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Interaction of a pseudo- π C—C bond with cuprous and argentous chlorides: Cyclopropane $\cdots$ CuCl and cyclopropane $\cdots$ AgCl investigated by rotational spectroscopy and *ab initio* calculations

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Strongly bound complexes $(\text{CH}_2)_3 \cdots \text{MCl}$ ($\text{M} = \text{Cu}$ or Ag), formed by non-covalent interaction of cyclopropane and either cuprous chloride or argentous chloride, have been generated in the gas phase by means of the laser ablation of either copper or silver metal in the presence of supersonically expanded pulses of a gas mixture containing small amounts of cyclopropane and carbon tetrachloride in a large excess of argon. The rotational spectra of the complexes so formed were detected with a chirped-pulse, Fourier transform microwave spectrometer and analysed to give rotational constants and Cu and Cl nuclear quadrupole coupling constants for eight isotopologues of each of $(\text{CH}_2)_3 \cdots \text{CuCl}$ and $(\text{CH}_2)_3 \cdots \text{AgCl}$. The geometry of each of these complexes was established unambiguously to have C_{2v} symmetry, with the three C atoms coplanar, and with the MCl molecule lying along a median of the cyclopropane C_3 triangle. This median coincides with the principal inertia axis a in each of the two complexes $(\text{CH}_2)_3 \cdots \text{MCl}$. The M atom interacts with the pseudo- π bond linking the pair of equivalent carbon atoms $^{\text{F}}\text{C}$ ($\text{F} = \text{front}$) nearest to it, so that M forms a non-covalent bond to one C—C edge of the cyclopropane molecule. The $(\text{CH}_2)_3 \cdots \text{MCl}$ complexes have similar angular geometries to those of the hydrogen- and halogen-bonded analogues $(\text{CH}_2)_3 \cdots \text{HCl}$ and $(\text{CH}_2)_3 \cdots \text{ClF}$, respectively. Quantitative details of the geometries were determined by interpretation of the observed rotational constants and gave results in good agreement with those from *ab initio* calculations carried out at the CCSD(T)(F12*)/aug-cc-pVTZ-F12 level of theory. Interesting geometrical features are the lengthening of the $^{\text{F}}\text{C}—^{\text{F}}\text{C}$ bond and the shrinkage of the two equivalent $^{\text{B}}\text{C}—^{\text{F}}\text{C}$ ($\text{B} = \text{back}$) bonds relative to the C—C bond in cyclopropane itself. The expansions of the $^{\text{F}}\text{C}—^{\text{F}}\text{C}$ bond are 0.1024(9) Å and 0.0727(17) Å in $(\text{CH}_2)_3 \cdots \text{CuCl}$ and $(\text{CH}_2)_3 \cdots \text{AgCl}$, respectively, according to the determined r_0 geometries. The C—C bond lengthening is in each case about four times that observed by similar methods in the corresponding complexes of MCl with ethyne and ethene, even though the cyclopropane complexes are more weakly bound than their ethyne and ethene analogues. Reasons for the larger increase in $r(\text{CC})$ in the pseudo- π complexes are discussed. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4934539>]

I. INTRODUCTION

We report here the rotational spectra of two complexes of the type $(\text{CH}_2)_3 \cdots \text{MCl}$, formed by the non-covalent interaction of cyclopropane $(\text{CH}_2)_3$ with either CuCl or AgCl. These hitherto unknown molecules were created by the reaction of laser-ablated copper or silver in the presence of a suitably timed pulse of a supersonically expanded gas mixture composed of small amounts of cyclopropane and carbon tetrachloride CCl_4 in a large excess of argon. The rotational spectra of the $(\text{CH}_2)_3 \cdots \text{MCl}$ molecules so generated were recorded by means of a chirped-pulse, Fourier-transform microwave (CP-FTMW) spectrometer.

The formation of a bond between a transition metal atom and an alkene, or alkyne, can lead to extensive geometrical

rearrangement within the hydrocarbon. For example, Walters *et al.*¹ performed a combined infrared spectroscopic and theoretical study of the structures of $\text{Ni}^+(\text{C}_2\text{H}_2)_n$, where n is an integer. They interpreted their observations to establish that the $\text{C}\equiv\text{C}$ bond of ethyne weakens on formation of $\text{Ni}^+(\text{C}_2\text{H}_2)$, with a concomitant displacement of hydrogen atoms from the $\text{C}\equiv\text{C}$ axis in the direction away from the approach of Ni^+ . The Dewar-Chatt-Duncanson interpretation² of the mechanism for this type of bond formation invokes donation of electron density from π orbitals of the hydrocarbon into unfilled d-orbitals on the metal, with a reciprocal transfer of electrons from occupied d-orbitals of the metal into π^* antibonding orbitals of the hydrocarbon. The reciprocal transfers cooperate to enhance the bond strength. We have initiated an extensive research program^{3–15} aimed at exploring the nature of the non-covalent interaction between simple Lewis bases B such as N_2 , NH_3 , H_2O , H_2S , C_2H_2 , and C_2H_4 and the metal atom in the transition metal halides CuX or AgX in isolated complexes $\text{B} \cdots \text{MX}$

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FIG. 1. (a) The geometries of complexes of ethyne with various Lewis acids, as determined from their rotational spectra. Drawings are to scale. In order of increasing non-covalent interaction strength, they are $\text{C}_2\text{H}_2 \cdots \text{HCl}$, $\text{C}_2\text{H}_2 \cdots \text{ClF}$, $\text{C}_2\text{H}_2 \cdots \text{AgCl}$, and $\text{C}_2\text{H}_2 \cdots \text{CuCl}$. In each, the Lewis acid lies along a C_2 axis of ethyne. Note the distortion of ethyne in the AgCl and CuCl complexes. (b) The geometries of complexes of ethene with various Lewis acids, as determined from their rotational spectra. Drawings are to scale. In order of increasing non-covalent interaction strength, they are $\text{C}_2\text{H}_4 \cdots \text{HCl}$, $\text{C}_2\text{H}_4 \cdots \text{ClF}$, $\text{C}_2\text{H}_4 \cdots \text{AgCl}$, and $\text{C}_2\text{H}_4 \cdots \text{CuCl}$. In each, the Lewis acid lies along the C_2 axis of ethene that is perpendicular to the plane of its nuclei. Note the distortion of ethene in the AgCl and CuCl complexes.

($\text{M} = \text{Cu}$ or Ag ; $\text{X} = \text{F}$, Cl , or I). Microwave spectroscopy and *ab initio* calculations were used to obtain quantitative information about the geometry, electronic structure, and dissociation energy of the complexes. Novick and co-workers have also conducted related investigations of $\text{B} \cdots \text{MX}$, for the interesting case in which B is the hydrogen molecule.^{16–19} When B is ethyne, ethene, or H_2 , the complexes $\text{B} \cdots \text{MX}$ provide particularly favourable examples of how rotational spectroscopy in combination with high-quality electronic structure calculations can yield precise quantitative details of the geometrical distortion of the molecule B that accompanies complex formation.

An early conclusion of our investigations of the $\text{B} \cdots \text{MX}$ species already mentioned is that their angular geometries are isomorphous with those of the corresponding members of the series of hydrogen-bonded complexes $\text{B} \cdots \text{HX}$ ($\text{X} = \text{F}$, Cl , Br , I , CN). Systematic investigations of the $\text{B} \cdots \text{HX}$ over a number of years led to a set of empirical rules^{20,21} that allowed angular geometries to be rationalized. These rules state that (i) the axis of the HX molecule coincides with the axis of a non-bonding pair of electrons carried by B , (ii) when B has no non-bonding electrons but carries π -bonding pairs, the axis of the HX molecule lies along the local symmetry axis of a π orbital, and (iii) when both non-bonding and π bonding electron pairs are present, the non-bonding pair is definitive of the angular geometry. Subsequently, it was shown through a parallel set of investigations of the series $\text{B} \cdots \text{XY}$ ($\text{XY} = \text{F}_2$, Cl_2 , Br_2 , ClF ,

BrCl , and ICl) that these rules (but modified by substituting HX by XY) also apply to halogen-bonded complexes.^{22,23} In the work reported here, we shall concentrate on rule (ii) and its applicability to $\text{B} \cdots \text{MX}$ molecules, where B carries π -bonding or pseudo- π bonding pairs but no non-bonding pairs.

Figure 1(a) shows the angular geometries of the complexes of ethyne with each of HCl ,²⁴ ClF ,²⁵ CuCl ,¹³ and AgCl ¹² (all drawn to scale), as determined by rotational spectroscopy. Apart from small distortions of the ethyne subunit by CuCl and AgCl (most obvious from the position of the acetylenic H atoms but also manifest in a small lengthening of the CC bond), it is clear that the four geometries are isomorphous and that rule (ii) applies. The same conclusion holds for the corresponding set of complexes^{9,13,26,27} with ethene, as shown in Figure 1(b). In each, the HCl , ClF , CuCl , or AgCl molecular axis lies along the symmetry axis of the π orbital and is therefore perpendicular to the plane of the ethene nuclei. Again, small distortions of ethene occur for the CuCl and AgCl complexes.

Many years ago, Coulson and Moffitt²⁸ proposed the pseudo- π bonding model for cyclopropane to explain, *inter alia*, the fact that it behaves like an alkene in some of its reactions. This model invokes sp^3 hybridised carbon atoms, with the CC bonds formed by overlap of the lobes of two sp^3 hybrid orbitals on adjacent C atoms to give a “bent,” pseudo- π bond, as illustrated in Figure 2. Does rule (ii) hold for such pseudo- π bonds? The experimental geometries of $(\text{CH}_2)_3 \cdots \text{HCl}$ ²⁹ and $(\text{CH}_2)_3 \cdots \text{ClF}$ ³⁰ (included in Figure 3 and drawn to scale) show

FIG. 2. The Coulson-Moffitt model of electron density in the C—C bonds of cyclopropane. Each C atom is assumed to be sp^3 hybridised and each C—C bond is formed by overlap of a singly occupied sp^3 orbital on two adjacent C atoms, as in (a), to give the pseudo- π bond shown in (b).

that it does. The questions to be addressed in this article are as follows: (a) Can the rotational spectra of $(CH_2)_3 \cdots CuCl$ and $(CH_2)_3 \cdots AgCl$ be observed? (b) Are the angular geometries of $(CH_2)_3 \cdots CuCl$ and $(CH_2)_3 \cdots AgCl$ isomorphous with those of their HCl and ClF analogues and consistent with rule (ii)? (c) Is the cyclopropane molecule distorted by complexation with the CuCl or AgCl molecule and, if so, how does this distortion compare with those observed for ethyne and ethene when they interact with these closed-shell, transition metal halides MCl?

II. EXPERIMENTAL AND THEORETICAL METHODS

The rotational spectra of cyclopropane $\cdots CuCl$ and cyclopropane $\cdots AgCl$ were observed by using a CP-FTMW spectrometer. The spectrometer has been described in detail elsewhere.^{31,32}

A gaseous sample mixture was introduced from a single pulsed nozzle oriented perpendicular to the direction of propagation of a microwave excitation pulse introduced from a horn antenna. The gas pulse contained $\sim 1\%$ CCl_4 and $\sim 1\%$ $c\text{-}C_3H_6$ balanced in 6 bar of argon and was flowed over either a silver or copper target rod, as appropriate, before undergoing expansion into a vacuum. The focussed pulse from a Nd:YAG laser (~ 10 mJ/pulse, 10 ns duration) was employed to ablate material from the rod target and thus introduce metal into each gaseous sample mixture. Synthetically enriched samples of 1,1- d_2 -cyclopropane (purchased from CDN isotopes) allowed measurements of spectra of deuterated isotopologues.

The molecular free induction decay (FID) was collected using a second horn antenna positioned opposite to the first. The pulsed nozzle repetition rate was 1.05 Hz, and 8 FIDs, each 20 μs in duration, were recorded per nozzle pulse. The final data sets represent time-domain averages of

FIG. 3. Geometries (drawn to scale) of the hydrogen-bonded and halogen-bonded complexes formed by cyclopropane with HCl and ClF, respectively.

multiple FIDs as indicated in brackets: $(\text{CH}_2)_3 \cdots \text{AgCl}$ (2.4M), $(\text{CD}_2)(\text{CH}_2)_2 \cdots \text{AgCl}$ (1.2M), $(\text{CH}_2)_3 \cdots \text{CuCl}$ (1.8M), and $(\text{CD}_2)(\text{CH}_2)_2 \cdots \text{CuCl}$ (1.32M). To obtain frequency-domain spectra of isotopologues containing silver, Fourier transformation was performed with an applied Kaiser-Bessel digital filter. However, for spectra of copper-containing species, it was necessary to apply a high resolution window function¹⁴ due to increased hyperfine structure. Spectral analysis was performed using the PGOPHER software package.³³

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.^{34,35} 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,³⁶ aug-cc-pV(T+d)Z for Cl,³⁷ and aug-cc-pVTZ-PP basis sets for Cu and Ag, in combination with the ECP-10-MDF and ECP-28-MDF effective core potentials on Cu and Ag, respectively, to account for scalar relativistic effects.^{37–39} At the optimised geometries, the approximate coupled cluster singles and doubles method CC2⁴⁰ was used to compute (unrelaxed) dipole moments. Dissociation energies at the CCSD(T)(F12*)/AVTZ level were computed using the counterpoise correction method where, for numerical stability, the singles correction was not included in the correction term. CCSD(T) calculations were performed us-

ing the MOLPRO package,⁴¹ CC2 response calculations using the TURBOMOLE package,⁴² and the frozen-core approximation was used throughout.

III. RESULTS

A. Determination of spectroscopic constants

The rotational spectrum observed for each of the isotopologues of $(\text{CH}_2)_3 \cdots \text{CuCl}$ and $(\text{CH}_2)_3 \cdots \text{AgCl}$ investigated exhibited only a -type transitions. These transitions fell into a pattern characteristic of a nearly prolate, asymmetric rotor, with only those of the type $(J+1)_{n,J+1} \rightarrow J_{n,J}$, where $n = 0, 1$, and 2 , having observable intensity for the most abundant isotopologue in each case. For other isotopologues, those with $K_{-1} = 2$ were too weak to observe. Figures 4 and 5 show broadband recordings of the region of the $J = 7 \rightarrow 6$ transitions of $(\text{CH}_2)_3 \cdots \text{CuCl}$ and $(\text{CH}_2)_3 \cdots \text{AgCl}$, respectively. Transitions with $K_{-1} = 1$ differed in intensity from those with $K_{-1} = 0$ because of three main effects. The first arises from nuclear-spin statistics. If the geometry of the complex is as predicted from rule (ii) and the Coulson-Moffitt pseudo- π model of cyclopropane, that is, if the MX internuclear axis lies along the extension of a median of the cyclopropane triangle and coincides with the principal inertia axis a , the operation C_2^a exchanges three

FIG. 4. Broadband rotational spectrum of $(\text{CH}_2)_3 \cdots \text{CuCl}$ recorded in the region of the $7 \rightarrow 6$ transitions. The downward pointing spectra are those simulated from the experimental spectroscopic constants given in Table I by using the PGOPHER program. The blue spectrum corresponds to the $(\text{CH}_2)_3 \cdots {}^{63}\text{Cu}^{35}\text{Cl}$ isotopologue while the red spectrum belongs to $(\text{CH}_2)_3 \cdots {}^{65}\text{Cu}^{35}\text{Cl}$. The natural abundances of ${}^{63}\text{Cu}$ and ${}^{65}\text{Cu}$ are 69.85% and 30.85%, respectively. The complicated nuclear quadrupole hyperfine structure arising from the quadrupolar nuclei Cu and Cl is evident in each of the three rotational transitions $7_{17} \rightarrow 6_{16}$, $7_{07} \rightarrow 6_{06}$ and $7_{16} \rightarrow 6_{15}$ of the lower spectrum, which are shown on an expanded frequency scale.

FIG. 5. Broadband rotational spectrum of $(\text{CH}_2)_3 \cdots \text{AgCl}$ recorded in the region of the $7 \rightarrow 6$ transitions. The downward pointing spectra are simulated from the experimental spectroscopic constants given in Table III by using the PGOPHER program. The blue spectrum corresponds to the $(\text{CH}_2)_3 \cdots {}^{107}\text{Ag}^{35}\text{Cl}$ isotopologue while the red spectrum belongs to the $(\text{CH}_2)_3 \cdots {}^{109}\text{Ag}^{35}\text{Cl}$. The natural abundances of ${}^{107}\text{Ag}$ and ${}^{109}\text{Ag}$ are 51.84% and 48.16%, respectively. The nuclear quadrupole hyperfine structure arising from the quadrupolar nucleus ${}^{35}\text{Cl}$ is evident in each of the three rotational transitions $7_{17} \rightarrow 6_{16}$, $7_{07} \rightarrow 6_{06}$, and $7_{16} \rightarrow 6_{15}$ in the lower spectrum, which are shown on an expanded frequency scale. The hyperfine structure is simpler in this spectrum than that in Figure 4 because the nuclear electric quadrupole moment of both Ag isotopes is zero.

pairs of equivalent protons and thereby endows the $K_{-1} = 1$ transitions with a nuclear spin statistical weight of 36 relative to a weight of 28 for the $K_{-1} = 0$ transitions. Second, the Cl (and where appropriate Cu) nuclear quadrupole hyperfine splitting tends to be larger and better resolved for $K_{-1} = 1$ transitions. Finally, the low effective temperature of the supersonic expansion will enhance the population of $K_{-1} = 0$ level, if collisional propensity rules permit such transfer of population.

Each rotational transition of $(\text{CH}_2)_3 \cdots \text{AgCl}$ carried the nuclear quadrupole hyperfine pattern expected for the presence of either a ${}^{35}\text{Cl}$ ($I = 3/2$) or a ${}^{37}\text{Cl}$ ($I = 3/2$) nucleus. For $(\text{CH}_2)_3 \cdots \text{CuCl}$, the additional quadrupolar nucleus ${}^{63}\text{Cu}$ ($I = 3/2$) or ${}^{65}\text{Cu}$ ($I = 3/2$) led to a more complex hyperfine structure, as is evident from Figure 5 when compared with Figure 4. Because of the fairly high J -value transitions that fall within the frequency range of the spectrometer, the hyperfine structure was not always well resolved. A least-squares fit of the hyperfine frequencies of all observed rotational transitions for each isotopologue was performed by using the program PGOPHER.³³ The Hamiltonian matrix

$$H = H_R + H_{Q(\text{Cl})} + H_{Q(\text{Cu})} \quad (1)$$

was constructed in the coupled symmetric-rotor basis $\mathbf{I}_{\text{Cl}} + \mathbf{J} = \mathbf{F}_1, \mathbf{F}_1 + \mathbf{I}_{\text{Cu}} = \mathbf{F}$, and diagonalized in blocks of the quantum number F for each isotopologue of $(\text{CH}_2)_3 \cdots \text{CuCl}$ investi-

gated. For $(\text{CH}_2)_3 \cdots \text{AgCl}$, the third term is zero. In Eq. (1), H_R is the rotational Hamiltonian appropriate for a semi-rigid asymmetric rotor, for which the Watson A reduction⁴³ in the I_r representation was chosen, and $H_{Q(X)} = -\frac{1}{6} Q_{\alpha\beta}^X V_{\alpha\beta}^X$ (α and β to be permuted over a , b , and c) accounts for the nuclear quadrupole coupling energy arising from the interaction of the nuclear electric quadrupole tensor $Q_{\alpha\beta}^X$ of nucleus X with the electric field gradient (e.f.g.) tensor $V_{\alpha\beta}^X$ at that nucleus. Only two (Δ_J and Δ_{JK}) of the five quartic centrifugal distortion constants were determinable (i.e., differed from zero by more than their standard error) for even the most abundant isotopologues because of the limited range of a -type transitions available and the fact that all isotopologues are nearly prolate, asymmetric rotors exhibiting only a -type transitions. Indeed, except for the most abundant isotopologues of $(\text{CH}_2)_3 \cdots \text{CuCl}$ and of $(\text{CH}_2)_3 \cdots \text{AgCl}$, insufficient transitions were available to determine even Δ_J and Δ_{JK} satisfactorily. Consequently, these constants were assumed unchanged from those of the most abundant isotopologue in each case. Only one diagonal element, namely, $\chi_{aa}(X)$, of each nuclear quadrupole coupling tensor $\chi_{\alpha\beta}(X) = -(eQ^X/h)V_{\alpha\beta}^X$ was necessary to produce fits with a rms deviation of magnitude similar to the estimated accuracy of frequency measurement. This implies that each anisotropy $\chi_{bb}(X) - \chi_{cc}(X)$ is zero within experimental error. This observation is readily

TABLE I. Ground-state spectroscopic constants determined for isotopologues of $(\text{CH}_2)_3 \cdots \text{CuCl}$ observed in natural abundance.

Spectroscopic constant	$(^{12}\text{CH}_2)_3 \cdots ^{63}\text{Cu}^{35}\text{Cl}$	$(^{12}\text{CH}_2)_3 \cdots ^{65}\text{Cu}^{35}\text{Cl}$	$(^{12}\text{CH}_2)_3 \cdots ^{63}\text{Cu}^{37}\text{Cl}$
A_0/MHz	18 059(17) ^a	18 058(19)	18 058(20)
B_0/MHz	1237.150 80(43)	1236.923 15(40)	1206.8128(14)
C_0/MHz	1185.541 19(42)	1185.329 51(52)	1157.9330(12)
Δ_{JK}/kHz^b	2.40(17)	[2.40]	[2.40]
Δ_J/kHz^b	0.1329(51)	[0.1329]	[0.1329]
$\chi_{aa}(\text{Cl})/\text{MHz}$	−24.252(69)	−24.50(16)	−18.68(21)
$\chi_{aa}(\text{Cu})/\text{MHz}$	57.307(85)	52.97(22)	57.69(39)
$P_a/\text{u} \text{ \AA}^2$ ^c	403.401(13)	403.476(15)	413.616(16)
$P_b/\text{u} \text{ \AA}^2$	22.884(13)	22.885(15)	22.832(16)
$P_c/\text{u} \text{ \AA}^2$	5.101(13)	5.101(15)	5.154(16)
N^d	91	32	13
$\sigma_{\text{rms}}/\text{kHz}^e$	10.8	10.7	10.1

^aNumbers in parentheses are one standard deviation in units of the last significant digits.^bCentrifugal distortion constants in square brackets are fixed in the fit at values unchanged from the most abundant isotopologue.^cPlanar moments P_a , etc. are defined in Eq. (2).^d N is the number of hyperfine frequencies included in the fit.^eRoot-mean square deviation of the fit.

understood by considering the experimental values $\chi_{bb}(\text{Cl}) - \chi_{cc}(\text{Cl}) = 0.09(14)$ and $0.47(1)$ MHz determined for the complexes $(\text{CH}_2)_3 \cdots \text{H}^{35}\text{Cl}$ and $(\text{CH}_2)_3 \cdots ^{35}\text{ClF}$, respectively.^{29,30} It will be shown in Section III B that $(\text{CH}_2)_3 \cdots \text{CuCl}$ and $(\text{CH}_2)_3 \cdots \text{AgCl}$ have geometries isomorphous with those of $(\text{CH}_2)_3 \cdots \text{HCl}$ and $(\text{CH}_2)_3 \cdots \text{ClF}$, which are displayed in Figure 3. Moreover, the distance of Cl from the centre of the cyclopropane ring is less in both of these complexes than in $(\text{CH}_2)_3 \cdots \text{AgCl}$, so it is expected that $\chi_{bb}(\text{Cl}) - \chi_{cc}(\text{Cl})$ will be even closer to zero in $(\text{CH}_2)_3 \cdots \text{AgCl}$. The distance of Cu from the centre of the ring in $(\text{CH}_2)_3 \cdots \text{CuCl}$ is only slightly less than that of Cl in $(\text{CH}_2)_3 \cdots \text{ClF}$ and therefore $\chi_{bb}(\text{Cu}) - \chi_{cc}(\text{Cu})$ is also likely to be very small. Accordingly, $\chi_{bb}(\text{X}) - \chi_{cc}(\text{X})$ was set to zero in all fits.

Assignments and measured frequencies of nuclear hyperfine components of all observed rotational transitions, together with residuals and spectroscopic constants from

the final cycle of the PGOPHER fits, are available as the supplementary material⁴⁴ for each of the isotopologues of $(\text{CH}_2)_3 \cdots \text{CuCl}$ and $(\text{CH}_2)_3 \cdots \text{AgCl}$ investigated. Table I contains the spectroscopic constants thus determined for the isotopologues of $(\text{CH}_2)_3 \cdots \text{CuCl}$ measured in natural abundance, namely, $(\text{CH}_2)_3 \cdots ^{63}\text{Cu}^{35}\text{Cl}$, $(\text{CH}_2)_3 \cdots ^{65}\text{Cu}^{35}\text{Cl}$, and $(\text{CH}_2)_3 \cdots ^{63}\text{Cu}^{37}\text{Cl}$. In order to determine the orientation of the cyclopropane subunit in the complex, it was necessary to use an isotopically enriched sample of $(\text{CH}_2)_2(\text{CD}_2)$. The spectroscopic constants of $(\text{CH}_2)_3 \cdots \text{CuCl}$ isotopologues containing $(\text{CH}_2)_2(\text{CD}_2)$ are given in Table II, namely, $(^{\text{B}}\text{CD}_2)(\text{CH}_2)_2 \cdots ^{63}\text{Cu}^{35}\text{Cl}$, $(^{\text{B}}\text{CD}_2)(\text{CH}_2)_2 \cdots ^{65}\text{Cu}^{35}\text{Cl}$, $(^{\text{F}}\text{CD}_2)(\text{CH}_2)_2 \cdots ^{63}\text{Cu}^{35}\text{Cl}$, $(^{\text{F}}\text{CD}_2)(\text{CH}_2)_2 \cdots ^{65}\text{Cu}^{35}\text{Cl}$, and $(^{\text{F}}\text{CD}_2)(\text{CH}_2)_2 \cdots ^{63}\text{Cu}^{37}\text{Cl}$, where the nomenclature anticipates the determined geometry of this complex, which is of the form displayed in Figure 6. Thus, a superscript B on C indicates that the D_2 substitution is at the unique C

TABLE II. Ground-state spectroscopic constants of $(\text{CH}_2)_3 \cdots \text{CuCl}$ isotopologues containing CD_2 groups at the front or back of the cyclopropane ring.^a

Spectroscopic constant	$(\text{CH}_2)_2(^{\text{F}}\text{CD}_2) \cdots ^{63}\text{Cu}^{35}\text{Cl}$	$(\text{CH}_2)_2(^{\text{F}}\text{CD}_2) \cdots ^{63}\text{Cu}^{37}\text{Cl}$	$(\text{CH}_2)_2(^{\text{F}}\text{CD}_2) \cdots ^{65}\text{Cu}^{35}\text{Cl}$	$(\text{CH}_2)_2(^{\text{B}}\text{CD}_2) \cdots ^{63}\text{Cu}^{35}\text{Cl}$	$(\text{CH}_2)_2(^{\text{B}}\text{CD}_2) \cdots ^{65}\text{Cu}^{35}\text{Cl}$
A_0/MHz	15 252.8(49)	15 252(18)	15 252(20)	17 040(12) ^b	17 039(15)
B_0/MHz	1217.567 91(29)	1187.963 30(53)	1217.290 97(42)	1159.443 21(29)	1159.122 42(36)
C_0/MHz	1162.837 57(30)	1135.824 84(48)	1162.582 31(40)	1118.177 72(26)	1117.872 61(32)
Δ_{JK}/kHz^c	[2.40]	[2.40]	[2.40]	[2.40]	[2.40]
Δ_J/kHz^c	[0.1329]	[0.1329]	[0.1329]	[0.1329]	[0.1329]
$\chi_{aa}(\text{Cl})/\text{MHz}$	−24.21(10)	−19.30(30)	−24.24(9)	−24.30(15)	−24.12(12)
$\chi_{aa}(\text{Cu})/\text{MHz}$	57.08(26)	53.32(18)	52.90(14)	57.32(38)	52.75(20)
$P_a/\text{u} \text{ \AA}^2$ ^d	408.273(5)	418.612(20)	408.367(22)	429.094(10)	429.215(13)
$P_b/\text{u} \text{ \AA}^2$	26.335(5)	26.332(20)	26.336(22)	22.872(10)	22.874(13)
$P_c/\text{u} \text{ \AA}^2$	6.799(5)	6.804(20)	6.799(22)	6.786(10)	6.786(13)
N^e	77	27	44	67	45
$\sigma_{\text{rms}}/\text{kHz}^f$	9.7	10.0	9.6	9.3	9.7

^aSuperscripts F and B on the CD_2 group indicate whether the D atoms are attached to one of the two equivalent C atoms closest to the metal atom M or to the C atom on the C_2 axis (see Figure 6).^bNumbers in parentheses are one standard deviation in units of the last significant digits.^cCentrifugal distortion constants in square brackets are fixed in the fit at values unchanged from the most abundant isotopologue.^dPlanar moments P_a , etc. are defined in Eq. (2).^e N is the number of hyperfine frequencies included in the fit.^fRoot-mean square deviation of the fit.

FIG. 6. The angular geometry of (a) $(\text{CH}_2)_3 \cdots \text{AgCl}$ and (b) $(\text{CH}_2)_3 \cdots \text{CuCl}$ drawn to scale. The three C atoms, the metal atom M, and the Cl atom are coplanar. The atoms ${}^{\text{B}}\text{C}$, M, and Cl lie on the principal inertia axis a in both molecules (superscript F refers to front C atoms, i.e., those closest to the metal, while the superscript B refers to the back, unique C atom). The MCl molecule lies along the local symmetry axis of the pseudo- π electron density shown schematically in Figure 2. The bond lengths and angles determined by fitting the principal moments of inertia for 8 isotopologues of each of $(\text{CH}_2)_3 \cdots \text{CuCl}$ and $(\text{CH}_2)_3 \cdots \text{AgCl}$ are recorded in Table VII. The most notable feature of each geometry is the significant distortion of the ${}^{\text{F}}\text{C}-{}^{\text{F}}\text{C}$ bond and a concomitant contraction of the two ${}^{\text{B}}\text{C}-{}^{\text{F}}\text{C}$ bonds on complex formation.

atom, i.e., the C atom on the a -axis and remote from CuCl. Correspondingly, superscript F on C delineates an isotopologue in which the D_2 substitution is at one of the two equivalent C atoms nearest the CuCl subunit. The set of spectroscopic constants determined for the corresponding isotopologues of $(\text{CH}_2)_3 \cdots \text{AgCl}$ are in Tables III and IV. Thus, Table III deals with $(\text{CH}_2)_3 \cdots {}^{107}\text{Ag}^{35}\text{Cl}$, $(\text{CH}_2)_3 \cdots {}^{109}\text{Ag}^{35}\text{Cl}$, $(\text{CH}_2)_3 \cdots {}^{107}\text{Ag}^{37}\text{Cl}$, and $(\text{CH}_2)_3 \cdots {}^{109}\text{Ag}^{37}\text{Cl}$, while Table IV contains the various $(\text{CH}_2)_2(\text{CD}_2) \cdots \text{AgCl}$ species. The values of the rms deviation of the fits σ_{rms} (included in Tables I–IV) are generally of the same order as the estimated accuracy of frequency measurement (15–20 kHz), indicating that

the chosen Hamiltonian of Eq. (1) was satisfactory. The rotational constants A_0 are less precisely determined than the other rotational constants because only a -type, R-branch transitions of nearly prolate asymmetric rotors were available.

B. Symmetry and geometry of $(\text{CH}_2)_3 \cdots \text{CuCl}$ and $(\text{CH}_2)_3 \cdots \text{AgCl}$

1. Molecular symmetry

There are several observations about the spectroscopic constants of both $(\text{CH}_2)_3 \cdots \text{CuCl}$ and $(\text{CH}_2)_3 \cdots \text{AgCl}$ that allow

TABLE III. Ground-state spectroscopic constants determined for isotopologues of $(\text{CH}_2)_3 \cdots \text{AgCl}$ observed in natural abundance.

Spectroscopic constant	$({}^{12}\text{CH}_2)_3 \cdots {}^{107}\text{Ag}^{35}\text{Cl}$	$({}^{12}\text{CH}_2)_3 \cdots {}^{109}\text{Ag}^{35}\text{Cl}$	$({}^{12}\text{CH}_2)_3 \cdots {}^{107}\text{Ag}^{37}\text{Cl}$	$({}^{12}\text{CH}_2)_3 \cdots {}^{109}\text{Ag}^{37}\text{Cl}$
A_0/MHz	18 495.501(10) ^a	18 493.480(38)	18 494(20)	18 494(19)
B_0/MHz	984.561 42(39)	984.423 25(32)	962.045 80(47)	961.948 99(50)
C_0/MHz	953.085 95(41)	952.956 98(30)	931.974 44(51)	931.882 57(46)
$\Delta_{JK}/\text{kHz}^{\text{b}}$	3.665(92)	[3.665]	[3.665]	[3.665]
$\Delta_J/\text{kHz}^{\text{b}}$	0.0991(23)	[0.0991]	[0.0991]	[0.0991]
$\chi_{aa}(\text{Cl})/\text{MHz}$	−31.26(26)	−31.18(26)	−25.17(54)	−25.57(47)
$P_a/\text{u } \text{\AA}^2$ ^c	508.116 34(15)	508.186 75(12)	520.128(15)	520.181(14)
$P_b/\text{u } \text{\AA}^2$	22.138 05(15)	22.139 40(12)	22.138(15)	22.139(14)
$P_c/\text{u } \text{\AA}^2$	5.186 33(15)	5.1879(12)	5.188(15)	5.188(14)
N^{d}	34	33	14	14
$\sigma_{\text{rms}}/\text{kHz}^{\text{e}}$	10.3	9.4	9.7	9.6

^aNumbers in parentheses are one standard deviation in units of the last significant digits.

^bCentrifugal distortion constants in square brackets are fixed at values unchanged from the most abundant isotopologue.

^cPlanar moments P_a , etc. are defined in Eq. (2).

^d N is the number of hyperfine frequencies included in the fit.

^eRoot-mean square deviation of the fit.

TABLE IV. Ground-state spectroscopic constants of cyclopropane...AgCl isotopologues containing CD₂ groups at the front or back of the cyclopropane ring.^a

Spectroscopic constant	(CH ₂) ₂ (^F CD ₂)... ¹⁰⁷ Ag ³⁵ Cl	(CH ₂) ₂ (^F CD ₂)... ¹⁰⁹ Ag ³⁵ Cl	(CH ₂) ₂ (^B CD ₂)... ¹⁰⁷ Ag ³⁵ Cl	(CH ₂) ₂ (^B CD ₂)... ¹⁰⁹ Ag ³⁵ Cl
A_0/MHz	15 675(17) ^b	15 674(19)	17 466(30)	17 466(32)
B_0/MHz	968.319 81(43)	968.157 11(41)	925.400 20(48)	925.2180(14)
C_0/MHz	934.967 19(45)	934.812 85(39)	900.263 47(50)	900.0888(12)
Δ_{JK}/kHz^c	[3.665]	[3.665]	[3.665]	[3.665]
Δ_J/kHz^c	[0.0991]	[0.0991]	[0.0991]	[0.0991]
$\chi_{aa}(\text{Cl})/(\text{MHz})$	−31.06(19)	−31.41(27)	−31.52(38)	−30.43(52)
$P_a/\text{u } \text{\AA}^2$ ^d	515.101(17)	515.188(20)	539.275(25)	539.383(27)
$P_b/\text{u } \text{\AA}^2$	25.429(17)	25.431(20)	22.092(25)	22.092(27)
$P_c/\text{u } \text{\AA}^2$	6.812(17)	6.812(20)	6.843(25)	6.843(27)
N^e	24	25	22	13
$\sigma_{\text{rms}}/\text{kHz}^f$	9.6	9.4	9.8	10.4

^aSuperscripts F and B on the CD₂ group indicate whether the D atoms are attached to one of the two equivalent C atoms closest to the metal atom M or to the C atom on the C₂ axis (see Figure 6).

^bNumbers in parentheses are one standard deviation in units of the last significant digits.

^cCentrifugal distortion constants in square brackets are fixed in the fit at values unchanged from the most abundant isotopologue.

^dPlanar moments P_a , etc. are defined in Eq. (2).

^e N is the number of hyperfine frequencies included in the fit.

^fRoot-mean square deviation of the fit.

the symmetries and angular geometries of the molecules to be established. These observations are common for both species and therefore, where appropriate, the two can be treated together. Once these qualitative aspects of geometry are established, attention will turn to the quantitative details, as described in Section III B 2.

Although the rotational constants A_0 are not as precisely determined as the rotational constants B_0 and C_0 (see Tables I–IV), we note that A_0 is similar in magnitude for each of the molecules containing the most abundant isotopologue of cyclopropane, (¹²CH₂)₃. Moreover, A_0 is invariant for these isotopologues within experimental error under isotopic substitution at both M and Cl. This observation requires that both M and Cl lie on (or very close to) the principal inertia axis a , suggesting that the a axis lies in the plane of the three C atoms of cyclopropane and that the centre of mass of the cyclopropane subunit lies on the a axis. However, while the mean value $A_0 = 18\,058(10)$ MHz for the three (¹²CH₂)₃ containing isotopologues when M = Cu is large and reasonably close to $B_0 = 20\,093.3348(33)$ MHz of the most

abundant form of free cyclopropane, it is significantly smaller (by 2035 MHz) (see Table V, in which are collected some properties of various isotopologues of cyclopropane, CuCl, and AgCl to be invoked here, including ground-state rotational constants).^{45–47} Similar conclusions hold for the A_0 values of the (¹²CH₂)₃...AgCl isotopologues, which are also invariant under substitution at Ag and Cl and for which the mean value is $A_0 = 18\,494(10)$ MHz, reduced by 1600 MHz from that of free (¹²CH₂)₃ (see Tables III–V).

The observations in the foregoing paragraph suggest, but do not prove, that both molecules have a geometry of the type shown in Figure 6, i.e., with the M and Cl atoms and the cyclopropane centre of mass lying on the a axis. However, the fact that the principal moment of inertia I_a^0 increases significantly from the corresponding quantity in free cyclopropane (see Table V) suggests that the front C—C bond of the cyclopropane ring expands on complex formation for both M = Cu and M = Ag, but more so in the case of Cu. This conclusion is reinforced by examination of A_0 values for the isotopologues (^BCD₂)(CH₂)₂...MCl, which also show

TABLE V. Some properties of isotopologues of cyclopropane, CuCl, and AgCl.

Property	(¹² CH ₂) ₃ ^a	(¹² CH ₂) ₂ (¹² CD ₂) ^b	⁶³ Cu ³⁵ Cl ^c	¹⁰⁷ Ag ³⁵ Cl ^c
A_0/MHz	20 093.3348(28)	18 835.662(18)	...	...
B_0/MHz	20 093.3348(28)	16 370.2703(70)	5328.549 98(23)	3678.0430(4)
C_0/MHz	12 555.7498(18)	11 409.2285(67)	5328.549 98(23)	3678.0430(4)
$P_a/\text{u } \text{\AA}^2$	20.125 401	24.168 212	...	...
$P_b/\text{u } \text{\AA}^2$	20.125 401	20.127 421 3	...	...
$P_c/\text{u } \text{\AA}^2$	5.026 173 2	6.703 544 6	...	...
$\chi_{aa}(\text{Cl})/\text{MHz}$	...	...	−32.1257(19)	−36.4408(20)
$\chi_{aa}(\text{Cu})/\text{MHz}$	...	...	16.1712(24)	...
$r_0(\text{C—C})/\text{\AA}$	...	1.515 321(25)	...	...
$r_0(\text{C—H})/\text{\AA}$	...	1.077 389(40)	...	...
$\angle\text{HCH}/\text{deg}$	...	115.5676(43)	...	...
$r_0(\text{M—Cl})/\text{\AA}$	...	...	2.054 11 ^d	2.283 56 ^d

^aReference 45.

^bReference 46.

^cReference 47.

^d $r_0(\text{M—Cl})$ was calculated from B_0 by using the equation $r = \{h/8\pi^2\mu B_0\}^{1/2}$.

invariance to isotopic substitution at M and Cl but which are substantially smaller than the appropriate rotational constant A_0 of the C_{2v} isotopologue 1,1-d₂ cyclopropane $(CD_2)(CH_2)_2$. The decrease is larger for M = Cu than for M = Ag. The much larger decreases in A_0 , the smaller change in $B_0 + C_0$, and the approximately doubled spectral intensity observed for the $(^FCD_2)(CH_2)_2 \cdots MCl$ isotopologues compared with those of $(^BCD_2)(CH_2)_2 \cdots MCl$ isotopologues also suggest that the orientation of the cyclopropane subunit is such that the MCl molecule interacts with the centre of one of the C—C bonds, as depicted in Figure 6. Finally, the fact that B_0 and C_0 are changed very little by isotopic substitution at M shows that this atom lies close to the molecular centre of mass for both M = Cu and Ag, and therefore it is the metal atom that is contiguous with the pseudo- π bond.

These qualitative conclusions are reinforced when the planar moments P_α of the various isotopologues of the $(CH_2)_3 \cdots MCl$ molecules are considered. P_α is defined by the following:

$$P_\alpha = \frac{1}{2}(-I_\alpha + I_\beta + I_\gamma) = \sum_i m_i \alpha_i^2, \quad (2)$$

where α , β , and γ are to be permuted cyclically over a , b , and c . The sum on the right-hand side is over the principal-axis coordinates α_i of all atoms i . Values of all three P_α are included in Tables I–IV for each isotopologue of both molecules $(CH_2)_3 \cdots MCl$ (M = Cu or Ag) investigated and the P_α of the free molecules $(^{12}CH_2)_3$ and $(CD_2)(CH_2)_2$ are given in Table V. Comparison of the cyclopropane and the $(CH_2)_3 \cdots MCl$ values allows the immediate conclusion that only the H (or D) atoms lie outside the ab principal plane in both $(CH_2)_3 \cdots CuCl$ and $(CH_2)_3 \cdots AgCl$. This is clear from (a) the close correspondence of $P_c = \sum_i m_i c_i^2$ for each $(^{12}CH_2)_3 \cdots MCl$ isotopologue with $P_c = \sum_i m_i c_i^2$ of $(^{12}CH_2)_3$ (note that the three C atoms of cyclopropane lie in the ab plane) and (b) their independence of the M or Cl isotope involved. The small differences can be attributed to a combination of minor changes in the geometry of the CH_2 groups on formation of the complex and zero-point motion differences between free cyclopropane and the complex. The fact that the more weakly bound $(CH_2)_3 \cdots AgCl$ exhibits a larger change from cyclopropane than does $(CH_2)_3 \cdots CuCl$ suggests that zero-point effects contribute more than geometry changes. When values for $(^BCD_2)(CH_2)_2 \cdots MCl$ and $(^FCD_2)(CH_2)_2 \cdots MCl$ are examined, we find a similar conclusion, namely, that $P_c = \sum_i m_i c_i^2$ for the complex is nearly the same as the corresponding quantity (also P_c) of 1,1-d₂ cyclopropane and is again independent of M or Cl isotope. Note also that for the CD_2 isotopologues, P_c is independent of the position of the substitution (front or back) and is almost identical for both M = Cu and Ag within experimental error.

A comparison of $P_b = \sum_i m_i b_i^2$ for the complexes with P_b for either $(^{12}CH_2)_3$ or 1,1-d₂ cyclopropane, as appropriate, shows that this quantity in the complex is always greater than that of the free cyclopropane molecule, with the values being about 2.8 u Å² larger for the complex when M = Cu but about 2.0 u Å² larger when M = Ag, independently of whether isotopic substitution is at M, Cl or ¹³C. This provides strong evidence that the front ^FC—^FC bond lengthens on complex

formation, the more so for M = Cu than for Ag. For FCD_2 isotopologues, the changes from P_b of 1,1-d₂ cyclopropane are 6.20 and 5.3 u Å² for M = Cu and Ag, respectively, again suggesting that the ^FC—^FC bond expansion is greater for M = Cu.

Finally, when zero-point moments of inertia are employed, the pseudo-inertia defect resulting from only the atoms that are coplanar, (i.e., from the C, M, and Cl atoms), after the contribution of the six H atoms have been removed, is given by

$$\Delta_0 \approx 2(P_c^{\text{cyclopropane}} - P_c^{\text{complex}}). \quad (3)$$

Eq. (3) is valid in the approximation that the contribution $6m_H c_H^2$ of the H atoms to the appropriate planar moments of the complex and free cyclopropane is identical.

For the isotopologue $(^{12}CH_2)_3 \cdots ^{107}Ag^{35}Cl$, $\Delta_0 = -0.320(1)$ u Å², while for $(^{12}CH_2)_3 \cdots ^{63}Cu^{35}Cl$, the result is $-0.150(13)$ u Å². For planar molecules, Δ_0 is usually small and positive. Small negative values do occur for planar molecules when large-amplitude, out-of-plane, low frequency vibrational modes contribute predominantly to the zero-point motion, however. The pseudo-inertia defects Δ_0 calculated for $(^{12}CH_2)_3 \cdots H^{35}Cl$ and $(^{12}CH_2)_3 \cdots ^{35}ClF$ from data in Refs. 29 and 30 are 0.25(4) and 0.17(2) u Å², respectively. Inertia defects Δ_0 of the corresponding (planar) complexes in which ethyne is the Lewis base are somewhat larger and positive and become smaller as the intermolecular binding becomes stronger. For example, the values are 1.2(3), 0.639(2), 0.34(4), and 0.285(4) u Å² for the T-shaped complexes of C_2H_2 with $H^{35}Cl$, ^{35}ClF , $^{107}Ag^{35}Cl$ and $^{63}Cu^{35}Cl$, respectively.^{24,25,12,13} Increasingly positive inertia defects are usually attributed to a predominant contribution of a low-lying, large-amplitude, in-plane vibration to the zero-point motion and this effect will presumably become more important as the intermolecular binding strength decreases. The order of binding strength in the C_2H_2 complexes is $HCl < ClF < AgCl < CuCl$. The different patterns of behaviour of the pseudo-inertia defect in the corresponding series when cyclopropane is the Lewis base are probably attributable to (1) small changes in the out-of-plane hydrogen coordinates c_H in the strongly bound species $(^{12}CH_2)_3 \cdots ^{63}Cu^{35}Cl$ and $(^{12}CH_2)_3 \cdots ^{107}Ag^{35}Cl$ coupled with (2) a decreasing importance of the contribution of the low-lying, in-plane vibration to the zero-point motion in the order $HCl > ClF > AgCl > CuCl$.

2. Quantitative geometry

The discussion in Section III B 1 suggests that the qualitative geometry of $(CH_2)_3 \cdots MCl$ (M = Cu or Ag) is of the type shown in Figure 6 and has C_{2v} symmetry. Thus, all atoms but H lie in the ab principal inertia plane, which is a plane of symmetry, and the atoms are in the indicated order. The mid-point of the ^FC—^FC bond (denoted by *) and the M and Cl nuclei all lie on the a -axis. Insufficient isotopic substitution was available in the cyclopropane subunit to allow a determination of an r_s geometry of cyclopropane when it is within either complex, and hence a r_0 geometry is more appropriate here. Isotopic substitution at M and Cl is available in both complexes, however, so that r_s coordinates of these atoms can be determined, as Costain⁴⁸ suggested, by using zero-point moments of inertia

TABLE VI. Comparison of r_s , r_0 , and r_e principal-axis coordinates and bond lengths determined for $(\text{CH}_2)_3 \cdots \text{MCl}$ ($\text{M} = \text{Cu}$ or Ag).^a

Coordinate/bond length	Parent isotopologue					
	$(^{12}\text{CH}_2)_3 \cdots ^{63}\text{Cu}^{35}\text{Cl}$			$(^{12}\text{CH}_2)_3 \cdots ^{107}\text{Ag}^{35}\text{Cl}$		
	r_s	$r_0(\text{fit } 1)^a$	<i>Ab initio</i> r_e^b	r_s	$r_0(\text{fit } 1)^a$	<i>Ab initio</i> r_e^b
$a_M/\text{\AA}$	0.196(76)	0.2076(22)	0.1919	0.191(79)	0.1891(18)	0.1850
$a_{\text{Cl}}/\text{\AA}$	2.2779(66)	2.2688(20)	2.2540	2.4658(60)	2.4764(30)	2.4612
$r(\text{M} \cdots \text{Cl})/\text{\AA}$	2.082(77)	2.0612(42)	2.0621	2.275(79)	2.2872(48)	2.2763

^aFit 1 is that in which the $r(\text{C}-\text{H})$ are released but the angular orientation of the CH_2 groups is fixed at the *ab initio* values (see text and Table VII).

^b*Ab initio* calculation conducted at the CCSD(T) (F12*)/aug-cc-pVTZ-F12 level of theory.

in the appropriate equilibrium expression due to the work of Kraitchman,⁴⁹ as reproduced in the following:

$$|a_{\text{M or Cl}}| = \{(\Delta I_b + \Delta I_c) / 2\mu_S\}^{\frac{1}{2}}, \quad (4)$$

where $\mu_S = \Delta m M / (\Delta m + M)$ and ΔI_b and ΔI_c are the changes in the principal moments of inertia that accompany a mass change Δm on substitution into a parent isotopologue of mass M . The values of a_M and a_{Cl} determined for each of $(^{12}\text{CH}_2)_3 \cdots ^{63}\text{Cu}^{35}\text{Cl}$ and $(^{12}\text{CH}_2)_3 \cdots ^{107}\text{Ag}^{35}\text{Cl}$ as parent molecules are given in Table VI, which also includes the substitution distances $r_s(\text{Cu} \cdots \text{Cl})$ and $r_s(\text{Ag} \cdots \text{Cl})$ that thereby become available. The signs of a_M were chosen so that these distances were in agreement with the r_0 values to be discussed later. The coordinates of the atoms M are small, but it has been shown elsewhere^{9,12,13} that substitution coordinates of heavy atoms, such as Cu or Ag, near the centre of mass do not suffer the serious underestimation that occurs for lighter atoms in the same situation. Nevertheless, the recommendation by Costain⁴⁸ that errors in r_s coordinates should be estimated as $\delta a = 0.015 \text{ \AA}/a$ has been followed for both a_M and a_{Cl} .

Initial attempts to determine the complete r_0 geometry of each molecule $(\text{CH}_2)_3 \cdots \text{MCl}$ ($\text{M} = \text{Cu}$ or Ag) failed because of high correlation and ill-conditioning, which led to large errors in bond lengths and angles. To avoid this problem, quantities well-determined in the *ab initio* calculation at the CCSD(T) (F12*)/aug-cc-pVTZ-F12 level, but of minor chemical interest

here, were assumed unchanged. Two such approaches were tested; in both, C_{2v} symmetry was assumed, with all heavy atoms coplanar, as concluded in Section III B 1. In the first, the angles defining the orientation of the two equivalent $^{\text{F}}\text{CH}_2$ groups and the angles $\text{H}^{\text{F}}\text{CH}$ and $\text{H}^{\text{B}}\text{CH}$ were so fixed (fit 1). The results obtained by using Kisiel's program STRFIT⁵⁰ to fit the three principal moments of inertia of all isotopologues investigated are shown in Table VII. In a second approach (fit 2), the distances $r(^{\text{F}}\text{C}-\text{H})$ and $r(^{\text{B}}\text{C}-\text{H})$ were fixed at their *ab initio* values while the angle $\text{H}-^{\text{F}}\text{C}-\text{H}$ and the angle made by the bisector of the $\text{H}-^{\text{F}}\text{C}-\text{H}$ group with the $^{\text{F}}\text{C}-^{\text{F}}\text{C}$ internuclear line were fitted. The geometry determined in this way is also given in Table VII. A comparison of the two approaches shows satisfactory agreement between the two, especially among the quantities of most chemical interest, namely, the distances $r_0(^{\text{F}}\text{C}-^{\text{F}}\text{C})$, $r_0(^{\text{B}}\text{C}-^{\text{F}}\text{C})$, $r_0(^*\cdots\text{M})$ (where * denotes the centre of the C—C bond) and $r_0(\text{M}-\text{Cl})$, the last of which is in both cases in excellent agreement with the r_s version available in Table VI. The two main features of note are the increase in $r_0(^{\text{F}}\text{C}-^{\text{F}}\text{C})$ and the decrease in $r_0(^{\text{B}}\text{C}-^{\text{F}}\text{C})$ relative to the C—C distance in free cyclopropane (see Table V) for both $\text{M} = \text{Cu}$ and Ag . Evidently, the interaction of the atom M of MCl with the front C—C bond of cyclopropane on forming molecules $(\text{CH}_2)_3 \cdots \text{MCl}$ ($\text{M} = \text{Cu}$ or Ag) is strong enough to perturb significantly the pseudo- π bond. It will be demonstrated in Section IV that the bond extension considerably

TABLE VII. r_0 and *ab initio* r_e geometries determined for $(\text{CH}_2)_3 \cdots \text{MCl}$ ($\text{M} = \text{Cu}$ or Ag).^a

Geometric quantity	$(\text{CH}_2)_3 \cdots \text{CuCl}$			$(\text{CH}_2)_3 \cdots \text{AgCl}$		
	$r_0(\text{fit } 1)^b$	$r_0(\text{fit } 2)^c$	<i>Ab initio</i> r_e^d	$r_0(\text{fit } 1)^b$	$r_0(\text{fit } 2)^c$	<i>Ab initio</i> r_e^d
$r(\text{M}-\text{Cl})/\text{\AA}$	2.0612(42)	2.0594(43)	2.0621	2.2872(48)	2.2793(36)	2.2763
$r(\text{M}-^*)/\text{\AA}^e$	1.9912(46)	1.9930(50)	1.9555	2.3069(54)	2.3078(46)	2.3047
$r(^{\text{F}}\text{C}-^{\text{F}}\text{C})/\text{\AA}$	1.6177(9)	1.6214(20)	1.6088	1.5880(17)	1.5966(29)	1.5750
$r(^{\text{F}}\text{C}-^{\text{B}}\text{C})/\text{\AA}$	1.469(4)	1.470(5)	1.4955	1.486(8)	1.501(9)	1.4968
$r(^{\text{F}}\text{C}-\text{H})/\text{\AA}$	1.0825(29)	[1.0836]	1.0836	1.0861(61)	[1.0820]	1.0820
$r(^{\text{B}}\text{C}-\text{H})/\text{\AA}$	1.0883(53)	[1.0797]	1.0797	1.092(10)	[1.0797]	1.0797
$\angle \text{H}-^{\text{F}}\text{C}-^*/\text{deg}$	[118.94]	118.5(3)	118.94	[118.67]	117.7(4)	118.67
$\angle \text{H}-^{\text{B}}\text{C}-^*/\text{deg}$	[122.34]	122.6(4)	122.34	[122.21]	121.7(6)	122.21
$\angle \text{H}-^{\text{F}}\text{C}-^*\text{B}/\text{deg}$	[104.49]	[104.49]	104.49	[105.20]	[105.20]	105.20

^aSee text for nomenclature used to label the front and back C atoms.

^bGeometry fitted to moments of inertia by assuming the angles enclosed in square brackets from the *ab initio* calculation.

^cGeometry fitted to moments of inertia by assuming the $r(\text{C}-\text{H})$ and the dihedral angle enclosed in square brackets from the *ab initio* calculation.

^dOptimised geometry calculated *ab initio* at the CCSD(T) (F12*)/aug-cc-pVTZ-F12 level of theory. See text for details.

^e* denotes the midpoint of the bond $^{\text{F}}\text{C}-^{\text{F}}\text{C}$.

TABLE VIII. A comparison of a range of properties determined for the complexes $B \cdots MCl$, where B is C_2H_2 , C_2H_4 or $(CH_2)_3$ and M is Cu or Ag.

$B \cdots MCl$	Ionicity i_c of MCl^a	Dipole moment enhancement/D of $B \cdots MX^b$	Dissociation energy $D_e/(kJ\ mol^{-1})^b$	Intermolecular force constant $k_{\sigma}/(N\ m^{-1})^c$	CC bond distortion $\delta r_0(CC)/(Å)^d$
$C_2H_2 \cdots CuCl$	0.80	...	148	94(12)	0.0268(25)
$C_2H_4 \cdots CuCl$	0.81	...	155	77(11)	0.0284(44)
$(CH_2)_3 \cdots CuCl$	0.78	2.65	108	72(5)	0.1024(9)
$C_2H_2 \cdots AgCl$	0.74	1.6	98	51(3)	0.0165(22)
$C_2H_4 \cdots AgCl$	0.75	1.5	94	56(2)	0.0132(18)
$(CH_2)_3 \cdots AgCl$	0.72	2.61	68	53(1)	0.0727(17)

^aAs calculated from $\chi_{aa}(Cl)$ with the aid of Eq. (5).^bFrom *ab initio* calculations reported in Refs. 12–14 and this work.^cFrom Refs. 12–14 and this work. Calculated from centrifugal distortion constants ΔJ by means of Eq. (6).^d $\delta r_0(CC) = r_0(CC)_{\text{complex}} - r_0(CC)_{\text{free B}}$, the increase in r_0 length of the C—C π - or pseudo- π bond of B in forming a complex $B \cdots MX$.

exceeds those in the corresponding molecules ethyne $\cdots MCl$ and ethene $\cdots MCl$. A reason for this will be presented.

C. Other experimental and *ab initio* calculated properties of $(CH_2)_3 \cdots MCl$

There are several properties, in addition to the detailed geometry discussed in Section III B, that are available from experimental and *ab initio* results reported here for $(CH_2)_3 \cdots MCl$ (M = Cu or Ag). These include information about the strength of the interaction of $(CH_2)_3$ and MCl, and the electric charge rearrangement on formation of $(CH_2)_3 \cdots MCl$.

The M and Cl nuclear quadrupole coupling constants carry information about how the components of the e.f.g. tensor $V_{\alpha\beta}^X$ (α and β to be permuted over a , b , and c , $X = Cu$ or Cl) at these nuclei change when $(CH_2)_3 \cdots MCl$ is formed from MCl. The coupling constants are defined as $\chi_{\alpha\beta}(X) = -(eQ/h)V_{\alpha\beta}^X$. Values of $\chi_{aa}(Cu)$ and $\chi_{aa}(Cl)$ observed for the isotopologues $(^{12}CH_2)_3 \cdots ^{63}Cu^{35}Cl$ and $(^{12}CH_2)_3 \cdots ^{107}Ag^{35}Cl$ are in Tables I and III, respectively. The corresponding experimental quantities⁴⁷ for the free molecules $^{63}Cu^{35}Cl$ and $^{107}Ag^{35}Cl$ are collected in Table V. Clearly, in forming $(CH_2)_3 \cdots MCl$ from MCl, the magnitude of the e.f.g. at Cl along the a axis direction (which coincides with the MCl internuclear axis) significantly decreases, both when M = Cu or Ag. Similarly, the aa component of the e.f.g. at Cu changes. (No equivalent comment about the e.f.g. at Ag is possible because the nuclear electric quadrupole moment for Ag is zero.)

The fractional ionic characters (or ionicities), i_c , of the free molecules $^{63}Cu^{35}Cl$ and $^{107}Ag^{35}Cl$ are available from their $\chi_{aa}(Cl)$ values recorded in Table V. The Townes-Dailey model^{51,52} for interpreting nuclear quadrupole coupling constants leads to the expression

$$i_c = 1 + \{\chi_{aa}(Cl)/eQq_{3,1,0}(Cl)\} \quad (5)$$

in which $eQq_{3,1,0}(Cl)$ ($=109.74\text{ MHz}$)⁵² is the contribution to the coupling constant from a single $3p_z$ electron of Cl. The results are $i_c = 0.70$ and 0.67 for $^{63}Cu^{35}Cl$ and $^{107}Ag^{35}Cl$, respectively. If the valence bond description of MCl is employed, these results imply contributions of 70% and 67% from the ionic form $M^+ Cl^-$ when M = Cu and Ag, respectively. For the complexes $(^{12}CH_2)_3 \cdots ^{63}Cu^{35}Cl$ and $(^{12}CH_2)_3 \cdots ^{107}Ag^{35}Cl$, the corresponding approach leads to $i_c = 0.78$ and 0.72 , respectively. The ionic character i_c has been similarly established for a number of complexes $B \cdots MCl$ in

which B is a simple Lewis base and M is either Cu or Ag, and are tabulated elsewhere,¹⁴ including those cases in which B is a π -electron donor. Table VIII compares the values of i_c for $C_2H_2 \cdots MCl$, $C_2H_4 \cdots MCl$, and $(CH_2)_3 \cdots MCl$ for M = Cu and Ag. We conclude that when MCl approaches the π -bond of either ethyne or ethene or the pseudo- π bond of cyclopropane, the existing partial positive charge on the M atom is stabilised by partial delocalisation onto the hydrocarbon and allows thereby an increase in the ionic character of MCl. The ionic character appears to be smaller in the case of the cyclopropane complexes, however. Unfortunately, the Townes-Dailey model cannot be applied in its simple form to the coupling constants $\chi_{aa}(^{63}Cu)$ of $^{63}Cu^{35}Cl$ and $(^{12}CH_2)_3 \cdots ^{63}Cu^{35}Cl$ in order to assess more directly the change in positive charge at Cu and the internal consistency of this approach. This is because the valence shell electrons are s electrons and predict, in the Townes-Dailey approximation, $\chi_{aa}(Cu) = 0$.

The electric dipole moments have been calculated *ab initio* at the level and by the method described in Section II. The results are 6.09 and 8.06 D for $(CH_2)_3 \cdots CuCl$ and $(CH_2)_3 \cdots AgCl$, respectively, corresponding to enhancements of 2.65 and 2.61 D over the values for CuCl and AgCl calculated at the same level of theory. These enhancements confirm the conclusion drawn from the Cl nuclear quadrupole coupling constants that there is significant electric charge redistribution when the complexes $(CH_2)_3 \cdots MCl$ (M = Cu or Ag) are formed from cyclopropane and MCl.

The fact of significant electric charge movement when each $(CH_2)_3 \cdots MCl$ is formed and the accompanying significant distortions of the cyclopropane ring identified in Section III B indicate that these complexes are strongly bound. This is confirmed by the equilibrium dissociation energy for the process $(CH_2)_3 \cdots MCl \rightarrow (CH_2)_3 + MCl$ which has been calculated at the CCSD(T)(F12*)/aug-cc-pVTZ-F12 level of theory for both M = Cu and M = Ag. The values after correction for basis set superposition error are $D_e = 108$ and 68 kJ mol^{-1} for M = Cu and Ag, respectively. Table VIII includes D_e obtained from *ab initio* calculations conducted at similar levels of theory for the π -type complexes ethyne $\cdots MCl$ ^{12,13} and ethene $\cdots MCl$ ^{9,13} as well as those reported here for cyclopropane $\cdots MCl$. Comparison of the D_e in Table VIII shows that the complex $B \cdots CuCl$ is significantly more strongly bound than the complex $B \cdots AgCl$ for a given B, whether B = ethyne, ethene, or cyclopropane, while, for a given M, the cyclopropane complex is more weakly bound

than those involving ethyne or ethene, according to the D_e criterion.

Another criterion of binding strength is the intermolecular stretching force constant k_σ which is the restoring force per unit infinitesimal displacement from equilibrium of the intermolecular bond along the molecular symmetry axis. For molecules such as $(\text{CH}_2)_3 \cdots \text{MCl}$ ($\text{M} = \text{Cu}$ or Ag), in which MCl lies along the molecular symmetry axis C_2^a , Millen⁵³ has shown that k_σ may be calculated from the centrifugal distortion constant Δ_J in the quadratic approximation by means of the expression

$$k_\sigma = \left(\frac{8\pi^2\mu}{\Delta_J} \right) [B^3(1-b) + C^3(1-c)]. \quad (6)$$

In Eq. (6), $\mu = (m_{\text{cyclo}}m_{\text{MCl}})/(m_{\text{cyclo}} + m_{\text{MCl}})$ and $b = (B/B_{\text{cyclo}} + B/B_{\text{MCl}})$ and there is a corresponding expression for c . The spectroscopic constants of the complex, free cyclopropane, and MCl should be equilibrium values but in their absence, zero-point values, which are available from Tables I–V, are employed. The component molecules are assumed rigid in deriving Eq. (6). For the most abundant isotopologues ($^{12}\text{CH}_2)_3 \cdots ^{63}\text{Cu}^{35}\text{Cl}$ and $(^{12}\text{CH}_2)_3 \cdots ^{107}\text{Ag}^{35}\text{Cl}$, the calculated values are $k_\sigma = 72(5)$ and $53(1) \text{ N m}^{-1}$, respectively, where the error quoted is that propagated from the error in Δ_J . Systematic errors arising from assumptions in deriving Eq. (6) will be significant here. For example, it is assumed that the geometry of both cyclopropane and MX are unchanged on formation of the complex and that the component molecules are rigid. It has been shown that the cyclopropane and MCl geometries do change when within $(\text{CH}_2)_3 \cdots \text{MCl}$. Moreover, CuCl and AgCl have force constants that are not very large (i.e., these diatomic molecules are not rigid). Hence, the values of k_σ presented should be treated cautiously. Table VIII includes k_σ values for the series $\text{B} \cdots \text{MCl}$ for $\text{B} = \text{ethyne}$,^{12,13} ethene,^{9,13} and cyclopropane and $\text{M} = \text{Cu}$ or Ag . Bearing in mind the caveat about its accuracy, the k_σ criterion suggests that the order of interaction strength is $\text{Cu} > \text{Ag}$ for a given B , as also indicated by D_e . The order ethyne $\approx$ ethene $>$ cyclopropane for a given M suggested by D_e values is reproduced by the k_σ for $\text{M} = \text{Cu}$, but is less clear for $\text{M} = \text{Ag}$, however.

Another property of the π and pseudo- π complexes that could be affected by the strength of the $\text{B} \cdots \text{MCl}$ interaction is the change $\delta r_0(\text{CC}) = r_0(\text{CC})_{\text{complex}} - r_0(\text{CC})_{\text{free B}}$ in the π or pseudo- π CC r_0 bond length from that of free B (ethyne, ethene, or cyclopropane) when subsumed into the complex. These quantities^{9,12,13} are included in Table VIII for $\text{B} \cdots \text{MX}$ for all three B and for $\text{M} = \text{Cu}$ or Ag . We note that the more strongly bound Cu complexes show larger distortions than the corresponding Ag complexes. The cyclopropane $\cdots \text{MCl}$ complexes, which are evidently more weakly bound than their ethyne or ethene counterparts for a given M , show a significantly greater lengthening $\delta r_0(\text{CC})$ than do the ethyne or ethene complexes. Reasons for this will be advanced in Section IV.

IV. CONCLUSIONS

Complexes $(\text{CH}_2)_3 \cdots \text{MCl}$ ($\text{M} = \text{Cu}$ or Ag), formed through the non-covalent interaction of cyclopropane with each of cuprous chloride or argentous chloride, have been

generated in the gas phase by the laser ablation of either copper or silver in the presence of supersonically expanded pulses of a gas mixture containing small amounts of cyclopropane and carbon tetrachloride in a large excess of argon. The rotational spectra of the complexes so formed were detected with a chirped-pulse, Fourier-transform microwave spectrometer and analysed to give rotational constants and Cu and Cl nuclear quadrupole coupling constants for eight isotopologues of each of $(\text{CH}_2)_3 \cdots \text{CuCl}$ and $(\text{CH}_2)_3 \cdots \text{AgCl}$. The geometry of each of these complexes was established unambiguously to be of the type shown in Figure 6, each having C_{2v} symmetry, with all C atoms coplanar, and with the MCl molecule lying along a median of the cyclopropane C_3 triangle. This median coincides with the principal inertia axis a in each of the two complexes $(\text{CH}_2)_3 \cdots \text{MCl}$. The M atom interacts with the pseudo- π bond linking the pair of equivalent carbon atoms $^{\text{F}}\text{C}$ nearest to it, so that M forms a non-covalent bond to one $\text{C}—\text{C}$ edge of the cyclopropane molecule. The $(\text{CH}_2)_3 \cdots \text{MCl}$ complexes have angular geometries (see Figure 6) which are isomorphous with those of their hydrogen- and halogen-bonded analogues $(\text{CH}_2)_3 \cdots \text{HCl}$ and $(\text{CH}_2)_3 \cdots \text{ClF}$, respectively, shown (drawn to scale) in Figure 3. Quantitative details of the geometries were determined by interpretation of the observed rotational constants of 8 isotopologues for each complex $(\text{CH}_2)_3 \cdots \text{CuCl}$ and $(\text{CH}_2)_3 \cdots \text{AgCl}$. The results are in good agreement with those from *ab initio* calculations carried out at the $\text{CCSD(T)}(\text{F12}^*)/\text{aug-cc-pVTZ-F12}$ level of theory. The most interesting geometrical feature is an elongation of the $^{\text{F}}\text{C}—^{\text{F}}\text{C}$ bond and a shrinkage of the two $^{\text{B}}\text{C}—^{\text{F}}\text{C}$ bonds relative to the $\text{C}—\text{C}$ bond in cyclopropane itself.

A comparison of various properties of $(\text{CH}_2)_3 \cdots \text{MCl}$ ($\text{M} = \text{Cu}$ or Ag), determined either by interpretation of spectroscopic constants or by *ab initio* calculation, with those of the ethyne and ethene analogues $\text{C}_2\text{H}_2 \cdots \text{MCl}$ and $\text{C}_2\text{H}_4 \cdots \text{MCl}$ similarly determined (see Table VIII) suggests the following general conclusions. For a given π or pseudo- π electron donor B , the order of the strength of the interaction is $\text{CuCl} > \text{AgCl}$ (whether measured by the experimental intermolecular stretching force constant k_σ or by the *ab initio* calculated dissociation energy D_e). Similarly, the increase in the ionicity i_c relative to that of free CuCl or AgCl (as calculated from the Cl nuclear quadrupole coupling constant) and the electric dipole moment enhancement also support this conclusion (see Table VIII). For a given MCl , the data collected in Table VIII suggest (but not as convincingly) that the order of binding strength is ethyne $\approx$ ethene $>$ cyclopropane. An apparent exception is the increase in the $r_0(\text{CC})$ bond length $\delta r_0(\text{CC}) = r_0(\text{CC})_{\text{complex}} - r_0(\text{CC})_{\text{free B}}$ when $\text{B} \cdots \text{MCl}$ is formed. We note that the more weakly bound species $(\text{CH}_2)_3 \cdots \text{MCl}$ have values of $\delta r_0(\text{CC})$ that are ca. 4 times larger than those of their $\text{C}_2\text{H}_2 \cdots \text{MCl}$ and $\text{C}_2\text{H}_4 \cdots \text{MCl}$ analogues, despite the fact that the last two are more strongly bound than the first. A possible explanation for this striking observation lies in the nature of the pseudo- π bond in cyclopropane, which is shown schematically in Figure 2. When MCl interacts with the pseudo- π bond, electron density is presumably transferred to MCl , thereby weakening the CC single bond. If ethene is the electron donor, removal of a similar amount of π -electron density to MCl would weaken the CC

bond less (and therefore not lengthen it as much) because there is still a single bond present, in addition to the weakened π bond. A similar argument applies to the $\text{C}\equiv\text{C}$ bond in ethyne.

The investigations of the complexes $\text{H}_2\cdots\text{CuF}$, $\text{H}_2\cdots\text{CuCl}$, $\text{H}_2\cdots\text{AgCl}$, and $\text{H}_2\cdots\text{AuCl}$ by Novick and co-workers^{16–19} lead to similar but with somewhat larger distortions, namely, that the $\text{H}-\text{H}$ bond increases in length by ca. 0.087 Å, 0.058 Å, 0.055 Å, and ~ 0.12 Å, respectively, i.e., by ca. 11.5%, 7.7%, 7.3%, and $\sim 16\%$, respectively, when H_2 becomes bound to MX. The percentage increases in length for the $\text{F}^\text{C}-\text{F}^\text{C}$ bond in $(\text{CH}_2)_3\cdots\text{CuCl}$ and $(\text{CH}_2)_3\cdots\text{AgCl}$ are 6.8% and 4.8%, respectively. The lengthening of the $\text{H}-\text{H}$ bond in $\text{H}_2\cdots\text{CuF}$ and $\text{H}_2\cdots\text{AgCl}$ might also be explained in a similar way to that proposed here for cyclopropane complexes, but the effects of changes in the zero-point motion will presumably make a more important contribution when hydrogen, rather than cyclopropane, is the Lewis base.

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- ¹R. S. Walters, P. v. R. Schleyer, C. Corminboeuf, and M. A. Duncan, *J. Am. Chem. Soc.* **127**, 1100 (2005).
- ²D. M. P. Mingos, *J. Organomet. Chem.* **635**, 1–8 (2001).
- ³S. G. Francis, S. L. Matthews, O. K. Poleshchuk, N. R. Walker, and A. C. Legon, *Angew. Chem., Int. Ed.* **45**, 6341–6343 (2006).
- ⁴S. J. Harris, A. C. Legon, N. R. Walker, and D. E. Wheatley, *Angew. Chem., Int. Ed.* **49**, 181–183 (2010).
- ⁵V. A. Mikhailov, D. P. Tew, N. R. Walker, and A. C. Legon, *Chem. Phys. Lett.* **499**, 16–20 (2010).
- ⁶V. A. Mikhailov, F. J. Roberts, S. L. Stephens, S. J. Harris, D. P. Tew, J. N. Harvey, N. R. Walker, and A. C. Legon, *J. Chem. Phys.* **134**, 134305 (2011).
- ⁷S. L. Stephens, D. P. Tew, N. R. Walker, and A. C. Legon, *J. Mol. Spectrosc.* **267**, 163–168 (2011).
- ⁸N. R. Walker, D. P. Tew, S. J. Harris, D. E. Wheatley, and A. C. Legon, *J. Chem. Phys.* **134**, 014307 (2011).
- ⁹S. L. Stephens, D. P. Tew, V. A. Mikhailov, N. R. Walker, and A. C. Legon, *J. Chem. Phys.* **135**, 024315 (2011).
- ¹⁰S. L. Stephens, W. Mizukami, D. P. Tew, N. R. Walker, and A. C. Legon, *J. Chem. Phys.* **136**, 064306 (2012).
- ¹¹S. Z. Riaz, S. L. Stephens, W. Mizukami, D. P. Tew, N. R. Walker, and A. C. Legon, *Chem. Phys. Lett.* **531**, 1–5 (2012).
- ¹²S. L. Stephens, W. Mizukami, D. P. Tew, N. R. Walker, and A. C. Legon, *J. Chem. Phys.* **137**, 174302 (2012).
- ¹³S. L. Stephens, D. M. Bittner, V. A. Mikhailov, W. Mizukami, D. P. Tew, N. R. Walker, and A. C. Legon, *Inorg. Chem.* **53**, 10722–10730 (2014).
- ¹⁴D. M. Bittner, D. P. Zaleski, S. L. Stephens, D. P. Tew, N. R. Walker, and A. C. Legon, *J. Chem. Phys.* **142**, 144302 (2015).

- ¹⁵D. P. Zaleski, S. L. Stephens, D. P. Tew, D. M. Bittner, J. C. Mullaney, N. R. Walker, and A. C. Legon, *Phys. Chem. Chem. Phys.* **17**, 19230 (2015).
- ¹⁶D. J. Frohman, G. S. Grubbs II, Z. Yu, and S. E. Novick, *Inorg. Chem.* **52**, 816–822 (2013).
- ¹⁷H. M. Pickett, D. A. Obenchain, G. S. Grubbs, and S. E. Novick, in *68th International Symposium on Molecular Spectroscopy [TH16]* (The Ohio State University, Columbus, OH, 2013).
- ¹⁸G. S. Grubbs II, D. A. Obenchain, H. M. Pickett, and S. E. Novick, *J. Chem. Phys.* **141**, 114306 (2014).
- ¹⁹D. A. Obenchain, G. S. Grubbs II, H. M. Pickett, and S. E. Novick, in *68th International Symposium on Molecular Spectroscopy [FC03]* (The Ohio State University, Columbus, OH, 2013).
- ²⁰A. C. Legon and D. J. Millen, *Faraday Discuss. Chem. Soc.* **73**, 71–87 (1982).
- ²¹A. C. Legon and D. J. Millen, *Chem. Soc. Rev.* **16**, 467–498 (1987).
- ²²A. C. Legon, *Chem. - Eur. J.* **4**, 1890–1897 (1998).
- ²³A. C. Legon, *Angew. Chem., Int. Ed.* **38**, 2686–2714 (1999).
- ²⁴A. C. Legon, P. D. Aldrich, and W. H. Flygare, *J. Chem. Phys.* **75**, 625–630 (1981).
- ²⁵K. Hinds, J. H. Holloway, and A. C. Legon, *J. Chem. Soc., Faraday Trans.* **92**, 1291–1296 (1996).
- ²⁶P. D. Aldrich, A. C. Legon, and W. H. Flygare, *J. Chem. Phys.* **75**, 2126–2134 (1981).
- ²⁷H. I. Bloemink, J. H. Holloway, and A. C. Legon, *Chem. Phys. Lett.* **250**, 567–575 (1996).
- ²⁸C. A. Coulson and W. E. Moffitt, *Philos. Mag.* **40**, 1 (1949).
- ²⁹A. C. Legon, P. D. Aldrich, and W. H. Flygare, *J. Am. Chem. Soc.* **104**, 1486–1490 (1982).
- ³⁰K. Hinds, J. H. Holloway, and A. C. Legon, *J. Chem. Soc., Faraday Trans.* **93**, 373–378 (1997).
- ³¹S. L. Stephens and N. R. Walker, *J. Mol. Spectrosc.* **263**, 27–33 (2010).
- ³²D. P. Zaleski, S. L. Stephens, and N. R. Walker, *Phys. Chem. Chem. Phys.* **16**, 25221–25228 (2014).
- ³³PGOPHER, a program for simulating rotational structure, version 6.0.202, designed by C. M. Western, University of Bristol, 2010. Available at <http://pgopher.chm.bris.ac.uk>.
- ³⁴K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, *Chem. Phys. Lett.* **157**, 479–483 (1989).
- ³⁵C. Hättig, D. P. Tew, and A. Köhn, *J. Chem. Phys.* **132**, 231102 (2010).
- ³⁶R. A. Kendall, T. H. Dunning, Jr., and R. J. Harrison, *J. Chem. Phys.* **96**, 6796 (1992).
- ³⁷T. H. Dunning, Jr., K. A. Peterson, and A. K. Wilson, *J. Chem. Phys.* **114**, 9244 (2001).
- ³⁸K. A. Peterson and C. Puzzarini, *Theor. Chem. Acc.* **114**, 283 (2005).
- ³⁹D. Figgen, G. Rauhut, M. Dolg, and H. Stoll, *Chem. Phys.* **311**, 227–244 (2005).
- ⁴⁰O. Christiansen, H. Koch, and P. Jørgensen, *Chem. Phys. Lett.* **243**, 409–418 (1995).
- ⁴¹H.-J. Werner, P. J. Knowles, R. Lindh, F. R. Manby, M. Schütz et al., MOLPRO, version 2009.1, a package of *ab initio* programs, 2009, see <http://www.molpro.net>.
- ⁴²C. Hättig and F. Weigend, *J. Chem. Phys.* **113**, 5154 (2000).
- ⁴³J. K. G. Watson, *J. Chem. Phys.* **48**, 4517 (1968).
- ⁴⁴See supplementary material at <http://dx.doi.org/10.1063/1.4934539> for fits of spectroscopic constants to observed transition frequencies for each isotopologue investigated.
- ⁴⁵T. Brubacher, C. Styger, B. Vogelsanger, I. Ozier, and A. Bauder, *J. Mol. Spectrosc.* **138**, 197–203 (1989).
- ⁴⁶Y. Endo, M. C. Chang, and E. Hirota, *J. Mol. Spectrosc.* **126**, 63–71 (1987).
- ⁴⁷K. D. Hensel, C. Styger, W. Jäger, A. J. Merer, and M. C. L. Gerry, *J. Phys. Chem.* **99**, 3320–3328 (1993).
- ⁴⁸C. C. Costain, *J. Chem. Phys.* **29**, 864 (1958).
- ⁴⁹J. Kraitchman, *Am. J. Phys.* **21**, 17–24 (1953).
- ⁵⁰Z. Kisiel, *J. Mol. Spectrosc.* **218**, 58–67 (2003).
- ⁵¹C. H. Townes and B. P. Dailey, *J. Chem. Phys.* **23**, 118–123 (1955).
- ⁵²W. Gordy and R. L. Cook, in *Microwave Molecular Spectra*, Technique of Organic Chemistry Vol. 9, edited by A. Weissberger (Interscience, New York, 1970), Chap. 14.
- ⁵³D. J. Millen, *Can. J. Chem.* **63**, 1477–1479 (1985).