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Mass Spectrometry & Purification Techniques

Commentry

Commentary on “J. Plaickner et al., Adsorption of toluene-3,4-dithiol on silver islands investigated by surface-enhanced Raman spectroscopy”: mass spectrum and sulfur bonds

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COMMENTRY

Mass spectrum of toluene-3,4-dithiol (TDT)

The TDT molecular gas flows into the main vacuum chamber from an external vacuum line. The gas flow is controlled by using a leak valve and observing the pressure change in the main chamber. The resulting gas in the main chamber is a mixture between TDT and residual components. In order to detect the presence of TDT in the main chamber, a mass spectrum was measured using a quadrupole mass spectrometer (QMS). The mass spectrum shows characteristic peaks of TDT at mass-to-charge ratios of 156, 123 and 92, in agreement with NIST Chemistry Webbook, as shown in (Figure 1).

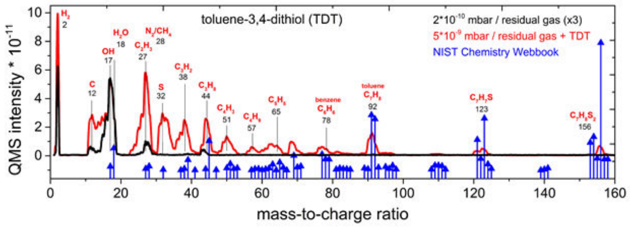

Figure 1: Mass spectrum of residual gas in the UHV chamber (black), of TDT gas + residual gas (red) and of TDT in literature (blue arrows). Assignment of elements is done according to tables provided by Pfeiffer Vacuum.

The mass spectrum measured before starting the TDT gas flow, indicating the initial conditions, is shown for comparison. In addition to the three TDT fingerprints, several other peaks are observed at lower masses, mainly associated to carbon compounds originated in secondary reactions. Two decomposition reactions of TDT are schematically depicted in (Figure 2).

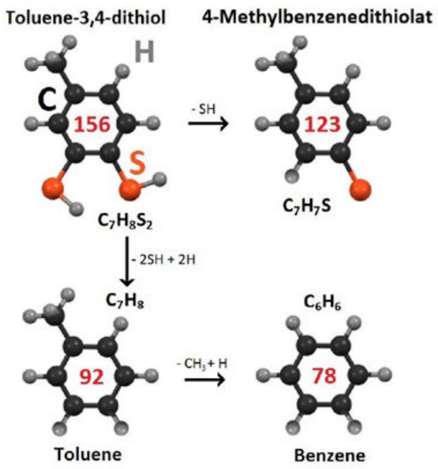

Figure 2: Schematic representation of two common decomposition reactions of toluene-3,4- dithiol.

From the observed mass spectrum we cannot exclude that other carbon compounds bind to the SERS substrate apart from TDT. However, the interpretation of these findings require following considerations:

- The distance between the leak valve and the QMS filament is much larger than the distance between leak valve and sample surface (which is only few centimeters). A fraction of the molecules attaches to the internal surfaces of the chamber and other obstacles before reaching the QMS filament.
- A fraction of the molecules is dissociated by the QMS filament itself.

Therefore, the measured QMS spectrum is not considered to be indicative of the relative TDT gas concentration in the vicinity of the sample. Nonetheless, the spectrum shows clearly the presence of TDT molecules in the main chamber.

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Considerations on the disordered adsorption

The SERS substrate used is composed by Ag islands, separated by gaps of SiO2, the native oxide layer on silicon (details on the preparation can be found in ref. [1]). The surface exhibits a high roughness due to the coexistence of Ag clusters of different dimensions. Thus, it is reasonable to expect that the molecular adsorption on the substrate can be only partially ordered. As known from literature, the SERS enhancement has its maximum at specific positions at interspaces between Ag islands [2].

Sulfur bonds

The intense vibration at 2552 cm-1 in the Raman spectrum of TDT powder (article: Figure 2) is assigned to S-H stretching, according to our DFT calculations. The clear absence of this band in the SERS spectrum is a strong argument in favor of a new chemical bond involving both sulfur atoms in the TDT molecule, which are no longer terminated by hydrogen. Let us consider the different possibilities:

- Both sulfur atoms are bonded to the substrate
- One sulfur atoms is bonded to the substrate, while the other is bonded to another molecule forming a TDT dimer through a S-S bond
- TDT dimers are attached to the substrate in other ways, e.g. through carbon atoms

The presence of clusters or multilayers of molecules should be accompanied by the appearance of new vibrational modes, for example S-S stretch vibrations if the molecules are bonded through S-S bonds (article: ref. [40]). For technical reasons, in our experiment, the SERS spectrum is not accessible in the spectral range between 470 and 560 cm-1, where S-S vibrations were observed for dimerized TDT molecules (article: Figure 3). However, we can support the scenario 1) with other arguments.

The presence of multilayers of TDT molecules on the surface can be excluded considering the following points:

- It was observed that the exposure of the SERS substrate to TDT gas for longer times is not affecting at all the SERS spectrum, indicating that surface is “saturated” with molecules.
- Several modes observed in Raman of TDT powder (article: Figure 3c) are largely unaffected in the SERS spectrum (article: Figure 3a), for example the vibrations at 1037 (sci-CH3), 1379 (wag-CH3) and 2912 cm-1 (ν-CH3), indicating that the CH3 group is exposed, and the vibrations at 629 (δ-ring), 867 (δ-ring) and 1270 cm-1 (ν-ring), suggesting the absence of multilayers formed through hydrogen bonds at the ring (article: Table 1, sites H13, H16, H17).

These points suggest that the surface is covered by 1 layer of TDT molecules and that his coverage is a saturation condition. Point b) is not compatible with the formation of clusters through other bonds than S-S bonds, since this should affect more clearly vibrations associated to ring or methyl group, thus excluding scenario 3). On the other hand, if only one sulfur atom is bonded to the metal, while the other is “pendent”, then both S-H stretching and metal-S stretching vibrations should be observed (article: ref. [18]), excluding scenario 2).

The adsorption of dithiols on Ag through both thiol groups, proved by the disappearance of the free S-H stretching Raman band and appearance of a Ag-S band, was reported in studies on other dithiols, such as 1,2-BDT (article: ref. [16]) and 1,3-BDT [4]. In the SERS spectrum we observe a feature at 224 cm-1, not visible in the ordinary Raman spectrum of TDT powder, which is compatible with the Ag-S stretching band observed for other dithiols (article: ref. [33]). Further, we observe features at 161 and 295 cm-1 that could be signatures of Agn-S-C complexes (article: ref [36]), indicating that the coordination of S with Ag occurs through different coordination mechanisms. These observations support scenario 1).

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