Distortions of ethyne when complexed with a cuprous or argentous halide: the rotational spectrum of $\text{C}_2\text{H}_2\cdots\text{CuF}^+$

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A new molecule $\text{C}_2\text{H}_2\cdots\text{CuF}$ 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 $^{12}\text{C}_2\text{H}_2\cdots^{63}\text{Cu}^{19}\text{F}$, $^{12}\text{C}_2\text{H}_2\cdots^{65}\text{Cu}^{19}\text{F}$, $^{13}\text{C}_2\text{H}_2\cdots^{63}\text{Cu}^{19}\text{F}$, $^{13}\text{C}_2\text{H}_2\cdots^{65}\text{Cu}^{19}\text{F}$, $^{12}\text{C}_2\text{D}_2\cdots^{63}\text{Cu}^{19}\text{F}$ and $^{12}\text{C}_2\text{D}_2\cdots^{65}\text{Cu}^{19}\text{F}$ were determined and interpreted to show that the molecule has a planar, T-shaped geometry belonging to the molecular point group $C_2v$ 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 $\text{C}≡\text{C}$ bond lengths (by $\delta r$) and the two H atoms cease to be collinear with the $\text{C}≡\text{C}$ internuclear line. The H atoms move symmetrically away from the approaching Cu atom of CuF, to increase each $\angle\text{C}≡\text{C}−\text{H}$ angle by $\delta\angle = 14.65(2)^\circ$, 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 $\delta\angle$, similarly determined, for four complexes $\text{C}_2\text{H}_2\cdots\text{MX}$ ($M = \text{Cu or Ag}; X = \text{F, Cl or CCH}$) are approximately linearly related to the energies $D_e$ for the dissociation process $\text{C}_2\text{H}_2\cdots\text{MX} = \text{C}_2\text{H}_2 + \text{MX}$.

1. Introduction

The coordination of transition metal atoms $M$, cations $M^+$ or polar salts $M^+X^-$ to alkenes 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 $\text{C}_2\text{H}_2\cdots\text{MX}$ which contain such interactions, where $M$ is a coinage metal atom and $X$ is a halogen atom.$^{4,5}$ 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 $\text{C}_2\text{H}_2\cdots\text{MX}$ 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$^{4,5}$ $\text{C}_2\text{H}_2\cdots\text{MX}$, where MX is AgCl, AgCCH, or CuCl.

In this article, we report the rotational spectra of six isotopologues of $\text{C}_2\text{H}_2\cdots\text{CuF}$. The complexes were produced by the laser ablation of metallic copper in the presence of a pulse of ethyne-$\text{SF}_6$-$\text{Ar}$ 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 $\text{C}_2\text{H}_2$ to MX = CuF, CuCl, AgCl and AgCCH (where M is copper or silver, and $X = \text{F, Cl or CCH}$ as appropriate). Variations in these distortions with (1) $M$ and (2) $X$ will be considered.
2. Experimental and theoretical methods

Experimental data for C2H2·CuF and C2D2·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.\(^8,9\) A gas sample was prepared containing approximately 1% C2H2 (or C2D2 as appropriate) and 1% SF6, 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 μs in duration. For C2H2·CuF a total of 480 k FID’s were acquired (16 h), for C2D2·CuF the total was 780 k (26 h), and 720 k (24 h) for 13C2H2·CuF. In each case, Fourier transformation used a digital Kaiser–Bessel window function.

For 12C2H2·CuF, data were also recorded on a Balle–Flygare cavity spectrometer,\(^10,11\) 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 CCSD(T)(F12\(^*\)),\(^12\) a coupled-cluster method with single and double excitations, explicit correlation,\(^13\) and a perturbative treatment of triple excitations.\(^14\) An AVTZ basis set combination was used, by which we mean that the aug-cc-pVTZ basis sets\(^15\) 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.\(^16,17\) The frozen-core approximation was used throughout, and all calculations were performed using the MOLPRO package.\(^18\) The equilibrium dissociation energy \(D_e\) for the process C2H2·CuF = C2H2 + CuF was also computed at the CCSD(T)-(F12\(^*\))/AVTZ level using the counterpoise correction method\(^19\) 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 core 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 et al.\(^20\) Post CCSD(T) calculations were performed using the MRCC program\(^21\) and yielded the fully corrected bond length \(r_{\text{Cu-F}} = 1.7430\; \text{Å}\), with a basis set uncertainty of 0.0006 Å. This result is in good agreement with the experimental value 1.74493 Å calculated from equilibrium rotational constants\(^22\) of 63CuF\(^{18}\) and 64CuF\(^{19}\) by using the expression \(r_e = \left( \frac{\hbar}{8\pi^2 \mu_{\text{CuF}}} \right)^{1/2}\). At the CCSD(T)(F12\(^*\))/(aug-cc-pVTZ level of theory, as used for C2H2·CuF, the equilibrium bond length for the free CuF molecule is predicted to be 1.7422(25) Å.

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

3. Results

3.1 Determination of spectroscopic constants

For all six isotopologues investigated, only vibrational ground-state, \(a\)-type R-branch transitions \((J + 1)_{K_a K_v} \rightarrow J K_a K_v^*\) with \(K_v = 0\) or 1 of the asymmetric-rotor complex C2H2·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 65Cu or 63Cu \((I = 3/2)\). Transition frequencies of each isotopologue were fitted by means of the program PGOPHER\(^23\) with the following choice of Hamiltonian:

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

in which \(\mathbf{Q}(\text{Cu})\) and \(\nabla \mathbf{E}(\text{Cu})\) 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\(^24\) chosen for \(H_{R0}\). In addition to the rotational constants, \(H_{R0}\) contains terms involving the five quartic centrifugal distortion constants \(\Delta a, \Delta b, \Delta c, \Delta d, \Delta e\).

The rotational constants of the most abundant isotopologue 12C2H2·63CuF 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 assignments will be presented to show that the geometry of C2H2·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 π 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 \(A_0\) is close in magnitude to the rotational constant \(B_0\) 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 C2H2·CuF.

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

\[
\Delta_0 = I_a - I_b - I_c,
\]

which is an important criterion of molecular planarity.

3. A rotation \(C^2\) exchanges a pair of equivalent protons \((I = 1/2)\) and this endows \(K_v = 1\) transitions with a nuclear spin statistical weight of 3 relative to that of 1 for \(K_v = 0\) transitions. This effect is evident in the set of 212 → 111, 202 → 101, 211 → 110 transitions, as can be seen from the recording of these transitions shown in Fig. 2. Similar arguments applied to...
the $^{12}$C$_2$D$_2$·Cu$^{19}$F and $^{13}$C$_2$H$_2$·Cu$^{19}$F isotopologues require the corresponding ratios to be 1:2 and 6:10, respectively, which were indeed as observed.

(4) Isotopic substitution of $^{63}$Cu by $^{65}$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 C$_2$H$_2$·Cu–F. Unfortunately, the (J + 1) $K_{a}K'_{a}$ → $J_{K-1}K'_{a}$ ($K_{a}$ = 0 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 C$_2$H$_2$·Cu–F can be calculated \textit{ab initio} with good accuracy.\footnote{Reference} For example, in the closely related species C$_2$H$_2$·Cu–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 ($A_J$, $A_{JK}$, $A_{KK'}$, $A_{KK''}$, and $B_{KK''}$) for C$_2$H$_2$·Cu–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\textsuperscript{25} for each isotopologue investigated. The calculated constants $A_J$ and $A_{JK}$ were then fixed in the PGOPHER fits of observed frequencies to determine the rotational constants $A_0$, $B_0$, and $C_0$ and the Cu nuclear quadrupole coupling constants $\chi_{dd}(\text{Cu})$ and $\chi_{bb}(\text{Cu}) = \chi_{cc}(\text{Cu})$ for the isotopologues $^{12}$C$_2$H$_2$·$^{63}$Cu$^{19}$F and $^{12}$C$_2$H$_2$·$^{65}$Cu$^{19}$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 C$_2$H$_2$·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 C$_2$H$_2$·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 $^{13}$C$_2$H$_2$·$^{63,65}$Cu$^{19}$F, and $^{12}$C$_2$D$_2$·$^{63,65}$Cu$^{19}$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)

| Spectroscopic constant | Balle–Flygare | Chirped-pulse |
|------------------------|---------------|---------------|
| $A_0$/MHz              | $^{12}$C$_2$H$_2$···$^{63}$CuF | $^{12}$C$_2$H$_2$···$^{65}$CuF | $^{12}$C$_2$H$_2$···$^{63}$CuF | $^{12}$C$_2$H$_2$···$^{65}$CuF |
| $A_0$/MHz              | 34 749(83)    | 34 930(270)   | 35 030(230)    | 35 020(180)    |
| $B_0$/MHz              | 3 431.4407(48)| 3 430.5201(55)| 3 430.5190(42)| 3 430.5190(42)|
| $C_0$/MHz              | 3 116.7391(44)| 3 115.9722(55)| 3 115.9721(39)| 3 115.9722(39)|
| $\Delta J_k$/kHz$^a$  | [0.61]        | [0.61]        | [0.61]        | [0.61]        |
| $\Delta J_k$/kHz$^a$  | [0.53]        | [0.53]        | [0.53]        | [0.53]        |
| $\langle \mu_0(Cu) - \mu_0(Cu) \rangle$/MHz | 69.991(47) | 64.721(53) | 64.720(40) | 64.720(40) |
| $N^b$                  | 20            | 16            | 18            | 19            |
| $\sigma_{\text{rms}}$/kHz | 30            | 33            | 34            | 26            |

$^a$ 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.

for these species were obtained in a similar way and are recorded in Table 2. Detailed fits are available as Supplementary Data28 at http://dx.doi.org/xxxxx. The effect of changes in the assumed values of the centrifugal distortion constants were investigated for the isotopologue $^{12}$C$_2$H$_2$···$^{63,65}$CuF. Changes of 10% in the assumed values of the distortion constants $A_0$ and $\Delta J_k$ lead to changes in $A$ that are small compared with the errors shown in Table 1. The standard deviations in $A_0$ values are higher than those identified in other B – MX studies because only one $J + 1 \rightarrow J$ transition is available within the bandwidth of the spectrometer in the present work.

It is significant that values of $A_0$ for $^{12}$C$_2$H$_2$···$^{63}$CuF and $^{12}$C$_2$H$_2$···$^{65}$CuF (Table 1) are equal within experimental error (as required if Cu lies on the a axis). These values of $A_0$ and their associated uncertainties strongly imply that the average of the two results provides the most reliable value for this quantity, namely 34 840(90) MHz (where the quoted error is the range about the mean). This value will be used in geometry determinations set out in Section 3.2, together with the mean value $A_0 = 33 100(150)$ MHz for the pair ($^{13}$C$_2$H$_2$···$^{63}$CuF, $^{13}$C$_2$H$_2$···$^{65}$CuF) and $A_0 = 25 182(26)$ MHz for the pair ($^{12}$C$_2$D$_2$···$^{63}$CuF, $^{12}$C$_2$D$_2$···$^{65}$CuF). We note that $A_0 = 34 840(90)$ MHz is smaller by 435(90) MHz than the $B_0$ value of free $^{12}$C$_2$D$_2$ (see Table 3 for various properties of isotopologues of the free molecules ethyne 27,28 and cuprous fluoride23). Similar conclusions (see Table 2) apply to the pair ($^{12}$C$_2$H$_2$···$^{63}$CuF, $^{12}$C$_2$H$_2$···$^{65}$CuF), for which the mean decrease from free $^{12}$C$_2$D$_2$ is 464(150) MHz, and the pair ($^{12}$C$_2$D$_2$···$^{63}$CuF, $^{12}$C$_2$D$_2$···$^{65}$CuF), for which a mean decrease of 236(26) MHz relative to $B_0$ of free $^{12}$C$_2$D$_2$ is observed. These decreases, although not well determined, indicate a change in the ethyne geometry when it becomes attached to CuF. Moreover, the very small change in all three rotational constants on substitution of $^{63}$Cu by $^{65}$Cu establishes that the Cu atom lies close to the centre of mass and therefore that the order along the a axis is $^*$Cu–F, where $^*$ indicates the centre of the C···C bond.

The Cu nuclear quadrupole coupling constants are reasonably well determined. The ratio of the values $\langle \mu_0(63Cu)/\mu_0(65Cu) \rangle = 1.0814(16)$ lies within experimental error of the known ratio $Q(63Cu)/Q(65Cu) = 1.0806(3)$ of the nuclear electric quadrupole moments of the copper nuclides. The large difference between $\langle \mu_0(Cu) \rangle = -74.58$ MHz and $\langle \mu_0(63Cu) \rangle = 4.59$ MHz is evidence of a large anisotropy in the electric field gradient at Cu along the b and c principal inertia axis directions arising from the facts that (1) the Cu atom is close to the ethyne $\pi$ bond and (2) the electron distribution within the triple bond C···C is different along the two directions. Indeed, the large difference $\langle \mu_0(63Cu) \rangle - \langle \mu_0(65Cu) \rangle = -79.17(11)$ MHz provides convincing evidence of the proximity of Cu to the C···C bond. In the related molecule $^{12}$C$_2$H$_2$···Ag···Cl, in which Cl is remote from the ethyne $\pi$ bond, values of the Cl nuclear quadrupole coupling constants are $\langle \mu_0(35Cl) \rangle = -28.9268(78)$ MHz and $\langle \mu_0(35Cl) \rangle - \langle \mu_0(37Cl) \rangle = -3.256(7)$ MHz.

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

| Spectroscopic constant | $^{12}$C$_2$H$_2$···$^{63}$CuF | $^{12}$C$_2$H$_2$···$^{65}$CuF | $^{12}$C$_2$D$_2$···$^{63}$CuF | $^{12}$C$_2$D$_2$···$^{65}$CuF |
|------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| $A_0$/MHz              | 33 250(240)                | 32 950(290)                | 25 208(19)                | 25 156(32)                |
| $B_0$/MHz              | 3 300.7667(62)             | 3 301.4981(98)             | 3 260.5869(86)            | 3 259.257(14)             |
| $C_0$/MHz              | 2 996.4700(43)             | 2 995.4204(47)             | 2 881.9524(88)            | 2 880.939(11)             |
| $\Delta J_k$/kHz$^a$  | [0.56]                     | [0.56]                     | [0.53]                     | [0.53]                     |
| $\Delta J_k$/kHz$^a$  | [0.56]                     | [0.56]                     | [0.53]                     | [0.53]                     |
| $\langle \mu_0(Cu) - \mu_0(Cu) \rangle$/MHz | 70.012(59) | 64.756(71) | 70.051(55) | 64.743(56) | 70.051(55) | 64.743(56) |
| $N^b$                  | 20                         | 15                         | 17                         | 13                         |
| $\sigma_{\text{rms}}$/kHz | 33.8                      | 32.2                      | 23.7                      | 22.8                      |

$^a$ 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.
Table 3  Some spectroscopic constants and bond lengths of C2H2 and CuF referred to in evaluating properties of C2H2 – CuF

| Quantity constant | 12C2H2 | 13C2H2 | 12C2D2 | 63Cu19F | 65Cu19F |
|-------------------|--------|--------|--------|---------|---------|
| Ethyne b0/MHz     | 33274.9693(54) | 33546.0054 | 25418.6291 | —       | —       |
| Geometry r[C(\equiv C)/Å] | r(C=C)/Å | r(C=C)/Å | r(C–D)/Å | —       | —       |
| r(C=C)/Å         | 1.206553(6) | 1.206553(6) | 1.20256(3) | —       | —       |
| r(C–H)/Å         | 1.06238(2) | 1.06011(3) | 1.06166(6) | —       | —       |

Cuprous fluoride

| r(Cu–F)/Å         | 1.7430(3) | 1.7430(3) | 1.7430(3) | —       | —       |

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 C2H2–CuF. The fourth is that the inertia defect, as defined in eqn (2), should be small.

By Chutjian30 planar.

For each of the related planar molecules C2H2 and 13C2H2, the inertia defect, as defined in eqn (2), should be small.

For both members of the pair. The results are A0 = 0.365(38) u Å2 and 0.366(38) u Å2 for the 12C2H2 and 12C2D2, respectively. The value obtained from calculations at the CCSD(T) level of theory.

In Table 3 the inertia defect, as defined in eqn (2), is given by the difference between the mean value of the inertia for the six isotopologues of C2H2 and C2D2 and the mean value of the inertia for the six isotopologues of C2H2 and C2H2–CuF. The values for A0 and B0 are given in Table 4. Each refers to the principal inertia axes of C2D2 and CuF investigated, namely a partial 30 geometry and an almost complete 30 geometry. These results will be compared with the full r0 geometry obtained from ab initio calculations carried out at the CCSD(T)[F12*/AVTZ] level of theory.

If equilibrium rotational constants (and therefore equilibrium principal moments of inertia) of the various isotopologues of C2H2–CuF investigated were available, the equilibrium principal-axis co-ordinates ac, bc, ah, and ac, could be determined by means of eqn (3)–(5). In view of the molecular planarity and the existence of the symmetry operation C2, the changes Ib and Ia in the equilibrium principal moments of inertia that accompany the double isotopic substitution of X by X′ (X = 14C or H; X′ = 13C or D, respectively) at symmetrically equivalent atoms are related to the equilibrium coordinates ac and bc by the expressions put forward by Chutjian30

| ac | = (Ia/μb)1/2, (3) |

where μb = (2ΔmM)/(M + 2Δm) is the reduced mass for the double substitution in the parent isotopologue of mass M leading to a mass change 2Δm. The equilibrium principal axis co-ordinate ac is that which lies on the a-axis, is is C, and so the value of ac is obtained from experimental results for C2H2–CuF, is given in terms of changes Δl∥ and Δl⊥ in equilibrium principal moments of inertia accompanying isotopic substitution at Cu by Kraitchman’s equation11

| ac | = [(Δl∥ + Δl⊥)/2μb]1/2, (5) |

where μb = (ΔmM)/(M + Δm) is the reduced mass for the substitution.

Thus, all the evidence so far presented is consistent with a geometry of C2H2–CuF of the planar, T-shaped type of C2H2 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 C2H2–CuF investigated, namely a partial r0 geometry and an almost complete r0 geometry. These results will be compared with the full r0 geometry obtained from ab initio calculations carried out at the CCSD(T)[F12*/AVTZ] level of theory.

If equilibrium rotational constants (and therefore equilibrium principal moments of inertia) of the various isotopologues of C2H2–CuF investigated were available, the equilibrium principal-axis co-ordinates ac, bc, ah, and ac, could be determined by means of eqn (3)–(5). In view of the molecular planarity and the existence of the symmetry operation C2, the changes Ib and Ia in the equilibrium principal moments of inertia that accompany the double isotopic substitution of X by X′ (X = 14C or H; X′ = 13C or D, respectively) at symmetrically equivalent atoms are related to the equilibrium coordinates ac and bc by the expressions put forward by Chutjian30

| ac | = (Ia/μb)1/2, (3) |

in which μb = (2ΔmM)/(M + 2Δm) is the reduced mass for the double substitution in the parent isotopologue of mass M leading to a mass change 2Δm. The equilibrium principal axis co-ordinate ac is that which lies on the a-axis, is is C, and so the value of ac is obtained from experimental results for C2H2–CuF, is given in terms of changes Δl∥ and Δl⊥ in equilibrium principal moments of inertia accompanying isotopic substitution at Cu by Kraitchman’s equation11

| ac | = [(Δl∥ + Δl⊥)/2μb]1/2, (5) |

in which μb = (ΔmM)/(M + Δm) is the reduced mass for the substitution. When equilibrium quantities are unavailable, Costain32,33 proposed using zero-point Δ0 values in place of their equilibrium counterparts Δ′ in eqn (3)–(5) and named the resulting coordinates as substitution or r0 coordinates.

The r0 coordinates ac, bc, ah, and ac, so obtained from eqn (3)–(5) are given in Table 4. Each refers to the principal inertia axes of the parent molecule and the chosen signs are those that lead to reasonable bond lengths. Note that the mean of Ac for pairs of 63Cu65F isotopologues, as given in Section 3.1, were used in the calculation of the bc and bh coordinates. The substantial uncertainties in bc and bh result from the relatively large errors assigned to Ac. A r0 coordinate ac is not available because fluorine possesses only one stable isotope and so the value of ac given in Table 4 was determined, as recommended by Costain,32 from the other r0 coordinates with the aid of the first moment condition,

| ac | = — (Σm|aj|)/mF, (6) |

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

The significantly larger magnitude of ah than ac 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≡C internuclear line when the complex is formed, with the two equivalent angles A = ∠H–C≡C (see Fig. 1 for definition) exceeding 180°. The value obtained from
Table 4 Various types of principal inertia axis coordinate and geometry determined for C$_2$H$_2$···Cu–F

| Atom | $r_\alpha$ geometry Coordinate $^a$ | $r_\beta$ geometry Coordinate $^a$ | $r_\gamma$ geometry Coordinate $^a$ |
|------|---------------------------------|---------------------------------|---------------------------------|
| H    | $a$/Å $b$/Å                      | $a$/Å $b$/Å                      | $a$/Å $b$/Å                      |
| C    | $-1.9764(8)$ $1.663(9)$         | $-1.9767(4)$ $1.6587(1)$        | $-1.9762$ $1.6501$             |
| Cu   | $-1.7066(9)$ $0.62(4)$          | $-1.7059(4)$ $0.6231(1)$        | $-1.6947$ $0.6182$            |
| F    | $0.142(10)$ $0.0000$            | $0.1415(3)$ $0.0000$            | $0.1412$ $0.0000$             |

Distance/angle $r$ geometry

| $r(C\equiv C)$/Å | $1.24(4)$ | $1.2461(1)$ | $1.2363$ |
|------------------|----------|------------|----------|
| $r(C\equiv H)$/Å | $1.07(7)$ | $[1.07041]^a$ | $1.0697$ |
| $r(Cu\equiv C)$/Å | $1.85(1)$ | $1.8474(7)$ | $1.8359$ |
| $r(Cu\equiv F)/Å$ | $1.753(10)$ | $1.7547(9)$ | $1.7392$ |
| Angle $\alpha^\circ$ | $194.5(6)$ | $194.52(2)$ | $195.3$ |

$^a$ The $r_\alpha$ geometry was optimized at the CCSD(T)(F12*)/aug-cc-pVTZ level of theory. $^b$ The errors in $r_\alpha$ coordinates $\delta a$ are those given by $\delta a = (0.0015 \AA)/a$, as suggested by Costain in ref. 32. The errors in $r_\beta$ coordinates $\delta b$ are those propagated from the poorly determined rotational constants $A_\alpha$. $^c$ Assumed value obtained by adding the difference $r_\beta(C-H) - r_\beta(C-H) = 0.00072$ Å of the quantities for free ethyne to $r_\beta(C-H)$ calculated for C$_2$H$_2$···Cu–F and given in the final column. See text for discussion.

The $r_\alpha$ coordinates in Table 3 is $A = 194.5(6)^\circ$ [see Table 4], where the large error is consequent upon the errors in the $A_\alpha$ values. These distortions are well reproduced in the optimized geometry of C$_2$H$_2$···Cu–F obtained from ab initio calculations carried out at the CCSD(T)(F12*)/AVTZ level of theory (see Table 4).

4. Discussion

The new molecule C$_2$H$_2$···Cu–F has been synthesized by interaction of the plasma produced by laser ablation of a copper rod with a supersonically-expanded pulse of gas containing SF$_6$ and C$_2$H$_2$ 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$_2$H$_2$ 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 $\alpha$ C–H angle increases from 180$^\circ$ to 194.65(2)$^\circ$. The C≡C bond lengthens by ca. 0.04 Å. These distortions are well reproduced in the optimized geometry of C$_2$H$_2$···Cu–F obtained from ab initio calculations carried out at the CCSD(T)(F12*)/AVTZ level of theory (see Table 4).

Similar distortions have now been observed in the series of molecules C$_2$H$_2$···CuF, C$_2$H$_2$···AgCl,$^4$ C$_2$H$_2$···AgCCH,$^5$ and C$_2$H$_2$···CuCl,$^6$ 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 $\delta \alpha$ in the angle $\alpha$ C–H and $\delta \sigma$ 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$_2$H$_2$ 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 $\delta \alpha$ and $\delta \sigma$ 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 $\delta \alpha$ and $\delta \sigma$ 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$_2$H$_2$···M–X (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 δ+ 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)²⁵ polarizes electron density preferentially from the π orbital (πₐ₀) in the molecular plane. The larger the polarization, the more the π bonding in the ethyne molecule will resemble that of an ethene molecule in which the symmetry plane of its bonding orbital is perpendicular to the C≡C axis. The larger the polarization, the more the C≡C bond of ethyne on formation is distorted away from the C₂ axis of C₂H₄ that is perpendicular to the molecular plane. The larger the polarization, the more the polarization of the π electrons, when both are completely removed from ethyne to yield the ion C₂H₂⁺, the distortions would be of the order δA ≈ 60° and δr ≈ 134.5 – 120.6 = 13.9 pm, where 134.5 and 120.6 pm are the CC distances in the ground state 3Σ⁺ of the dication C₂H₂⁺ and in ethyne,²⁷ respectively. Similar distortions have been observed in C₂H₄•••M-X (M = Cu or Ag),³⁷ in which M-X lies on the C₂ axis of C₂H₄ that is perpendicular to the plane of the C₂H₄ nuclei. Similar arguments can be used to rationalize the distortions in these molecules, but with C₂H₄⁺ as the limiting dication.

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