Distortions of ethyne when complexed with a cuprous or argentous halide: the rotational spectrum of C$_2$H$_2$···CuF

Daniel P. Zaleski, Susanna L. Stephens, David P. Tew, Dror M. Bittner, Nicholas R. Walker, and Anthony C. Legon

A new molecule C$_2$H$_2$···CuF has been synthesized in the gas phase by means of the reaction of laser-ablated metallic copper with a pulse of gas consisting of a dilute mixture of ethyne and sulfur hexafluoride in argon. The ground-state rotational spectrum was detected by two types of Fourier-transform microwave spectroscopy, namely that conducted in a microwave Fabry–Perot cavity and the chirped-pulse broadband technique. The spectroscopic constants of the six isotopologues $^{12}$C$_2$H$_2$···$^{63}$Cu$^{19}$F, $^{12}$C$_2$H$_2$···$^{65}$Cu$^{19}$F, $^{13}$C$_2$H$_2$···$^{63}$Cu$^{19}$F, $^{13}$C$_2$H$_2$···$^{65}$Cu$^{19}$F, $^{12}$C$_2$D$_2$···$^{63}$Cu$^{19}$F and $^{12}$C$_2$D$_2$···$^{65}$Cu$^{19}$F were determined and interpreted to show that the molecule has a planar, T-shaped geometry belonging to the molecular point group $C_s$ with CuF forming the stem of the T. Quantitative interpretation reveals that the ethyne molecule is distorted when subsumed into the complex in such a manner that the C=C bond lengths (by $\delta r$) and the two H atoms cease to be collinear with the C=C internuclear line. The H atoms move symmetrically away from the approaching Cu atom of CuF, to increase each $\equiv$C–H angle by $\delta \theta = 14.65(2)^\circ$, from 180$^\circ$ to 194.65(2)$^\circ$. 

$Ab initio$ calculations at the explicitly-correlated level of theory CCSD(T)(F12*)/aug-cc-pVTZ lead to good agreement with the experimental geometry. It is shown that similar distortions $\delta r$ and $\delta \theta$, similarly determined, for four complexes C$_2$H$_2$···MX (M = Cu or Ag; X = F, Cl or CCH) are approximately linearly related to the energies $D_0$ for the dissociation process C$_2$H$_2$···MX = C$_2$H$_2$ + MX.

1. Introduction

The coordination of transition metal atoms M, cations M$^+$ or polar salts M$^+$X$^-$ to alkynes and alkenes has been described in terms of the interaction of the $\pi$ electrons of the latter compounds with the $\pi^*$ orbitals of the metal atom or ion.$^{1,2}$ Such interactions achieve importance by virtue of their presence in coordination compounds that feature in hydrogenation and polymerization reactions.$^3$ For that reason, we have recently been investigating systematically a series of simple, gas-phase complexes of the type C$_2$H$_2$···MX which contain such interactions, where M is a coinage metal atom and X is a halogen atom.$^{4-6}$ The advantage of working in the gas phase is that distortions of the alkyne on complex formation are free from lattice or solvent effects and are therefore intrinsic to the interaction of interest. The technique employed in the synthesis of C$_2$H$_2$···MX complexes is laser ablation of the metal M in the presence of both ethyne and a source of halogen atom X in a preponderating excess of argon gas. The subsequent, rapid supersonic expansion of the mixture into a vacuum cools and stabilizes the product molecules and allows their rotational spectra to be observed. By these methods it has been possible to determine, with all the precision associated with microwave spectroscopy, the geometries of several species$^{4-6}$ C$_2$H$_2$···MX, where MX is AgCl, AgCCH, or CuCl.

In this article, we report the rotational spectra of six isotopologues of C$_2$H$_2$···CuF. The complexes were produced by the laser ablation of metallic copper in the presence of a pulse of ethyne–SF$_6$–Ar gas mixture and their spectra were detected by two versions of the Fourier-transform microwave technique. Interpretation of the spectroscopic constants thereby determined leads to a precise characterization of the distortion that ethyne undergoes when it is coordinated to CuF. The distortions will be compared with those predicted by an $ab initio$ calculation conducted at the CCSD(T)(F12*)/AVTZ level of theory. Such distortions have now been established, both experimentally and $ab initio$, as accompanying the attachment of C$_2$H$_2$ to MX = CuF, CuCl, AgCl and AgCCH (where M is copper or silver, and X = F, Cl or CCH as appropriate). Variations in these distortions with (1) M and (2) X will be considered.

$^a$ School of Chemistry, Newcastle University, Bedson Building, Newcastle-upon-Tyne, NE1 7RU, UK. E-mail: nick.walker@newcastle.ac.uk
$^b$ School of Chemistry, University of Bristol, Cantock’s Close, Bristol, BS8 1TS, UK. E-mail: a.c.legon@bristol.ac.uk
$^\dagger$ Electronic supplementary information (ESI) available. See DOI: 10.1039/c5cp02248g
2. Experimental and theoretical methods

Experimental data for \( \text{C}_2\text{H}_2\cdot\cdot\cdot\text{CuF} \) and \( \text{C}_2\text{D}_2\cdot\cdot\cdot\text{CuF} \) were recorded on a chirped-pulse Fourier transform microwave spectrometer\(^7\) operating between 7 and 18.5 GHz. The instrument has been previously described in detail.\(^\text{8,9}\) A gas sample was prepared containing approximately 1\% \( \text{C}_2\text{H}_2 \) (or \( \text{C}_2\text{D}_2 \) as appropriate) and 1\% \( \text{SF}_6 \), balanced in 6 bar argon. The gas mixture then pulsed over a copper target rod which was ablated with a Nd:YAG laser. The gas pulse was subsequently expanded into a vacuum chamber. For these experiments, the pulsed nozzle was placed perpendicular to the axis of microwave propagation. During each sample injection cycle, 8 free induction decays (FID’s) were measured, each 20 \( \mu \)s in duration. For \( \text{C}_2\text{H}_2\cdot\cdot\cdot\text{CuF} \) a total of 480 k FID’s were acquired (16 h), for \( \text{C}_2\text{D}_2\cdot\cdot\cdot\text{CuF} \) the total was 780 k (26 h), and 720 k (24 h) for \( \text{C}_2\text{H}_2\cdot\cdot\cdot\text{CuF} \). In each case, Fourier transformation used a digital Kaiser–Bessel window function.

For \( ^{12}\text{C}_2\text{H}_2\cdot\cdot\cdot\text{CuF} \), data were also recorded on a Balle–Flygare cavity spectrometer,\(^\text{10,11}\) with an equivalent gas sample. These measurements were acquired with the pulsed nozzle placed coaxial with the direction of microwave propagation. Transitions measured in this arrangement appear as Doppler doublets, each normally with a full-width half maximum (FWHM) of 5 kHz (but see Section 3.1); this is compared to a FWHM of approximately 150 kHz for the perpendicular arrangement found in the broadband instrument. Only samples containing isotopes in natural abundance were employed when using this spectrometer.

Geometry optimizations were performed using CASSCF(T)(F12\(^*\)),\(^\text{12}\) a coupled-cluster method with single and double excitations, explicit correlation,\(^\text{13}\) and a perturbative treatment of triple excitations.\(^\text{14}\) An AVTZ basis set combination was used, by which we mean that the aug-cc-pVTZ basis sets\(^\text{15}\) were used for the C, F and H atoms and the aug-cc-pVTZ-PP basis for Cu, in combination with the ECP-10-MDF effective core potential on Cu to account for scalar relativistic effects.\(^\text{16,17}\) The frozen-core approximation was used throughout, and all calculations were performed using the MOLPRO package.\(^\text{18}\) The equilibrium dissociation energy \( D_e \) for the process \( \text{C}_2\text{H}_2\cdot\cdot\cdot\text{CuF} \rightarrow \text{C}_2\text{H}_2 + \text{CuF} \) was also computed at the CCSD(T)- (F12\(^*\))/AVTZ level using the counterpoise correction method\(^\text{19}\) where, for numerical stability, the CABS singles correction was not included in the correction term. The result was \( D_e = 170 \, \text{kJ mol}^{-1} \).

For the free CuF, the bond length was optimised on a series of potential curves including successive corrections for core correlation, computed at the CCSD(T) level by using the cc-pCVQZ basis, full triplets at the frozen-core level with a cc-pVQZ basis and perturbative quadruples using the cc-pVTZ basis, following a similar procedure to that employed by Gauss \textit{et al.}\(^\text{20}\) Post CCSD(T) calculations were performed using the MRCC program\(^\text{21}\) and yielded the fully corrected bond length \( r_e(\text{Cu-F}) = 1.7430 \, \text{Å} \), with a basis set uncertainty of 0.0006 \( \text{Å} \). This result is in good agreement with the experimental value 1.74493 \( \text{Å} \) calculated from equilibrium rotational constants\(^\text{22}\) of \( ^{12}\text{CuF} \) and \( ^{13}\text{CuF} \) by using the expression \( r_e = (\hbar/8\pi^2 m_k \mu_k)^{1/2} \). At the CCSD(T)(F12\(^*\))/aug-cc-pVTZ level of theory, as used for \( \text{C}_2\text{H}_2\cdot\cdot\cdot\text{CuF} \), the equilibrium bond length for the free CuF molecule is predicted to be 1.7422(25) \( \text{Å} \),

where the error is that estimated \( \text{(via gaussian error propagation)} \) to arise from basis set incompleteness (0.0007 \( \text{Å} \)), core valence correlation error (0.0021 \( \text{Å} \)) and higher-order correlation (0.0011 \( \text{Å} \)).

3. Results

3.1 Determination of spectroscopic constants

For all six isotopologues investigated, only vibrational ground-state, \( a \)-type R-branch transitions \( (J + 1)^{K\cdot\cdot\cdot K'} \rightarrow J^{K\cdot\cdot\cdot K'} \) with \( K' = 0 \) or 1 of the asymmetric-rotor complex \( \text{C}_2\text{H}_2\cdot\cdot\cdot\text{CuF} \) were observed under the experimental conditions described in Section 2. Each transition carried a resolvable nuclear quadrupole hyperfine structure resulting from a single quadrupolar nucleus \( ^{63}\text{Cu} \) or \( ^{65}\text{Cu} \) \( (I = 3/2) \). Transition frequencies of each isotopologue were fitted by means of the program PGOPHER\(^\text{23}\) with the following choice of Hamiltonian:

\[
H = H_R - \frac{1}{2} Q(Cu) \cdot \nabla E(Cu),
\]

in which \( Q(Cu) \) and \( \nabla E(Cu) \) are the Cu nuclear electric quadrupole tensor and the electric field gradient tensor at the Cu nucleus, respectively. \( H_R \) is the familiar Hamiltonian for a semi-rigid, asymmetric-rotor molecule and contains both rotational constants and centrifugal distortion constants. The \( H \) matrix was constructed in the coupled symmetric rotor basis, with the Watson \( A \) reduction\(^\text{24}\) chosen for \( H_R \). In addition to the rotational constants, \( H_R \) contains terms involving the five quartic centrifugal distortion constants \( A_J, A_{K\cdot\cdot\cdot K'}, A\cdot\cdot\cdot B, \delta_J \) and \( \delta_K \).

The rotational constants of the most abundant isotopologue \( ^{12}\text{C}_2\text{H}_2\cdot\cdot\cdot^{63}\text{CuF} \) are large enough that only one group of \( J + 1 \rightarrow J \) transitions, namely that with \( J = 1 \), could be measured in the frequency range available. A set of internally consistent arguments will be presented to show that the geometry of \( \text{C}_2\text{H}_2\cdot\cdot\cdot\text{CuF} \) is of the planar, T-shaped type in which the non-covalent interaction of the two component molecules involves primarily the Cu atom of CuF and the \( \pi \) bond of ethyne, as shown in Fig. 1. The experimental consequences of such a geometry are as follows:

1. The molecule is a nearly prolate, planar asymmetric rotor of molecular point group \( C_{2v} \), with the \( a \) axis coincident with the \( C_2 \) axis. The rotational constant \( A_\theta \) is close in magnitude to the rotational constant \( B_\theta \) of free ethyne. Any difference of the two rotational constants will provide quantitative information about the extent of any geometrical distortion of the ethyne molecule when subsumed into \( \text{C}_2\text{H}_2\cdot\cdot\cdot\text{CuF} \).

2. The ground-state molecule will have a small positive inertia defect

\[
A_\theta = I_a - I_b - I_c,
\]

which is an important criterion of molecular planarity.

3. A rotation \( C_2^\alpha \) exchanges a pair of equivalent protons \( (I = 1/2) \) and this ends \( K' = 1 \) transitions with a nuclear spin statistical weight of 3 relative to that of 1 for \( K' = 0 \) transitions. This effect is evident in the set of \( 2_{11} \rightarrow 1_{11}, 2_{02} \rightarrow 1_{01}, 2_{11} \rightarrow 1_{10} \) transitions, as can be seen from the recording of these transitions shown in Fig. 2. Similar arguments applied to
the \(^{12}\text{C}_2\text{D}_2\cdot \cdot \cdot \text{Cu}^{19}\text{F}\) and \(^{13}\text{C}_2\text{H}_2\cdot \cdot \cdot \text{Cu}^{19}\text{F}\) isotopologues require the corresponding ratios to be 1:2 and 6:10, respectively, which were indeed as observed.

(4) Isotopic substitution of \(^{63}\text{Cu}\) by \(^{65}\text{Cu}\) should leave \(A_0\) unchanged.

It is evident that the rotational constant \(A_0\) has a central role to play in drawing conclusions about the symmetry and geometry of \(\text{C}_2\text{H}_2\cdot \cdot \cdot \text{Cu}–\text{F}\). Unfortunately, the \((J + 1)_{K, \pm K_1} \rightarrow J_{K, \pm K_0}\) \((K_1 = 0 \text{ or } 1)\) transition frequencies have a very weak dependence on \(A_0\) and it was not possible from the measured transition frequencies to determine \(A_0\) independently of the two centrifugal distortion constants \(A_J\) and \(A_{JK}\). (There is insignificant dependence on the remaining centrifugal distortion constants.) This difficulty was circumvented by the following approach.

It has been shown elsewhere that centrifugal distortion constants of molecules similar to \(\text{C}_2\text{H}_2\cdot \cdot \cdot \text{Cu}–\text{F}\) can be calculated \textit{ab initio} with good accuracy.\(^4\) For example, in the closely related species \(\text{C}_2\text{H}_2\cdot \cdot \cdot \text{Cu}–\text{Cl}\) calculations at the MP2/cc-pVTZ level of theory reproduced \(A_J\) and \(A_{JK}\) to within a few standard deviations of the well-determined experimental values. Here, the five quartic constants \((A_J, A_{JK, A_{KK}}, \delta_J, \delta_{JK})\) for \(\text{C}_2\text{H}_2\cdot \cdot \cdot \text{Cu}–\text{F}\) were calculated for the optimized geometry at the higher level of theory MP2/aug-cc-pVQZ with the aid of the Gaussian electronic structure package\(^{25}\) for each isotopologue investigated. The calculated constants \(A_J\) and \(A_{JK}\) were then fixed in the POGOPHER\(^{21}\) fits of observed frequencies to determine the rotational constants \(A_0, B_0\) and \(C_0\) and the Cu nuclear quadrupole coupling constants \(\chi_{ab}(\text{Cu})\) and \(\chi_{bb}(\text{Cu}) - \chi_{cc}(\text{Cu})\) for the isotopologues \(^{12}\text{C}_2\text{H}_2\cdot \cdot \cdot \text{Cu}^{19}\text{F}\) and \(^{12}\text{C}_2\text{H}_2\cdot \cdot \cdot \text{Cu}^{65}\text{F}\) in the first instance.

The spectroscopic constants so determined both from measurements made with the Balle–Flygare and the chirped-pulse spectrometers are displayed in Table 1. The residuals of the fit to frequencies collected with the Balle–Flygare spectrometer were poorer than the usual few kHz. This arises because \(\text{C}_2\text{H}_2\cdot \cdot \cdot \text{CuF}\) carries four nuclei (H, H, Cu and F) with magnetic moments of significant magnitude, in addition to the electric quadrupolar moment of the Cu nucleus. Moreover, only the lowest \(J\) transitions were available because of the relatively large rotational constants. The magnetic coupling of these nuclei (Cu, F spin–spin coupling, for example) can lead to further complicated but minor, partially resolved splitting or broadening and/or lineshape distortion of each Cu nuclear quadrupole component and is most significant at the lowest \(J\). Therefore assignment of the magnetic sub-structure was not possible in the observed transitions of \(\text{C}_2\text{H}_2\cdot \cdot \cdot \text{CuF}\), particularly those with \(K_1 = 1\), and hence larger than normal residuals in the fit of the Cu nuclear quadrupole hyperfine structure resulted. When measured with the lower resolution, chirped-pulse instrument, fitted frequencies assigned to Cu quadrupole components gave similar magnitude residuals. Reassuringly, the spectroscopic constants determined independently with the two spectrometers are identical within experimental error.

Measurements for \(^{13}\text{C}_2\text{H}_2\cdot \cdot \cdot \text{Cu}^{19}\text{F}\) and \(^{12}\text{C}_2\text{D}_2\cdot \cdot \cdot \text{Cu}^{65}\text{F}\) were made exclusively on the chirped-pulse instrument to conserve the more expensive isotopic materials. The spectroscopic constants...
Table 1  Ground-state spectroscopic constants of $^{12}$C$_2$H$_2$·$^{63,65}$CuF as determined with two different pulsed-jet, Fourier-transform microwave spectrometers (Balle–Flygare and chirped-pulse types).

<table>
<thead>
<tr>
<th>Spectroscopic constant</th>
<th>Balle–Flygare</th>
<th>Chirped-pulse</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_0$/MHz</td>
<td>$^{12}$C$_2$H$_2$·$^{63}$CuF</td>
<td>$^{12}$C$_2$H$_2$·$^{63,65}$CuF</td>
</tr>
<tr>
<td>$B_0$/MHz</td>
<td>$^{12}$C$_2$H$_2$·$^{63}$CuF</td>
<td>$^{12}$C$_2$H$_2$·$^{63,65}$CuF</td>
</tr>
<tr>
<td>$C_{6s}$/MHz</td>
<td>$^{12}$C$_2$H$_2$·$^{63}$CuF</td>
<td>$^{12}$C$_2$H$_2$·$^{63,65}$CuF</td>
</tr>
<tr>
<td>$\Delta_J/kHz^a$</td>
<td>$^{12}$C$_2$H$_2$·$^{63}$CuF</td>
<td>$^{12}$C$_2$H$_2$·$^{63,65}$CuF</td>
</tr>
<tr>
<td>$\delta_{\text{r.m.s.}}$/kHz</td>
<td>$^{12}$C$_2$H$_2$·$^{63}$CuF</td>
<td>$^{12}$C$_2$H$_2$·$^{63,65}$CuF</td>
</tr>
</tbody>
</table>

Values calculated at the MP2/aug-cc-pVQZ level of theory and fixed in the fit. b Number of nuclear quadrupole components included in the fit. c Standard deviation of fit.

Table 2  Ground-state spectroscopic constants of $^{12}$C$_2$H$_2$·$^{63,65}$CuF and $^{12}$C$_2$D$_2$·$^{63,65}$CuF as determined with a chirped-pulse, pulsed-jet, Fourier-transform microwave spectrometer.

<table>
<thead>
<tr>
<th>Spectroscopic constant</th>
<th>$^{12}$C$_2$H$_2$·$^{63,65}$CuF</th>
<th>$^{12}$C$_2$D$_2$·$^{63,65}$CuF</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_0$/MHz</td>
<td>$^{12}$C$_2$H$_2$·$^{63,65}$CuF</td>
<td>$^{12}$C$_2$D$_2$·$^{63,65}$CuF</td>
</tr>
<tr>
<td>$B_0$/MHz</td>
<td>$^{12}$C$_2$H$_2$·$^{63,65}$CuF</td>
<td>$^{12}$C$_2$D$_2$·$^{63,65}$CuF</td>
</tr>
<tr>
<td>$C_{6s}$/MHz</td>
<td>$^{12}$C$_2$H$_2$·$^{63,65}$CuF</td>
<td>$^{12}$C$_2$H$_2$·$^{63,65}$CuF</td>
</tr>
<tr>
<td>$\Delta_J/kHz^a$</td>
<td>$^{12}$C$_2$H$_2$·$^{63,65}$CuF</td>
<td>$^{12}$C$_2$H$_2$·$^{63,65}$CuF</td>
</tr>
<tr>
<td>$\delta_{\text{r.m.s.}}$/kHz</td>
<td>$^{12}$C$_2$H$_2$·$^{63,65}$CuF</td>
<td>$^{12}$C$_2$H$_2$·$^{63,65}$CuF</td>
</tr>
</tbody>
</table>

Values calculated at the MP2/aug-cc-pVQZ level of theory and fixed in the fit. b Number of nuclear quadrupole components included in the fit. c Standard deviation of fit.
Table 3 Some spectroscopic constants and bond lengths of C\(_2\)H\(_2\) and CuF referred to in evaluating properties of C\(_2\)H\(_2\)–CuF

<table>
<thead>
<tr>
<th>Quantity constant</th>
<th>(^{12})C(_2)H(_2)</th>
<th>(^{13})C(_2)H(_2)</th>
<th>(^{12})C(_2)D(_2)</th>
<th>(^{65})Cu(^{19})F</th>
<th>(^{65})Cu(^{18})F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyne (b_0/\text{MHz})</td>
<td>33574.9693(54)(^a)</td>
<td>33564.0058(^a)</td>
<td>25418.6291(^a)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Geometry (r(C\equiv C)/\text{Å})</td>
<td>(r(C_1/C_1)/\text{Å})</td>
<td>(r(C_2/D)/\text{Å})</td>
<td>(r(C_1/H)/\text{Å})</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Cuprous fluoride</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

\(^a\) Calculated from ref. 22. \(^b\) Estimated from Dunham constants in ref. 22. \(^c\) Calculated by fitting the moments of inertia \(e_0\) of \(^{12}\)C\(_2\)H\(_2\) and \(^{13}\)C\(_2\)H\(_2\) from ref. 27. See text. \(^d\) Calculated from Dunham constants in ref. 22.

3.2 Molecular geometry

Of the four consequences of a planar geometry of the type shown in Fig. 1, it was indicated in Section 3.1 that three were satisfied by experimental results for C\(_2\)H\(_2\)–CuF. The fourth is that the inertia defect, as defined in eqn (2), should be small and positive. If the Cu atom does lie on the \(a\) axis, it is reasonable to use the mean \(e_0\) value for a pair of isotopologues \(^{63}\)Cu\(^{19}\)F and \(^{65}\)Cu\(^{19}\)F in calculating \(\Delta\) for both members of the pair. The results are \(\Delta_0 = 0.365(38)\) \(\text{Å}^2\) and 0.366(38) \(\text{Å}^2\) for the \(^{12}\)C\(_2\)H\(_2\)–\(^{63}\)Cu\(^{19}\)F pair, 0.373(69) \(\text{Å}^2\) and 0.373(69) \(\text{Å}^2\) for the \(^{13}\)C\(_2\)H\(_2\)–\(^{63}\)Cu\(^{19}\)F pair, and 0.295(22) \(\text{Å}^2\) and 0.293(22) \(\text{Å}^2\) for the \(^{12}\)C\(_2\)D\(_2\)–\(^{63}\)Cu\(^{19}\)F pair. The very similar values, observed across a similar range of isotopologues, for each of the related planar molecules C\(_2\)H\(_2\)–CuCl\(^b\) and C\(_2\)H\(_2\)–AgCl\(^b\) reinforce the conclusion that C\(_2\)H\(_2\)–CuF is also planar.

Thus, all the evidence so far presented is consistent with a geometry of C\(_2\)H\(_2\)–CuF of the planar, T-shaped type of C\(_2\)\(v\) symmetry illustrated in Fig. 1, with the atoms in the indicated order. Quantitative detail of the geometry can be determined experimentally in two ways from the zero-point rotational constants of the six isotopologues of C\(_2\)H\(_2\)–CuF investigated, namely a partial \(r_s\) geometry and an almost complete \(r_0\) geometry. These results will be compared with the full \(r_s\) geometry obtained from ab initio calculations carried out at the CCSD(T)[\(\text{F12}^*/\text{AVTZ}\)] level of theory.

If equilibrium rotational constants (and therefore equilibrium principal moments of inertia) of the various isotopologues of C\(_2\)H\(_2\)–CuF investigated were available, the equilibrium principal-axis co-ordinates \(a_{Cu}\), \(b_{Cu}\), \(a_{Ch}\), and \(a_{Co}\), could be determined by means of eqn (3)–(5). In view of the molecular planarity and the existence of the symmetry operation \(C_2\), the changes \(I_0\) and \(I_0\) in the equilibrium principal moments of inertia that accompany the double isotopic substitution of X by \(X'\) \((X = ^{12}\text{C} \text{H}_2 \text{ or } X' = ^{13}\text{C} \text{H}_2 \text{ or } D_2\text{, respectively})\) at symmetrically equivalent atoms are related to the equilibrium coordinates \(a_X\) and \(b_X\) by the expressions put forward by Chutjian\(^{10}\):

\[|a_X| = (\Delta I_0/\mu I_0)^{1/2},\]

\[|b_X| = (\Delta I_0/\mu I_0)^{1/2},\]

in which \(\mu_0 = (2\mu M)/(M + 2\mu M)\) is the reduced mass for the double substitution in the parent isotopologue of mass \(M\) leading to a mass change \(2\mu M\). The equilibrium principal axis co-ordinate \(a_{Cu}\) of the atom Cu, which lies on the \(a\)-axis of C\(_2\)H\(_2\)–CuF, is given in terms of changes \(\Delta I_0\) and \(\Delta I_0\) in equilibrium principal moments of inertia accompanying isotopic substitution at Cu by Kraitchman’s equation\(^{11}\):

\[|a_{Cu}| = \left|\Delta I_0 + \Delta I_0/2\mu I_0\right|^{1/2},\]

where \(\mu_0 = (\mu M)/(M + \mu M)\) is the reduced mass for the substitution. When equilibrium quantities are unavailable, Costain\(^{32,33}\) proposed using zero-point \(\Delta\) values in place of their equilibrium counterparts \(\Delta\) in eqn (3)–(5) and named the resulting coordinates as substitution or \(r_0\) coordinates. The \(r_s\) coordinates \(a_{Cu}, b_{Cu}, a_{Ch}, b_{Ch}\) and \(a_{Co}\) so obtained from eqn (3)–(5) are given in Table 4. Each refers to the principal inertia axis of \(^{12}\)C\(_2\)H\(_2\)–\(^{63}\)Cu\(^{19}\)F as the parent molecule and the chosen signs are those that lead to reasonable bond lengths. Note that the mean of \(a_{Ch}\) for pairs of \(^{63,65}\)Cu isotopologues, as given in Section 3.1, were used in the calculation of the \(b_{Ch}\) and \(b_{Ch}\) coordinates. The substantial uncertainties in \(b_{Ch}\) and \(b_{Ch}\) result from the relatively large errors assigned to \(a_{Cu}\). A \(r_s\) coordinate \(a_F\) is not available because fluorine possesses only one stable isotope and so the value of \(a_F\) given in Table 4 was determined, as recommended by Costain\(^{32}\) from the other \(r_s\) coordinates with the aid of the first moment condition,

\[a_F = -\left(\sum m_j a_j\right) / m_F,\]

in which the sum over \(j\) indicates that all atoms but F are included.

The significantly larger magnitude of \(a_{Ch}\) than \(a_C\) provides experimental evidence that the angular geometry of ethyne is distorted in the manner shown in Fig. 1, that is the H atoms move away from the C\(\equiv\)C internuclear line when the complex is formed, with the two equivalent angles \(\alpha = \angle H\cdot \text{C} \cdot \equiv\) (see Fig. 1 for definition) exceeding 180°. The value obtained from
The $r_s$ coordinates in Table 3 is $A = 194.5(6)^\circ$ [see Table 4], where the large error is consequent upon the errors in the $A_0$ values. This distortion is established with greater accuracy in the experimental $r_0$ and $ab\ initio$ $r_s$ geometries discussed later (see below). The bond distances implied by the $r_s$ coordinates are also included in Table 4.

When the minimum number of bond lengths and angles required to establish a molecular geometry uniquely is fitted to a sufficient number of zero-point principal moments of inertia by the least-squares method, the result is called a $s$ geometry. Additional $r_s$ and $r_0$ geometries were determined through the investigation of six isotopologues. A significant finding is that the ethyne subunit is considerably distorted by the interaction of its C≡C bond with the Cu atom of $CuF$. The H atoms move from the C≡C internuclear line, in the direction away from the approaching Cu atom, so that the $\angle \equiv C-H$ angle increases from $180^\circ$ to $194.65(2)^\circ$. The $C\equiv C$ bond lengths by ca. $0.04\ Å$. These distortions are well reproduced in the optimized geometry of $CuF$, $C_2H_2$, $CuF$, and $C_2H_2$ calculated at the CCSD(T)(F12*)/AVTZ level of theory (see Table 4).

Similar distortions have now been observed in the series of molecules $CuF$, $C_2H_2$, $AgCl$, $C_2H_2$, $AgCCH_2$, $C_2H_2$, $CuCl$, each of which has the planar $T$-shaped, $C_{2v}$ geometry with the metal atom adjacent to the ethyne $\pi$ bond (see Fig. 1). The changes $\Delta \angle$ in the angle $\equiv C-H$ and $\Delta \theta$ in the distance $r(C\equiv C)$ are [14.65(2)$^\circ$, 4.0(1) pm], [7.70(4)$^\circ$, 2.86(4) pm], [5.9(1)$^\circ$, 2.61(3) pm] and [12.5(2)$^\circ$, 2.7(3) pm], respectively, along the series. The corresponding energy changes $D_e$ accompanying dissociation into $C_2H_2$ and $MX$ have been calculated $ab\ initio$ [at the CCSD(T)(F12*)/AVTZ or AVDZ levels] to be 170, 97.5, 92 and 148 kJ mol$^{-1}$, respectively. Fig. 3 displays a plot of each of $\Delta \theta$ and $\Delta \theta$ versus $D_e$ for these molecules. The origin has been included as a point in each plot because when the interaction energy $D_e$ is zero, presumably there is no distortion of the ethyne subunit. Fig. 3 shows that there is an approximate linear relationship between each of the two types of distortion $\Delta \theta$ and $\Delta \theta$ and the strength of the interaction $D_e$.

The nature of the ethyne distortions can be understood with the aid of a simple model. The nuclei of each of the $C_2H_2\cdots MX$ ($M=Cu$ or Ag, $X=F$ or Cl) molecules all lie in the $ab$ principal inertia plane. Let the symmetry plane of one of the ethyne $\pi$ bonding orbitals lie in this plane, with that of the other $\pi$ orbital perpendicular to it. When $M-X$ approaches from large separation and takes up its position along a $C_2$ axis of ethyne (which then becomes the $a$ axis of the new molecule), the partial

<table>
<thead>
<tr>
<th>Atom</th>
<th>$r_s$ geometry</th>
<th>$r_0$ geometry</th>
<th>$r_e$ geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$a/\text{Å}$</td>
<td>$b/\text{Å}$</td>
<td>$a/\text{Å}$</td>
</tr>
<tr>
<td>H</td>
<td>-1.9764(8)</td>
<td>±1.663(9)</td>
<td>-1.9767(4)</td>
</tr>
<tr>
<td>C</td>
<td>-1.7066(9)</td>
<td>±0.62(4)</td>
<td>-1.7059(4)</td>
</tr>
<tr>
<td>Cu</td>
<td>0.142(10)</td>
<td>0.0000</td>
<td>0.1415(3)</td>
</tr>
<tr>
<td>F</td>
<td>1.893(33)</td>
<td>0.0000</td>
<td>1.8961(6)</td>
</tr>
</tbody>
</table>

$^a$ The $r_e$ geometry was optimized at the CCSD(T)(F12*)/aug-cc-pVTZ level of theory. $^b$ The errors in $r_s$ coordinates $\alpha_0$ are those given by $\delta \alpha = (0.0015 \text{ Å})/\alpha$, as suggested by Costain in ref. 32. The errors in $r_s$ coordinates $\beta_0$ are those propagated from the poorly determined rotational constants $A_0$. $^c$ Assumed value obtained by adding the difference $\Delta\left(\equiv C-H\right) = 0.00072\text{ Å}$ for free ethyne $^{27,28}$

### 4. Discussion

The new molecule $C_2H_2\cdots CuF$ has been synthesized by interaction of the plasma produced by laser ablation of copper rod and a supersonically-expanded pulse of gas containing $SF_6$ and $C_2H_2$ diluted with a large excess of argon. It was detected by means of its ground-state rotational spectrum and was shown to have a planar, $T$-shaped geometry of $C_{2v}$ symmetry, with the $CuF$ molecule lying along a $C_2$ axis of the $C_2H_2$ molecule. Quantitative aspects of the molecular geometry were determined through the investigation of six isotopologues. A significant finding is that the ethyne subunit is considerably distorted by the interaction of its C≡C bond with the Cu atom of $CuF$. The H atoms move from the C≡C internuclear line, in the direction away from the approaching Cu atom, so that the $\angle \equiv C-H$ angle increases from $180^\circ$ to $194.65(2)^\circ$. The $C\equiv C$ bond lengths by ca. $0.04\ Å$. These distortions are well reproduced in the optimized geometry of $CuF$, $C_2H_2$, $CuF$, and $C_2H_2$ calculated at the CCSD(T)(F12*)/AVTZ level of theory (see Table 4).

Similar distortions have now been observed in the series of molecules $CuF$, $C_2H_2$, $AgCl$, $C_2H_2$, $AgCCH_2$, $C_2H_2$, $CuCl$, each of which has the planar $T$-shaped, $C_{2v}$ geometry with the metal atom adjacent to the ethyne $\pi$ bond (see Fig. 1). The changes $\Delta \angle$ in the angle $\equiv C-H$ and $\Delta \theta$ in the distance $r(C\equiv C)$ are [14.65(2)$^\circ$, 4.0(1) pm], [7.70(4)$^\circ$, 2.86(4) pm], [5.9(1)$^\circ$, 2.61(3) pm] and [12.5(2)$^\circ$, 2.7(3) pm], respectively, along the series. The corresponding energy changes $D_e$ accompanying dissociation into $C_2H_2$ and $MX$ have been calculated $ab\ initio$ [at the CCSD(T)(F12*)/AVTZ or AVDZ levels] to be 170, 97.5, 92 and 148 kJ mol$^{-1}$, respectively. Fig. 3 displays a plot of each of $\Delta \theta$ and $\Delta \theta$ versus $D_e$ for these molecules. The origin has been included as a point in each plot because when the interaction energy $D_e$ is zero, presumably there is no distortion of the ethyne subunit. Fig. 3 shows that there is an approximate linear relationship between each of the two types of distortion $\Delta \theta$ and $\Delta \theta$ and the strength of the interaction $D_e$.

The nature of the ethyne distortions can be understood with the aid of a simple model. The nuclei of each of the $C_2H_2\cdots MX$ ($M=Cu$ or Ag, $X=F$ or Cl) molecules all lie in the $ab$ principal inertia plane. Let the symmetry plane of one of the ethyne $\pi$ bonding orbitals lie in this plane, with that of the other $\pi$ orbital perpendicular to it. When $M-X$ approaches from large separation and takes up its position along a $C_2$ axis of ethyne (which then becomes the $a$ axis of the new molecule), the partial
positive charge $\delta^+$ that exists on the M atom in the species M-X (the metal halides have large electric dipole moments in the range ~5 or 6 D)\textsuperscript{35} polarizes electron density preferentially from the $\pi$ orbital ($\pi_{ab}$) in the molecular plane. The larger the polarization, the more the $\pi$ bonding in the ethyne molecule will resemble that of an ethene molecule in which the symmetry plane of its $\pi$ bonding orbital is perpendicular to the $ab$ plane and the C-H bond lies in the $ab$ plane. In the limit of very large polarization of the $\pi_{ab}$ electrons, when both are completely removed from ethyne to yield the ion C\textsubscript{2}H\textsubscript{2}\textsuperscript{2+}, the distortions would be of the order $\Delta \delta \approx 60^\circ$ and $\delta^\prime \approx 134.5 - 120.6 = 13.9$ pm, where 134.5 and 120.6 pm are the CC distances in the ground state $^3\Sigma^+$ of the dication\textsuperscript{26} C\textsubscript{2}H\textsubscript{2}\textsuperscript{2+} and in ethyne,\textsuperscript{27} respectively. Similar distortions have been observed in C\textsubscript{2}H\textsubscript{2}...MX (M = Cu or Ag),\textsuperscript{27} in which M-X lies on the C\textsubscript{2} axis of C\textsubscript{2}H\textsubscript{4} that is perpendicular to the plane of the C\textsubscript{2}H\textsubscript{4} nuclei. Similar arguments can be used to rationalize the distortions in these molecules, but with C\textsubscript{2}H\textsubscript{4}\textsuperscript{2+} as the limiting dication.

**Acknowledgements**

We thank the European Research Council for postdoctoral fellowships awarded to D.P.Z. and S.L.S., and for project funding (CPFTMW-307000). ACL thanks the University of Bristol for a Senior Research Fellowship and Newcastle University for a Faculty of SAgE Visiting Professorship. D.P.Z. thanks Newcastle University for the award of a Faculty of SAgE Research Fellowship. D.P.T. gratefully acknowledges the award by the Royal Society of a University Research Fellowship.

**References**


21. M. Kállay, MRCC, a generalized CC/CI program, see http://www.mrcc.hu.


26 See ESI† for assignments of all observed transitions and the fits used to determine the spectroscopic constants of six isotopologues of C$_2$H$_2$···Cu–F.


