A combined experimental and theoretical study on dissociative ionization and
dissociative electron attachment to the heteronuclear FEBID precursor;
HFeCo$_3$(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; HFeCo$_3$(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 depo-
sition (FEBID) [2,3]. For the fabrication of alloy nanostructures through FEBID, the use of hetero-
nuclear 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 mol-
cules are limited. In fact, the only FEBID work with heteronuclear precursors we are aware of are that
with HFeCo$_3$(CO)$_{12}$ [4] and unpublished work with H$_2$FeRu$_3$(CO)$_{13}$ [5]. In the first case, i.e., HFeCo$_3$(CO)$_{12}$
a typical metal purity of 80% with 1:3 FeCo ratio was reached, clearly attesting the feasibility of using bimetal-
lic precursors for pure alloy deposition.

Motivated by the successful deposition of alloy structures using HFeCo$_3$(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 decomposi-
tion of this compound through dissociative electron attachment and dissociative ionization.

The two main channels observed in DEA to HFeCo$_3$(CO)$_{12}$ are the loss of the apical Fe-group, mainly as Fe(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 con-
sistuent picture of our experimental observations with weakening of the bonding of the apex Fe(CO)$_3$ group
to the CO plane and appreciable spin density at the apical iron, reflecting the observed efficiency of the
Fe(CO)$_4^-$ formation. The sequential CO loss, the sec-
dominateing 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 en-
ergy - 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
attaching process is thus ascribed to a quasi-
continuum of resonant states associated with multiple
electronic excitations within the metal-CO anti
bonding "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 differ-
ent from that in DEA. Here, the apex loss appears
through formation of Fe(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 mecha-
nisms behind the observed DEA processes in conjunc-
tion 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 HFeCo$_3$(CO)$_{12}$ at surfaces. These will be
presented in a separate poster.

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