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# The C–S bond in ethylthiols: a study of the characteristic Raman vibrational spectral band

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A range of ethylthiol copper clusters (EtSCu<sub>n</sub> where n = 1 to 4) have had their structures and Raman spectra calculated. The calculated spectra were compared to an experimental surface enhanced Raman scattering (SERS) spectrum of ethanethiol (EtSH) on a copper electrode which showed good agreement in peak position. To further analyse the calculated spectra, potential energy distributions (PEDs) of the calculated spectra were obtained and special emphasis was put on the position and PED of the commonly labelled ν(CS) stretch (~650 cm<sup>-1</sup>). The structures (with Cu<sub>n</sub> ≥ 3) appear to be promising avenues for development of an acceptable model of the SERS from EtSH on copper.

**Key words:** ethanethiol, SERS, copper clusters, computational chemistry

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## INTRODUCTION

The use of computational techniques is becoming increasingly common throughout all of the various fields of chemistry [1]. When coupled with spectroscopic investigations it becomes a powerful tool, particularly comparing calculated and experimental spectra. There is also a growing interest [2] in the properties of self-assembled monolayers (SAMs) of thiols on metal surfaces, although there is a considerable amount of uncertainty concerning fundamental properties of these SAMs such as the nature of the sulphyl group – metal bond.

The majority of published *ab initio* calculations utilise Hartree–Fock (HF) theory; this study has utilised density functional theory (DFT). DFT relies on the total electron density, with the electrons “placed” in non-interacting Kohn–Sham (KS) orbitals [3]. But the B3LYP method is a hybrid DFT/HF theory where the physical meaning of the eigenvalues (energies) of the KS orbital still isn’t clear [4]. DFT, particularly B3LYP, geometries and harmonic frequencies of simple models of ethanol trimers [5], hydrogen bonds [6, 7], Cu homogenous catalysts [8] and Cu clusters [9, 10] have been shown to give reliable results.

As part of this group’s ongoing research, these methods have been combined to investigate the Raman scattering (both “normal” and SERS) from a

series of ethylthiols, EtSX, (where X = H, D, and Cu<sub>1</sub> to Cu<sub>4</sub>). The planar copper clusters were used, as one of the aims of the present work was to build an acceptable model of adsorption complexes at Cu electrodes. There are two complications in this relatively simple treatment:

1. The sulphur atom is capable of “binding” either monodentate or bidentate, *i.e.* the sulphur can bond to one (labelled EtSCu<sub>1</sub>Cu<sub>2</sub>) or two atoms (denoted EtSCu<sub>2</sub>Cu<sub>1</sub>) in the Cu<sub>3</sub> complexes.

2. The EtSCu<sub>n</sub> complexes are capable of two conformers: where the torsional angle CCSCu<sub>n</sub> (τ) can be in one of two conformations, τ~60° (*gauche*), and τ~180° (*trans*).

Previous work [11] has shown that for all the conformer pairs, the *gauche* conformer corresponds to the global energy minimum. All of the complexes are neutral with the exception of EtSCu<sub>2</sub><sup>+</sup>, which is believed to be unrepresentative (from the PED data, Table) and thus can be excluded from any further consideration. From the structures, Raman spectra have been calculated (for the molecules in the gas phase at 298 K and 1 atm using the most abundant atomic isotopes) and are presented with a Lorentzian distribution (peak width of 5.0 cm<sup>-1</sup> and a data point spacing of 0.1 cm<sup>-1</sup>). Both of the spectra (Fig. 2 and 3) show an excellent peak position agreement with the experimental SER spectra [12]. The differences in peak intensity between theoretical and experimental spectra can be easily explained as SER peak intensities arise from a very different process compared to “normal” Raman.

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## EXPERIMENTAL

The models of the thiols have had their potential energy surfaces (PESs) derived and it has been found that there were always two minima. The two minima are from two conformers of the EtSX, arising from two values of the C-C-S-X torsion ( $\tau$ ):  $\tau \sim 180^\circ$  (*trans*) and  $\tau \sim 60^\circ$  (*gauche*). In all cases *gauche* was the minimum energy conformer. We have calculated [13] gas phase spectra and force constants. From these potential energy distributions [14, 15] (PEDs) of the principal force constants for all of the vibrational modes have been derived (using redundant internal coordinates [15, 16] to form the normal coordinates). To summarise the results, a term  $E^{C-S}$  is introduced which is defined as the contribution to the PED of the C-S stretch (of length  $r / \text{\AA}$ ) to the commonly labelled  $\nu(\text{CS})$  vibrational mode ( $\sim 650 \text{ cm}^{-1}$ ) in the Raman spectra. This is particularly useful as the CS bond length is both a unique internal coordinate and a normal coordinate.

## RESULTS AND DISCUSSION

The structures of some of the obtained  $\text{EtSCu}_n$  complexes are given in Fig. 1. The obtained calcu-

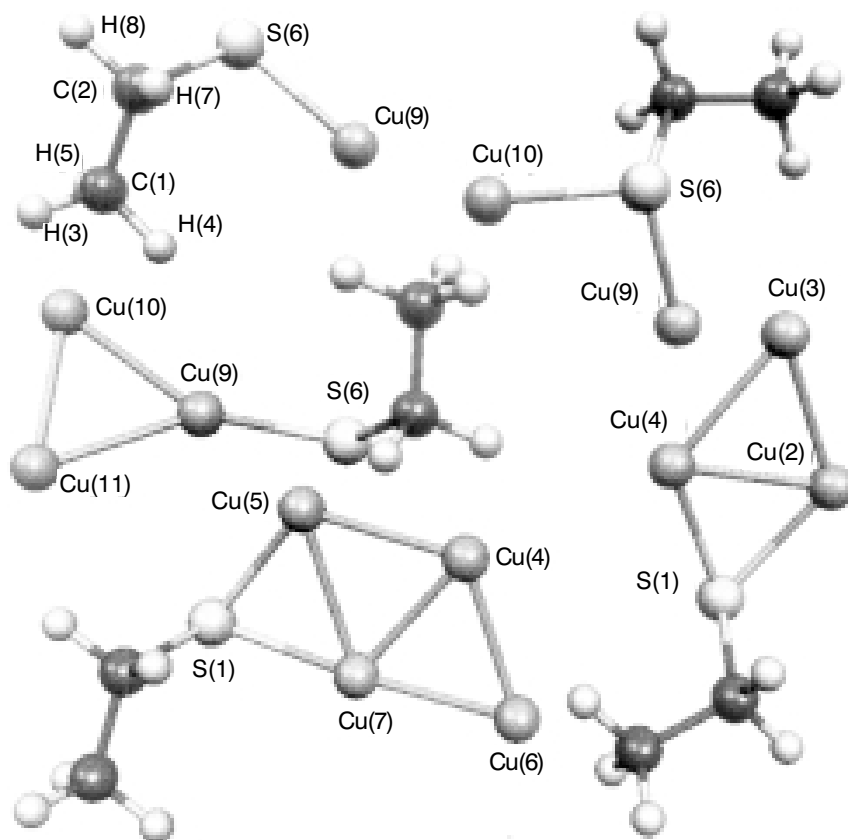


Fig. 1. Representation of the obtained ethylthiol copper clusters (for brevity only the *gauche* conformers are shown). From top to bottom (and left to right as applicable)  $\text{EtSCu}$ ,  $\text{EtSCu}_2$ ,  $\text{EtSCu}_1\text{Cu}_2$ ,  $\text{EtSCu}_2\text{Cu}_1$  and  $\text{EtSCu}_4$

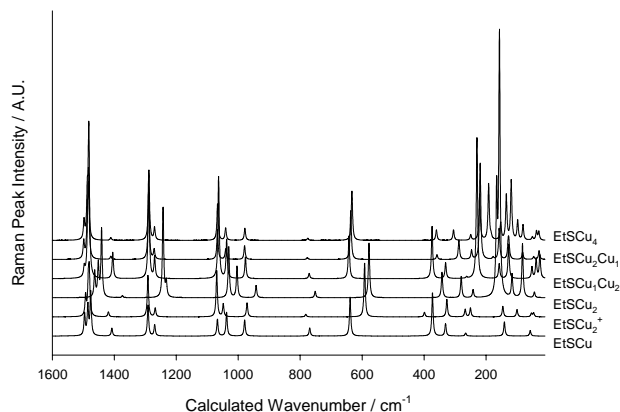


Fig. 2. Calculated Raman spectra of the *gauche*  $\text{EtSCu}_n$  complexes

lated spectra (Fig. 2 and 3) show good agreement in peak position with previously obtained SERS spectra. Before the results are discussed it is worth highlighting the three limitations of the techniques used. The first is that the computational technique used has inherent approximations and it is well known that a full *ab initio* calculation is all but impossible except for the simplest molecules. The other two relate to the spectral calculations and analysis: the calculations assume harmonic motion

(*i.e.* there is no anharmonicity in the calculated vibrations) and that the PED calculations use only the principle force constants (the diagonal values of the force constant matrix) and “ignore” the force constant interactions (the off diagonal values) [17]. Discounting these points, there is good agreement between the calculated and experimental peak positions and the peak “shift” from EtSH to the Cu complexes has also been accurately modelled (Table). The peak shift also indicates a weakening of the bond strength which may be modelled by the increasing bond length. The calculations suggest that the EtSH SAM is *gauche* (based upon the PES data). The effect of  $\tau$  on the conformer pairs is indicative of a steric interaction between X and the  $\text{CH}_2$  group. The effect of deuteration is as expected, with a small change in  $\nu$  and also in  $E^{C-S}$ , indicating a considerable mode mixing as the molecule is of both

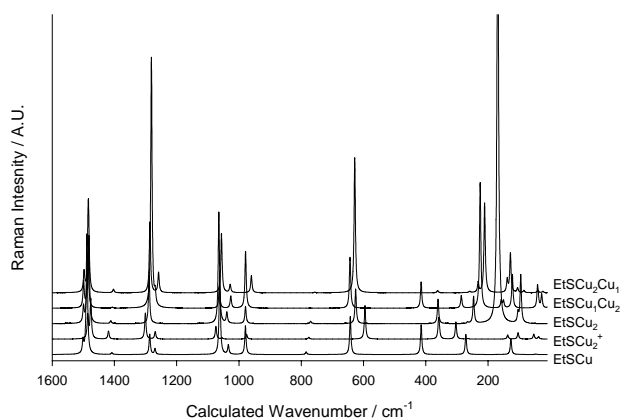


Fig. 3. Calculated Raman spectra of the *trans* EtSCu<sub>n</sub> complexes

to monodentate), as well as to alter the conformation to *trans*, to the copper clusters for EtSCu<sub>4</sub> and EtSCu<sub>3</sub>, but the resultant structures were identical to those presented. The remarkable result for *trans* EtSCu<sub>2</sub> can be easily explained by the fact that this was the only calculated structure that gave a Raman spectrum that had a virtual vibrational mode (*i.e.* one with a vibration with a negative wavenumber) indicating that the molecule is not at a global minimum. Although its position (at  $\nu = 625 \text{ cm}^{-1}$ ) is identical to the experimental result, it must be discounted as a credible model.

The majority of the *trans* conformers (notably in the dimer and EtSCuCu<sub>2</sub>) appear to have lowered values for E<sup>C-S</sup> than for the *gauche*. There appears

Table. Summary of peak position ( $\nu$ ), bond length ( $r$ ) and E<sup>C-S</sup> for the calculated *gauche* and *trans* EtSX complexes and experimental spectra (Expt.)

Molecule	<i>Gauche</i>			<i>Trans</i>			Expt.
	$\nu / \text{cm}^{-1}$	%E <sup>C-S</sup>	$r / \text{Å}$	$\nu / \text{cm}^{-1}$	%E <sup>C-S</sup>	$r / \text{Å}$	
EtS <sup>-</sup>	–	–	–	655	39	1.840	656 <sup>a</sup>
EtSH	645	46	1.844	656	40	1.849	659 <sup>b</sup>
(EtSH) <sub>2</sub> <sup>c</sup>	643	87	1.846	658	15	1.849	659 <sup>b</sup>
EtSH <sup>g</sup> EtSD <sup>t</sup>	657	84	1.846	–	–	1.849	No expt.
EtSD <sup>g</sup> EtSH <sup>t</sup>	629/643	34/82	1.846	699	15	1.849	No expt.
(EtSD) <sub>2</sub>	610/657	34/79	1.846	–	–	1.849	670 <sup>d</sup>
EtSD	660	33	1.844	616/689	21/33	1.849	670 <sup>d</sup>
EtSCu	639	81	1.852	643	40	1.858	625 <sup>e</sup>
EtSCu <sub>2</sub>	578	49	1.891	625	0	1.871	625 <sup>e</sup>
EtS <sup>+</sup> Cu <sub>2</sub>	592	47	1.883	595	47	1.874	625 <sup>e</sup>
EtSCuCu <sub>2</sub>	643	50	1.854	643	13	1.859	625 <sup>e</sup>
EtSCu <sub>2</sub> Cu	637	49	1.862	636	51	1.855	625 <sup>e</sup>
EtSCu <sub>4</sub>	633	25	1.864	f	f	f	625 <sup>e</sup>

<sup>a</sup> 1M EtSH + 3.2 M NaOH; <sup>b</sup> Liquid; <sup>c</sup> *g* and *t* denote *gauche* and *trans* conformers, (EtSX)<sub>2</sub> denotes a dimeric form; <sup>d</sup> EtSD formed by stirring a D<sub>2</sub>O emulsion of EtSH (5%) for a week at room temperature, removing the non-aqueous fraction and drying it over sodium sulphate; <sup>e</sup> SERS: EtSH adsorbed on Cu electrode at E = -0.400 V, solution: 0.1 M Na<sub>2</sub>SO<sub>4</sub> + 0.01M H<sub>2</sub>SO<sub>4</sub>; <sup>f</sup> no *trans* structure obtained.

small size and low symmetry [18, 19] (the symmetry group C<sub>s</sub> has been assumed for all of the calculations).

Comparison of the calculated  $\nu(\text{CS})$  peak position and the calculated CS bond lengths for the *gauche* and *trans* ethylthiol copper clusters shows clear trends, although the *gauche* conformers appear to be “better” results – this may be an effect of *gauche* being the preferred conformation, *i.e.* it is the lower energy conformer for each of the pairs (Fig. 4).

Attempts were made to alter the position of the sulphur bond (and to change the S bonding from bidentate

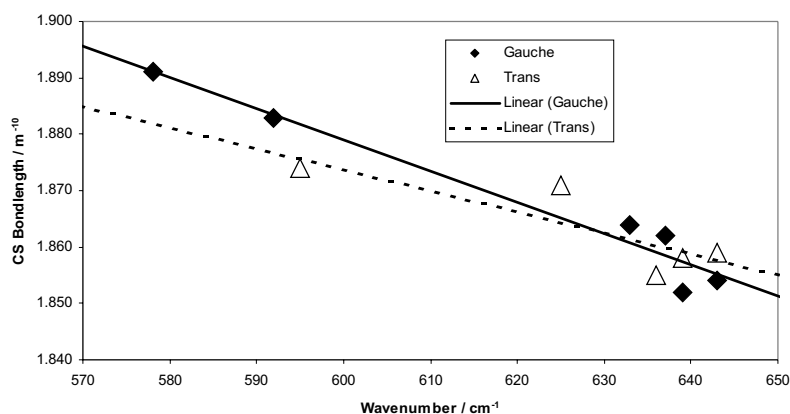


Fig. 4. Comparison of the CS bond length (for the complexes EtSCu<sub>n</sub>, where n = 1 to 4) with the position of the  $\nu(\text{CS})$  vibration at  $\sim 650 \text{ cm}^{-1}$ . Linear trends are shown for the *gauche* and *trans* conformers

to be no clear pattern regarding the effect of X (in EtSX) on either  $\nu$  or  $E^{C-S}$ .

## CONCLUSIONS

From our data the EtSCu and EtSCu<sub>2</sub> complexes appear to be good candidates for further study, yet it is believed that these copper clusters are too simple to provide a “believable” model of the Cu surface. Thus, complexes with three or more Cu atoms seem to be better candidates for further analysis. The spectral data (Figs. 2 and 3) show that this relatively trivial treatment is a promising avenue for development of a sufficiently accurate model of the SERS of SAMs. “Fast” and “powerful” PCs have been used in the majority of previous studies that used “supercomputers” trying to build small models of a copper surface. The present study has aimed to develop simple models, as part of the analysis is derivation of PEDs. The effect of deuteration on the dimers (and the *gauche* / *trans* structures) is as yet unexplained. Full PEDs of the complexes are available from the authors.

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## S. Bloxham, O. Eicher-Lorka, R. Jakubėnas, G. Niaura ETANTIOLIŲ C–S JUNGTIŠ: BŪDINGOS JUOSTOS RAMAN SPEKTRUOSE TYRIMAS

### S a n t r a u k a

Apskaičiuotos etantiolio–vario kompleksų (EtSCu<sub>n</sub>; ėia n kito nuo 1 iki 4) struktūros ir Ramano spektrai. Eksperimentiniai etantiolio, adsorbuoto ant vario elektrodo, sustiprinti paviršiumi Ramano spektrai palyginti su apskaičiuotaisiais. Spektrinių juostų dažniai gerai sutapo. Ypaė daug dėmesio skirta C–S jungties virpesių ties ~650 cm<sup>-1</sup> analizei. Parodyta, kad perspektyviausi kompleksai modeliuojant etantiolio adsorbciją ant Cu elektrodo yra tie, kuriuose Cu<sub>n</sub> ≥ 3.