Medcraft C, Bittner DM, Tew DP, Walker NR, Legon AC. [Geometries of H₂S-MI \(M = Cu, Ag, Au\) complexes studied by rotational spectroscopy: The effect of the metal atom](#). *Journal of Chemical Physics* 2016, 145(19), 194306.

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Date deposited:

28/11/2016

Embargo release date:

18 November 2017

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Geometries of $\text{H}_2\text{S}\cdots\text{MI}$ ($\text{M}=\text{Cu}, \text{Ag}, \text{Au}$) Complexes Studied by Rotational Spectroscopy: The Effect of the Metal Atom

Chris Medcraft,[†] Dror M. Bittner,[†] David P. Tew,[‡] Nicholas R. Walker^{†*} and Anthony C. Legon^{‡*}

[†] School of Chemistry, Bedson Building, Newcastle University, Newcastle upon Tyne, Tyne and Wear, NE1 7RU, U.K.

[‡] School of Chemistry, University of Bristol, Bristol, BS8 1TS, U.K.

*Corresponding authors email: nick.walker@newcastle.ac.uk, a.c.legon@bristol.ac.uk

KEYWORDS: hydrogen sulfide, rotational spectroscopy, microwave spectroscopy.

ABSTRACT

Complexes formed between H_2S and each of CuI , AgI and AuI have been isolated and structurally characterised in the gas phase. The $\text{H}_2\text{S}\cdots\text{MI}$ complexes (where M is the metal atom) are generated through laser vaporisation of a metal rod in the presence of a low concentration of H_2S and CF_3I in a buffer gas of argon undergoing supersonic expansion. The microwave spectra of six isotopologues of each of $\text{H}_2\text{S}\cdots\text{CuI}$ and $\text{H}_2\text{S}\cdots\text{AgI}$; and three isotopologues of $\text{H}_2\text{S}\cdots\text{AuI}$ have been measured by chirped-pulse Fourier transform microwave (CP-FTMW) spectroscopy. The spectra are interpreted to determine geometries for the complexes and to establish the values of structural parameters. The complexes have C_s symmetry at equilibrium and have a pyramidal configuration about the sulfur atom. The local C_2 axis of the hydrogen sulfide molecule intersects the linear axis defined by the three heavy atoms at an angle, $\phi = 75.00(47)^\circ$ for $\text{M}=\text{Cu}$, $\phi = 78.43(76)^\circ$ for $\text{M}=\text{Ag}$ and $\phi = 71.587(13)^\circ$ for $\text{M}=\text{Au}$. The trend in the molecular geometries is consistent with significant relativistic effects in the gold-containing complex. The force constant describing the interaction between the H_2S and MI sub-units is determined from the measured centrifugal distortion constant, Δ_f , of each complex. Nuclear quadrupole coupling constants, $\chi_{aa}(\text{M})$ and $\chi_{aa}(\text{I})$ (where M denotes the metal atom), are determined for $\text{H}_2\text{S}\cdots\text{CuI}$ and $\text{H}_2\text{S}\cdots\text{AuI}$ for the first time.

1. INTRODUCTION

This article is one of a series in which the non-covalent interactions of the simple Lewis bases H_2O and H_2S with various Lewis acids has been investigated by means of rotational spectroscopy. Initially, the Lewis acids were chosen to be the hydrogen halides HX ($\text{X} = \text{F}, \text{Cl}, \text{Br}$ or I), thereby leading to the hydrogen bond in complexes $\text{H}_2\text{O} \cdots \text{HX}^{1-5}$ and $\text{H}_2\text{S} \cdots \text{HX}^{6-10}$ as the non-covalent interaction. Later, halogen bonds were characterised by using homo- and hetero-nuclear dihalogen molecules X_2 or XY (X or $\text{Y} = \text{F}, \text{Cl}, \text{Br}$ or I) as the Lewis acids in complexes $\text{H}_2\text{O} \cdots \text{XY}^{11-17}$ and $\text{H}_2\text{S} \cdots \text{XY}^{18-23}$. More recently, it has been possible to generate coinage metal monohalides MX ($\text{M} = \text{Cu}$ or Ag ; $\text{X} = \text{F}, \text{Cl}$ or I) in the gas phase by laser-ablation techniques and thereby to observe the rotational spectra of complexes $\text{H}_2\text{O} \cdots \text{MX}$ ($\text{X} = \text{F}$ or Cl)²⁴⁻²⁶ and $\text{H}_2\text{S} \cdots \text{MX}$ ($\text{X} = \text{Cl}$ or I)^{24,27,28} in which MX is the Lewis acid.

The Lewis bases H_2O and H_2S played a central role in establishing a set of rules²⁹⁻³² for predicting the angular geometries of hydrogen- and halogen-bonded complexes. These rules state that the angular geometries of hydrogen-bonded complexes $\text{B} \cdots \text{HX}$ or halogen-bonded complexes $\text{B} \cdots \text{XY}$ in the gas phase can be predicted by assuming that, in the equilibrium conformation, the internuclear axis of the HX or XY molecule lies

- (1) along the axis of a non-bonding electron pair (n-pair) carried by B, or
- (2) along the local symmetry axis of a π bonding orbital, if B carries no n-pairs, or
- (3) if B carries both n- and π -pairs, rule (1) takes precedence.

All $\text{H}_2\text{O} \cdots \text{HX}$, $\text{H}_2\text{S} \cdots \text{HX}$, $\text{H}_2\text{O} \cdots \text{XY}$ and $\text{H}_2\text{S} \cdots \text{XY}$ complexes so far investigated have been shown to have an equilibrium geometry of the general type shown in Figure 1, that is a conformation of C_s symmetry, in which HX (or XY) forms a hydrogen bond (or halogen bond) to either O or S and lies along the axis of one of the n-pairs carried by O or S. There is, however, a significant difference between the

H₂O complexes and the H₂S complexes, as revealed by the one-dimensional potential energy (PE) as a function of the angle ϕ (see Figure 1 for definition of ϕ).

Typical one-dimensional PE functions, with vibrational energy levels, for such complexes, are shown in Figure 2. Figure 2(a) refers to H₂O...HCl while Figure 2(b) applies to H₂S...HCl. The level of theory (MP2/cc-pVDZ) and the method of calculating energy levels used in each case are described in detail in ref. 3. Both functions are of the double-minimum type and both have a potential energy barrier at the C_{2v}, planar conformation (angle $\phi = 0^\circ$). A well-known property of such PE functions is that as the energy barrier increases from zero, the vibrational energy levels associated with the motion described by ϕ begin to draw together in inversion pairs. In the limit of a very high barrier, the inversion splitting in the lower pairs of levels becomes negligibly small. The main difference between the two types of function shown in Figure 2 is that in (a) there is a low potential energy barrier and a large separation of the lowest inversion pair while in (b) the barrier is higher and wider, leading to an almost complete quenching in the inversion motion in the lowest vibrational state. Those complexes of the type H₂O...HX and H₂O...XY for which PE functions have been calculated^{1,3,12,14-17,25,26,32,33} exhibit similar general characteristics (low barrier, large inversion splittings, small angles ϕ_e) to that shown in Figure 2(a), with the shape and barrier height relatively insensitive to the level of theory used in the *ab initio* calculations. Likewise, H₂S...HX and H₂S...XY complexes^{20,32,33} have PE functions with properties similar to those of the function shown in Figure 2(b) (high barriers, very small inversion splittings, large equilibrium angle ϕ_e) independently of level of theory used. As a result, most H₂S...HX and H₂S...XY are permanently pyramidal (C_s symmetry) in the two lowest energy vibrational levels $\nu=0$ and 1 (the only levels populated in the low-temperature spectroscopy described here), with a negligibly small rate of inversion relative to the observation time for rotational spectroscopy. (Exceptions are H₂S...HI¹⁰ and H₂S...F₂¹⁸, which, although still steeply pyramidal exhibit, some evidence of a slightly higher inversion rate). On the other hand, for H₂O...HX and H₂O...XY complexes, inversion doubling is large and only the lowest vibrational level is populated. The vibrational

wavefunctions therefore have C_{2v} symmetry and the H_2O complexes are effectively planar but, importantly in connection with the rules, the equilibrium geometry is non-planar ($\phi_e > 0$). As will be discussed later, the two types of PE function shown in Figure 2 have consequences for the appearance of the rotational spectra³⁴

The experimental values of ϕ for all $H_2S \cdots HX$ ⁶⁻¹⁰ and $H_2S \cdots XY$ ¹⁸⁻²³ complexes so far investigated are $\approx 90^\circ$, while for all $H_2O \cdots HX$ ¹⁻⁵ and $H_2O \cdots XY$ ¹¹⁻¹⁷ complexes $\phi \approx 50^\circ$. These results are consistent with the rules, given the electronic models of H_2S and H_2O familiar to chemists^{30,33}, namely having angles between the two n-pair axes of 180° and 109.5° (the tetrahedral angle), respectively. The fact that $H_2S \cdots CuCl$ and $H_2S \cdots AgCl$ ²⁷ have been shown to be non-inverting in the lowest vibrational state with $\phi \approx 80^\circ$ while $H_2O \cdots CuCl$, $H_2O \cdots AgCl$ [25] and $H_2O \cdots AgF$ [26] are effectively planar with $\phi \approx 50^\circ$ in the zero-point energy state suggests that the rules for angular geometries also apply to coinage metal complexes $B \cdots MX$ in which the metal monohalide acts as the Lewis acid. We present in this article the results of investigating the ground-state rotational spectra of the family of three complexes $H_2S \cdots CuI$, $H_2S \cdots AgI$ and $H_2S \cdots AuI$. The aims of this work were (1) to discover whether complexes $H_2S \cdots MI$ exhibited angular geometries in the zero-point state similar to those of $H_2S \cdots HX$, $H_2S \cdots XY$ and $H_2S \cdots MX$ referred to earlier, that is non-inverting, pyramidal angular geometries having $\phi \approx 80^\circ$, and (2) to discover whether any significant changes in the geometry of $H_2S \cdots MI$ result from changing the metal atom from Cu to Ag to Au.

II. EXPERIMENTAL

The instruments and methods employed have been described in detail previously.^{35,36} The generation of molecular complexes is achieved by laser-vaporising material from a solid target such that it becomes entrained in a gaseous sample undergoing supersonic expansion. For all the experiments described herein, the prepared sample contained a low concentration of CF_3I ($\approx 1\%$) in argon at a pressure of 6 bar. The gas

sample also includes a low concentration ($\approx 2\%$) of H_2S , D_2S or a $\text{H}_2\text{S}/\text{D}_2\text{S}$ mixture as necessary to allow measurement of the spectra of isotopologues containing $\text{H}_2\text{S}\cdots\text{MI}$, $\text{D}_2\text{S}\cdots\text{MI}$ and $\text{HDS}\cdots\text{MI}$. Either pure metal rods (for Cu or Ag) or gold foil wrapped around a glass rod were used as laser vaporisation targets as appropriate to the metal complex studied. The frequency doubled output of a Nd:YAG laser (532 nm, 10 mJ pulse⁻¹, 10 ns duration) is focussed on the target which is continually rotated and translated to ensure fresh surface material is exposed to each laser pulse.

An arbitrary waveform generator (AWG) is used to supply a chirped microwave pulse that sweeps from 0.5–12 GHz over a duration of 1 μs . This chirped pulse passes through a 12.2 GHz low-pass filter and is mixed against the filtered output of a phase-locked dielectric resonant oscillator (PDRO) that supplies a 19.00 GHz signal. The AWG and PDRO are each phase-locked to a 10 MHz frequency accurate to 1 part in 10^{11} . The output after mixing passes through a 7–18.5 GHz bandpass filter and is amplified prior to irradiation of the molecular sample. The data presented herein were acquired using a 300W travelling wave tube amplifier. The microwave frequency sweep is introduced perpendicular to the propagation direction of the expanding gas via a microwave horn. The molecular emission signal (free induction decay, or FID, of the polarisation) is detected by a second horn antenna and amplified by a low noise amplifier. The FID is mixed down against the 19.00 GHz reference signal supplied by the PDRO and then passes through a 12.5 GHz low-pass filter before detection. Each FID is measured over a 20 μs period following each chirped polarisation pulse. A fast digital oscilloscope is phase-locked to the same 10 MHz external frequency reference used by the PDRO and AWG and used to digitise the molecular FID. The above sequence of microwave polarisation pulse, detection and recording of FID is repeated eight times following each individual nozzle (i.e. gas sample introduction) pulse to maximise the duty cycle of the spectrometer. In order to record the spectrum of $\text{D}_2\text{S}\cdots^{63}\text{CuI}$ during this study, 697k FIDs (acquired from 87k valve pulses and requiring 23 hours of real time). FID's are averaged in the time domain before Fourier transforming to yield the frequency domain spectrum spanning from 7 to 18.5 GHz. After application of a Kaiser-Bessel window function, all observed transitions have a full width at half maximum (FWHM) of 150 kHz.

III. AB INITIO CALCULATIONS

Structure optimisations and counterpoise corrected dissociation energies were calculated using the MOLPRO³⁷ package at the CCSD(T)(F12*)³⁸ level of theory, a coupled-cluster method with single and double excitations, a perturbative treatment of triple excitations³⁹ and explicit correlation.⁴⁰ Only valence electrons are included in the correlation treatment. A basis set combination consisting of aug-cc-pVTZ on H, aug-cc-pV(T+d)Z on S, aug-cc-pVTZ-PP on Cu, I and Au atoms was used and will be referred to by AVTZ. The effective core potentials ECP-10-MDF^{41,42}, ECP-28-MDF^{43,44} and ECP-60-MDF⁴⁵ were used on Cu, I and Au, respectively, to account for scalar relativistic effects. For the density fitting approximation used to accelerate the CCSD(T)(F12*) calculation, the respective def2-QZVPP⁴⁵ basis sets were employed for the MP2⁴⁶ and Fock⁴⁷ terms. For the complementary auxiliary basis required for the F12 treatment,⁴⁸ the def2-TZVPP MP2 density fitting basis sets were used.⁴⁹ Force constants were calculated from the second derivative of the energy with respect to the internal coordinates.

IV. RESULTS

A. Determination of Spectroscopic Constants

The preparative method generates a range of molecules and complexes that have been studied previously including CF₃I,³⁵ CF₃I...H₂S⁵⁰ and MI. The spectra^{51,52} of CuI, AgI and AuI have all been measured previously. The initial identification of transitions of H₂S...MI was informed by previous studies of H₂S...MX which established the C_s geometry shown in Figure 1 as typical for this family. All heavy atoms are located very close to the a inertial axis implying that each H₂S...MI complex will have a comparatively high value of A_0 and low value of B_0-C_0 . The electric dipole moment of each can be expected to be nearly aligned with the a inertial axis implying that a type transitions will be observed. Hence, $J' \rightarrow J''$ transitions separated by regular intervals of B_0+C_0 were observed and reported during a previous study

of $\text{H}_2\text{S}\cdots\text{AgI}$ and again during this work. Tentative initial assignments of the spectra of $\text{H}_2\text{S}\cdots\text{CuI}$ and $\text{H}_2\text{S}\cdots\text{AuI}$ also followed the identification of groups of transitions separated by intervals consistent with the expected values of B_0+C_0 for each of these complexes. Transitions of $\text{H}_2\text{S}\cdots\text{MI}$ are typically less intense than those of CF_3I (figure 3) by a factor of 500 and less intense than those of MI by a factor of 10. The spectrum obtained when probing a sample containing CF_3I , Cu and H_2S is shown in Figure 3.

Western's PGOPHER [53] was used to fit parameters in the Hamiltonian shown below to the observed transitions of all the complexes studied during this work;

$$H = H_R - \frac{1}{6}\mathbf{Q}(\text{M}):\nabla\mathbf{E}(\text{M}) - \frac{1}{6}\mathbf{Q}(\text{I}):\nabla\mathbf{E}(\text{I}) \quad (1)$$

where H_R is Watson's A-reduced Hamiltonian⁵⁴ in the Ir representation for a semi-rigid, prolate symmetric rotor. The second, and third terms on the right hand side describe the coupling of the nuclear electric quadrupole moment with the electric field gradient at each of the M and I nuclei. The interaction is given by the scalar (or inner) product of the nuclear quadrupole moment dyadic, $\mathbf{Q}$, and the dyadic of the electric field gradient arising from extra nuclear charges, $\nabla\mathbf{E}$. The nuclear quadrupole coupling constants are denoted by $\chi_{aa}(\text{M})$ (where M is Cu, Au or I) and can be determined from the nuclear quadrupole hyperfine structure. Neither of the two naturally-abundant isotopes of silver possesses $I \geq 1/2$ so the term of Eqn.(1) that applies to the metal atom is omitted when fitting the spectra of $\text{H}_2\text{S}\cdots\text{AgI}$. The coupling scheme used is $\mathbf{F}_1=\mathbf{J}+\mathbf{I}_\text{I}$ and $\mathbf{F}_2=\mathbf{F}_1+\mathbf{I}_\text{M}$. Distinctive features of the spectrum of $\text{D}_2\text{S}\cdots^{63}\text{CuI}$ were groups of transitions on either side of the $K_{-1} = 0$ transitions. Transitions in these groups were readily assigned as having $K_{-1} = 1$ allowing for the separate determination of the B_0 and C_0 rotational constants and Δ_{JK} for this isotopologue.

The observation of these transitions having $K_{-1}=1$ prompted re-measurement of the spectrum of $\text{D}_2\text{S}\cdots^{107}\text{AgI}$, which was recorded with higher sensitivity than achieved during the earlier study. Transitions having $K_{-1}=1$ were thus observed for both $\text{D}_2\text{S}\cdots^{107}\text{AgI}$ and $\text{D}_2\text{S}\cdots^{109}\text{AgI}$. It was not possible to unambiguously assign $K_{-1}=1$ transitions for any isotopologue of $\text{H}_2\text{S}\cdots\text{AuI}$ because of complex spectral overlap between hyperfine components of $K_{-1}=0$ and $K_{-1}=1$. Transitions having $K_{-1}=1$ were also not

observed for other isotopologues of $\text{H}_2\text{S}\cdots\text{CuI}$ and $\text{H}_2\text{S}\cdots\text{AgI}$ preventing determination of a value of B_0-C_0 in these cases. The A_0 rotational constant was not determinable for any of the complexes studied so calculated values are assumed by the simulations displayed in Figure 3 in order to reproduce relative intensities of $K_{-1}=1$ transitions. Hyperfine splittings introduced by deuterium nuclei were not resolved by the present experiments. The results of all fits of spectroscopic parameters are provided in Tables 1, 2 and 3 for $\text{H}_2\text{S}\cdots\text{CuI}$, $\text{H}_2\text{S}\cdots\text{AgI}$ and $\text{H}_2\text{S}\cdots\text{AuI}$ respectively. In total, approximately 1000 transitions from $\text{H}_2\text{S}\cdots\text{MI}$ complexes were successfully assigned. Complete details of all spectroscopic fits and measured transition frequencies are available as supplementary data.⁵⁵

The observation of a -type, $K_{-1}=1$ transitions of the type $(J+1)_{1,J+1} \rightarrow J_{1,J}$ and $(J+1)_{1,J} \rightarrow J_{1,J-1}$ in this study is curious. In previous studies of similar complexes of the form $\text{H}_2\text{S}\cdots\text{HX}$ ⁵⁻⁹, $\text{H}_2\text{S}\cdots\text{XY}$ ¹⁸⁻²³ and $\text{H}_2\text{S}\cdots\text{MX}$ ^{25,27,28} the $K_{-1}=1$ transitions are either absent or appear with greatly reduced intensities. For example, in $\text{H}_2\text{S}\cdots\text{HF}$ the $K_{-1}=1$ transitions are approximately 100 times weaker than the $K_{-1}=0$ transitions in the $J=2$ triplet⁷. For $\text{H}_2\text{S}\cdots\text{HCl}$ ⁸, $\text{H}_2\text{S}\cdots\text{HI}$ ¹⁰, $\text{H}_2\text{S}\cdots\text{ClF}$ ¹⁹, $\text{H}_2\text{S}\cdots\text{Cl}_2$ ²⁰, $\text{H}_2\text{S}\cdots\text{BrCl}$ ²¹ and $\text{H}_2\text{S}\cdots\text{Br}_2$ ²², no $K_{-1}=1$ transitions were observed, while for $\text{H}_2\text{S}\cdots\text{ICl}$ the two $K_{-1}=1$ transitions of a given $J+1 \rightarrow J$ transition were weaker by at least a factor of 10 than the corresponding $K_{-1}=0$ transition. However, it has been observed that $K_{-1}=1$ transitions are significantly stronger than the corresponding $K_{-1}=0$ transition $(J+1)_{0,J+1} \rightarrow J_{0,J}$ in the rotational spectra of all complexes $\text{H}_2\text{O}\cdots\text{HX}$,¹⁻⁴ $\text{H}_2\text{O}\cdots\text{XY}$ ¹¹⁻¹⁷ and $\text{H}_2\text{O}\cdots\text{MX}$ ²⁴⁻²⁶ observed using supersonic jet spectroscopy. This behaviour can be explained³⁴ by invoking the collisional propensity rules for population transfer during the supersonic cooling that follows formation of the complexes.

Figure 4 (a) shows a schematic diagram of the rotational energy levels $1_{1,0}$, $1_{0,1}$, and $1_{1,1}$ of a generic molecule $\text{H}_2\text{O}\cdots\text{HX}$ in both the vibrational ground state and lowest lying vibrationally excited state $V_{\beta(0)}=1$ (the mode $\nu_{\beta(0)}$ is the lowest frequency, out-of-plane bending mode, and corresponds approximately to changes in the internal coordinate ϕ defined in Figure 1). As discussed in the Introduction, $\text{H}_2\text{O}\cdots\text{HX}$

complexes are effectively planar in both states and there is a relatively large separation ($\approx 100 \text{ cm}^{-1}$) between the ground state and the excited state $V_{\beta(0)} = 1$. A rotation C_2^a exchanges the pair of equivalent protons (fermions, $I = 1/2$) and therefore the total wavefunction $\psi_{\text{tot}} = \psi_e \psi_{\text{vib}} \psi_{\text{rot}} \psi_{\text{spin}}$ must change sign under this operation. Since the electronic and vibrational ground states of $\text{H}_2\text{O} \cdots \text{HX}$ are both symmetric under C_2^a , it follows that the rotational level $1_{0,1}$ (symmetric under C_2^a) can occur only in combination with the singlet spin state (antisymmetric) of the two equivalent protons in the vibrational ground state while the levels $1_{1,0}$ and $1_{1,1}$ (antisymmetric under C_2^a) must appear in combination with the three triplet spin states (symmetric), (see Figure 4(a)). Thus, the levels $1_{1,0}$ and $1_{1,1}$ have a nuclear spin statistical weight of 3 while the level $1_{0,1}$ has a weight of 1. The state $V_{\beta(0)} = 1$ is antisymmetric with respect to the operation C_2^a and hence the combinations of spin functions and rotational functions is reversed in this state, as indicated. During the formation of the complexes and the subsequent supersonic expansion of the gas pulse, transfer of populations between the singlet and triplet levels within a given vibrational state, as indicated in Figure 4(a), is evidently forbidden by collisional propensity rules. Thus, unless differential cooling occurs, the ratio of the population of triplet to singlet states will be determined mainly by the nuclear spin statistical weight ratio of 3:1. Similar conclusions apply to the rotational energy levels $2_{1,2}$, $2_{0,2}$ and $2_{1,1}$, etc. In all complexes $\text{H}_2\text{O} \cdots \text{HX}$, $\text{H}_2\text{O} \cdots \text{XY}$ and $\text{H}_2\text{O} \cdots \text{MX}$ so far investigated by pulsed-jet spectroscopy the ratios of the intensities of the $(J+1)_{1,J+1} \rightarrow J_{1,J}$ and $(J+1)_{1,J} \rightarrow J_{1,J-1}$ transitions to that of the $(J+1)_{0,J+1} \rightarrow J_{0,J}$ transition in the ground vibrational state are consistent with the 3:1 statistical weighting. In the $V_{\beta(0)} = 1$ state, the nuclear spin statistical weights are reversed. Although rotational transitions in this state have not been observed in pulsed-jet spectroscopy, the three transitions $2_{1,2} \leftarrow 1_{1,1}$, $2_{0,2} \leftarrow 1_{0,1}$, $2_{1,1} \leftarrow 1_{1,0}$ in the $V_{\beta(0)} = 1$ state of $\text{H}_2\text{O} \cdots \text{HF}$ were observed when the spectrum was recorded at 200 K in an equilibrium gas mixture of water and hydrogen fluoride and they do exhibit the predicted 1:3 intensity pattern.¹

Figure 4(b) shows what happens to the rotational energy levels in the $V_{\beta(0)} = 1$ state of complexes of the type $\text{H}_2\text{S} \cdots \text{HX}$. As discussed in the Introduction, such complexes have a rigidly pyramidal, nearly

right-angled geometry with a high PE barrier to inversion of configuration at S (see Figure 2). This results in inversion doubling of only a few kHz in the lowest pair of vibrational states ($V_{\beta(0)} = 0$ and 1), which is very much less than the separation of the $K_{-1} = 1$ states from the $K_{-1} = 0$ state of a given J , as indicated schematically for $J = 1$ in Figure 4(b). The indicated red-blue level population transfers shown in Figure 4(b), for example ($V_{\beta(0)} = 1_{1,1} \rightarrow V_{\beta(0)} = 0, 1_{0,1}$), are not spin forbidden and can occur by collision. Hence, population from the $K_{-1} = 1$ states can be transferred to the $K_{-1} = 0$ state, leading to a population ratio at the end of the expansion appropriate to the usual temperature of ~ 1 -2K. Moreover, the rotational constants of the nearly degenerate $V_{\beta(0)} = 0$ and 1 states are so nearly identical that the $(J + 1)_{0,J+1} \rightarrow J_{0,J}$ transitions in these states are usually unresolved. The spectrum is then identical to that expected of the permanently pyramidal C_s molecule in which the $K_{-1} = 1$ transitions are unobservable or greatly weakened. The extent of population loss depends on the efficiency of the collisional transfer process. Evidently, the efficiency is greater under the conditions used to observe $H_2S \cdots HF$ (intensity ratio of $\approx 1:100$ for the $2_{1,2} \rightarrow 1_{1,1}$, $2_{1,1} \rightarrow 1_{1,0}$ transitions to the $2_{0,2} \rightarrow 1_{0,1}$ transition) than those used to observe $H_2S \cdots ICl$, (intensity ratio $\approx 1:10$ or worse for $K_{-1} = 1: K_{-1} = 0$ of a given J). For other $H_2S \cdots HX$ complexes, the intensities of the $(J + 1)_{0,J+1} \rightarrow J_{0,J}$ transitions were smaller than those of $H_2S \cdots HF$, so their $K_{-1} = 1$ counterparts would not be observed if they were lower in intensity by a factor of ≈ 100 . Likewise, ratios in the range 1:10 to 1:100 would likely preclude observation of $K_{-1} = 1$ transitions in all $H_2S \cdots XY$ (other than $XY = ICl$) and all $H_2S \cdots MX$ previously investigated. Exceptions are the very weakly bound $H_2S \cdots HI^{10}$ and $H_2S \cdots F_2^{18}$, for both of which two sets of transitions, very close in frequency but resolved, were observed.

During the present investigation, weak $(J + 1)_{1,J+1} \rightarrow J_{1,J}$ and $(J + 1)_{1,J} \rightarrow J_{1,J-1}$ transitions were observed for $D_2S \cdots CuI$ and $D_2S \cdots AgI$ in addition to $(J + 1)_{0,J+1} \rightarrow J_{0,J}$ transitions. The energy separation between the $K_{-1} = 1$ and $K_{-1} = 0$ levels of a given J in these very nearly symmetric-top complexes is $\Delta E \approx (A - B)h$. The rotational constant A is estimated to decrease from 147 GHz in $H_2S \cdots CuI$ to 75 GHz in $D_2S \cdots CuI$, so the energy separation ΔE is approximately halved. Under a given set of experimental

conditions, the population of $K_{-1}=1$ rotational levels might therefore be greater initially in $\text{D}_2\text{S}\cdots\text{CuI}$ than in $\text{H}_2\text{S}\cdots\text{CuI}$. If collisional transfer from a $K_{-1}=1$ to a $K_{-1}=0$ level of a given J has the same probability per collision for both isotopologues, the population loss from $K_{-1}=1$ should be similar for both during the expansion process. Since the initial population is greater for $\text{D}_2\text{S}\cdots\text{CuI}$ than $\text{H}_2\text{S}\cdots\text{CuI}$, the former should emerge with a greater $K_{-1}=1$ level population. This is a possible mechanism leading to an observable intensity of the $K_{-1}=1$ transitions in $\text{D}_2\text{S}\cdots\text{CuI}$.

B. Molecular Geometry

Structural parameters were fitted to the measured spectroscopic constants using Kisiel's least squares fitting program, STRFIT,⁵⁶ in order to obtain ground state experimental (r_0) structures for each complex. There is only one naturally-abundant isotope of each of gold, iodine and sulfur. It is therefore necessary to make various assumptions during the fitting of structural parameters. It is assumed that the r_0 geometry of isolated H_2S does not change on formation of the complex. This assumption is sufficient to allow $r(\text{M}\cdots\text{I})$, $r(\text{M}\cdots\text{S})$ and ϕ (the angle formed from the intersection of the C_2 axis of H_2S and the $\text{S}\cdots\text{MI}$ backbone) to be fitted for $\text{H}_2\text{S}\cdots\text{CuI}$ and $\text{H}_2\text{S}\cdots\text{AgI}$. Fitting of the $r(\text{M}\cdots\text{S})$ distance of $\text{H}_2\text{S}\cdots\text{AuI}$ requires the further assumption that the Au-I distance is equal to a value obtained by correcting the *ab initio* calculated r_e -value for the difference between the experimental and values of r_0 and r_e in AuI . The geometry of $\text{H}_2\text{S}\cdots\text{AgI}$ was the subject of a previous work²⁸ however the measurement of B_0-C_0 provided herein now allows a more reliable geometry to be provided for this complex. The structural parameters for all three molecules and bond lengths of the isolated metal halides are presented in tables 4 and 5.

It is known that relativistic effects in gold reverse the periodic trends of many molecular properties progressing down group 11.⁵⁷ Bond lengths generally increase when a copper atom is replaced by silver but then decrease when silver is replaced by gold. Whilst the decrease of $r_e(\text{M-I})$ when replacing silver for gold is modest, the observed decreases in $r(\text{S-M})$ and ϕ are greater. The trend in the experimentally-determined

quantities is reproduced in the calculated results. Although the experimental data is analysed to obtain an r_0 result while the *ab initio* calculation yields an r_e quantity, the experimental and calculated results are in very good agreement for $\text{H}_2\text{S}\cdots\text{CuI}$ and $\text{H}_2\text{S}\cdots\text{AgI}$. The experimental and calculated results for $r(\text{S}-\text{Au})$ of $\text{H}_2\text{S}\cdots\text{AuI}$ are less consistent, perhaps because core-valence correlation was not taken into consideration (*vide infra*) which may have affected the experimental $r_0(\text{Au}-\text{S})$ value as it was necessary to assume $r(\text{Au}-\text{I})$ in order to determine $r_0(\text{Au}-\text{S})$.

Contributions to the calculated *ab initio* geometry of AuI were discussed in detail in a previous work.⁵⁸ It was shown that extrapolation beyond CCSD(T)(F12*)/AVTZ to the basis set limit does not yield a significant change in the $r(\text{Au}-\text{I})$ distance calculated for free AuI. However, the inclusion of core-valence correlation reduces this bond length by 0.014 Å. At the level of the calculations employed herein, the low level treatment of relativity employed will contribute to differences between the experimentally-determined and *ab initio* calculated results for $r(\text{Au}-\text{I})$ and $r(\text{S}-\text{Au})$ of $\text{H}_2\text{S}\cdots\text{AuI}$. Uncertainty also arises in the experimentally-determined geometry of $\text{H}_2\text{S}\cdots\text{AuI}$ because of the limited number of isotopic substitutions possible for this molecule. The values of $r(\text{Au}-\text{I})$ and ϕ provided in Table 5 are determined under the assumption of an $r_0(\text{Au}-\text{I})$ bond distance as described above. Where both $r_0(\text{Au}-\text{I})$ and ϕ are assumed (as 2.5191 Å and 73.6° respectively), the fitted result for $r(\text{S}-\text{Au})$ is 2.2595(5) Å. Evidently, this bond distance is dependent on the choice of parameters to be fitted and the residuals quoted alongside parameters in Table 5 are underestimated.

C. Force Constants

The experimentally-determined force constants are calculated by applying a model⁵⁹ which accounts for contributions to the centrifugal distortion constants from both the $\text{M}-\text{X}$ and $\text{S}\cdots\text{M}$ bonds. The force constants of these bonds are denoted by F_{11} and F_{22} respectively in Eq 3;

$$hD_J = \frac{1}{2} \left\{ \frac{\hbar^4}{I_{bb}^4} \right\} \{ (m_1 a_1)^2 (F^{-1})_{11} + (m_1 a_1 + m_2 a_2)^2 (F^{-1})_{22} \} \quad (3)$$

where m_1 and m_2 are the masses of the halogen and metal atoms respectively. The principal axis coordinates of the halogen and metal atoms are a_1 and a_2 respectively. This model does not strictly apply to complexes of C_s symmetry but may be expected to give good results because of the near-prolate symmetry and bonds between the heavy atoms which are close to coincident with the a -inertial axis. This model allows the calculation of either F_{11} or F_{22} provided the other is known by assuming the cross term, F_{12} , is negligible. Even where neither parameter is accurately known, a good estimate of one will allow an approximate value and uncertainty limits to be assigned to the other. In order to estimate F_{22} for $\text{H}_2\text{S}\cdots\text{CuI}$, $\text{H}_2\text{S}\cdots\text{AgI}$ and $\text{H}_2\text{S}\cdots\text{AuI}$, F_{11} for each complex is assumed equal to that of the isolated metal halide diatomic and the r_0 values of geometrical parameters are used to determine the principal axis coordinates.

These experimentally determined values of F_{11} and F_{22} are shown in Table 6 along with values obtained from *ab initio* calculations. The *ab initio* results for F_{11} are very similar to k_σ for the free MI molecules, in similarity with previous works on $\text{B}\cdots\text{MX}$ complexes. The calculations suggest that F_{11} and F_{22} are similar in magnitude for each of $\text{H}_2\text{S}\cdots\text{CuI}$, $\text{H}_2\text{S}\cdots\text{AgI}$ and $\text{H}_2\text{S}\cdots\text{AuI}$ and especially so for the latter. It is initially assumed that $F_{11} = 208.0(13) \text{ N m}^{-1}$ and is thus equal to F_{AuI} of the isolated AuI molecule. The value of F_{22} thus obtained is $236.1(20) \text{ N m}^{-1}$ (with the uncertainty in F_{22} being that implied by the uncertainty in the determined centrifugal distortion constants) in fairly poor agreement with an *ab initio* calculated result of 150 N m^{-1} for the same parameter. An analysis of the interdependence of F_{11} and F_{22} for $\text{H}_2\text{S}\cdots\text{AuI}$ is presented in Figure 5. Where $F_{11} \cong F_{22}$, as is the case for $\text{H}_2\text{S}\cdots\text{AuI}$, any change in the assumed value of F_{11} implies a very significant change in the determined value of F_{22} . For the copper and silver species we repeat the assumption that F_{11} is equal to F_{MI} for the respective, isolated metal halides. Values of F_{11} of $172.1(8) \text{ N m}^{-1}$ and $145.8(12) \text{ N m}^{-1}$ are assumed for $\text{H}_2\text{S}\cdots\text{CuI}$ and $\text{H}_2\text{S}\cdots\text{AgI}$ which lead to F_{22} of $153.6(15)$ and $92.0(17) \text{ N m}^{-1}$ respectively. The values of F_{22} are less sensitive to the assumed values of F_{11} in $\text{H}_2\text{S}\cdots\text{CuI}$ and $\text{H}_2\text{S}\cdots\text{AgI}$ than in $\text{H}_2\text{S}\cdots\text{AuI}$. The agreement between the results obtained from the experimental data and those calculated *ab initio* is satisfactory given the assumptions involved.

D. Ionicities

The measured nuclear quadrupole coupling constants of iodine, $\chi_{aa}(\text{I})$, allow for calculation of the ionicity (i_c in table 5) of the M–I bond in each complex according to the Townes-Dailey model;⁶⁰

$$i_c = 1 + \frac{\chi_{aa}(I)}{eQq_{5,1,0}(I)}$$

where $eQq_{5,1,0}(I) = 2292.71 \text{ MHz}$ ⁶⁰ is the coupling constant that would result from a single $5p_z$ electron in an isolated iodine atom. The results are shown in Table 7 alongside those for other $\text{B}\cdots\text{MX}$ complexes and MX diatomic molecules. For any given B and X, the ionicity of the M–X bond decreases when proceeding from $\text{Cu} > \text{Ag} > \text{Au}$. The attachment of CO or H_2S to MX causes an increase in the ionicity of the metal halide bond, relative to that found in the free MX diatomic, with the induced change being greater where $\text{B}=\text{CO}$. The fractional changes are greater for $\text{X}=\text{I}$ than for $\text{X}=\text{Cl}$. Similar trends have been noted previously in studies of $\text{B}\cdots\text{MCl}$ complexes.

V. CONCLUSIONS

It has been shown that isolated complexes where H_2S is bound to MI (where $\text{M} = \text{Cu}, \text{Ag}, \text{Au}$) can be generated in the gas phase through laser ablation of a metal rod in the presence of a low concentration of CF_3I in an argon buffer gas undergoing supersonic expansion. The resulting complexes adopt model geometries analogous to those previously identified for $\text{H}_2\text{S}\cdots\text{CuCl}$ and $\text{H}_2\text{S}\cdots\text{AgCl}$, each having a C_s geometry in which all heavy atoms lie on the same axis which is nearly collinear with the inertial a axis. Table 8 presents a comparison of the geometries of $\text{H}_2\text{S}\cdots\text{MCl}$ and $\text{H}_2\text{S}\cdots\text{MI}$. The $r(\text{S}-\text{M})$ parameter is slightly longer for $\text{X}=\text{I}$ than for $\text{X}=\text{Cl}$. Changing the halogen atom induces very little change in φ while substitution of the metal atom has a far more significant effect, with $\varphi(\text{H}_2\text{S}\cdots\text{AgI}) > \varphi(\text{H}_2\text{S}\cdots\text{CuI}) > \varphi(\text{H}_2\text{S}\cdots\text{AuI})$. This angle is determined to be $78.43(26)^\circ$ for $\text{H}_2\text{S}\cdots\text{AgI}$ but only $71.587(13)^\circ$ for $\text{H}_2\text{S}\cdots\text{AuI}$. Geometrical changes seen in $\text{OC}\cdots\text{MX}$ on progressing from $\text{Cu} > \text{Ag} > \text{Au}$ have been discussed previously.

The changes observed on substitution of the metal atom during this work are analogous to those observed previously for $\text{OC}\cdots\text{MX}$ and are also a result of relativistic effects.

It is apparent that the values of ϕ determined for $\text{H}_2\text{S}\cdots\text{AgI}$ and $\text{H}_2\text{S}\cdots\text{CuI}$ are very similar to those previously identified for the analogous $\text{H}_2\text{S}\cdots\text{MCl}$ complexes. Geometrical parameters of selected hydrogen- and halogen-bonded complexes are given alongside details of the complexes studied during this work in Table 8. The values of $r(\text{I}-\text{S})$ and $r(\text{Br}-\text{S})$, respectively of $\text{H}_2\text{S}\cdots\text{ICl}$ and $\text{H}_2\text{S}\cdots\text{BrCl}$, are each longer than $r(\text{S}-\text{M})$ of the $\text{H}_2\text{S}\cdots\text{MX}$ complexes studied herein. The angle, ϕ , is significantly greater in $\text{H}_2\text{S}\cdots\text{ICl}$, $\text{H}_2\text{S}\cdots\text{BrCl}$ and $\text{H}_2\text{S}\cdots\text{HCl}$ than in $\text{H}_2\text{S}\cdots\text{MX}$, consistent with a bond between B and M–X of each metal-containing complex which is significantly stronger than a hydrogen- or halogen bond. Additional evidence for a strong bond between each metal iodide and H_2S is apparent in the experimentally-determined force constants (F_{22}) and in the dissociation energies, D_e , calculated *ab initio* for $\text{H}_2\text{S}\cdots\text{MX} \rightarrow \text{H}_2\text{S} + \text{MX}$. The dissociation energies are in the order $\text{Au} > \text{Cu} > \text{Ag}$, mirroring the trend in the force constants, with $D_e = 140 \text{ kJ mol}^{-1}$ for $\text{H}_2\text{S}\cdots\text{AuI}$.

Acknowledgments

The authors thank the EPSRC and the School of Chemistry at Newcastle University for the award of a DTA postgraduate studentship (EPK5028931) to D.M.B., the European Research Council for the postdoctoral fellowship awarded to C.M. and for project funding (Grant No. CPFTMW-307000). A.C.L. thanks the University of Bristol for a Senior Research Fellowship and Newcastle University for a Visiting Professor award. D.P.T. is pleased to acknowledge the Royal Society for the award of a University Research Fellowship. We are also grateful to the EPSRC UK National Service for Computational Chemistry Software (NSCCS) at Imperial College London.

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Table 1. Determined spectroscopic constants of six isotopologues of $\text{H}_2\text{S}\cdots\text{CuI}$

	$\text{H}_2\text{S}\cdots^{63}\text{CuI}$	$\text{H}_2\text{S}\cdots^{65}\text{CuI}$	$\text{HDS}\cdots^{63}\text{CuI}$
$\frac{1}{2}(B_0+C_0)$ / MHz	783.01594(15) ^a	780.60144(25)	767.97639(26)
Δ_J / Hz	48.47(82)	48.2(16)	48.1(11)
Δ_{JK} / kHz	-	-	-
$\chi_{aa}(\text{Cu})$ / MHz	55.629(33)	51.468(45)	55.61(18)
$[\chi_{bb}(\text{Cu})-\chi_{cc}(\text{Cu})]$ / MHz	-	-	-
$\chi_{aa}(\text{I})$ / MHz	-632.40(16)	-632.34(22)	-631.19(44)
$[\chi_{bb}(\text{I})-\chi_{cc}(\text{I})]$ / MHz	-	-	-
N^c	121	65	65
$\sigma_{\text{r.m.s.}}^d$ / kHz	8.7	10.1	11.9
	$\text{D}_2\text{S}\cdots^{63}\text{CuI}$	$\text{D}_2\text{S}\cdots^{65}\text{CuI}$	$\text{HDS}\cdots^{65}\text{CuI}$
B_0 / MHz	754.16334(19)	751.52287(31)	765.72370(31)
C_0 / MHz ^b	753.08379(20)	-	-
Δ_J / Hz	38.64(77)	47.3(13)	46.6(15)
Δ_{JK} / kHz	3.27(18)	-	-
$\chi_{aa}(\text{Cu})$ / MHz	52.627(69)	51.376(99)	52.13(41)
$[\chi_{bb}(\text{Cu})-\chi_{cc}(\text{Cu})]$ / MHz	-12.7(12)	-	-
$\chi_{aa}(\text{I})$ / MHz	-630.39(51)	-631.66(53)	-632.20(51)
$[\chi_{bb}(\text{I})-\chi_{cc}(\text{I})]$ / MHz	-16.8(26)	-	-
N^c	145	51	38
$\sigma_{\text{r.m.s.}}^d$ / kHz	20.0	12.7	11.2

^a Numbers in parentheses are one standard deviation in units of the last significant figure.^b Where no value for C_0 is given, B_0 refers to $\frac{1}{2}(B_0+C_0)$ ^c N is the number of fitted transitions,^d $\sigma_{\text{r.m.s.}}$ denotes the r.m.s. deviation of the fit.

Table 2. Determined spectroscopic constants of six isotopologues of $\text{H}_2\text{S}\cdots\text{AgI}$.

	$\text{H}_2\text{S}\cdots^{107}\text{AgI}^{\text{a}}$	$\text{H}_2\text{S}\cdots^{109}\text{AgI}^{\text{a}}$	$\text{HDS}\cdots^{107}\text{AgI}^{\text{a}}$
$\frac{1}{2}(B_0+C_0) / \text{MHz}$	625.39310(2)	624.16348(2)	615.35566(2)
Δ_J / Hz	34.82(8)	34.62(5)	(33.55) ^a
Δ_{JK} / kHz	-	-	-
$\chi_{aa}(\text{I}) / \text{MHz}$	-807.36(4)	-807.29(9)	-806.36(7)
$[\chi_{bb}(\text{I})-\chi_{cc}(\text{I})] / \text{MHz}$	-	-	-
N^{d}	-	-	-
$\sigma_{\text{r.m.s.}}^{\text{e}} / \text{kHz}$	-	-	-
	$\text{HDS}\cdots^{109}\text{AgI}^{\text{a}}$	$\text{D}_2\text{S}\cdots^{107}\text{AgI}$	$\text{D}_2\text{S}\cdots^{109}\text{AgI}$
B_0 / MHz	614.19979(1)	605.99267(16)	604.90322(14)
$C_0 / \text{MHz}^{\text{c}}$	-	605.42504(16)	604.33962(15)
Δ_J / Hz	(33.48) ^a	32.25(35)	31.27(31)
Δ_{JK} / kHz	-	1.609(77)	1.502(69)
$\chi_{aa}(\text{I}) / \text{MHz}$	-806.68(10)	-805.24(30)	-805.89(26)
$[\chi_{bb}(\text{I})-\chi_{cc}(\text{I})] / \text{MHz}$	-	-9.6(12)	-9.50(92)
N^{d}	-	120	97
$\sigma_{\text{r.m.s.}}^{\text{e}} / \text{kHz}$	-	9.4	7.8

^a From Ref. 28^b Numbers in parentheses are one standard deviation in units of the last significant figure.^c Where no value for C_0 is given, B_0 refers to $\frac{1}{2}(B_0+C_0)$.^d N is the number of fitted transitions.^e $\sigma_{\text{r.m.s.}}$ denotes the r.m.s. deviation of the fit.

Table 3. Determined spectroscopic constants of three isotopologues of $\text{H}_2\text{S}\cdots\text{AuI}$.

	$\text{H}_2\text{S}\cdots\text{AuI}$	$\text{HDS}\cdots\text{AuI}$	$\text{D}_2\text{S}\cdots\text{AuI}$
$\frac{1}{2}(B_0+C_0) / \text{MHz}$	617.209051(87)	608.77377(14)	600.611173(97)
Δ_J / Hz	22.72(26)	21.47(58)	20.18(29)
$\chi_{aa}(\text{Au}) / \text{MHz}$	-1087.02(16)	-1085.95(22)	-1085.17(17)
$\chi_{aa}(\text{I}) / \text{MHz}$	-753.29(17)	-755.93(17)	-757.17(26)
N^b	155	84	100
$\sigma_{\text{r.m.s.}}^c / \text{kHz}$	7.8	8.8	7.2

^a Numbers in parentheses are one standard deviation in units of the last significant figure.

^b N is the number of fitted transitions.

^c $\sigma_{\text{r.m.s.}}$ denotes the r.m.s. deviation of the fit.

Table 4. Determined structural parameters of $\text{H}_2\text{S}\cdots\text{CuI}$ and $\text{H}_2\text{S}\cdots\text{AgI}$.

	$\text{H}_2\text{S}\cdots\text{CuI}$		$\text{H}_2\text{S}\cdots\text{AgI}$	
	r_0 (exp.)	r_e	r_0 (exp.)	r_e
$r(\text{M}-\text{I}) / \text{\AA}$	2.3603(83)	2.3655	2.5484(94) ^a	2.5540
$r(\text{S}-\text{M}) / \text{\AA}$	2.175(14)	2.1648	2.409(18) ^a	2.4187
$\phi / ^\circ$	75.00(47)	74.387	78.43(76) ^a	77.074
$a_{\text{M}} / \text{\AA}$	1.0054	1.0101	0.9002	0.9017
$a_{\text{I}} / \text{\AA}$	-1.3545	-1.3553	-1.6479	-1.6523
$a_{\text{S}} / \text{\AA}$	3.1804	3.1748	3.3096	3.3203
$a_{\text{H}} / \text{\AA}$	3.4374	3.4324	3.5108	3.5351
$b_{\text{H}} / \text{\AA}$	± 0.9686	± 0.9739	± 0.9686	± 0.9719
	^{63}CuI		^{107}AgI	
	r_0 (exp.)	r_e (exp)	r_0 (exp.)	r_e (exp)
$r(\text{M}-\text{I}) / \text{\AA}$	2.34059082(2) ^b	2.3383236(15) ^c	2.54662697(7) ^b	2.5446165(12) ^d

^a Ref. 28 yielded a molecular geometry for $\text{H}_2\text{S}\cdots\text{AgI}$ where $r(\text{Ag}-\text{I}) = 2.5416(9) \text{\AA}$, $r(\text{S}-\text{Ag}) = 2.4228(18) \text{\AA}$ and $\phi = 78.94(7)^\circ$. The parameters determined during this work are thus consistent with those provided earlier.

^b Ref. 51

^c Ref. 61

^d Ref. 62

Table 5. Determined structural parameters of $\text{H}_2\text{S}\cdots\text{AuI}$.

$\text{H}_2\text{S}\cdots\text{AuI}$		
	r_0 (exp.)	r_e
$r(\text{Au-I}) / \text{\AA}$	$[2.5191]^a$	2.5208
$r(\text{S-Au}) / \text{\AA}$	2.256665(19)	2.3049
$\phi / ^\circ$	71.587(13)	73.586
$a_{\text{Au}} / \text{\AA}$	0.6497	0.6735
$a_{\text{I}} / \text{\AA}$	-1.8210	-1.8473
$a_{\text{S}} / \text{\AA}$	3.0215	2.9783
$a_{\text{H}} / \text{\AA}$	3.2362	3.2474
$b_{\text{H}} / \text{\AA}$	± 0.9686	± 0.9724
AuI		
	r_0 (exp.)	r_e (exp)
$r(\text{Au-I}) / \text{\AA}$	2.472804^b	2.4711022^c

^a Fixed to the value obtained by correcting the r_e result of the *ab initio* calculation for the difference between the experimental values of r_0 and r_e of AuI.

^b Ref. 61

^c Ref. 52

Table 6

Experimentally-determined and *ab initio* calculated values of F_{11} and F_{22} for $\text{H}_2\text{S}\cdots\text{CuI}$, $\text{H}_2\text{S}\cdots\text{AgI}$ and $\text{H}_2\text{S}\cdots\text{AuI}$.

	Exp.		Calc. ^a		$D_e / \text{kJ mol}^{-1}$
	$F_{11} / (\text{N m}^{-1})^b$	$F_{22} / (\text{N m}^{-1})$	$F_{11} / (\text{N m}^{-1})$	$F_{22} / (\text{N m}^{-1})$	
$\text{H}_2\text{S}\cdots\text{CuI}$	[172.1(8)]	153.6(15)	172	127	127
$\text{H}_2\text{S}\cdots\text{AgI}$	[145.8(12)]	92.0(17)	150	84	92
$\text{H}_2\text{S}\cdots\text{AuI}$	[208.0(13)]	236.1(20)	201	150	145

^{a.} Calculated at the CCSD(T)(F12*)/AVTZ level.

^{b.} Experimental values of F_{11} are fixed to the values obtained for the diatomic (M-I) molecules

Table 7: Ionicities i_c for M–I, H₂S···MI and OC···MI complexes

M	MI	H ₂ S···MI	OC···MI
Cu	0.59 ^a	0.72 ^c	0.74 ^d
Ag	0.53 ^a	0.65 ^c	0.66 ^e
Au	0.26 ^b	0.53 ^c	0.58 ^f
M	MCl	H ₂ S···MCl	OC···MCl
Cu ^g	0.71	0.79	0.80
Ag ^g	0.67	0.73	0.74

^a Ref. 51^b Ref. 52^c This work^d Ref. 63^e Ref. 64^f Ref. 64^g Ref. 65 and refs therein.

Table 8: Geometries of $\text{H}_2\text{S}\cdots\text{MX}$ complexes

	$r(\text{M}-\text{X}) / \text{\AA}$	$r(\text{M}-\text{S}) / \text{\AA}$	$\phi / ^\circ$
$\text{H}_2\text{S}\cdots\text{CuCl}$	2.0633(3) ^c	2.1531(3)	74.46(2)
$\text{H}_2\text{S}\cdots\text{CuI}$	2.3603(83)	2.175(14)	75.00(47)
$\text{H}_2\text{S}\cdots\text{AgCl}$	2.26882(13)	2.38384(12)	78.052(6)
$\text{H}_2\text{S}\cdots\text{AgI}$	2.5484(94)	2.409(18)	78.43(76)
$\text{H}_2\text{S}\cdots\text{AuI}$	[2.5191] ^a	2.256665(19)	71.587(13)
$\text{H}_2\text{S}\cdots\text{ICl}$	[2.3236]	3.154(3)	91.9(12)
$\text{H}_2\text{S}\cdots\text{BrCl}$	[2.1388]	3.094(7)	96.0(13)
$\text{H}_2\text{S}\cdots\text{HCl}$	[1.2746]	2.535	93.81(4)

^a Fixed to the value obtained by correcting the r_e result of the *ab initio* calculation for the difference between the experimental values of r_0 and r_e of AuI.

Figure 1

Figure 1: Definitions of the internal coordinates of the molecules in this study (M=Cu, Ag, Au)

Figure 2

Figure 2: Potential energy as a function of the angle ϕ (figure 1) for (a) $\text{H}_2\text{O} \cdots \text{HCl}$ and (b) $\text{H}_2\text{S} \cdots \text{HCl}$.

The potential energy functions are reproduced with permission from ref. [2]

Figure 3

Figure 3: (a) $J' \rightarrow J'' = 12 \rightarrow 11$ transition of $D_2S \cdots {}^{63}\text{CuI}$ showing the experimental (top) and the simulation from the fitted constants (lower) (b) $J' \rightarrow J'' = 15 \rightarrow 14$ transition of $D_2S \cdots {}^{105}\text{AgI}$ experimental top and simulation lower (grey) the overlapping lines are due to CF_3I (c) $J' \rightarrow J'' = 12 \rightarrow 11$ transition of $D_2S \cdots \text{AuI}$ (d) overview spectrum of $D_2S \cdots \text{CuI}$ showing the various precursors and products that are observed.

Figure 4

Figure 4: Rotational energy diagram. “nssw” = nuclear spin statistical weight.

Figure 5

Figure 5: Variation of F_{22} as a function of the assumed value of F_{11} for $\text{H}_2\text{S}\cdots\text{AuI}$. The value of F_{22} when F_{11} is assumed equal to $F_{\text{AuI}} = 208.0(13) \text{ N m}^{-1}$ in $\text{H}_2\text{S}\cdots\text{AuI}$ is indicated by dashed lines.