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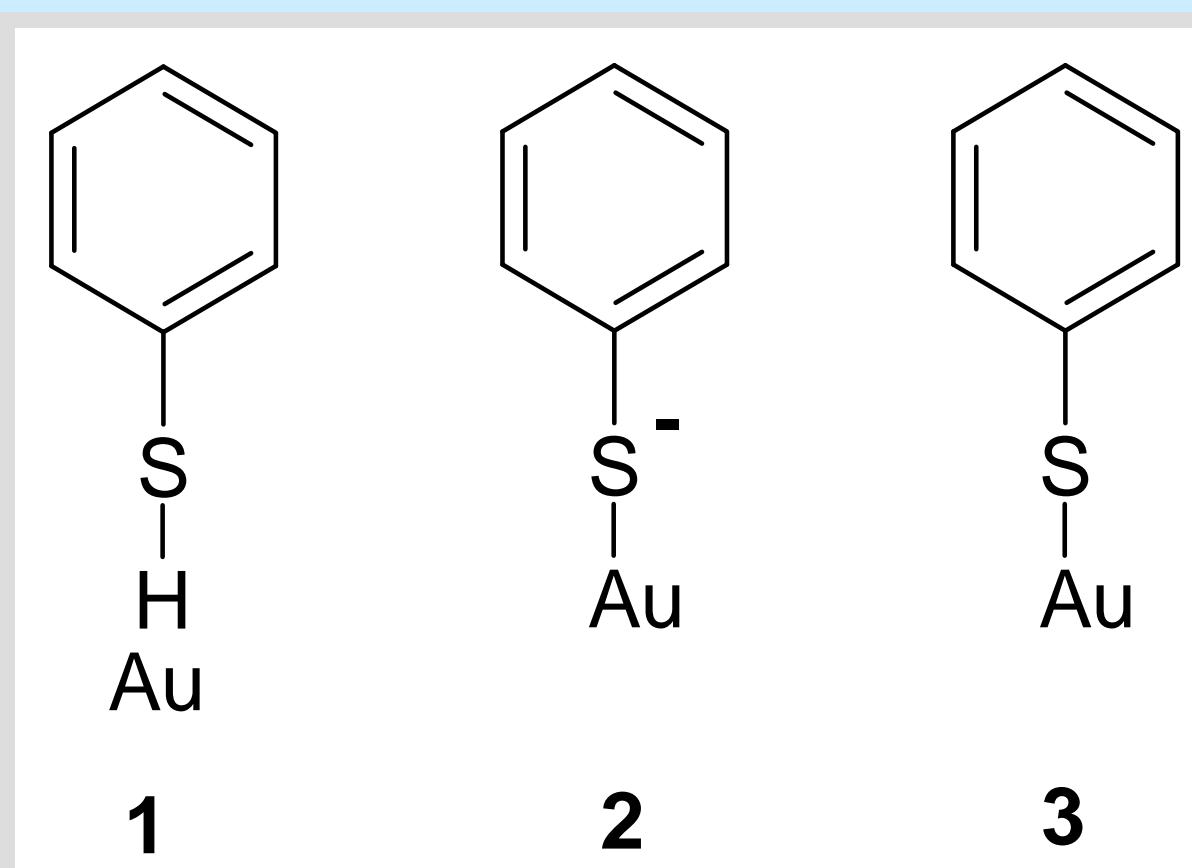
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Introduction

Self-assembled monolayers SAMs on various substrates have attracted large interest from scientists and engineers because of their fundamentally interesting properties and their attractive applications. In electrochemistry SAMs with gold as the substrate and sulfur-containing molecules as building blocks have been studied intensely. The large binding energy of the gold-sulfur bond ($167.15 \text{ kJ}\cdot\text{mol}^{-1}$)¹ provides the driving force for strong and stable attachment, a wide variety of organic molecules offer structural variations finally affecting the intermolecular interactions and thus structure and properties of the SAM. Of particular interest are molecules and building blocks with multiple bonds, they offer structural rigidity and options of electronic intermolecular interaction. Somewhat surprisingly studies of the behavior of thiophene TP as the most simple molecule are scant and incomplete. The results presented here are an attempt to close this gap.

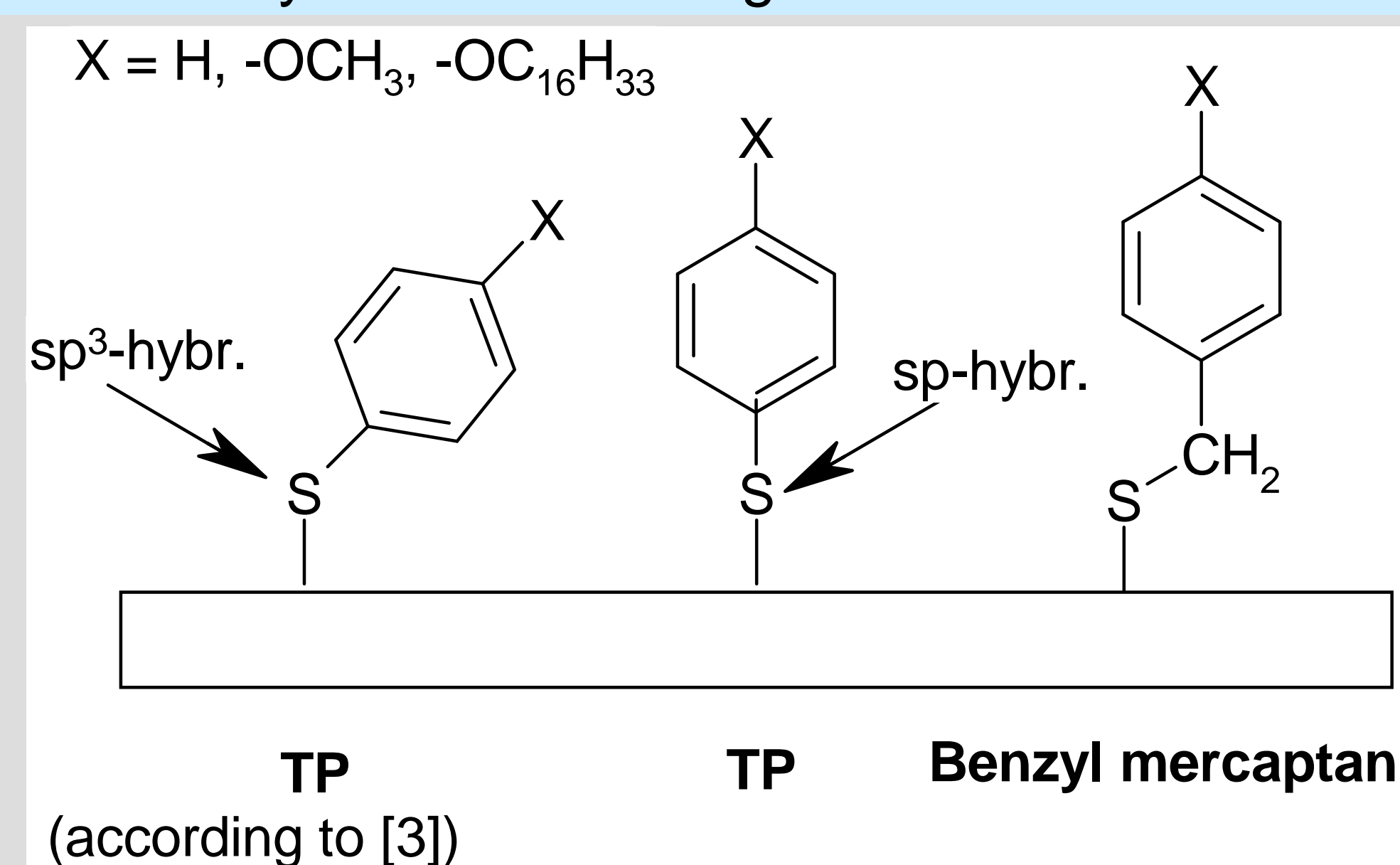
The molecule

Various modes of interaction have been modeled²:



Adsorption as thiolate **2** was concluded, but the calculated wavenumber of the Au-S-stretching mode of 334 cm^{-1} differed wildly from the experimentally observed one at 275 cm^{-1} implying a rather limited predictive value, possibly because of the assumption of only one gold atom representing the metal surface.

Data obtained with infrared spectroscopy and various surface-analytical techniques by Tao et al.³ for a variety of sulfur-containing molecules yield the following overview:

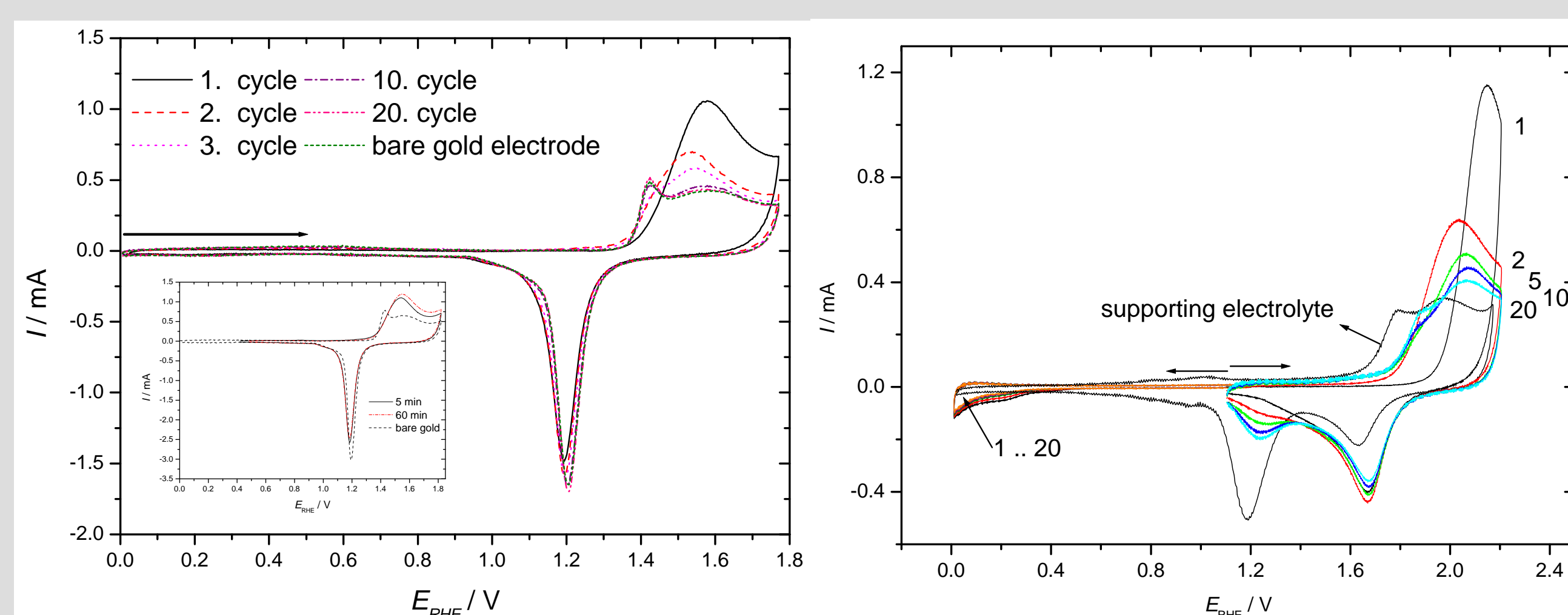


Experimental approach

Cyclic voltammetry of a polycrystalline gold electrode in contact with unbuffered neutral and acidic electrolyte solutions was performed to identify the electrode potential window of double layer behavior without Faradaic processes, it also helped in identifying possible modes of TP desorption. *in situ*-Surface enhanced Raman spectroscopy under the same experimental conditions in a wide range of wavenumbers was employed to identify the mode of TP-gold interaction, the adsorbate molecule orientation and – if any – possible intramolecular interactions.

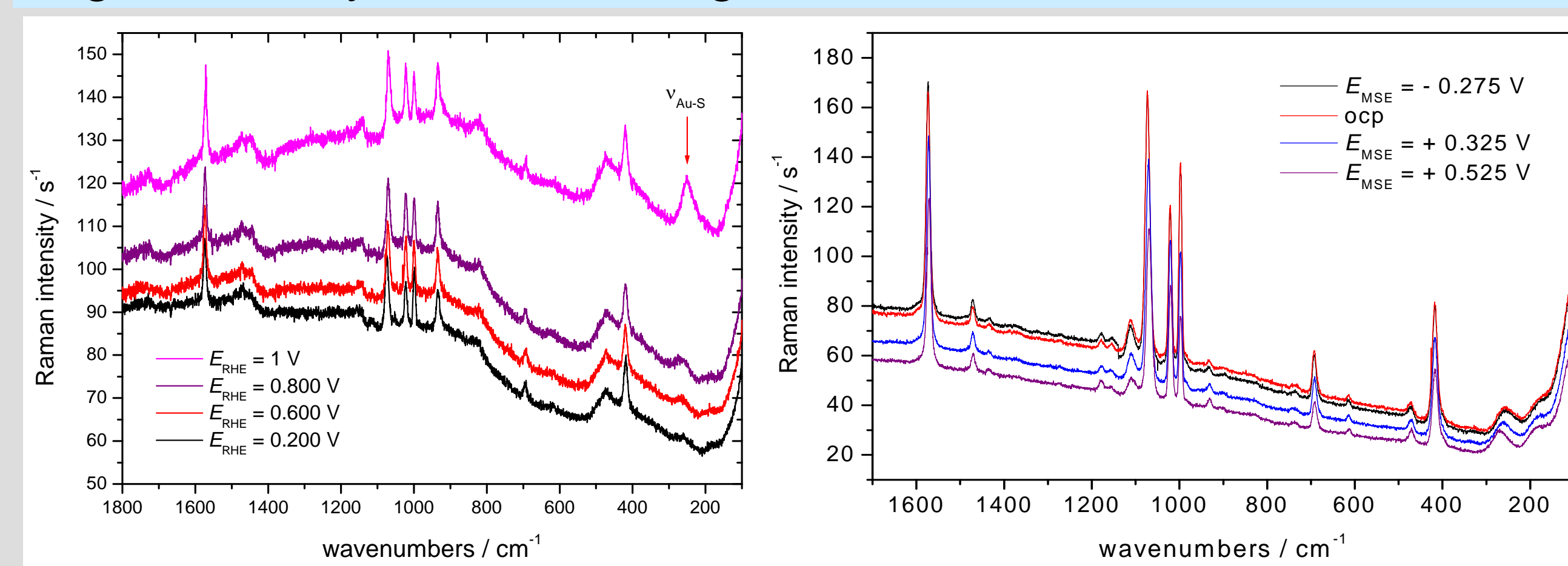


Results and Discussion



Cyclic voltammograms of a gold sheet electrode without/with adsorbed TP in an aqueous solution of left: 1 M HClO_4 ; right: 0.1 M KClO_4 (full cycles, partial cycles starting at spontaneous established rest potential, arrows indicate direction of scan with starting point of arrow indicating initial electrode potential); $dE/dt = 0.1 \cdot \text{V}\cdot\text{s}^{-1}$, room temperature, nitrogen purged. Insert: Effect of adsorption time

In both solutions anodic oxide layer formation is inhibited by the adsorbed TP, the anodic current finally observed is larger with the neutral solution. Taking corresponding changes in the cathodic reduction of the anodically formed layer the amount of adsorbed TP is larger in case of the neutral solution, this corresponds to a larger intensity of scattered light in SERS.



SER-spectra of TP adsorbed on a polycrystalline gold electrode in contact with an aqueous solution of left: 1 M HClO_4 ; right: 0.1 M KClO_4 , room temperature, nitrogen purged.

A new band around 265 cm^{-1} with its position hardly depending on electrode potential in acidic solution (left) and shifting to higher wavenumbers with more positive electrode potential in neutral solution (right) support in the latter solution the suggested adsorption as thiolate (**2**), in the acidic solution molecular adsorption (**1**) is more likely. The majority of bands is attributed to in plane motions of the adsorbed molecule (assuming C_{2v}^y symmetry) implying a more or less perpendicular orientation.

Literature

- 1 A. Ulman, Chem. Rev. **96** (1996) 1533.
- 2 S.J. Li, D.Y. Wu, X.Y. Xu, R.N. Gu, J. Raman Spectrosc. **38** (2007) 1436.
- 3 Y.-T. Tao, C.-C. Wu, J.-Y. Eu, W.-L. Lin, K.-C. Wu, C.-h. Chen, Langmuir **13** (1997) 4018.

Conclusions and Outlook

A mode of interaction between thiophenol and a poly-crystalline gold surface involving formation of a gold-sulfur bond is concluded from appearance of the respective band of the associated stretching mode, a perpendicular orientation is deduced from the dominance of in-plane vibrational modes.

Acknowledgements

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