

# Vibrational spectroscopic identification of carbon absorbed beneath the metal surface

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**Abstract:** Carbon dissolved in transition metals, also known as subsurface or bulk carbon, plays a critically important role in many technological processes. Subsurface carbon atoms have been recognized as essential for the catalytic growth of carbon nanotubes, graphene synthesis, and operation of direct carbon fuel cells. Despite the recognition of carbon bound beneath the surface of a metal as a crucial species in many chemical and catalytic processes, it has not been identified spectroscopically using methods that do not destroy the sample. We report the first vibrational spectroscopic identification of bulk carbon in a Au-Ni(111) surface alloy by high-resolution electron energy loss spectroscopy (HREELS) and its unambiguous synthesis via collision-induced absorption (CIA). The vibrational modes of carbon embedded beneath the surface alloy are shown to be distinguishable from surface-bound carbon based on their intensity dependence on the incident electron energy. Three distinct peak features, centered around 690, 500, and 380  $\text{cm}^{-1}$ , are assigned to modes of subsurface carbon atoms that are located at octahedral sites and triangular misfit dislocation loops of the second layer of Au/Ni surface alloy. Additional confirmation of these assignments come from their appearance after CIA experiments, in which surface bound carbon atoms are hammered into the bulk by collisions with energetic gas phase Xe atoms, accompanied by a decreased intensity of the surface carbon mode at 540  $\text{cm}^{-1}$ . This work reports for the first time a new method to spectroscopically identify interstitial carbon below the surface of a solid metal and a non-thermal method to synthesize it.

