

Measuring Orientation and Surface Interactions of Heterogeneous Catalysts using 2D SFG

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Using 2D SFG spectroscopy, we characterize a CO₂ reduction catalyst on gold surface. We find that by analyzing lineshape of cross-peaks, the interactions between vibrational modes and gold surface can be revealed. Further, we demonstrate a general method to measure the molecular orientation and its distribution on surface.

In this abstract, by studying a CO₂ reduction catalyst, Re(diCN-bpy)(CO)₃Cl on gold surface, we demonstrated that heterodyne 2D SFG is (1) sensitive to interaction between molecules and metal substrates,¹ and (2) can unambiguously determine the molecular orientation on an ensemble-averaged monolayers,² which overcome a 17-year challenge that limited SFG spectroscopy from accurately measuring the surface molecular orientations.³

1. The 2D SFG spectrum (Fig.1a) of the CO modes of Re-complex all show large inhomogeneous broadening. However, the center-line-slope analysis indicates that the A'(1) peak of Re-complex are more tilted than the A'(2) peak from the same complex. By analyzing the lineshape of the cross-peaks, we concluded that the lineshape difference between A'(2) is more homogeneously broadened than the A'(1) mode. The cause of additional homogeneous broadening is likely that A'(2) interact stronger with the image dipole of gold surface than the A'(1) mode, which also indicate that A'(2) are spatial more close to the surface than A'(1). The sensitivity of 2D SFG to surface interactions could be extended to many other interfaces, such as liquid membrane and water interfaces.
2. We demonstrate the 2D SFG can unambiguously determine orientation information (mean-tilt-angle and angular distribution) for an ensemble-averaged surface monolayer. Using this method, we successfully circumvent the 'narrow angular distribution' assumption that could introduce inaccuracy in molecular angle measurements. As a result, we solve the well-known 'magic angle' ambiguity in SFG spectroscopy.

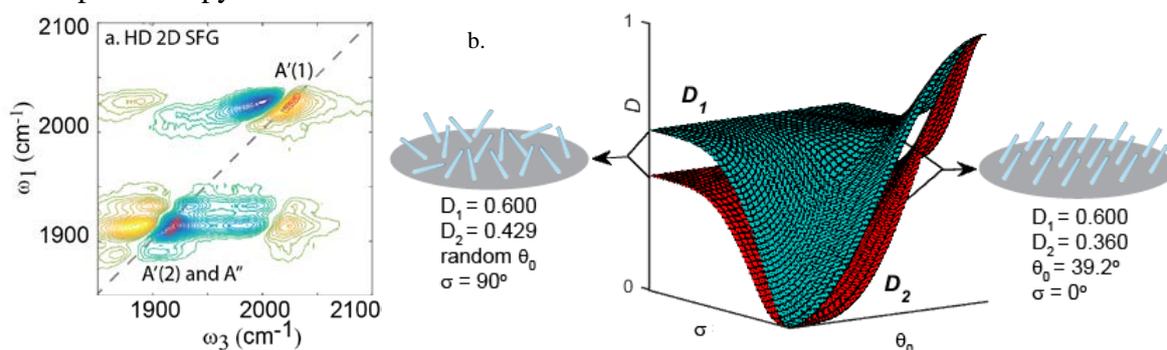


Figure 1. (a) HD 2D SFG spectrum of Re(diCN-bpy)(CO)₃Cl on gold surface. The center-line-slope indicate that A'(2) mode has stronger interactions with the surface than A'(1) mode. (b) by determine two independent orientation parameters, the mean orientation and orientation distribution of an ensemble averaged monolayer can be unambiguously determined.

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