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Reply to Comment on 'Local methylthiolate adsorption geometry on Au(111) from photoemission core-level shifts'

The key contention of Cossaro *et al.*[1], in criticising our interpretation of the relative photoemission intensities of the Au 4f core-level-shifted components from the Au(111)($\sqrt{3}\times\sqrt{3}$)R30°-CH₃S surface [2], is that photoelectron diffraction prevents one relating these intensities to the relative occupation of surface Au atoms in different bonding states. They show independently-obtained data from both the clean and thiolate-covered surface, under conditions similar to those of our original paper, but at two different polar emission angles, normal emission and 60 degrees. These spectra show clear differences in both the surface-to-bulk component ratios, and in the ratio of the two surface components *S*, and *T*, that they attribute (most probably correctly) to photoelectron diffraction.

Photoelectron diffraction can lead to strong variations in both the angle- and energy-dependence of photoemission from core levels of atoms at the surface of a solid. This elastic backscattering effect can be particularly strong at the low kinetic energies (~50 eV) used in these studies. Our measurements of these effects from ~90 different adsorbate systems [3] show that, particularly for emitter atoms in high-symmetry sites (as is expected in the present case), one generally sees the strongest effects (up to ~50%) in the most-symmetric directions, relative to either the crystal, or the local bonding geometry; one such direction is normal emission. At larger polar angles, like 60 degrees, the modulations seen are usually much weaker (<10%), unless the emission is in a strong backscattering direction in a high-symmetry azimuth. The data we reported in our Letter [2] were measured in two different low-symmetry azimuths, namely 5° from <110>, and 9° from <211>. These two sets of measurements yielded identical values of the intensity ratios of the core-level-shifted components, *S:T* and *S+T:B*. This observation, and the fact that these high-angle low-symmetry geometries are ones in which photoelectron diffraction may be expected to play a much reduced role, lead us to conclude that photoelectron diffraction is most unlikely to have significantly influenced the assumed linearity between detected photoemission signal and relative site occupation in our data.

By contrast, the very large difference seen in the experiments of Cossaro *et al.* at normal emission is entirely consistent with the expectation of much stronger photoelectron diffraction effects in this direction.

A further issue raised by the analysis of Cossaro *et al.* concerns the extent to which the multiple-peak fitting of the measured spectra should be constrained, particularly with regard to spectral widths. Free-parameter fits are always superior in quality, but are not necessarily physically meaningful. The fits we showed in our Letter used constraints that we judged to be physically reasonable and gave a $S:T$ intensity ratio of 3.1 ± 0.2 . For unconstrained fits, as used by Cossaro *et al.*, we reported a $S:T$ ratio of 2.2 ± 0.2 , identical to their value in a similar emission geometry. However, our constrained fits ensured that the relative intensities of the bulk and surface signals remained similar before and after thiolate adsorption. By contrast, Cossaro *et al.* argue that the reduced intensity of the S peak of their fits is to be expected; other studies of longer-chain alkane thiol adsorption on gold have indicated that the S peak vanishes. Why should the relative intensity of the surface and bulk emission signals be significantly changed by an adsorbed layer that will have a similar attenuation effect on both signals? There seems no physical argument to justify this large change of relative intensities. In earlier studies, the core-level-shift of the S peak relative to the B peak may have been too small to detect, making the S peak *appear* to vanish, but in the present case a clearly-identified S peak, albeit with a reduced core-level-shift relative to that on the clean (reconstructed) surface, is still identified after thiol adsorption.

Of course, our analysis is based on the assumption that the thiolate-covered surface is well-ordered, and that the Au 4f photoemission spectra can be described by three components, although we discussed the possible influence of a fourth component [2]. Cossaro *et al.* prefer the complex disordered structural model of Mazzarello *et al.* [4], but at least one aspect of this model, a significant co-occupation of bridging sites by thiolate species, is clearly incompatible with other experimental data [5].

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