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# An Isolated Complex of Ethyne and Gold Iodide Characterized by Broadband Rotational Spectroscopy and Ab initio Calculations

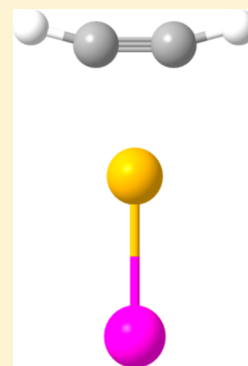
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## Supporting Information

**ABSTRACT:** A molecular complex of  $C_2H_2$  and AuI has been generated and isolated in the gas phase through laser ablation of a gold surface in the presence of an expanding sample containing small percentages of  $C_2H_2$  and  $CF_3I$  in a buffer gas of argon. Rotational,  $B_0$ , centrifugal distortion,  $\Delta_J$  and  $\Delta_{JK}$ , and nuclear quadrupole coupling constants,  $\chi_{aa}(Au)$ ,  $\chi_{bb}(Au) - \chi_{cc}(Au)$ ,  $\chi_{aa}(I)$ , and  $\chi_{bb}(I) - \chi_{cc}(I)$ , are measured for three isotopologues of  $C_2H_2 \cdots AuI$  through broadband rotational spectroscopy. The complex is  $C_{2v}$  and T-shaped with  $C_2H_2$  coordinating to the gold atom via donation of electrons from the  $\pi$ -orbitals of ethyne. On formation of the complex, the  $C \equiv C$  bond of ethyne extends by 0.032(4) Å relative to  $r(C \equiv C)$  in isolated ethyne when the respective  $r_0$  geometries are compared. The geometry of ethyne distorts such that  $\angle(*-C-H)$  (where \* indicates the midpoint of the  $C \equiv C$  bond) is 194.7(12)° in the  $r_0$  geometry of  $C_2H_2 \cdots AuI$ . *Ab initio* calculations at the CCSD(T)(F12\*)/AVTZ level are consistent with the experimentally determined geometry and further allow calculation of the dissociation energy ( $D_0$ ) as 136 kJ mol<sup>-1</sup>. The  $\chi_{aa}(Au)$  and  $\chi_{aa}(I)$  nuclear quadrupole coupling constants of AuI and also the Au—I bond length change significantly on formation of the complex consistent with the strong interaction calculated to occur between  $C_2H_2$  and AuI.



## INTRODUCTION

Although less reactive than its group 11 counterparts, gold has important uses as both a heterogeneous<sup>1,2</sup> and homogeneous<sup>3,4</sup> catalyst. It can exist in a variety of oxidation states from (–I) to (V), with (I) and (III) being the most common states. Au(I) is particularly prevalent<sup>5,6</sup> in modern catalysis where it is often used in combination with a halide counterion and neutral ligands such as phosphines. Relativistic effects are highly significant in the chemistry of gold. At the focus of the present work is the interaction between the gold atom of diatomic gold iodide and ethyne. A molecular complex of  $C_2H_2 \cdots AuI$  is isolated in the gaseous phase and probed by pure rotational spectroscopy to determine the molecular geometry of the complex.

It has been shown that the hydrogenation of ethyne<sup>7</sup> can be facilitated by gold-containing catalysts. According to the Dewar–Chatt–Duncanson model<sup>8</sup> the geometry adopted by an alkyne or alkene when bonding to an individual metal atom results from overlap of  $\pi$  orbitals on the unsaturated hydrocarbon with d orbitals on the metal atom. Complexes formed between group 11 metal ions and each of  $C_2H_2$  and  $C_2H_4$  have been the subject of a computational study of molecular geometries and binding strengths.<sup>9</sup> As a consequence of relativistic effects, the bond distance separating  $M^+$  and  $C_2H_{2n}$  subunits in  $M^+ - C_2H_{2n}$  complexes follows a V-shaped trend on descending group 11. The dissociation energy ( $D_0$ ) calculated for the  $Au^+ - C_2H_4$  complex (with respect to breaking the  $M^+ - C_2H_4$  bond) is higher than those calculated for either  $Cu^+ - C_2H_4$  or  $Ag^+ - C_2H_4$ . Electronic photo-

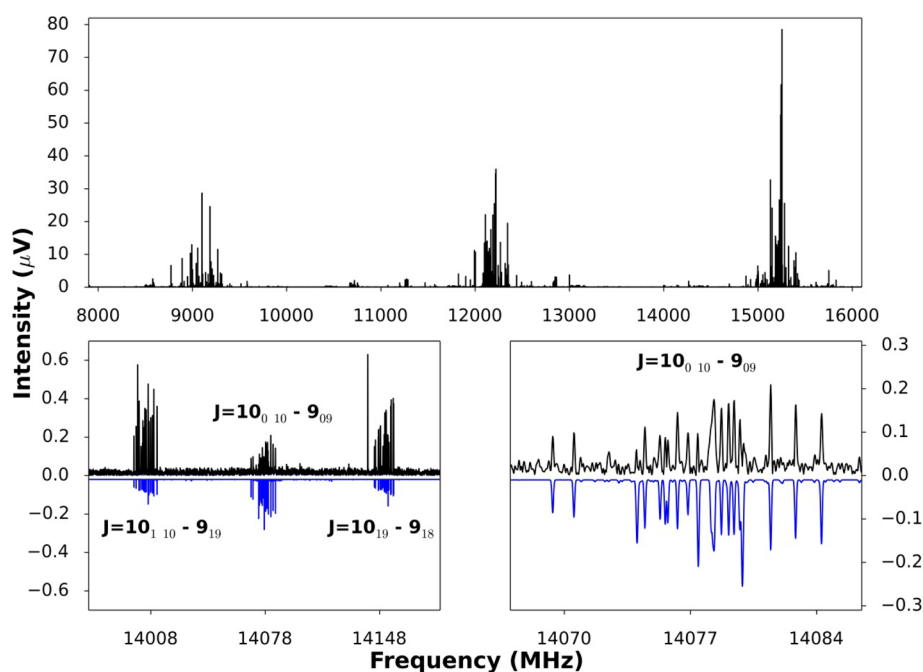
dissociation spectra have also been measured and reported for  $Au^+(C_2H_4)$ .<sup>10</sup> Pure rotational spectroscopy contributes quantitative information and benchmarks against which the results of high level calculations can be tested. The present study reports the geometry of a neutral unit and follows a number of recent computational works that have examined the geometries and binding energies of complexes where either  $C_2H_2$  or  $C_2H_4$  is bound to a group 11 metal atom contained within a neutral molecule.<sup>11–13</sup>

A set of empirical rules<sup>14,15</sup> have been shown to predict correctly the geometries of a very wide range of metal-containing, hydrogen- and halogen-bonded complexes. For example, it was shown that each of  $C_2H_4 \cdots MCl$ ,<sup>16,17</sup>  $C_2H_2 \cdots MCl$ <sup>16,18,19</sup> (where M is Cu or Ag), and  $C_2H_2 \cdots AgCCH$ <sup>20</sup> adopt  $C_{2v}$  T-shaped geometries in which the  $C_2H_2$  subunit forms the bar of the “T”. The geometries of  $C_2H_2$  and  $C_2H_4$  respectively distort from linearity/planarity on their attachment to CuCl. In addition, the C—C bond within the  $C_2H_2$  or  $C_2H_4$  subunit extends relative to its length in the free molecule. The changes are greatest with respect to  $C_2H_2 \cdots CuCl$  where  $\angle(CCH)$  expands to 192.4(7)°, allowing the hydrogen atoms to move away from the metal atom on formation of the complex. The C=C bond extends by 0.027(3) Å relative to its value in free  $C_2H_2$ . The corresponding changes in the geometry of  $C_2H_2$  on formation of  $C_2H_2 \cdots AgCl$  are 187.7(4)° and

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**Figure 1.** Upper panel shows the rotational spectrum observed (780 k FIDs) with the conditions described in the experimental text. Transitions assigned to other species such as AuI and  $\text{CF}_3\text{I}$  are present, and those assigned to  $\text{C}_2\text{H}_2\cdots\text{AuI}$  are significantly less intense and not apparent in the survey spectrum. Expansions of the horizontal and vertical scales (in the bottom panels) reveals features assigned to  $\text{C}_2\text{H}_2\cdots\text{AuI}$  with the strongest transitions having  $S/N \sim 15:1$ . The bottom left panel shows the  $J' \rightarrow J'' = 10 \rightarrow 9$  transition for the  $\text{C}_2\text{H}_2\cdots\text{AuI}$  species, with the measured spectrum in black and the simulation inverted and in blue. The intensities of transitions in the experimental spectrum result from the nuclear spin statistical weightings associated with exchange of equivalent protons by a  $\text{C}_2$  rotation. Nuclear spin statistical weight effects are not included in the simulated spectrum. The bottom right panel shows an expansion of the  $K_{-1} = 0$  of  $J' \rightarrow J'' = 10 \rightarrow 9$ . Hyperfine splitting arising from nuclear quadrupole coupling of each of Au and I is present and shown in the bottom panels.

0.017(2) Å. Although the geometry of  $\text{C}_2\text{H}_4$  also changes on attachment to each of CuCl and AgCl, again so as to move the hydrogen atoms away from the metal atom and extend the  $\text{C}=\text{C}$  bond, the magnitudes of the changes are smaller than those seen for  $\text{C}_2\text{H}_2$ . Evidently, the extent of the distortion of each of  $\text{C}_2\text{H}_2$  and  $\text{C}_2\text{H}_4$  from their free molecule geometries depends upon the identity of the attached metal atom. The greatest distortions of ethyne induced by attachment to a metal atom and observed to date were identified by Kukolich et al.<sup>21</sup> during a study of acetylenemethyldioxorhenium in 2000. It was reported that the  $\text{C}\equiv\text{C}$  bond extends by 0.09 Å whereas  $\angle(\text{CCH})$  expands by  $26^\circ$  on attaching to a rhenium atom, where the quoted changes are relative to the values for the free ethyne molecule in each case. The purpose of the present work is to reveal the extent of structural changes in  $\text{C}_2\text{H}_2$  on attaching to the gold atom of the AuI diatomic. This may be the first quantitative experimental study to measure directly the geometrical change in an unsaturated hydrocarbon following its attachment to a single gold atom within a neutral molecule.

## EXPERIMENTAL SECTION

**Materials and Methods.** A gaseous mixture of precursors is introduced into an evacuated chamber through the circular orifice (0.5 mm in diameter) of a pulsed nozzle (Parker-Hannifin General Valve, Series 9). The prepared gaseous sample contains  $\sim 5\%$   $\text{C}_2\text{H}_2$  and  $\sim 2\%$   $\text{CF}_3\text{I}$ , and the remainder is a buffer gas of argon held at a pressure of 6 bar. The mixture of gaseous precursors undergoes supersonic expansion allowing efficient collisional cooling of molecular rotational energies and the formation of weakly bound species such as  $\text{C}_2\text{H}_2\cdots\text{ICF}_3$  within the supersonic jet. The generation of gas phase

complexes of  $\text{C}_2\text{H}_2\cdots\text{AuI}$  is achieved through vaporization of the surface of a gold metal target (gold foil attached to a brass rod) by a focused pulse of 532 nm radiation from a Nd:YAG laser (Continuum Minilite) in the presence of the expanding sample. The rod target is continually rotated and translated to expose fresh surface material to each laser pulse. As described within earlier publications,<sup>22,23</sup> the plasma induced by the focused laser pulse contains a mixture of species that may undergo fragmentation, react, and/or recombine with each other. The time intervals between the laser, solenoid valve, and microwave pulses are optimized to maximize the intensities of transitions of the target complex in measured spectra. With respect to the particular case of  $\text{C}_2\text{H}_2\cdots\text{AuI}$ , it will be shown that the bond between  $\text{C}_2\text{H}_2$  and Au is considerably stronger than a typical van der Waals interaction.

Studies of the most abundant isotopologue of ethyne were facilitated by a commercially sourced cylinder of ethyne, which also contains a significant subfraction of acetone. It is standard practice for the latter to be used as a stabilizing solvent for the former in mitigation of hazards associated with high-pressure storage of ethyne. Isotopically enriched samples of  $^{13}\text{C}_2\text{D}_2$  and  $^{12}\text{C}_2\text{D}_2$  were employed when measuring the spectra of isotopologues containing  $^{13}\text{C}$  and/or D atoms. Broadband rotational spectra were measured using a CP-FTMW spectrometer<sup>24</sup> that probes all transitions between 7.5 and 18 GHz simultaneously. Detailed descriptions of both the microwave spectrometer<sup>22,25–27</sup> and laser ablation source<sup>23,28</sup> used during this work have been given elsewhere. Following supersonic expansion of the prepared sample, a pulse of microwave radiation induces a macroscopic rotational polarization on resonance with a molecular rotational transition. The

Table 1. Spectroscopic Constants Determined for Three Isotopologues of C<sub>2</sub>H<sub>2</sub>...AuI

spectroscopic constant	<sup>12</sup> C <sub>2</sub> H <sub>2</sub> ...AuI	<sup>12</sup> C <sub>2</sub> D <sub>2</sub> ...AuI	<sup>13</sup> C <sub>2</sub> D <sub>2</sub> ...AuI
A <sub>0</sub> /MHz	34399(36) <sup>a</sup>	25179(13)	24213(13)
B <sub>0</sub> /MHz	711.28170(6)	692.747417(73)	678.257387(92)
C <sub>0</sub> /MHz	696.65502(6)	673.887794(76)	659.504581(85)
Δ <sub>JK</sub> /kHz	4.001(16)	3.461(24)	3.403(26)
[Δ <sub>J</sub> × 10 <sup>2</sup> ]/kHz	3.172(21)	3.026(25)	2.618(31)
χ <sub>aa</sub> (Au)/MHz	−808.678(53)	−809.865(79)	−810.30(11)
[χ <sub>bb</sub> (Au) − χ <sub>cc</sub> (Au)]/MHz	358.20(11)	360.35(29)	360.72(35)
χ <sub>aa</sub> (I)/MHz	−1013.001(43)	−1012.442(82)	−1012.29(12)
[χ <sub>bb</sub> (I) − χ <sub>cc</sub> (I)]/MHz	−219.67	−219.87(27)	−218.94(33)
N <sup>b</sup>	532	443	364
σ <sub>rms</sub> /kHz <sup>c</sup>	6.7	7.3	8.0
Δ <sub>0</sub> /(u Å <sup>2</sup> ) <sup>d</sup>	0.23(2)	0.35(1)	0.31(1)
P <sub>a</sub> /(u Å <sup>2</sup> )	710.6(7)	745.3(4)	729.7(4)
P <sub>b</sub> /(u Å <sup>2</sup> )	14.80(2)	20.24(1)	21.03(1)
P <sub>c</sub> /(u Å <sup>2</sup> )	−0.113(1)	−0.174(1)	−0.157(1)

<sup>a</sup>Numbers in parentheses are one standard deviation in units of the last significant figure. <sup>b</sup>Number of hyperfine components included in the fit. <sup>c</sup>rms deviation of the fit. <sup>d</sup>Inertia defect as defined in eq 2.

subsequent molecular emission, detected as the free induction decay (FID) of the polarization, is Fourier transformed to obtain the frequency domain spectrum. The experiment is repeated and averaged in the time domain to improve S/N. Propagation of the molecular beam is perpendicular to the orientation of the detecting horn such that each transition is observed as a single peak with full-width at half-maximum (fwhm)  $\cong$  150 kHz after application of a Kaiser-Bessel digital filter. All frequency signals are locked to an external reference source accurate to 1 part per 10<sup>11</sup>.

**Ab Initio Calculations.** Geometry optimizations were performed using CCSD(T)(F12\*), a coupled-cluster method with single and double excitations, explicit correlation, and a perturbative treatment of triple excitations.<sup>29–31</sup> An AVTZ basis set combination was used, by which we mean that aug-cc-pVTZ basis sets were used for the C and H atoms<sup>32</sup> and cc-pVTZ-PP basis sets were used for Au and I, in combination with the ECP-28-MDF and ECP-60-MDF effective core potentials on I and Au, respectively, to account for scalar relativistic effects.<sup>33–35</sup> The frozen-core approximation was used throughout and all calculations were performed using the MOLPRO package.<sup>36</sup> Dissociation energies at the CCSD(T)-(F12\*)/AVTZ level were computed using the counterpoise correction method where, for numerical stability, the CABS singles correction was not included in the correction term.

## RESULTS

**Initial Observations.** The broadband spectrum probed as described in the Experimental Section is displayed in Figure 1. Intense signals are observed for CF<sub>3</sub>I and AuI, which have each been previously characterized. A molecular complex formed between CF<sub>3</sub>I and C<sub>2</sub>H<sub>2</sub> is observed but yields transitions of somewhat lower intensities than those of CF<sub>3</sub>I and AuI. It has previously been shown<sup>16,19</sup> that the geometries of C<sub>2</sub>H<sub>2</sub>...CuCl and C<sub>2</sub>H<sub>2</sub>...AgCl are each C<sub>2v</sub> and T-shaped with the C<sub>2</sub>H<sub>2</sub> subunit forming the bar of the “T”. These previous studies justify the initial assumptions that a complex of C<sub>2</sub>H<sub>2</sub> and AuI will adopt the same basic geometry as each of C<sub>2</sub>H<sub>2</sub>...CuCl and C<sub>2</sub>H<sub>2</sub>...AgCl and yield a spectrum that is typical of a near-prolate asymmetric rotor. Consistent with these expectations, groups of transitions are observed in the spectrum at intervals of  $\sim$ 1400 MHz. Each group is itself observed to be composed

of three distinct bands of transitions and is tentatively assigned to a different J'  $\rightarrow$  J'' transition implying a rotational constant of  $\sim$ 700 MHz for the molecular carrier.

The frequency intervals separating distinct bands within each J'  $\rightarrow$  J'' transition are observed to increase with J in a pattern consistent with assignment of the central band in each J'  $\rightarrow$  J'' transition to components having K<sub>−1</sub> = 0 whereas components within the other two bands are assigned with K<sub>−1</sub> = 1. This pattern is consistent with the expected distribution of a-type transitions in the spectrum of a near-prolate asymmetric rotor in the described, T-shaped, C<sub>2v</sub> geometry. As described in previous works,<sup>16</sup> where two equivalent nuclei are exchanged by a C<sub>2</sub> rotation, collisional propensity rules inhibit relaxation from K<sub>−1</sub> = 1 into K<sub>−1</sub> = 0 states of a complex. Relative intensities of the observed K<sub>−1</sub> = 1 and K<sub>−1</sub> = 0 transitions reflect the nuclear spin statistical weightings expected of a molecule containing hydrogen atoms exchanged by a C<sub>2</sub> rotation. The extensive and intricate splittings within each band are a consequence of hyperfine structure arising from the presence of Au (I = 3/2) and I (I = 5/2) nuclei within the complex and are further confirmation that the carrier of the observed spectrum is a complex of C<sub>2</sub>H<sub>2</sub> and AuI in the described C<sub>2v</sub>, T-shaped geometry.

**Spectral Assignment and Spectroscopic Constants.** Measured transitions were assigned with quantum numbers to determine spectroscopic parameters through fitting to measured transition frequencies. Western's PGOPHER program<sup>37</sup> was used to perform all quantum number assignments and fitting. The model Hamiltonian used to describe C<sub>2</sub>H<sub>2</sub>...AuI was constructed as follows;

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

The rotational Hamiltonian of a semirigid asymmetric top is denoted by H<sub>R</sub>, which includes terms in the rotational constants, A<sub>0</sub>, B<sub>0</sub>, and C<sub>0</sub>, that respectively describe rotation of the complex about the a, b, and c inertial axes of the complex. Though a complex in the described C<sub>2v</sub> geometry does not have an electric dipole moment on either the b- or c-inertial axes, the observation of J<sub>0 K<sub>−1</sub></sub>  $\rightarrow$  (J + 1)<sub>0 K<sub>−1</sub></sub> and J<sub>1 K<sub>−1</sub></sub>  $\rightarrow$  (J + 1)<sub>1 K<sub>−1</sub></sub>



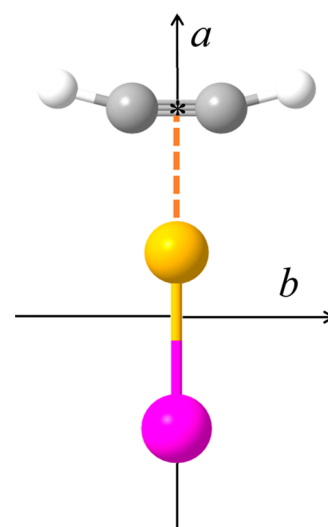
transitions allows the determination of all three rotational constants, with  $B_0$  and  $C_0$  fitted to somewhat higher precision than  $A_0$ . The centrifugal distortion constants,  $\Delta_J$  and  $\Delta_{JK}$ , are included in  $H_R$  and fitted for all measured isotopologues of  $C_2H_2\cdots AuI$ . The second and third terms of eq 1 describe the nuclear quadrupole coupling interactions between the nuclear electric quadrupole moments of the respective gold and iodine nuclei and the electric field gradients at each of these nuclei. The projections of the nuclear quadrupole coupling tensors of Au and I onto the  $a$ -axis, respectively, denoted by  $\chi_{aa}(Au)$  and  $\chi_{aa}(I)$ , are fitted in addition to  $\chi_{bb}(Au) - \chi_{cc}(Au)$  and  $\chi_{bb}(I) - \chi_{cc}(I)$ .

**Molecular Geometry.** The observations reported above strongly imply a T-shaped,  $C_{2v}$  geometry for  $C_2H_2\cdots AuI$ . It is possible to examine this proposal more quantitatively through analysis of the fitted rotational constants. An important test of planarity involves calculation of the inertia defect,  $\Delta_0$ ,

$$\Delta_0 = I_c^0 - I_a^0 - I_b^0 \quad (2)$$

where  $I_a^0$ ,  $I_b^0$ , and  $I_c^0$  are the moments of inertia determined from the experimentally measured  $A_0$ ,  $B_0$ , and  $C_0$  rotational constants. The evaluated  $\Delta_0$  are 0.23(2), 0.37(2), and 0.31(1) u Å<sup>2</sup> for  $^{12}C_2H_2\cdots AuI$ ,  $^{12}C_2D_2\cdots AuI$ , and  $^{13}C_2D_2\cdots AuI$ , respectively. These are very similar to the inertia defects established for various isotopologues<sup>16</sup> of  $C_2H_2\cdots CuCl$  and are slightly smaller than those determined for  $C_2H_2\cdots AgCl$ .<sup>19</sup> These small positive results are consistent with planar geometries for these complexes. It has been noted previously<sup>16</sup> that there is an inverse correlation between the stiffness of the intermolecular bond and the evaluated inertia defect such that  $\Delta_0$  decreases along the series  $C_2H_2\cdots HCl$ ,  $C_2H_2\cdots ClF$ ,  $C_2H_2\cdots AgCCH$ ,  $C_2H_2\cdots AgCl$ ,  $C_2H_2\cdots CuCl$ . The results for  $C_2H_2\cdots AuI$  are consistent with this trend given that the dissociation energy calculated for the complex is similar to that calculated for  $C_2H_2\cdots CuCl$  (discussed below). The inertia defects calculated for the various isotopologues of  $C_2H_2\cdots AuI$  are displayed alongside the values of the planar moments,  $P_a$ ,  $P_b$ , and  $P_c$  in Table 1.

Rotational constants,  $A_0$ ,  $B_0$ , and  $C_0$  are available for three isotopologues of  $C_2H_2\cdots AuI$ , allowing further information about the molecular geometry to be obtained through fitting of structural parameters to the experimentally determined moments of inertia using Kisiel's STRFIT.<sup>38</sup> It is convenient to define various structural parameters with respect to the midpoint of the  $C\equiv C$  bond, represented by an asterisk in the geometry of the complex illustrated in Figure 2. Only one isotope of each of gold and iodine is naturally abundant, reducing the confidence and precision with which the  $r(*-Au)$  and  $r(Au-I)$  distances can be determined from the experimental data. The results displayed in Table 2 are obtained by fitting  $r(*-Au)$ ,  $r(Au-I)$ ,  $r(C\equiv C)$ , and  $\angle(*-C-H)$  while holding  $r(C-H)$  fixed at the value of the parameter calculated at the CCSD(T)(F12\*)/AVTZ level after correcting for the difference between the experimentally measured  $r_0$  and  $r_e$  values of  $r(C-H)$  in  $C_2H_2$ . Alternative procedures that (i) fix  $r(*-Au)$  at the *ab initio* result yields values of  $r(Au-I) = 2.5008(5)$  Å,  $r(C\equiv C) = 1.234(3)$  Å,  $\angle(*-C-H) = 193.3(6)^\circ$  or (ii) fix  $r(Au-I)$  at the *ab initio* result yields  $r(*-Au) = 2.005(3)$  Å,  $r(C\equiv C) = 1.248(6)$  Å, and  $\angle(*-C-H) = 198.0(12)^\circ$ . Evidently, the results are somewhat sensitive to the parameter set chosen, but consistently yield an extended  $C\equiv C$  bond length and increased  $\angle(*-C-H)$  compared with the geometry of free  $C_2H_2$ . The results obtained



**Figure 2.** Geometry of  $C_2H_2\cdots AuI$  showing the orientation of the principal inertial axes  $a$  and  $b$ . All of the atoms lie in the  $ab$  plane, and  $a$  is a  $C_2$  axis of rotation. The \* indicates the midpoint of the  $C\equiv C$  bond. Bond lengths and angles are to scale.

**Table 2.** Geometry of  $C_2H_2\cdots AuI^a$

	$r_0$ (exp)	$r_s$ (exp)	$r_e$ (CCSD(T)(F12*)/AVTZ)
$r(*-Au)/\text{\AA}$	2.057(15)		2.077
$r(Au-I)/\text{\AA}$	2.507(4)		2.522
$r(C\equiv C)/\text{\AA}$	1.239(4)	1.264(4)	1.234
$r(C-H)/\text{\AA}$	[1.0692] <sup>b</sup>	1.038(2)	1.068
$\angle(*-C-H)/\text{deg}$	194.7(12)	195.1(7)	193.9
$a_{Au}/\text{\AA}$	-0.737(3)		-0.741
$a_I/\text{\AA}$	1.752(2)		1.780
$a^* = a_C/\text{\AA}$	-2.793(12)	-2.795(1)	-2.818
$b_C/\text{\AA}$	$\pm 0.619(2)$	$\pm 0.632(2)$	$\pm 0.617$
$a_H/\text{\AA}$	-3.065(12)	-3.065(2)	-3.074
$b_H/\text{\AA}$	$\pm 1.653(4)$	$\pm 1.635(1)$	$\pm 1.655$

<sup>a</sup>Numbers in parentheses are one standard deviation in units of the last significant figure. <sup>b</sup>Fixed to the value obtained by correcting the  $r_e$  result calculated at the CCSD(T)(F12\*)/AVTZ level for the difference between the experimentally measured  $r_0$  and  $r_e$  distances of  $C_2H_2$ .

while fitting all of  $r(*-Au)$ ,  $r(Au-I)$ ,  $r(C\equiv C)$ , and  $\angle(*-C-H)$  in the  $r_0$  geometry are closest to CCSD(T)(F12\*)/AVTZ calculated results displayed alongside the  $r_0$  and  $r_s$  results in Table 2.

Changes in the moments of inertia on isotopic substitution can also be used to calculate coordinates for each atom and thus generate an  $r_s$  substitution geometry. Unfortunately, only one isotope of each of gold and iodine is naturally abundant so this analysis of  $r_s$  coordinates will consider only the locations of C and H atoms within the  $C_2H_2$  subunit. For a T-shaped complex where a double substitution is performed on atoms exchanged by a  $C_2$  rotation, the  $b$ -coordinate of the substituted atom is given by<sup>39</sup>

$$|b_X| = \left\{ \frac{\Delta I_a}{2\Delta m} \right\}^{1/2} \quad (3)$$

where  $\Delta I_a$  is the change in the moment of inertia,  $I_a$ , on isotopic substitution of atom X and  $\Delta m$  is the associated mass change on substitution. The  $^{12}C_2D_2\cdots AuI$  isotopologue is

selected as the parent allowing the *b*-coordinate for C to be determined from  $\Delta I_a$  on substitution of  $^{12}\text{C}$  for  $^{13}\text{C}$  and the *b*-coordinate for H to be determined from  $\Delta I_a$  on substitution of H for D. The *a* coordinate shared by the C atoms is calculated using

$$|a_X| = \left\{ \frac{\Delta I_b}{\mu_D} \right\}^{1/2} \quad (4)$$

where  $\mu_D = (2\Delta m M)/(M + 2\Delta m)$  is the reduced mass for the double substitution in the parent isotopologue of mass *M* leading to mass change  $2\Delta m$ . The values of  $r(\text{C}\equiv\text{C})$  and  $\angle(*-\text{C}-\text{H})$  implied by the  $r_s$  results are provided in Table 2 alongside the coordinates themselves. It is apparent that the calculated substitution ( $r_s$ ) coordinates are less consistent with the *ab initio* results than those in the  $r_0$  geometry, particularly with respect to  $b_C$  and  $b_H$ . The  $b_C$  and  $b_H$  substitution coordinates are calculated from selected  $I_a$  values only, whereas  $I_b$  and  $I_c$  for each isotopologue provide additional input parameters in the fitted  $r_0$  geometry. However,  $\angle(*-\text{C}-\text{H})$  is somewhat insensitive to the results for  $b_C$  and  $b_H$ . The CCSD(T)(F12\*)/AVTZ values of these parameters are  $b_C = \pm 0.617 \text{ \AA}$  and  $b_H = \pm 1.655 \text{ \AA}$ , and using these results alongside the  $r_s$  coordinates of  $a_H$  and  $a_C$  would yield  $\angle(*-\text{C}-\text{H}) = 194.6(7)^\circ$ .

It is possible to assess the level of agreement that should be expected between *ab initio* calculations of  $r_e$  geometries at the stated level and experimentally determined  $r_0$  parameters through calculations performed on isolated AuI and  $\text{C}_2\text{H}_2$ , for which highly accurate experimental geometries are available (Table 3). The experimentally determined and CCSD(T)-

correlation are much greater and their inclusion reduces the value of the calculated parameter by  $0.014 \text{ \AA}$ . The remaining difference between the calculated and experimentally determined  $r_e$  values for  $r(\text{Au}-\text{I})$  arises because of the low-level treatment of relativity used.

Examining the results for the  $\text{C}_2\text{H}_2\cdots\text{AuI}$  complex, it must first be noted that the experiment yields an  $r_0$  geometry whereas the CCSD(T)(F12\*)/AVTZ calculation is for the  $r_e$  geometry. The implication of vibrational motion in the zero-point state, as stated above, is that the value of the  $r(\text{Au}-\text{I})$  parameter in the  $r_0$  geometry can be expected to be  $\sim 0.002 \text{ \AA}$  longer than that in the  $r_e$  geometry. Noting the discussion above, the  $\sim 0.02 \text{ \AA}$  difference between the CCSD(T)(F12\*)/AVTZ ( $r_e$ ) and experimentally determined ( $r_0$ ) results for the  $r(\text{Au}-\text{I})$  parameter arises because core–valence correlation is excluded from the present calculation and only a low-level treatment of relativity is used. Allowing for an  $r(*-\text{Au})$  bond that extends slightly in the  $r_0$  geometry relative to the  $r_e$  value, the CCSD(T)(F12\*)/AVTZ calculated ( $r_e$ ) and experimentally determined ( $r_0$ ) results given in Table 3 are in very good agreement. The implication of both experimental ( $r_0$ ) and CCSD(T)(F12\*)/AVTZ ( $r_e$ ) results is that the  $\text{C}\equiv\text{C}$  bond of  $\text{C}_2\text{H}_2$  extends by  $0.03 \text{ \AA}$  on attachment to AuI. The angular geometry of ethyne is distorted by  $\sim 14^\circ$  relative to the linear geometry of the free molecule. There is an associated lengthening of the Au–I bond relative to its length in the isolated diatomic<sup>41</sup> of  $0.034(7) \text{ \AA}$ . The changes in the geometries of the monomer subunits on formation of  $\text{C}_2\text{H}_2\cdots\text{AuI}$  will be discussed further in the Conclusions.

It is possible to estimate a force constant from rotational and centrifugal distortion constants by making the approximation that each complex is a pseudodiatom molecule<sup>39</sup> in which the  $\text{C}_2\text{H}_2$  and AuI subunits can each be represented as point masses (Tables 1–3). The simplest treatment neglects the internal structure of each of the subunits whereas the more sophisticated model provided by Millen<sup>42</sup> accounts for differing monomer geometries and also been applied to many  $\text{B}\cdots\text{MX}$  complexes. Each of the described methods of calculating a force constant applies only in the quadratic approximation and assumes that the intermolecular stretching mode,  $\sigma$ , lies much lower in wavenumber than other modes of the same symmetry. It has previously been noted<sup>43</sup> that the *ab initio*-calculated frequency of the  $\Sigma^+$  CAu stretch is lower than that for  $\Sigma^+$  AuX in OCAuF whereas this ordering is reversed in OCAuCl and OCAuBr. It was also noted that good agreement was obtained between the vibrational frequency predicted under the simple pseudodiatom approximation and the  $\Sigma^+$  AuX stretch, rather than the  $\Sigma^+$  CAu stretch, where  $\text{X} = \text{Cl}$  and  $\text{Br}$  in OCAuX. The vibrational frequencies of  $\text{C}_2\text{H}_2\cdots\text{AuI}$  calculated at the CCSD(T)(F12\*)/AVTZ level are shown in Table 4. The wavenumber of the Au–I stretch is calculated to be  $206 \text{ cm}^{-1}$  whereas that for  $*-\text{Au}$  is  $343 \text{ cm}^{-1}$ . Evidently, the assumption that the vibrational stretching motion of lowest frequency is well-separated from others of the same symmetry is unreliable with respect to  $\text{C}_2\text{H}_2\cdots\text{AuI}$ . No attempt is made to calculate a force constant from the measured spectroscopic constants during the present work. A counterpoise-corrected dissociation energy ( $D_e$ ) of  $136 \text{ kJ mol}^{-1}$  is calculated *ab initio* with respect to dissociation into  $\text{C}_2\text{H}_2$  and AuI subunits. This result is similar to the  $D_e$  of  $148 \text{ kJ mol}^{-1}$  established<sup>16</sup> with respect to the dissociation of  $\text{C}_2\text{H}_2\cdots\text{CuCl}$  into  $\text{C}_2\text{H}_2$  and CuCl. The value of  $D_0$  for  $\text{C}_2\text{H}_2\cdots\text{AuI}$ , obtained after subtracting the appropriate

Table 3. Geometries of Isolated  $\text{C}_2\text{H}_2$  and AuI

	AuI		
	$r_0$ (exp) <sup>a</sup>	$r_e$ (exp) <sup>a</sup>	$r_e$ (CCSD(T)(F12*)/AVTZ)
$r(\text{Au}-\text{I})/\text{\AA}$	2.4728	2.4711	2.4896 2.4881 [fc-CCSD(T)/CV5Z] 2.4758 [+CV/CV5Z] 2.4792 [+T] 2.4793 [+Q]
	$\text{C}_2\text{H}_2$		
	$r_0$ (exp) <sup>b</sup>	$r_e$ (exp) <sup>b</sup>	$r_e$ (CCSD(T)(F12*)/AVTZ)
$r(\text{C}\equiv\text{C})/\text{\AA}$	1.206553(6)	1.20286(3)	1.2055
$r(\text{C}-\text{H})/\text{\AA}$	1.06238(2)	1.06166(6)	1.0631
$^{12}\text{C}_2\text{H}_2$		$^{12}\text{C}_2\text{D}_2$	$^{13}\text{C}_2\text{D}_2$
$B_0/\text{MHz}$	35274.9693(54) <sup>b</sup>	25418.629 <sup>b</sup>	24484.418 <sup>c</sup>

<sup>a</sup>Reference 41. <sup>b</sup>Reference 19. <sup>c</sup>Calculated using data from ref 40.

(F12\*)/AVTZ values of  $r(\text{C}\equiv\text{C})$  in isolated<sup>40</sup>  $\text{C}_2\text{H}_2$  are within  $0.003 \text{ \AA}$  of each other in the  $r_e$  geometry. There is a similar level of agreement between theory and experiment with respect to the  $r(\text{C}-\text{H})$  parameter. As expected, bond distances in the  $r_0$  geometry are slightly longer (by  $0.001 \text{ \AA}$ ) than those in the  $r_e$  geometry as a consequence of vibrational motion in the zero-point state. Calculation of  $r(\text{Au}-\text{I})$  of free AuI at the stated level of theory yields a result that is  $0.02 \text{ \AA}$  longer than the experimentally determined  $r_e$  parameter. Extrapolating the calculation to the basis set limit yields only a very small ( $0.001 \text{ \AA}$ ) reduction in the calculated bond length and a full treatment of triple and quadruple excitations also has only a very small effect. However, contributions from core–valence

Table 4. Calculated Vibrational Wavenumbers of C<sub>2</sub>H<sub>2</sub>...AuI

	C <sub>2</sub> H <sub>2</sub> ...AuI		C <sub>2</sub> H <sub>2</sub> + AuI	
	sym	wavenumber/cm <sup>-1</sup>	sym	wavenumber/cm <sup>-1</sup>
*—Au—I bend	B <sub>1</sub>	89		
*—Au—I bend	B <sub>2</sub>	167		
Au—I stretch	A <sub>1</sub>	206	Σ <sup>+</sup>	212
*—Au stretch	A <sub>1</sub>	343		
Au—HCCH rock	B <sub>2</sub>	380		
HCCH wag	B <sub>2</sub>	742	Π <sub>g</sub>	617
HCCH wag	A <sub>2</sub>	1423	Π <sub>g</sub>	617
HCCH bend	B <sub>1</sub>	733	Π <sub>u</sub>	751
HCCH bend	A <sub>1</sub>	783	Π <sub>u</sub>	751
C—C stretch	A <sub>1</sub>	1858	Σ <sub>g</sub> <sup>+</sup>	2011
C—H stretch	B <sub>2</sub>	3349	Σ <sub>u</sub> <sup>-</sup>	3411
C—H stretch	A <sub>1</sub>	3435	Σ <sub>g</sub> <sup>+</sup>	3505

contribution to the calculated zero point energy of the complex from  $D_0$  is 126 kJ mol<sup>-1</sup>.

**Nuclear Quadrupole Coupling Constants.** A perspective on the strength of the interaction between C<sub>2</sub>H<sub>2</sub> and AuI can be obtained from examination of the measured nuclear quadrupole coupling constants. The sign of  $\chi_{aa}(\text{Au})$  changes when C<sub>2</sub>H<sub>2</sub> is attached to AuI and there is also a significant change in the magnitude of the parameter. A significant change is also observed in  $\chi_{aa}(\text{I})$ , which can be used to calculate the ionicity<sup>39</sup> of the Au—I bond

$$i_c = 1 + \frac{\chi_{aa}(\text{I})}{eQq_{(n,l,0)}(\text{I})} \quad (6)$$

where  $eQq_{(n,l,0)}(\text{I})$  is the coupling constant that would result from a single np<sub>z</sub> electron in the isolated iodine atom<sup>39</sup> and is 2292.44 MHz.

Measured values of  $\chi_{aa}$  and ionicities for AuI, OCAuI, and C<sub>2</sub>H<sub>2</sub>...AuI are shown in Table 5. It is apparent that attachment

Table 5. Nuclear Quadrupole Coupling Constants and Ionicities of C<sub>2</sub>H<sub>2</sub>...AuX

	$\chi_{aa}(\text{Au})/\text{MHz}$	$\chi_{aa}(\text{X})/\text{MHz}$	$i_c$	$\Delta r^a/\text{\AA}$
AuI <sup>b</sup>	78.27	-1707.9	0.26	
C <sub>2</sub> H <sub>2</sub> ...AuI	-808.678	-1013.001	0.56	+0.036(15)
OC...AuI <sup>c</sup>	-961.3	-981.0	0.58	+0.030 <sup>d</sup>
AuBr	37.3	492.3	0.38	
OC...AuBr <sup>c</sup>	-999.1	285.1	0.64	+0.020
AuCl	9.6	-62.0	0.44	
OC...AuCl <sup>c</sup>	-1026.0	-36.4	0.67	+0.018
AuF	-53.3			
OC...AuF <sup>c</sup>	-1006.3			-0.009

<sup>a</sup>Extension in Au—I bond relative to the same distance in the isolated AuI molecule ( $r_0$  geometry). <sup>b</sup>Reference 41. <sup>c</sup>References 43 and 44. <sup>d</sup>Determined through calculation rather than fitting so no standard deviation is assigned to this value.

of either C<sub>2</sub>H<sub>2</sub> or CO to AuI causes a significant increase in the ionicity of the AuI bond. Changes in the various  $\chi_{aa}$  for C<sub>2</sub>H<sub>2</sub>...AuI are almost as great as those accompanying the formation of OCAuI from the monomer subunits implying a similar strength of interaction. It was previously noted<sup>43,44</sup> that the fractional increase in ionicity of the AuX bond on attachment of CO is greatest where X is iodine. Evidence that the interaction between Au and I weakens when C<sub>2</sub>H<sub>2</sub> attaches to AuI is also

available in the calculated and experimentally determined geometries presented above. When experimentally determined results for the  $r_0$  geometries are compared, the length of the AuI bond extends by 0.036(15) Å on attachment of C<sub>2</sub>H<sub>2</sub> to AuI. A similar change was observed in the earlier study of OCAuI. The fractional changes in both ionicity and the length of the AuX bond are lower on attaching CO to each of AuF, AuCl, and AuBr (Table 5).

Values for  $\chi_{bb}(\text{Au}) - \chi_{cc}(\text{Au})$  and  $\chi_{bb}(\text{I}) - \chi_{cc}(\text{I})$  are also measured for C<sub>2</sub>H<sub>2</sub>...AuI, as shown in Table 1. The calculated significant differences between  $\chi_{bb}$  and  $\chi_{cc}$  for each of Au and I are consistent with the proposed bonding mechanism, which involves the donation of electrons from  $\pi$ -orbitals of ethyne into unfilled bonding orbitals of the metal atom. The geometry of this interaction is the source of the asymmetry in the nuclear quadrupole coupling tensors. In contrast, the spectrum of OCAuI was fitted while assuming a linear molecular geometry implying donation of electron density from a lone pair on the C atom into unfilled orbitals on Au.

## CONCLUSIONS

The first significant conclusion to arise from this work is that the molecular geometry of the isolated C<sub>2</sub>H<sub>2</sub>...AuI complex is C<sub>2v</sub> (T-shaped). Evidence for this geometry is available from the measured rotational constants, nuclear quadrupole coupling constants, and *ab initio* calculations at the CCSD(T)(F12\*)/AVTZ level. The  $r(\text{C}\equiv\text{C})$  parameter of C<sub>2</sub>H<sub>2</sub>...AuI is longer than that in isolated ethyne by ~0.032(4) Å whereas the value of  $\angle(*-\text{C}-\text{H}) = 194.7(12)^\circ$  implies distortion of the linear geometry of isolated ethyne by 14.7(12)<sup>o</sup> (where the comparison is between  $r_0$  geometries). It is apparent that the ionicity and length of the Au—I bond also change significantly on the attachment of C<sub>2</sub>H<sub>2</sub> to AuI, consistent with previous studies of OCAuX, which identified much smaller changes in the geometries of AuX subunits where complexes have X = F, Cl, or Br. The large, calculated ( $D_0$ ) binding energy of 136 kJ mol<sup>-1</sup> with respect to dissociation into C<sub>2</sub>H<sub>2</sub> and AuI subunits implies that the bond between the two monomers is stronger than that found in a typical van der Waals complex and involves significant  $\pi$  electron donation from C<sub>2</sub>H<sub>2</sub> to Au.

The geometry of the C<sub>2</sub>H<sub>2</sub>...AuI complex is consistent with empirical rules originally provided by Legon and Millen,<sup>14,15</sup> which state that in the absence of a nonbonding pair on the Lewis base, B, the axis of an MX subunit (where MX is a Lewis acid) in a complex of the general form B...MX intersects the internuclear axis of atoms that form a  $\pi$ -bond and is perpendicular to the [nodal] plane of the  $\pi$ -orbital. The rules were originally formulated to allow prediction of the geometries of a wide variety of hydrogen- and halogen-bonded complexes but have recently been shown to predict the basic geometries of a wide variety of much more strongly bound B...MX complexes where M is either copper or silver. This work is believed to provide the first evidence that the empirical rules may also serve to predict the geometries of gold-containing complexes.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.5b06593.

Fits of spectroscopic parameters to measured transition frequencies for <sup>12</sup>C<sub>2</sub>H<sub>2</sub>...AuI (TXT)



Fits of spectroscopic parameters to measured transition frequencies for  $^{12}\text{C}_2\text{D}_2\cdots\text{AuI}$  (TXT)

Fits of spectroscopic parameters to measured transition frequencies for  $^{13}\text{C}_2\text{D}_2\cdots\text{AuI}$  (TXT)

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### Notes

The authors declare no competing financial interest.

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