

A combined experimental and theoretical study on dissociative ionization and dissociative electron attachment to the heteronuclear FEBID precursor; $\text{HFeCo}_3(\text{CO})_{12}$

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Synopsis Here we present a combined experimental and theoretical study on dissociative ionization (DI) and dissociative electron attachment (DEA) to the heteronuclear FEBID precursor; $\text{HFeCo}_3(\text{CO})_{12}$ with the emphasis on the DEA process, the nature of the attachment and the dissociation dynamics.

Low energy electron interaction with organometallics has received appreciable attention in recent years [1], specifically in relation to the use of these compounds as precursors in focused electron beam induced deposition (FEBID) [2,3]. For the fabrication of alloy nanostructures through FEBID, the use of heteronuclear precursors is an attractive alternative to mixed gas or multiple gas inlet systems. To date, however, the use of heteronuclear organometallics in FEBID and related studies on such potential precursor molecules are limited. In fact, the only FEBID work with heteronuclear precursors we are aware of are that with $\text{HFeCo}_3(\text{CO})_{12}$ [4] and unpublished work with $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$ [5]. In the first case, i.e., $\text{HFeCo}_3(\text{CO})_{12}$ a typical metal purity of 80% with 1:3 FeCo ratio was reached, clearly attesting the feasibility of using bimetallic precursors for pure alloy deposition.

Motivated by the successful deposition of alloy structures using $\text{HFeCo}_3(\text{CO})_{12}$ and the role of low energy secondary electrons in FEBID (see e.g. ref [1] and refs. therein), we have studied the gas phase decomposition of this compound through dissociative electron attachment and dissociative ionization.

The two main channels observed in DEA to $\text{HFeCo}_3(\text{CO})_{12}$ are the loss of the apical Fe-group, mainly as $\text{Fe}(\text{CO})_4^-$, and sequential CO loss [5]. The first of these two channels agrees well with quantum chemical calculations conducted at the BP86/def2-TZVP level of theory [6]. The calculations offer a consistent picture of our experimental observations with weakening of the bonding of the apex $\text{Fe}(\text{CO})_3$ group to the Co_3 plane and appreciable spin density at the apical iron, reflecting the observed efficiency of the $\text{Fe}(\text{CO})_4^-$ formation. The sequential CO loss, the second dominating channel, comprises the loss of 1 and 2 CO close to 0 eV up to the loss of all 12 CO ligands, which appears at around 20 eV incident electron energy – about 12 eV above its ionisation energy. To elucidate this remarkable attachment of electrons about 12 eV above the ionisation limit, we conducted calculations of the state densities of this compound in comparison to model compounds both with and without the metal core [7]. The calculations reveal a

high density of metal-CO antibonding orbitals about 3 eV above the HOMO, while the density of antibonding metal-metal orbitals is low. The accommodation of the large amount of excess energy associated with the attachment process is thus ascribed to a quasi-continuum of resonant states associated with multiple electronic excitations within the metal-CO antibonding "band".

In dissociative ionization, the fragmentation pattern observed is similar to DEA in the sense that the loss of the iron-centred apex and the sequential CO loss are the dominating channels. However, in DI the intensity ratios within the respective channels are very different from that in DEA. Here, the apex loss appears through formation of $\text{Fe}(\text{CO})_n^+$ with $n = 1-5$, all with comparable intensity, and the main CO loss channels are associated with the loss of 5 to 12 CO; the bulk of the intensity in DEA is on the loss of 2 CO ligands.

In the current contribution, we discuss the mechanisms behind the observed DEA processes in conjunction with our calculations, as well as the efficiency of the DI vs. the DEA channels in conjunction with the decomposition pathways and deposit formation from thin layers of $\text{HFeCo}_3(\text{CO})_{12}$ at surfaces. These will be presented in a separate poster.

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