro program package³³ and the MRCC program package,³⁴ respectively.

IV. RESULTS

A. Qualitative interpretation

The transitions displayed in Figure 1 were measured while probing the expanding gas sample containing C_2H_2 , SF_6 , Ag, and argon. The displayed section is only a very small portion of the 12 GHz bandwidth probed during the experiment. Neither C_2H_2 nor SF_6 possess an electric dipole moment and the various introduced components of the prepared gas sample do not possess any nuclei with $I > 1/2$. For these reasons, intense molecular transitions are comparatively sparse within the broad frequency range probed. Some transitions assign to acetone that is unavoidably introduced from the commercially supplied cylinder of ethyne (in which acetone is used as a stabilising solvent for ethyne). Consistent with a previous study³⁵ that probed expanding samples containing Ag and SF_6 , transitions can be observed for ^{109}AgF and ^{107}AgF at 15 829.646 and 15 873.548 MHz, respectively.

Further to the described signatures of known species, there are also new transitions in the spectrum which have not previously been measured. Many of these are distributed in patterns that are qualitatively similar to those observed previously during a study¹⁰ of $\text{C}_2\text{H}_2 \cdots \text{AgCl}$. It proves possible to connect sequential $J \leftarrow (J+1)$ transitions using a preliminary value of $\frac{B_0+C_0}{2}$ while assuming the geometry of a near-prolate asymmetric top. Each $J \leftarrow (J+1)$ transition consists of a central component (tentatively assigned as $J_{0K''+1} \leftarrow (J+1)_{0K'+1}$) and others at increments that suggest tentative assignment as

FIG. 1. The black trace is a 20 $\times$ magnification of the CP-FTMW spectrum of $\text{C}_2\text{H}_2 \cdots \text{AgCCH}$ after 600 000 FID acquisitions (8 FID acquisitions per valve pulse for 75 000 valve pulses). The insets highlight the tightly spaced transitions of $\text{C}_2\text{H}_2 \cdots ^{107}\text{AgCCH}$ (higher frequency) and $\text{C}_2\text{H}_2 \cdots ^{109}\text{AgCCH}$ (lower frequency) isotopologues. Panels (a), (c), and (b), respectively, show the $2_{12} \leftarrow 3_{13}$, $2_{02} \leftarrow 3_{03}$, and $2_{11} \leftarrow 3_{12}$ rotational transitions for $\text{C}_2\text{H}_2 \cdots \text{AgCCH}$.

$J_{1K'_{+1}} \leftarrow (J+1)_{1K'_{+1}}$ components. The patterns are consistent with expectations for a molecule or complex with very large A_0 rotational constant and B_0 and C_0 rotational constants where $B_0 - C_0 < 150$ MHz. The transitions tentatively assigned with $K_{-1} = 1$ are observed with a nuclear spin statistical weight of 3 relative to a weight of 1 for the $K_{-1} = 0$ transitions. Consistent with the previous study of $\text{C}_2\text{H}_2 \cdots \text{AgCl}$, this pattern of intensities implies a complex of C_{2v} geometry and the presence of hydrogen nuclei that are interchanged by a C_2 symmetry operation. The transitions are observed with greatest intensity where SF_6 and C_2H_2 are simultaneously present within the gas sample. They are also found to depend on the presence of ablated Ag within the expanding gas pulse and it is possible to identify two distinct series of transitions corresponding to ^{107}Ag - and ^{109}Ag -containing isotopologues. It is evident in Figure 1 that the frequency shift resulting from substitution of the silver isotope is very small (of the order of 200 kHz for a transition at ~ 9.3 GHz). It is therefore concluded that the silver atom is very close to the centre of mass in the carrier species.

All of the above observations mirror those made during an earlier study¹⁰ of $\text{C}_2\text{H}_2 \cdots \text{AgCl}$ and suggest that the new transitions should be assigned to another complex of C_{2v} (and T-shaped) symmetry. The preliminary determination of B_0 and C_0 from the measured transition frequencies allows an initial assessment of whether $\text{C}_2\text{H}_2 \cdots \text{AgF}$ is the carrier of the observed spectrum. Previous studies^{5,7,9,10,17} of $\text{B} \cdots \text{AgX}$ ($X = \text{F}, \text{Cl}$) complexes repeatedly found that the AgX bond length is within 1% of the equivalent length in the isolated AgX monomer. Applying the reasonable assumption that this level of similarity will also hold between $\text{C}_2\text{H}_2 \cdots \text{AgF}$ and AgF , the implication is that the $\cdots \text{Ag}$ bond length (defined in Figure 2) would have to be of the order of 3.1 Å for $\text{C}_2\text{H}_2 \cdots \text{AgF}$ to be the carrier of the observed spectrum. This is approximately 50% longer than predicted by calculations at the CCSD(T)(F12*) level of theory which have reliably predicted the geometries of other $\text{B} \cdots \text{MX}$ complexes with accuracies that are better than $\pm 1\%$. This suggests that $\text{C}_2\text{H}_2 \cdots \text{AgF}$ is a highly unlikely carrier of the spectrum and other possibilities require examination.

FIG. 2. The T-shaped, planar geometry of $\text{C}_2\text{H}_2 \cdots \text{AgCCH}$ with inertial axes indicated. The asterisk indicates the midpoint of the $\text{HC}\equiv\text{CH}$ bond.

It has been concluded that the carrier must be C_{2v} , T-shaped with symmetrically equivalent hydrogen nuclei interchanged by a C_2 symmetry operation and that the unit possesses a silver atom very close to the centre of mass. The requirement that the A_0 rotational constant is very large further suggests that most of the mass in the complex is located on the a -inertial axis. All these considerations together imply that the number of possible carrier species other than $\text{C}_2\text{H}_2 \cdots \text{AgF}$ is actually very small. One attractive possibility is that C_2H_2 binds to AgCCH to yield a T-shaped, C_{2v} complex of $\text{C}_2\text{H}_2 \cdots \text{AgCCH}$. The isolated AgCCH monomer has been generated by laser ablation and previously detected by microwave spectroscopy.^{12,13} It is known that C_2H_2 is present in the expanding gas sample with sufficient abundance to form molecular complexes. To explore this new possibility, the broadband spectrum can be examined for evidence of the isolated AgCCH monomer. Transitions of both $^{107}\text{AgCCH}$ and $^{109}\text{AgCCH}$ are indeed present with similar intensities to those of ^{107}AgF and ^{109}AgF . Comparisons of the preliminary values of the rotational constants with theoretical predictions for $\text{C}_2\text{H}_2 \cdots \text{AgCCH}$ at the CCSD(T)(F12*) level provide further encouragement. Experiments employing isotopically enriched samples of $^{13}\text{C}_2\text{H}_2$ and C_2D_2 were performed to allow isotopic shifts of the target complex to be tested against the model geometry of $\text{C}_2\text{H}_2 \cdots \text{AgCCH}$ (shown in Figure 2). It will be shown below that the observations unambiguously confirm that $\text{C}_2\text{H}_2 \cdots \text{AgCCH}$ is the carrier for the observed spectrum. The FP-FTMW spectrometer was used to perform measurements of transition frequencies at high resolution (± 0.5 kHz) and sensitivity prior to determination of the molecular geometry as described in Sec. IV C. Examples of transitions measured using the FP-FTMW spectrometer are displayed in Figure 3. One puzzling aspect of the observations remains. It was noted earlier that the presence of SF_6 within the gas sample significantly enhances the intensities of transitions now assigned to $\text{C}_2\text{H}_2 \cdots \text{AgCCH}$. It is not clear why this should

FIG. 3. The black trace shows the $3_{12} \leftarrow 4_{13}$ rotational transition of $\text{C}_2\text{H}_2 \cdots \text{AgCCH}$ as measured on the FP-FTMW spectrometer. The carrier of the lower frequency doublet is $\text{C}_2\text{H}_2 \cdots ^{109}\text{AgCCH}$ and that for the higher frequency doublet is $\text{C}_2\text{H}_2 \cdots ^{107}\text{AgCCH}$.

TABLE I. Spectroscopic parameters fitted for various isotopologues of AgCCH during this and previous works.

	$^{107}\text{AgCCH}$	$^{109}\text{AgCCH}$	$^{107}\text{AgCCD}$	$^{109}\text{AgCCD}$
B_0 (MHz)	3197.285220(60) ^{a,b}	3186.977263(38) ^a	2933.05547(41) ^a	2923.38049(41) ^a
D_J (kHz)	0.837307(23) ^a	0.832253(14) ^a	0.657(11) ^a	0.655(11) ^a
χ_{aa} (D) (kHz)	...	...	0.1540(94)	0.1474(95)
B_0 (MHz)	3197.28504(181) ^c	3186.97714(181) ^c	...	...
D_J (kHz)	0.799(120) ^c	0.832(120) ^c	...	...
B_0 (MHz)	3197.28507(23) ^d	3186.977519(34) ^d	2933.054723 ^d	2923.379302 ^d
D_J (kHz)	0.811(15) ^d	0.8417(22) ^d	0.6217 ^d	0.5908 ^d
χ_{aa} (D) (kHz)	...	...	0.154 ^e	0.147 ^e
N^f	3	3	2	2
$\sigma_{\text{r.m.s}}$ (kHz)	0.6	0.1	...	...

^aReference 13.^bNumbers in parentheses are one standard deviation in units of the last significant figure.^cReference 12.^dThis work. B_0 and D_J for $^{107}\text{AgCCD}$ and $^{109}\text{AgCCD}$ are the results of a fit of two constants to two frequencies and the errors are zero.^eFixed to the result presented in Ref. 13.^f N is the number of transitions included in the fit.

be true but an answer may ultimately be found through a greater understanding of the potentially complex sequence of reactions that yield $\text{C}_2\text{H}_2 \cdots \text{AgCCH}$ within the expanding gas pulse.

B. Spectral assignment and fitting

Measurements were performed on the AgCCH monomer and the $\text{C}_2\text{H}_2 \cdots \text{AgCCH}$ complex. The former is known to be a linear molecule^{12,13} while it will be shown that the latter adopts a C_{2v} , T-shaped geometry. The frequencies of all observed transitions are fitted using Western's PGOPHER³⁶ spectral assignment and fitting program. The Hamiltonian used for AgCCH is the simple expression appropriate to a linear molecule,

$$\mathbf{H}_R = B_0 \mathbf{J}^2 - D_J \mathbf{J}^4, \quad (6)$$

where B_0 and D_J are rotational and centrifugal distortion constants, respectively. Each of the spectrometers used during these experiments has an operational bandwidth that spans from ~ 6 GHz to 18.5 GHz. Given that B_0 is of the order of 3 GHz for $^{107}\text{AgCCH}$, it was possible to observe three different $J \leftarrow (J+1)$ transitions for $^{107}\text{Ag}^{12}\text{C}^{12}\text{CH}$ and $^{109}\text{Ag}^{12}\text{C}^{12}\text{CH}$ isotopologues, but only two such transitions for each of the analogous ^{13}C - and D -containing species. As a consequence, the two parameters (B_0 and D_J) are fitted to three frequencies for each of $^{107}\text{Ag}^{12}\text{C}^{12}\text{CH}$ and $^{109}\text{Ag}^{12}\text{C}^{12}\text{CH}$ but calculated from only two frequencies for each of $^{107}\text{Ag}^{13}\text{C}^{13}\text{CH}$, $^{109}\text{Ag}^{13}\text{C}^{13}\text{CH}$, $^{107}\text{Ag}^{12}\text{C}^{12}\text{CD}$, and $^{109}\text{Ag}^{12}\text{C}^{12}\text{CD}$. The results for isotopologues containing ^{12}C are compared with those of previous works in Table I while those for $^{107}\text{Ag}^{13}\text{C}^{13}\text{CH}$ and $^{109}\text{Ag}^{13}\text{C}^{13}\text{CH}$ are presented in Table II. The Hamiltonian applied for $\text{C}_2\text{H}_2 \cdots \text{AgCCH}$ has the form

$$\mathbf{H}_R = A J_a^2 + \left(\frac{B_0 + C_0}{2} \right) (\mathbf{J}^2 - J_a^2) + \left(\frac{B_0 - C_0}{2} \right) (J_+^2 + J_-^2) - \Delta_J \mathbf{J}^4 - \Delta_{JK} \mathbf{J}^2 J_a^2, \quad (7)$$

where A_0 , B_0 , and C_0 are rotational constants and Δ_J , Δ_{JK} are the centrifugal distortion constants for a semi-rigid, near-prolate asymmetric top. Under the assumption of a nearly prolate, asymmetric rotor molecule for which $(J+1)_{0,J+1} \leftarrow J_{0,J}$ and $(J+1)_{1,J+1} \leftarrow J_{1,J}$ transitions can be observed, the determinable spectroscopic constants are A_0 , B_0 , C_0 and the centrifugal distortion constants Δ_J and Δ_{JK} . The data are most complete and authoritative for the $^{12}\text{C}_2\text{H}_2 \cdots ^{107/109}\text{Ag}^{12}\text{C}^{12}\text{CH}$ isotopologues, which were studied in natural abundance. However, a value was obtained for each parameter for all isotopologues studied. In the case of the $^{13}\text{C}_2\text{H}_2 \cdots ^{107/109}\text{Ag}^{13}\text{C}^{13}\text{CH}$ isotopologues, generated using a synthetically enriched sample of $^{13}\text{C}_2\text{H}_2$, an unfavourable nuclear spin statistical weight ratio (see below) means that $K_{-1} = 1$ transitions are of weaker intensity and because of the limited amount of $^{13}\text{C}_2\text{H}_2$ available, the number of measurements only just exceeds the number of spectroscopic constants to be fitted. The centrifugal distortion constant Δ_J is strongly correlated with the rotational constant A_0 . To check that this constant was properly determined for the $^{13}\text{C}_2\text{H}_2$ based species, the values were calculated by using the GAUSSIAN³⁷ electronic structure package. The geometry of $\text{C}_2\text{H}_2 \cdots \text{AgCCH}$ was optimised at the MP2/aug-cc-pVQZ level of theory and the various vibration-rotation constants calculated. In particular, the quartic centrifugal distortion constant Δ_J is found to be in agreement within experimental error with those observed for all isotopologues of $\text{C}_2\text{H}_2 \cdots \text{AgCCH}$ reported here. Hence, the values of Δ_J determined in the fits of frequencies

TABLE II. Spectroscopic parameters fitted for ^{13}C -containing isotopologues of AgCCH during this work.

	$^{107}\text{Ag}^{13}\text{C}^{13}\text{CH}$	$^{109}\text{Ag}^{13}\text{C}^{13}\text{CH}$
B_0 (MHz)	3014.833680 ^a	3004.494493
D_J (kHz)	0.7600	0.7617
N	2	2

^a B_0 and D_J for $^{107}\text{Ag}^{13}\text{C}^{13}\text{CH}$ and $^{109}\text{Ag}^{13}\text{C}^{13}\text{CH}$ are the results of a fit of two constants to two frequencies and the errors are zero.

TABLE III. Spectroscopic parameters fitted for various isotopologues of $\text{C}_2\text{H}_2\cdots\text{AgCCH}$ during this work.

Spectroscopic constant	$\text{C}_2\text{H}_2\cdots^{107}\text{AgCCH}$	$\text{C}_2\text{H}_2\cdots^{109}\text{AgCCH}$	$^{13}\text{C}_2\text{H}_2\cdots^{107}\text{Ag}^{13}\text{C}^{13}\text{CH}$
A_0 (MHz)	34 936(50) ^a	34 950(120)	33 239(41)
B_0 (MHz)	1579.56940(26)	1579.53918(61)	1468.430876(91)
C_0 (MHz)	1509.70215(26)	1509.67502(60)	1404.913582(95)
Δ_J (kHz)	0.1711(39)	0.1714(92)	0.1500(43)
Δ_{JK} (kHz)	23.86(28)	23.58(67)	20.38(17)
$\Delta_0 = (I_c^0 - I_a^0 - I_b^0)/(\text{u}\text{\AA}^2)$	0.34(2)	0.35(5)	0.356(19)
N^b	14	14	6
$\sigma_{\text{r.m.s}}$ (kHz)	1.5	3.6	0.4
	$^{13}\text{C}_2\text{H}_2\cdots^{109}\text{Ag}^{13}\text{C}^{13}\text{CH}$	$\text{C}_2\text{D}_2\cdots^{107}\text{AgCCD}$	$\text{C}_2\text{D}_2\cdots^{109}\text{AgCCD}$
A_0 (MHz)	33 234(171)	25 262.8(52)	25 292(17)
B_0 (MHz)	1468.40136(46)	1446.39579(32)	1446.37455(64)
C_0 (MHz)	1404.88712(45)	1366.52161(29)	1366.50275(50)
Δ_J (kHz)	0.145(16)	0.1215(47)	0.1340(86)
Δ_{JK} (kHz)	20.6(7)	20.102(87)	19.77(15)
$\Delta_0 = (I_c^0 - I_a^0 - I_b^0)/(\text{u}\text{\AA}^2)$	0.35(5)	0.42(4)	0.418(13)
N^b	7	13	12
$\sigma_{\text{r.m.s}}$ (kHz)	1.9	2.4	4.2

^aNumbers in parentheses are one standard deviation in units of the last significant figure.^bNumber of transitions included in the fit.

for the two $^{13}\text{C}_2\text{H}_2\cdots^{107/109}\text{Ag}^{13}\text{C}^{13}\text{CH}$ isotopologues by the same method are clearly satisfactory, as are those for the other isotopologues, for which more transitions are included in the fits. This permits confidence in the determined values of the rotational constants A_0 , which are important in the arguments about geometry given in Sec. IV C 2. The results of fits of all spectroscopic parameters for $\text{C}_2\text{H}_2\cdots\text{AgCCH}$ are displayed in Table III. Transition frequencies and details of all spectroscopic fits are available in the supplementary material.³⁸

The value of $\frac{B_0+C_0}{2}$ for $\text{C}_2\text{H}_2\cdots\text{AgCCH}$ is of the order of 1.5 GHz allowing five different $J \leftarrow (J+1)$ transitions to be measured for $^{12}\text{C}_2\text{H}_2\cdots^{107/109}\text{Ag}^{12}\text{C}^{12}\text{CH}$ while only four distinct $J \leftarrow (J+1)$ transitions could be measured for ^{13}C - and D-containing isotopologues. It has been explained that the intensity of a $K_{-1} = 1$ component of a given $J \leftarrow (J+1)$ transition compares with that where $K_{-1} = 0$ in a 3:1 ratio for a T-shaped, planar, C_{2v} complex. Exchanging each hydrogen ($I = 1/2$) for a deuterium ($I = 1$) alters the nuclear spin statistics such that the ratio of relative intensities is 1:2 in favour of transitions where $K_{-1} = 0$. Likewise, exchanging $^{12}\text{C}_2\text{H}_2$ for $^{13}\text{C}_2\text{H}_2$ yields an intensity ratio of 6:10 in favour of $K_{-1} = 0$ transitions. As a consequence, fewer $J_{1K'_{-1}} \leftarrow (J+1)_{1K'_{-1}}$ transitions are accessible to measurement for ^{13}C -containing isotopologues than for ^{12}C -containing species. The fact that observation is consistent with these arguments from nuclear spin statistical weightings supports the hypothesis that the complex has the basic geometry shown in Figure 2. Additional to transitions where $K_{-1} = 0$ or 1, it was possible to measure and assign a small number of transitions where $K_{-1} = 2$ for $\text{C}_2\text{D}_2\cdots^{107/109}\text{AgCCD}$ isotopologues. This was not possible for undeuterated isotopologues and is presumably a consequence of values for A_0 that are significantly lower for deuterated species than their undeuterated counterparts. The result is evidently a greater population of complexes in excited K_{-1} states subsequent to the supersonic expansion and

more intense transitions involving $K_{-1} = 2$ states. The inclusion of transitions where $K_{-1} = 2$ allows the A_0 rotational constant to be fitted with reasonable precision even for deuterated isotopologues. Figure 4 displays a transition measured using the FP-FTMW spectrometer where $K_{-1} = 2$.

C. Molecular geometry

1. AgCCH

The molecular geometries of CuCCH , AgCCH , and AuCCH have been examined by several recent works. The most complete determination is available for CuCCH where rotational constants have been measured for 6 isotopologues.³⁹ Measurements of the transitions of

FIG. 4. The $5_{24} \leftarrow 6_{25}$ rotational transition of $\text{C}_2\text{D}_2\cdots^{107}\text{AgCCD}$ as measured on the FP-FTMW spectrometer.

$^{63}\text{Cu}^{12}\text{C}^{12}\text{CH}$, $^{65}\text{Cu}^{12}\text{C}^{12}\text{CH}$, $^{63}\text{Cu}^{12}\text{C}^{13}\text{CH}$, $^{63}\text{Cu}^{13}\text{C}^{13}\text{CH}$, $^{63}\text{Cu}^{13}\text{C}^{12}\text{CH}$, and $^{63}\text{Cu}^{12}\text{C}^{12}\text{CD}$ allowed a complete r_s geometry to be determined with respect to a $^{63}\text{Cu}^{12}\text{C}^{12}\text{CH}$ parent and also permitted a r_0 geometry to be established. These measurements revealed that the complex is linear, and that the $\text{C}\equiv\text{C}$ bond length in CuCCH is greater by 0.06 Å than that found in C_2H_2 in the r_0 geometry. Okabayashi *et al.*¹³ acquired rotational spectra for two isotopologues of AuCCH allowing $r(\text{Au}-\text{C}) = 1.903$ Å and $r(\text{C}-\text{H}) = 1.055$ Å to be determined under the assumption that $r(\text{C}\equiv\text{C})$ is the same as the equivalent distance of 1.212 Å in CuCCH .

Two recent works have explored the geometry of AgCCH which has also been shown to be a linear molecule. Cabezas *et al.*¹² measured transitions for the $^{107}\text{Ag}^{12}\text{C}^{12}\text{CH}$ and $^{109}\text{Ag}^{12}\text{C}^{12}\text{CH}$ isotopologues and reported that $r(\text{Ag}-\text{C}) \cong 2.02$ Å if the values of $r(\text{C}\equiv\text{C})$ and $r(\text{C}-\text{H})$ are assumed equal to those in C_2H_2 . Okabayashi *et al.*¹³ obtained additional data for $^{107}\text{Ag}^{12}\text{C}^{12}\text{CD}$ and $^{109}\text{Ag}^{12}\text{C}^{12}\text{CD}$ isotopologues allowing the determination of other parameters. Their published data allow the calculation of r_s coordinates for the Ag and H atoms according to the expression provided by Kraitchman,⁴⁰

$$\left(\frac{\Delta I_b}{\mu_s}\right)^{\frac{1}{2}} = |a_{\text{Ag}}|, \quad (8)$$

where $\mu_s = (\Delta m M)/(M + \Delta m)$ is the reduced mass on isotopic substitution of one atom within the molecule. The mass of the parent isotopologue is denoted by M and the mass change resulting from the isotopic substitution is represented by Δm . The resulting principal axis coordinates are $a_{\text{Ag}} = -0.509(3)$ Å for Ag and $a_{\text{H}} = +3.776(1)$ Å for H where the uncertainties are calculated using $\Delta a_{\text{Ag}} = 0.0015/|a_{\text{Ag}}|$ as recommended by Costain.⁴¹ The data acquired during the present work are consistent with these substitution coordinates for the silver and hydrogen atoms. It is possible to assume a value of $r(\text{C}\equiv\text{C})$ and employ the first moment condition to determine a partial r_s geometry. However, in the absence of data from a greater range of isotopologues, we prefer to employ the results of accurate theory to perform a partial r_s fit to determine the $r(\text{Ag}-\text{C})$ bond distance as described in Sec. IV C 2 below.

An r_0 geometry was provided by Okabayashi *et al.*¹³ Rotational constants have been measured for ^{13}C -containing isotopologues during the present work (Table II). These provide an opportunity to fit a r_0 geometry with reference to a more extensive set of isotopologues. Under the assumption that the molecule is linear, the $r(\text{Ag}-\text{C})$, $r(\text{C}\equiv\text{C})$, and $r(\text{C}-\text{H})$ bond distances are fitted to the rotational constants of $^{107}\text{Ag}^{13}\text{C}^{13}\text{CH}$, $^{109}\text{Ag}^{13}\text{C}^{13}\text{CH}$, $^{107}\text{Ag}^{12}\text{C}^{12}\text{CH}$, $^{109}\text{Ag}^{12}\text{C}^{12}\text{CH}$, $^{107}\text{Ag}^{12}\text{C}^{12}\text{CD}$, and $^{109}\text{Ag}^{12}\text{C}^{12}\text{CD}$ to determine the r_0 geometry provided in Table IV. Data from $\text{Ag}^{12}\text{C}^{13}\text{CH}$ and $\text{Ag}^{13}\text{C}^{12}\text{CH}$ isotopologues are not available and it should be noted that the results of this unconstrained fit of all parameters are highly correlated. It can be expected that the fit will be relatively insensitive to the locations of the carbon atoms and that the standard deviations quoted will not provide a good indication of the precision of the results. This is presumably the reason for the differences between the unconstrained r_0 geometry presented by Okabayashi *et al.*,¹³

that presented herein and the results from our calculations at a high level of theory. Values of parameters in the r_s geometry will be discussed below alongside the results of the *ab initio* calculations.

2. *Ab initio* calculations

For C_2H_2 , the agreement between the highest level of theory and experiment is 5×10^{-4} Å and 2×10^{-4} Å for the $r_e(\text{C}\equiv\text{C})$ and $r_e(\text{C}-\text{H})$ bond lengths, respectively (Table IV). The accuracy of the *ae*-CCSD(T)(F12*) geometries (V_2) is already excellent and the effect of higher-order correlation is less than 1×10^{-3} Å. For the CuCCH , AgCCH , and AuCCH molecules, the magnitude and sign of the post *fc*-CCSD(T) effects on $r_e(\text{C}-\text{C})$ and $r_e(\text{C}-\text{H})$ are very similar to C_2H_2 and we therefore assign error bars of 1×10^{-3} Å to the values predicted by the V_2 potential surfaces. For the $r_e(\text{M}-\text{C})$ bond length, again higher order correlation (ΔTQ) does not appear to be important. For the CuCCH and AuCCH molecules, it is possible to account for relativistic effects explicitly rather than implicitly (ΔDK), which lengthens $r_e(\text{Cu}\equiv\text{C})$ by 3.4×10^{-3} Å. We therefore assign conservative error bars of 5×10^{-3} Å for the $r_e(\text{M}-\text{C})$ bond lengths predicted by our V_2 potential surfaces. The calculated results are somewhat different to those determined through unconstrained fitting to the experimentally determined moments of inertia. It has been noted that the fits to the experimental data involve extensively correlated parameters.

The described high accuracy of the calculations permits an alternative approach to determination of the molecular geometry of AgCCH . First, the differences, δr , between the r_e values calculated at the highest level of theory for each of $r(\text{C}\equiv\text{C})$ and $r(\text{C}-\text{H})$ and the corresponding r_0 parameters in the isolated C_2H_2 monomer are determined. Next, each value of δr so obtained is added to the r_e value calculated at the V_3 level of theory for each individual parameter in AgCCH . The resulting parameters are fixed in a fit to obtain a partial r_0 value for $r(\text{Ag}-\text{C})$ in AgCCH as shown in Table IV. The result of 2.0096(1) Å is consistent with the calculated result to within 5×10^{-3} Å as expected. In order to test the described procedure, an equivalent calculation employing both theoretical and experimental results is also performed for CuCCH drawing upon the experimental data provided in Ref. 39. The result of 1.8114(1) Å so obtained for $r(\text{Cu}-\text{C})$ is in excellent agreement with the V_4 result of 1.8144 Å and also with that obtained through the unconstrained fit to experimental data made available in Ref. 39. The experimentally determined r_s result for the $r(\text{Cu}-\text{C})$ parameter presented in Ref. 39 and the r_e value calculated herein are also within 5×10^{-3} Å of each other. However, the r_s results for $r(\text{C}\equiv\text{C})$ and $r(\text{C}-\text{H})$ are not within the expected 1×10^{-3} Å of the r_e bond lengths calculated at the V_4 level.

3. $\text{C}_2\text{H}_2 \cdots \text{AgCCH}$

A_0 , B_0 , and C_0 rotational constants are available for $^{12}\text{C}_2\text{H}_2 \cdots ^{107}\text{Ag}^{12}\text{C}^{12}\text{CH}$, $^{12}\text{C}_2\text{H}_2 \cdots ^{109}\text{Ag}^{12}\text{C}^{12}\text{CH}$, $^{13}\text{C}_2\text{H}_2 \cdots ^{107}\text{Ag}^{13}\text{C}^{13}\text{CH}$, $^{13}\text{C}_2\text{H}_2 \cdots ^{109}\text{Ag}^{13}\text{C}^{13}\text{CH}$,

TABLE IV. Parameters in the geometries of CuCCH, AgCCH, and AuCCH determined experimentally and by *ab initio* calculation.

	CuCCH		
	$r(\text{C}\equiv\text{C})$ (Å)	$r(\text{C}-\text{H})$ (Å)	$r(\text{Cu}-\text{C})$ (Å)
V_0 [fc-CCSD(T)(F12*)/ACVDZ] ^{a,b}	1.2229	1.0666	1.8138
V_1 [fc-CCSD(T)(F12*)/ACVTZ] ^b	1.2209	1.0649	1.8104
V_2 [$V_1 + \Delta\text{CV}$] ^b	1.2181	1.0636	1.8104
V_3 [$V_2 + \Delta\text{TQ}$] ^b	1.2190	1.0636	1.8110
V_4 [$V_3 + \Delta\text{DK}$] ^b	1.2188	1.0636	1.8144
Exp. (r_0) ^c	1.212(2)	1.058(1)	1.818(1)
Exp. (r_0) ^d	[1.2222]	[1.0641]	1.8114(1)
Exp. (r_s) ^c	1.213	1.058	1.819
	AgCCH		
	$r(\text{C}\equiv\text{C})$ (Å)	$r(\text{C}-\text{H})$ (Å)	$r(\text{Ag}-\text{C})$ (Å)
V_0 [fc-CCSD(T)(F12*)/ACVDZ] ^b	1.2222	1.0668	2.0230
V_1 [fc-CCSD(T)(F12*)/ACVTZ] ^b	1.2202	1.0651	2.0191
V_2 [$V_1 + \Delta\text{CV}$] ^b	1.2170	1.0638	2.0064
V_3 [$V_2 + \Delta\text{TQ}$] ^b	1.2178	1.0638	2.0070
Exp. (r_0) ^e	[1.203]	[1.060]	≈ 2.02
Exp. (r_0) ^f	1.227	1.052	2.007
Exp. (r_0) ^g	1.2444(30)	1.0452(11)	1.9954(20)
Exp. (r_0) ^h	[1.2210]	[1.0643]	2.0096(1)
Exp. (r_s) ⁱ	[1.2210]	[1.0643]	2.000(3)
	AuCCH		
	$r(\text{C}\equiv\text{C})$ (Å)	$r(\text{C}-\text{H})$ (Å)	$r(\text{Au}-\text{C})$ (Å)
V_0 [fc-CCSD(T)(F12*)/ACVDZ] ^b	1.2160	1.0658	1.9151
V_1 [fc-CCSD(T)(F12*)/ACVTZ] ^b	1.2143	1.0643	1.9135
V_2 [$V_1 + \Delta\text{CV}$] ^b	1.2114	1.0631	1.9052
V_3 [$V_2 + \Delta\text{TQ}$] ^b	1.2121	1.0631	1.9061
Exp. (r_0) ^f	[1.212]	1.055	1.903
	C_2H_2		
	$r(\text{C}\equiv\text{C})$ (Å)	$r(\text{C}-\text{H})$ (Å)	
V_0 [fc-CCSD(T)(F12*)/ACVDZ] ^b	1.2059	1.0647	...
V_1 [fc-CCSD(T)(F12*)/ACVTZ] ^b	1.2051	1.0631	...
V_2 [$V_1 + \Delta\text{CV}$] ^b	1.2027	1.0619	...
V_3 [$V_2 + \Delta\text{TQ}$] ^b	1.2034	1.0619	...
Exp. (r_0) [C_2H_2] ^j	1.206553(6)	1.06238(2)	...
$\delta r = [\text{Exp. } (r_0) - \text{calc. } (V_3, (r_e))]$	0.003153(6)	0.00048(2)	...
Exp. (r_0) [C_2D_2] ^j	[1.206553]	1.060113	...
Exp. (r_e) [C_2H_2] ^k	1.20286(3)	1.06166(6)	...
	C_2H_2	$^{13}\text{C}_2\text{H}_2$	C_2D_2
Exp. (B_0) (MHz) ^l	35 274.9693(54)	33 564.005	25 418.6291

^aStandard deviations are enclosed within parentheses immediately after fitted results in this table. Where no standard deviation is given, the result is a direct calculation. Square brackets indicate values that are held fixed while other parameters are fitted.

^bThis work.

^cReference 39.

^d $r(\text{Cu}-\text{C})$ bond distance fitted to data provided in Ref. 20 with $r(\text{C}\equiv\text{C})$ and $r(\text{C}-\text{H})$ fixed to the values obtained by adding δr to the r_e results calculated at the fc-CCSD(T)(F12*)/ACVTZ + ΔCV + ΔTQ level.

^eFrom Ref. 12, where the approach taken was to assume $r(\text{C}\equiv\text{C}) = 1.203$ Å and $r(\text{C}-\text{H}) = 1.060$ Å allowing determination of $r(\text{Ag}-\text{C})$.

^fReference 13.

^gThis work. Coordinates for the various atoms in the fitted r_0 geometry are $a_{\text{H}} = 3.776(2)$ Å, $a_{\text{C1}} = 2.731(2)$ Å, $a_{\text{C2}} = 1.486(2)$ Å, $a_{\text{Ag}} = -0.509(2)$ Å. The standard deviations are determined from those in the bond lengths.

^hThis work. $r(\text{C}\equiv\text{C})$ and $r(\text{C}-\text{H})$ are fixed to the values obtained by adding δr to the r_e results calculated at the fc-CCSD(T)(F12*)/ACVTZ + ΔCV + ΔTQ level. Coordinates for the various atoms are $a_{\text{H}} = 3.7853(1)$ Å, $a_{\text{C1}} = 2.7210(1)$ Å, $a_{\text{C2}} = 1.5001(1)$ Å, $a_{\text{Ag}} = -0.5095(1)$ Å.

ⁱThis work. $r(\text{C}\equiv\text{C})$ and $r(\text{C}-\text{H})$ are fixed to the values obtained by adding δr to the r_e results calculated at the fc-CCSD(T)(F12*)/ACVTZ + ΔCV + ΔTQ level to allow a partial r_s determination of $r(\text{Ag}-\text{C})$. The experimental results obtained during this work and Ref. 13 consistently find the r_s coordinates of Ag and H to be $-0.509(3)$ Å and $3.776(1)$ Å, respectively.

^jCalculated by fitting the moments of inertia, I_0 , of $^{12}\text{C}_2\text{H}_2$ and $^{13}\text{C}_2\text{H}_2$ from Ref. 42.

^kReference 49.

^lReference 42.

$^{12}\text{C}_2\text{D}_2 \cdots ^{107}\text{Ag}^{12}\text{C}^{12}\text{CD}$, and $^{12}\text{C}_2\text{D}_2 \cdots ^{109}\text{Ag}^{12}\text{C}^{12}\text{CD}$. Attempts to generate and study isotopologues containing a combination of ^{12}C and ^{13}C atoms involved mixing $^{12}\text{C}_2\text{H}_2$ with isotopically enriched samples of $^{13}\text{C}_2\text{H}_2$, but were not successful. It has thus been possible to generate isotopologues that are the result of multiple isotopic substitutions at C or H atoms but not their singly substituted analogues. For this reason, it is not possible to establish a full set of r_s coordinates for C and H atoms within the complex, although as indicated below it is possible to determine the r_s coordinates b_{C} and b_{H} as well as a value for the a -coordinate of Ag. The data allow for a more complete but still partial determination of the r_0 molecular geometry. The r_s coordinates will be discussed first, together with arguments about the molecular symmetry. The r_0 geometry will then be presented.

Ground-state rotational constants of three isotopologues of free ethyne⁴² and the various r_0 geometries of the molecule that can be determined from them are collected together in Table IV. It is clear that the A_0 values for the two isotopologues of $\text{C}_2\text{H}_2 \cdots \text{AgCCH}$ containing ^{12}C shown in Table III are identical within the large experimental errors and each is only slightly reduced from the B_0 value of $\text{H}^{12}\text{C}^{12}\text{CH}$ (Table IV). Similar relationships exist between the A_0 values of either of $^{12}\text{C}_2\text{D}_2 \cdots ^{107}\text{Ag}^{12}\text{C}^{12}\text{CD}$ or $^{12}\text{C}_2\text{D}_2 \cdots ^{109}\text{Ag}^{12}\text{C}^{12}\text{CD}$ and B_0 for free $\text{D}^{12}\text{C}^{12}\text{CD}$, and also between the corresponding species containing $\text{H}^{13}\text{C}^{13}\text{CH}$. These observations, when taken together with the nuclear spin statistical weight arguments presented earlier, offer strong evidence of a planar, T-shaped molecule, in which C_2H_2 forms the bar of the T while AgCCH lies along a C_2 axis to form the stem. It will be shown later that zero-point angular oscillations of both components of the T will be small because the intermolecular bond in $\text{C}_2\text{H}_2 \cdots \text{AgCCH}$ is strong. This motion is unlikely, therefore, to be responsible for the majority of the reduction in A_0 with respect to B_0 of free C_2H_2 . A similar reduction is not observed in complexes of C_2H_2 that are more weakly bound such as $\text{C}_2\text{H}_2 \cdots \text{ClF}$, for example.⁴³ The change can be ascribed mainly to distortions of the C_2H_2 subunit in $\text{C}_2\text{H}_2 \cdots \text{AgCCH}$. The suggestion of a planar, T-shaped geometry is supported by the values of the inertia defects Δ_0 of the various isotopologues.

The inertia defect, Δ_0 , of a planar molecule is defined by

$$\Delta_0 = I_c^0 - I_a^0 - I_b^0, \quad (9)$$

where I_a^0 , I_b^0 , and I_c^0 are zero-point principal moments of inertia. Values of Δ_0 for the various isotopologues investigated are included in Table III. The errors in Δ_0 are large as a result of the relatively poor determination of the A_0 , but nevertheless it is clear that Δ_0 is indeed small and positive, with a mean value of $0.38(5) \text{ u } \text{\AA}^2$. For small, planar covalent molecules that do not have low-energy vibrational modes, Δ_0 usually falls in the range $0.05\text{--}0.15 \text{ u } \text{\AA}^2$. On the other hand, complexes that are relatively weakly bound, such as the hydrogen- and halogen-bonded molecules $\text{C}_2\text{H}_2 \cdots \text{HCl}$ and $\text{C}_2\text{H}_2 \cdots \text{ClF}$,^{43,44} both of which have a T-shaped geometry, have larger Δ_0 values [$1.2(3)$ and $0.636(2) \text{ u } \text{\AA}^2$, respectively] as a result of low-wavenumber, intermolecular vibrational modes that contribute to the zero-point motion. The complex $\text{C}_2\text{H}_2 \cdots \text{AgCl}$ is also planar and T-shaped¹⁰ but is

more strongly bound than its hydrogen and halogen-bonded analogues, resulting in the smaller $\Delta_0 = 0.34(3) \text{ u } \text{\AA}^2$. Smaller values of Δ_0 are evidently a reflection of an increased rigidity of the intermolecular bond. This is confirmed by the intermolecular stretching force constants, k_σ , which take the values $6.9(4)$, $10.0(1)$, $51(3)$, and $59(2) \text{ N m}^{-1}$, respectively, for the series $\text{C}_2\text{H}_2 \cdots \text{HCl}$, $\text{C}_2\text{H}_2 \cdots \text{ClF}$, $\text{C}_2\text{H}_2 \cdots \text{AgCl}$, and $\text{C}_2\text{H}_2 \cdots \text{AgCCH}$.^{10,43,44} According to this criterion at least, $\text{C}_2\text{H}_2 \cdots \text{AgCl}$ and $\text{C}_2\text{H}_2 \cdots \text{AgCCH}$ have a similar intermolecular binding strength. A simple model⁴⁵ relates Δ_0 to the wavenumber ω/c of the lowest energy, in-plane vibration of the molecule according to

$$\Delta_0 \approx 4K/\omega, \quad (10)$$

where $K = (h/8\pi^2c) = 16.8576 \text{ u } \text{\AA}^2 \text{ cm}^{-1}$. For $^{12}\text{C}_2\text{H}_2 \cdots \text{Ag}^{12}\text{C}^{12}\text{CH}$, Eq. (10) predicts the lowest, in-plane vibrational harmonic wavenumber $\omega/c = 198 \text{ cm}^{-1}$, when the mean value $\Delta_0 = 0.34 \text{ u } \text{\AA}^2$ for the ^{107}Ag and ^{109}Ag species from Table III is used. $\text{C}_2\text{H}_2 \cdots \text{AgCCH}$ is a much more complicated molecule than those for which Eq. (10) was originally derived.

In order to distinguish the various parameters within the C_2H_2 monomer from those within AgCCH during a discussion of the molecular geometry of $\text{C}_2\text{H}_2 \cdots \text{AgCCH}$, the $r(\text{C}\equiv\text{C})$, and $r(\text{C}-\text{H})$ parameters within the C_2H_2 sub-unit of $\text{C}_2\text{H}_2 \cdots \text{AgCCH}$ will hereafter be termed $r(\text{HC}\equiv\text{CH})$ and $r(\text{HC}_2-\text{H})$. The AgCCH sub-unit is assumed to be linear throughout this work so the $\angle(\text{CCH})$ label applies only to the $\text{C}\equiv\text{C}-\text{H}$ angle within the C_2H_2 sub-unit. A complete r_s or r_0 determination of the molecular geometry would require data from each of three forms of singly substituted isotopologue in which a ^{12}C atom is substituted for ^{13}C . The isotopic combinations available to this work permit only partial r_s and r_0 geometries to be determined on the basis of single isotopic substitution at the Ag atom and multiple substitutions at the C and H atoms (Table V). In all cases, the $^{12}\text{C}_2\text{H}_2 \cdots ^{107}\text{Ag}^{12}\text{C}^{12}\text{CH}$ isotopologue is selected as the parent species during the calculation of r_s coordinates. The B_0 rotational constant available for $^{12}\text{C}_2\text{H}_2 \cdots ^{109}\text{Ag}^{12}\text{C}^{12}\text{CH}$ permits the a_{Ag} coordinate of the silver atom in the r_s geometry to be determined as $0.055(27) \text{ \AA}$ using the method (appropriate to a planar asymmetric rotor) and expression for calculating the uncertainty in the parameter proposed by Costain.⁴¹ The analysis does not specify the sign for the coordinate but only a positive result yields a physically realistic level of agreement with the $\text{CCSD(T)}(\text{F12}^*)$ calculations and the r_0 geometry presented below. High uncertainties are generally associated with small coordinates in r_s geometries. However, comparisons^{9,10} with results from other methods of geometry determination have previously shown that the Ag atoms within $\text{C}_2\text{H}_2 \cdots \text{AgCl}$ and $\text{C}_2\text{H}_4 \cdots \text{AgCl}$ are located with reasonably high precision. It is also possible to calculate r_s coordinates for Ag with respect to $^{13}\text{C}_2\text{H}_2 \cdots ^{107}\text{Ag}^{13}\text{C}^{13}\text{CH}$ or $\text{C}_2\text{D}_2 \cdots ^{107}\text{AgCCH}$ parent species. The results are $0.057(26) \text{ \AA}$ and $0.051(29) \text{ \AA}$, respectively, mainly reflecting the changed location of the centre of mass of the complex when substituting all ^{12}C or H atoms for their heavier isotopes.

TABLE V. Parameters in the geometry of $\text{C}_2\text{H}_2\cdots\text{AgCCH}$ determined experimentally.

	r_s I_a^0	r_0 (I_a^0, I_b^0, I_c^0)	r_0 (I_b^0, I_c^0)
$r(\text{C-H})^a$ (Å)	...	[1.0646]	[1.0646]
$r(\text{C}\equiv\text{C})^a$ (Å)	...	[1.2237]	[1.2237]
$r(\text{Ag}-\text{C})^a$ (Å)	...	[2.0094]	[2.0094]
$r(\text{Ag}\cdots)^*$ (Å)	...	2.2104(10)	2.2096(2)
$r(\text{HC}\equiv\text{CH})$ (Å)	1.213(5)	1.2200(24)	1.2327(3)
$r(\text{HC}_2-\text{H})^b$ (Å)	[1.0665]	[1.0665]	[1.0665]
$\angle(\text{CCH})$ (deg)	189.4(1)	186.0(5)	185.88(8)
a_{Ag} (Å)	0.055(27) ^c	0.06024(11)	0.06040(2)
b_{H} (Å)	$\pm 1.659(1)$	$\pm 1.6707(24)$	$\pm 1.6772(18)$
b_{C} (Å)	$\pm 0.607(4)$	$\pm 0.6100(12)$	$\pm 0.6163(3)$

^a $r(\text{C}\equiv\text{C})$ and $r(\text{C-H})$ are fixed at values obtained by adding Δr_e (see Table VI) to the r_0 results for isolated AgCCH determined as described in footnote h of Table IV. The value of $r(\text{Ag}-\text{C})$ is fixed at the r_0 result obtained by fitting this parameter to the experimentally determined moments of inertia for the AgCCH monomer while $r(\text{C}\equiv\text{C}) = 1.2210$ Å and $r(\text{C-H}) = 1.0643$ Å are assumed.

^bFixed to the value obtained by adding the experimentally determined r_0 result for isolated C_2H_2 to Δr_e , the calculated change on formation of the complex (see Tables IV and VI).

^cIt is also possible to calculate r_s coordinates for Ag with respect to substitution of ^{109}Ag into $^{13}\text{C}_2\text{H}_2\cdots^{107}\text{Ag}^{13}\text{C}^{13}\text{CH}$ or $\text{C}_2\text{D}_2\cdots^{107}\text{AgCCD}$ parent species. The results are 0.057(26) Å and 0.051(29) Å, respectively (see text).

A semi-empirical method can be used to test whether the very small coordinate a_{Ag} evaluated by the r_s method is seriously underestimated. The approach is based on the fact that substitution of an atom by one of its more massive isotopes attenuates the zero-point motion of that atom and the bonds attached to it appear to shrink.^{45,46} As a result, the r_s coordinate obtained is often underestimated in magnitude. The semi-empirical method involves correcting the moments of inertia of the substituted molecule for this shrinkage and then using the values so corrected in Kraitichman's equation to give a revised r_s coordinate of the atom in question. The bond shrinkage in the diatomic molecule AgCl is 3.6×10^{-6} Å, as discussed in Ref. 10. In the absence of more appropriate data, we assume that the $\cdots\text{Ag}$ and $\text{Ag}-\text{C}$ bonds in $\text{C}_2\text{H}_2\cdots\text{Ag}-\text{CCH}$ both shrink by this amount on substitution of ^{109}Ag into $^{12}\text{C}_2\text{H}_2\cdots^{107}\text{Ag}^{12}\text{C}^{12}\text{CH}$. The changes to the moments of inertia of $^{12}\text{C}_2\text{H}_2\cdots^{109}\text{Ag}^{12}\text{C}^{12}\text{CH}$ attendant on such a shrinkage are $\Delta I_b^{\text{shrink}} = -0.000902 \text{ u Å}^2$ and $\Delta I_c^{\text{shrink}} = -0.000900 \mu\text{Å}^2$, if the r_0 geometry given in Table V (and calculated as described below) is used in their calculation. The values $I_b + \Delta I_b^{\text{shrink}}$ and $I_c + \Delta I_c^{\text{shrink}}$ are then the principal moments of inertia of $^{12}\text{C}_2\text{H}_2\cdots^{109}\text{Ag}-^{12}\text{C}^{12}\text{CH}$ corrected for bond shrinkage and when used in the version of Eq. (8) appropriate to a planar asymmetric top yield the value $|a_{\text{Ag}}^{\text{corr}}| = 0.059(27)$ Å. This should be compared with the uncorrected r_s coordinate of 0.055(27) Å and the value 0.06024(11) Å from the r_0 geometry of Table V. The change is very small indeed. If the atom in question were a first row atom, the uncorrected coordinate would undoubtedly be imaginary and the shrinkage correction large. In the limit of isotopic substitution at an atom of very large (essentially infinite) mass, the zero-point change and the correction to the coordinate are both negligible. There is now evidence that substitutions at ^{107}Ag fall into this category.^{7,9}

The calculation of b_{C} and b_{H} coordinates is assisted by the T-shaped symmetry of the complex and employs ΔI_a^0 calculated from the fitted values of the A_0 rotational constants. In view of the molecular planarity and the existence of the symmetry operation C_2^a , the change ΔI_a^0 in the equilibrium principal moment of inertia that accompanies the double isotopic substitution of X by X' (X = ^{12}C or H; X' = ^{13}C or D) at symmetrically equivalent atoms is related to the equilibrium co-ordinate b_{X} by the expression⁴⁷

$$|b_{\text{X}}| = \left\{ \frac{\Delta I_a}{2\Delta m} \right\}^{\frac{1}{2}} \quad (11)$$

in which $2\Delta m$ is the mass change on the double substitution. The evaluated coordinates of the C atoms imply $r(\text{HC}\equiv\text{CH})$ of 1.213(5) Å, representing a lengthening of the bond relative to unbound C_2H_2 . It is not possible to independently determine $\angle(\text{CCH})$ and $r(\text{HC}_2-\text{H})$ from only the b_{H} coordinate but the assumption that $r(\text{HC}_2-\text{H})$ is equal to the r_0 distance in free C_2H_2 leads to $\angle(\text{CCH})$ of 189.4(1) $^\circ$.

Three moments of inertia, I_a^0 , I_b^0 , and I_c^0 are available for each of the isotopologues studied. These can be employed to determine parameters in the r_0 geometry of the complex. Owing to the lack of data from isotopologues containing a single substitution at a selected carbon atom, it is first necessary to make some initial assumptions about the geometry of the AgCCH unit. Previous works^{9,10,17,35} have revealed small differences between the fitted r_0 and *ab initio* r_e geometries where the same theoretical approaches have been applied. Our calculations predict that each of the $r(\text{Ag}-\text{C})$, $r(\text{C}\equiv\text{C})$, and $r(\text{C-H})$ parameters changes slightly by a quantity defined here as Δr_e (Table VI) when AgCCH coordinates to C_2H_2 . The values of $r(\text{C}\equiv\text{C})$ and $r(\text{C-H})$ that were earlier held fixed in the partial r_0 fit to determine $r(\text{Ag}-\text{C})$ for the AgCCH monomer are thus added to the respective values of Δr_e to reflect their changes on formation of the complex. The value of $r(\text{Ag}-\text{C})$ obtained through the partial r_0 fit of the geometry of monomer AgCCH, and the value of $r(\text{C-H})$ in the r_e geometry of the C_2H_2 sub-unit are corrected for their changes on complex formation in the same way. The resulting values of all these parameters are held fixed in fits to determine the geometry of $\text{C}_2\text{H}_2\cdots\text{AgCCH}$ from the experimental data. It is thus possible to arrive at the values for $r(\text{Ag}\cdots)^*$, $r(\text{HC}\equiv\text{CH})$, and $\angle(\text{CCH})$ in the r_0 geometry that are shown in the second column of Table V. The symmetry of the complex and multiple isotopic substitutions at the ^{12}C atoms assist the determination of the $r(\text{HC}\equiv\text{CH})$ bond length which is found to be 1.2200(24) Å. The $\angle(\text{CCH})$ parameter is determined to be 186.0(5) $^\circ$. These results indicate significant changes from the r_0 geometry of the isolated C_2H_2 molecule and will be the subject of further discussion in Sec. V. Excluding the I_a^0 moments of inertia which are less well-determined than the I_b^0 and I_c^0 values yields slightly altered results (final column) for the $\angle(\text{CCH})$ and $r(\text{HC}\equiv\text{CH})$ parameters.

It has been shown that the formation of a complex between C_2H_2 and AgCl results in measurable changes from the r_0 molecular geometries of both the C_2H_2 and AgCl sub-units.¹⁰ Some caution is warranted given that $r(\cdots\text{Ag})$ in the r_0 geometry of $\text{C}_2\text{H}_2\cdots\text{AgCCH}$ is sensitive to the

TABLE VI. Parameters in the geometry of $C_2H_2 \cdots AgCCH$ determined by *ab initio* calculation.

	AgCCH + C_2H_2 $r_e(\text{ae-CCSD(T)}(F12^*))^a$		$C_2H_2 \cdots AgCCH$ $r_e(\text{ae-CCSD(T)}(F12^*))$		Δr_e^b
	ACVDZ	ACVTZ	ACVDZ	ACVTZ	
$r(C-H)$ (Å)	1.0664	1.0638	1.0661	1.0641	+0.0003
$r(C \equiv C)$ (Å)	1.2217	1.2170	1.2221	1.2197	+0.0027
$r(Ag-C)$ (Å)	2.0145	2.0064	2.0101	2.0062	-0.0002
$r(Ag \cdots *)$ (Å)	...	...	2.1966	2.1887	...
$r(HC \equiv CH)$ (Å)	1.2054	1.2027	1.2184	1.2164	+0.0137
$r(HC_2-H)$ (Å)	1.0642	1.0619	1.0680	1.0660	+0.0041
$\angle(CCH)$ (deg)	180.00	180.00	187.18	187.16	+7.16

^aThe ae-CCSD(T)(F12*)/ACVTZ level of theory is equivalent to the V_2 level defined in Table IV.^b Δr_e is obtained by subtracting the value of the parameter in the r_e geometry calculated at the CCSD(T)(F12*)/ACVTZ level for AgCCH from the corresponding quantity in the r_e geometry of $C_2H_2 \cdots AgCCH$.

geometry assumed for AgCCH. Bond lengths and angles within the C_2H_2 sub-unit are significantly less sensitive to the geometry assumed for the AgCCH sub-unit. The excellent level of agreement between the experimental and calculated geometries of AgCCH as shown in Table IV provides confidence.

D. Intermolecular stretching force constant k_σ of $C_2H_2 \cdots AgCCH$

The quadratic force constant, k_σ , associated with stretching the intermolecular bond in a complex is one measure of the strength of that bond. For weakly bound complexes formed between rigid subunits, the centrifugal distortion constant Δ_J can be used to give k_σ at two levels of approximation. The most appropriate here is that due to Millen,⁴⁸ which relates Δ_J to k_σ under the assumption of subunits that are rigid and unperturbed in geometry when subsumed into the complex. For a planar T-shaped molecule of C_{2v} symmetry, such as $C_2H_2 \cdots AgCCH$ in which component AgCCH is perpendicular to the internuclear axis of the linear subunit C_2H_2 , the required expression is

$$k_\sigma = (8\pi^2\mu/\Delta_J)[B^3(1-b) + C^3(1-c) + \frac{1}{4}(B-C)^2(B+C)(2-b-c)]. \quad (12)$$

In Eq. (12), $\mu = (m_{C_2H_2}m_{AgCCH})/(m_{C_2H_2} + m_{AgCCH})$, $b = (B/B_{C_2H_2}) + (B/B_{AgCCH})$, and $c = (C/B_{C_2H_2}) + (C/B_{AgCCH})$, where $B_{C_2H_2}$ and B_{AgCCH} are rotational constants of the component molecules and strictly should be equilibrium values and the spectroscopic constants B , C , and Δ_J of $C_2H_2 \cdots AgCCH$ should also be equilibrium values. Usually zero-point values (see Table III) are used, given that equilibrium quantities are rarely available. Equation (12) applies only in the quadratic approximation and only if the intermolecular stretching mode σ lies much lower in wavenumber of the other modes of the same symmetry. The values of k_σ calculated for the six isotopologues of $C_2H_2 \cdots AgCl$ for which Δ_J is available experimentally (Table III) by using Eq. (12) and the appropriate spectroscopic constants yields values of 58.0(13), 57.7(31), 57.8(17), 59.6(66), 64.5(71), and 58.5(38) $N m^{-1}$ for the isotopologues $C_2H_2 \cdots ^{107}AgCCH$, $C_2H_2 \cdots ^{109}AgCCH$,

$^{13}C_2H_2 \cdots ^{107}Ag^{13}C^{13}CH$, $^{13}C_2H_2 \cdots ^{109}Ag^{13}C^{13}CH$, $C_2D_2 \cdots ^{107}AgCCD$, and $C_2D_2 \cdots ^{109}AgCCD$, respectively. The relatively large errors quoted are those propagated from the errors in Δ_J only. The mean value of 59(4) $N m^{-1}$ leads to the wavenumber $\omega_\sigma/c = 211(4) cm^{-1}$. The value of $\omega_\sigma/c = 283 cm^{-1}$ was determined in harmonic wavenumber calculations at the CCSD(T)(F12*)/ACVDZ level of theory (Table VII). The significant difference from the Δ_J based result suggests that Eq. (12) is not entirely appropriate for $C_2H_2 \cdots AgCCH$ and it is noted from the *ab initio* calculations that there is another low-wavenumber stretching mode (predicted at 445 cm^{-1}). In the approximation that both component molecules are point masses and using $(1/2)(B+C)$

TABLE VII. Results of *ab initio* calculations of harmonic vibrational wavenumbers for $C_2H_2 \cdots AgCCH$, C_2H_2 , and AgCCH.

	Symmetry	$C_2H_2 \cdots AgCCH$ Wavenumber (cm^{-1})	Fragment ^a Wavenumber (cm^{-1})
		$C_2H_2 \cdots AgCCH$	AgCCH
*...Ag-C bend ^b	B ₂	59	...
*...Ag-C bend	B ₁	60	...
*...Ag stretch	A ₁	283	...
$C_2H_2 \cdots Ag$ rock	B ₁	294	...
Ag-C-C bend	B ₁	207	181
Ag-C-C bend	B ₂	224	181
Ag-C stretch	A ₁	445	417
C-C-H bend	B ₂	617	628
C-C-H bend	B ₁	631	628
C-C stretch	A ₁	2035	2033
C-H stretch	A ₁	3437	3439
C-C-H bend	A ₂	604	590
C-C-H bend	B ₁	674	590
H-C-C-H wag	B ₂	744	743
H-C-C-H wag	A ₁	778	743
C-C stretch	A ₁	1952	2011
C-H stretch	B ₁	3379	3413
C-H stretch	A ₁	3465	3508

^aWavenumbers listed in this column apply to modes within the isolated monomers, AgCCH or C_2H_2 , respectively, and as indicated.^bThe symmetry labels are those appropriate to modes within the $C_2H_2 \cdots AgCCH$ complex.

as the rotational constant of the resulting diatomic molecules, Eq. (12) becomes

$$k_{\sigma} = 16\pi^2\mu \left\{ \frac{1}{2}(B+C) \right\}^3 / \Delta_J \quad (13)$$

which leads to a mean value of $k_{\sigma} = 300 \text{ N m}^{-1}$ and the wavenumber $\omega_{\sigma/C} = 126 \text{ cm}^{-1}$, clearly both in serious disagreement with the results from Millen's model. The dissociation energy of the complex has been calculated to be 92 kJ mol^{-1} at the CCSD(T)(F12*)/ACVDZ level.

V. CONCLUSIONS

The data acquired from ^{13}C -containing isotopologues have allowed the geometry of the AgCCH monomer to be examined in greater detail than previously. The results confirm that the coordinates of the Ag and H atoms in the r_s geometry are $-0.509(3) \text{ \AA}$ and $3.776(1) \text{ \AA}$, respectively. This is consistent with the positions of those atoms given by a r_0 fit to the moments of inertia. The present r_0 determinations of $r(\text{C-H})$ and $r(\text{Ag-C})$ are in moderate agreement with calculations at the CCSD(T)(F12*)/ACVTZ level of theory. The spectra of $\text{Ag}^{13}\text{C}^{12}\text{CH}$ and $\text{Ag}^{12}\text{C}^{13}\text{CH}$ isotopologues will be required before a reliable $r(\text{C}\equiv\text{C})$ distance can be provided in the experimental r_0 geometry of the free AgCCH molecule.

The most significant conclusions of the present study arise from the data acquired for the $\text{C}_2\text{H}_2 \cdots \text{AgCCH}$ complex. Both the r_s geometry determined by fitting to the A_0 rotational constant and the r_0 geometry determined from the B_0 and C_0 rotational constants show that $r(\text{HC}\equiv\text{CH})$ is extended relative to the equivalent parameter in free C_2H_2 . Comparing the r_0 geometries⁴² of free C_2H_2 and $\text{C}_2\text{H}_2 \cdots \text{AgCCH}$, the fits of the geometry to the experimentally determined rotational constants imply an extension of between 0.014 and $0.026 \text{ \AA}$ whereas the *ab initio* result (Table VI) suggests an extension of $0.014 \text{ \AA}$ in the r_e geometry. Distortion of the geometry of C_2H_2 on attachment to AgCCH is also evident in the $\angle(\text{CCH})$ parameter which is 180° in the free C_2H_2 molecule. This angle is $186.0(5)^\circ$ in the experimental r_0 geometry of $\text{C}_2\text{H}_2 \cdots \text{AgCCH}$ and 187.2° in the calculated r_e geometry. The possibility of large amplitude, zero-point angular oscillation of the C_2H_2 subunit about its equilibrium position in the T-shaped molecule $\text{C}_2\text{H}_2 \cdots \text{AgCCH}$ has been ignored in deducing the reported distortion of the ethyne subunit. In the much more weakly bound, isomorphous complex $\text{C}_2\text{H}_2 \cdots \text{ClF}$,⁴³ for which distortion of the C_2H_2 geometry is expected to be negligible, the effect of the C_2H_2 zero-point oscillation is to increase the rotational constant A_0 by $\sim 200 \text{ MHz}$ from that expected if there were no change in C_2H_2 geometry, namely, a value close to B_0 of free C_2H_2 . In fact, A_0 of $\text{C}_2\text{H}_2 \cdots \text{AgCCH}$ is decreased by $\sim 340 \text{ MHz}$ from the latter quantity. If the C_2H_2 oscillation were significant in $\text{C}_2\text{H}_2 \cdots \text{AgCCH}$ (as it is for $\text{C}_2\text{H}_2 \cdots \text{ClF}$), this decrease would require us to invoke a much larger distortion of the C_2H_2 subunit when subsumed into $\text{C}_2\text{H}_2 \cdots \text{AgCCH}$ than is deduced here. Given the excellent agreement between the experimental and *ab initio* results and the much greater binding

TABLE VIII. Comparison of parameters in the geometry of $\text{C}_2\text{H}_2 \cdots \text{AgCCH}$ with those in other complexes that contain C_2H_2 .

	$k_{\sigma} \text{ (N m}^{-1}\text{)}$	$r(\text{HC}\equiv\text{CH}), \angle(\text{CCH})$	
$\text{C}_2\text{H}_2 \cdots \text{HBr}$	5.5	...	Ref. 44
$\text{C}_2\text{H}_2 \cdots \text{Cl}_2$	5.6	...	Ref. 50
$\text{C}_2\text{H}_2 \cdots \text{BrCl}$	9.4	...	Ref. 51
$\text{C}_2\text{H}_2 \cdots \text{ClF}$	10	...	Ref. 43
$\text{C}_2\text{H}_2 \cdots \text{ICl}$	12.2	...	Ref. 52
$\text{C}_2\text{H}_2 \cdots \text{AgCl}$	51	$1.2231(28) \text{ \AA}, 187.7(4)^\circ$	Ref. 10
$\text{C}_2\text{H}_2 \cdots \text{AgCCH}$	59	$1.2200(24) \text{ \AA}, 186.0(5)^\circ$	This work

strength, the assumption of a significant zero-point angular oscillation of C_2H_2 seems unnecessary for $\text{C}_2\text{H}_2 \cdots \text{AgCCH}$.

Table VIII compares the k_{σ} values determined for a range of T-shaped, C_{2v} complexes in which C_2H_2 binds to a hydrogen, halogen, or silver atom. It is apparent that the silver-containing complexes are more strongly bound than the hydrogen- or halogen-bonded species. The strength of these binding interactions are consistent with the observed lengthening of $r(\text{HC}\equiv\text{CH})$ in the $\text{C}_2\text{H}_2 \cdots \text{AgCCH}$ complex and the deformation away from the linear geometry observed for unbound C_2H_2 . It is satisfying to note that the effects are predicted with high accuracy by calculations at the CCSD(T)(F12*)/ACVTZ level.

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