Low Energy Electron Interactions with Precursor Molecules Relevant to Focused Electron Beam Induced Deposition

Sarah Franziska Engmann

Faculty of Physical Sciences
School of Engineering and Natural Sciences
University of Iceland
2013
LOW ENERGY ELECTRON INTERACTIONS WITH PRECURSOR MOLECULES RELEVANT TO FOCUSED ELECTRON BEAM INDUCED DEPOSITION

Sarah Franziska Engmann

180 ECTS thesis submitted in partial fulfillment of a Doctor Philosophiae degree in Chemistry (Physical Chemistry)

Ph.D. Supervisor:
Prof. Oddur Ingólfsson

Ph.D. committee:
Prof. Michael J. Brunger
Prof. Štefan Matejčík

Opponents:
Prof. Michael Allan
University of Fribourg, Switzerland

Prof. Cornelis W. Hagen
Delft University of Technology, The Netherlands

Faculty Representative:
Prof. Hafliði Pétur Gíslason

Faculty of Physical Sciences
School of Engineering and Natural Sciences
University of Iceland
Reykjavík, March 2013
Low Energy Electron Interactions with Precursor Molecules Relevant to Focused Electron Beam Induced Deposition

Dissertation submitted in partial fulfillment of a Doctor Philosophiae degree in Chemistry (Physical Chemistry)

Copyright © 2013 Sarah Franziska Engmann, unless otherwise stated. Some rights reserved.

This work is licensed under a Creative Commons Attribution 3.0 Unported License, unless otherwise stated.

Faculty of Physical Sciences
School of Engineering and Natural Sciences
University of Iceland
VRII, Hjarðahaga 2-6
107 Reykjavík
Iceland
Telephone: +354 525 4800

Bibliographic information:
Sarah Franziska Engmann,
“Low Energy Electron Interactions with Precursor Molecules Relevant to Focused Electron Beam Induced Deposition” Ph.D. dissertation, Faculty of Physical Sciences, University of Iceland, 2013.

ISBN 978-9935-9069-7-7

Printing:
Háskólaprent ehf., Fálkagötu 2, 107 Reykjavík

Reykjavík, Iceland, March 2013
I would like to start with thanking the University of Iceland research fund for my stipend and RANNÍS for project related funding. I would also like to acknowledge the ECCL COST Action CM0601 for funding my visits to Comenius University, Bratislava.

I would like to thank my supervisor Prof. Oddur Ingólfsson for an interesting and challenging project, as well as the basement crew Bennedikt Ómarsson, Elias H. Bjarnason, Frímann H. Ómarsson and Dr. Helga D. Flosadóttir for the past few years. Frímann deserves special thanks for taking care of everything Icelandic in this thesis.

I specifically wish to thank Dr. Michal Stano and Prof. Štefan Matejčík for hosting me during my stays in Bratislava, where I could perform the bulk part of my Ph.D. work. I also thank Prof. Štefan Matejčík and Prof. Michael J. Brunger for serving on my PhD committee and scrutinizing my writing. I also want to thank Prof. Michael Allan and Prof. Cornelis W. Hagen for acting as my opponents during the doctoral defense.

Furthermore, I would like to acknowledge Katrín Lilja Sigurðardóttir and Prof. Ingvar H. Árnason for teaching me, and allowing me, to use their glovebox. I would also like to thank Prof. Sveinn Ólafsson and Dr. Kristján Leósson to enable me an excursion to thin film physics and clean-room work. Special thanks also to Tryggvi K. Tryggvason and Mohammad Shayesteh for welcoming me on their territory. Furthermore, I would like to take the time to thank the administrative staff at Rauno and HÍ, particularly Anna Kristín, Alda, and Tona.

Last, but definitely not least, I would like to thank Dr. Simon Klüpfel for an excellent thesis template and Dr. Peter Klüpfel for both scientific and moral support during the past years, his love, and a great time outside the lab.
Abstract

In his 1959 speech “There is plenty of room at the bottom” \(^1\), Richard Feynman shared his visions on how to manipulate matter on a small scale, down to individual atoms. Fifty years later, nanotechnology has become an essential tool in various disciplines, including advanced electronics, biotechnology and medicine. As a result, there exists an increasing demand for novel nano structures with tuneable physical and chemical properties. One viable way to meet this demand is through focused electron beam induced deposition (FEBID), which allows deposition of structures on the nanometer scale. Remarkable milestones have already been reached, yet there remain some challenges and goals to be met. For example, FEBID structures generally contain levels of impurities that adversely influence their properties. In addition, the theoretically possible sub-nanometer scale has still to be reached experimentally. These limitations are partially attributed to low energy electrons (< 50 eV) generated during the FEBID process, yet no systematic study on their mode of action in FEBID has been carried out.

This Ph.D. project addresses the question of how low energy electrons may affect the purity and resolution in FEBID, with a special focus on dissociative electron attachment (DEA) and dissociative ionization (DI). It aims at laying down a stepping stone for understanding the underlying physics of the deposition process by identifying and characterizing the processes operative at a molecular level, unburdened by the high degree of complexity encountered in FEBID. More specifically, gas phase DEA and DI studies of the precursor molecules cobalt tricarbonyl nitrosyl, trimethyl (methylcyclopentadienyl) platinum (IV), palladium (II) and copper (II) hexafluoroacetylacetate and titanium (IV) iso-propoxide were carried out. Fundamental insights gained from each study are presented in this thesis and are related

\(^1\)R. Feynman, “There’s Plenty of Room at the Bottom” APS meeting at the California Institute of Technology, 1959.
to surface science studies where available. The research in this field is still in its infancy and it is hoped that this work can spark interest for extended investigations, eventually taking the FEBID technique beyond its current empirical approach.
Í ræðu Richards Feynman: „Það er nægt pláss á botninum“,\(^1\), lýsti hann þeirri sýn sinni að vilja stjórna efni á smáum skala – atóm fyrir atóm. Nú, rúmum 50 árum síðar, hefur nanótaeknin rutt sér rúms á ýmsum sviðum t.a.m. í rafeindataekni, lítetakni og læknisfræði. Ein af afleiðingum þess er sú að nú til dags er aukiin áhugi og eftirspurn eftir strúktúrum á nanómetraskala með ákveðna eðlis- og efnafræði eiginleika. Ein aðferð sem mögulega getur mætt þessari eftirspurn er öppuntun með skörpum rafeindageisla (e. Focused Electron Beam Induced Deposition, FEBID). Þónokkur árangur hefur náðst með þessari aðferð, enn er þó þörf á frekari þróun. Sérstaklega er mikilvægt að leita leíða til að koma í veg fyrir öhrinindir í strúktúrum sem prentaðir eru því slik öhrinindi geta haft tölverð áhrif á eiginleika þeirra. Auk þess má nefna að upplausn upp á innan við nanómeter, sem fræðilega ætti að vera möguleg, hefur ekki enn náðst. Að einhverju leiti má tengja þessa annmáka við óhrinindi í strúktúrum (með hreyfiorkur undir 50 eV) sem losna í ferlinu. Hingað til hefur þó engin kerfisbundin rannsókn farið fram á áhrifum þessara þeirra í FEBID.

Rannsóknarspurning þessa doktorsverkefnis er að hvaða leyti lágorkurafeindir hafa áhrif á hreinleika og upplausn öðrprentana í FEBID. Sérstaklega er horft til rjúfandi rafeindarálagningar (e. Dissociative Electron Attachment, DEA) og rjúfandi jónuna (e. Dissociative Ionization, DI). Markmiðið er að auka skilning á þeim eðlisfræðilegu ferlum sem liggja að baki FEBID með því að rannsaka þá á sameindaskala. Í þessu samehengi voru köbalt-tríkarbónylíntróxyln, trimethyl (methylcyklopentadienyln)-plátína(IV), palladium- og kopar-hexaflúroórasetýl- asetonat og titanium-isoprópoxyrannsakaðar með tilliti til rafeindadrifinnar sundrunar.

\(^1\)R. Feynman, “There’s Plenty of Room at the Bottom” APS meeting at the California Institute of Technology, 1959.

Útdráttur
Niðurstöður okkar gefa innsýn í ferlin sem eiga sér stað og eru þær bornar
saman við yfirborðseðlisfræðilegar niðurstöður, þar sem við á. Rannsóknir á
þessum áhrifum lágorkurafeinda á FEBID sameindir hafa ekki verið miklar
hingað til. Það er von okkar að með þessu verkefni sé tekið mikilvægt
skref í að reyna fræðilegum stoðum undir FEBID ferlið og leggi þannig að
mörkum til frekari próunar FEBID við örprentun yfirborða.
# List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>acac</td>
<td>acetylacetonate</td>
</tr>
<tr>
<td>AD</td>
<td>Autodetachment</td>
</tr>
<tr>
<td>AE</td>
<td>Appearance Energy</td>
</tr>
<tr>
<td>AES</td>
<td>Auger Electron Spectroscopy</td>
</tr>
<tr>
<td>BDE</td>
<td>Bond Dissociation Energy</td>
</tr>
<tr>
<td>BSE</td>
<td>Backscattered Electron</td>
</tr>
<tr>
<td>CU</td>
<td>Comenius University</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical Vapor Deposition</td>
</tr>
<tr>
<td>DEA</td>
<td>Dissociative Electron Attachment</td>
</tr>
<tr>
<td>DI</td>
<td>Dissociative Ionization</td>
</tr>
<tr>
<td>EA</td>
<td>Electron Affinity</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy Dispersive X-ray Spectroscopy</td>
</tr>
<tr>
<td>EI</td>
<td>Electron Ionization</td>
</tr>
<tr>
<td>ESD</td>
<td>Electron Stimulated Desorption</td>
</tr>
<tr>
<td>ETS</td>
<td>Electron Transmission Spectroscopy</td>
</tr>
<tr>
<td>FCF</td>
<td>Franck-Condon Factor</td>
</tr>
<tr>
<td>FEBID</td>
<td>Focused Electron Beam Induced Deposition</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full Width at Half Maximum</td>
</tr>
<tr>
<td>hfac</td>
<td>Hexafluoroacetylacetonate</td>
</tr>
<tr>
<td>Hhfac</td>
<td>Hexafluoroacetylacetone</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
</tr>
<tr>
<td>HREELS</td>
<td>High Resolution Electron Energy Loss Spectroscopy</td>
</tr>
<tr>
<td>HV</td>
<td>High Vacuum</td>
</tr>
<tr>
<td>IE</td>
<td>Ionization Energy</td>
</tr>
<tr>
<td>KER</td>
<td>Kinetic Energy Release</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest Unoccupied Molecular Orbital</td>
</tr>
<tr>
<td>MC</td>
<td>Monte Carlo</td>
</tr>
<tr>
<td>MeCpPtMe₃</td>
<td>Trimethyl (methylcyclopentadienyl) platinum (IV)</td>
</tr>
</tbody>
</table>
MO Molecular Orbital
MS Mass Spectrometry
ND Neutral Dissociation
NDA Non-Dissociative Attachment
PE Primary Electron
QMS Quadrupole Mass Spectrometer
RAIRS Reflection Absorption Infrared Spectroscopy
RC Radiative Cooling
SE Secondary Electron
SEM Secondary Electron Multiplier
TEM Trochoidal Electron Monochromator
TIPO Titanium iso-propoxide
TNI Temporary Negative Ion
UHV Ultra High Vacuum
UI University of Iceland
UV/Vis Ultraviolet/Visible
vtms Vinyltrimethylsilane
XPS X-ray Photoelectron Spectroscopy
List of Publications

Publications included in the thesis

• The Role of Dissociative Electron Attachment in Electron Beam Induced Deposition – A Case Study on Cobalt Tricarbonyl Nitrosyl
  Sarah Engmann, Michal Stano, Štefan Matejčík and Oddur Ingólfsson

• Die Rolle dissoziativer Elektronenanlagerung in Prozessierungsverfahren mit fokussierten Elektronenstrahlen – eine Fallstudie an Tricarbonyl(nitrosyl)cobalt
  Sarah Engmann, Michal Stano, Štefan Matejčík and Oddur Ingólfsson

• Gas Phase Low Energy Electron Induced Decomposition of the Focused Electron Beam Induced Deposition (FEBID) precursor Trimethyl (Methylocyclopentadienyl) Platinum(IV) (MeCpPtMe₃)
  Sarah Engmann, Michal Stano, Štefan Matejčík and Oddur Ingólfsson

• Absolute Cross Sections for Dissociative Electron Attachment and Dissociative Ionization of Cobalt Tricarbonyl Nitrosyl in the Energy Range from 0 eV to 140 eV
  Sarah Engmann, Michal Stano, Peter Papp, Michael J. Brunger, Štefan Matejčík and Oddur Ingólfsson

• Dissociative Electron Attachment to Hexafluoroacetylacetone and its Bidentate Metal Complexes [M(hfac)₂], M = Cu, Pd
Publications not included in the thesis

- A Combined Experimental and Theoretical Study on Structural Parameters and Energetics in Electron Induced Ionization and Dissociation of Cobalt Tricarbonyl Nitrosyl
  Peter Papp, Sarah Engmann, Marek Kučera, Michal Stano, Štefan Matejčík and Oddur Ingólfsson
  Manuscript March 2013
Contents

1 Introduction .............................................. 1

2 Electron-Molecule Interactions .................. 7
   2.1 Positive Ion Formation through Electron Impact ............... 8
      2.1.1 Ionization and Appearance Energies .................. 9
      2.1.2 Ionization and Dissociation Cross-Sections .......... 11
   2.2 Negative Ion Formation through Electron Attachment .......... 11
      2.2.1 Formation and Stability ................................ 12
      2.2.2 Relaxation of the Temporary Negative Ion .......... 14
      2.2.3 Dissociative Electron Attachment (DEA) ............. 15
   2.3 Cross Sections ..................................... 18
   2.4 Condensed Phase ...................................... 20

3 Experimental Configuration ...................... 23
   3.1 General Remarks .................................... 23
   3.2 Crossed Beam Setups ................................ 23
      3.2.1 The Electron Monochromator ......................... 23
      3.2.2 The Effusive Molecular Beam ....................... 26
   3.3 Calibration Procedures and Data Processing .................. 27
      3.3.1 Energy Scales and Electron Energy Resolution ....... 27
      3.3.2 Determination of Absolute Cross Sections ........... 29

4 Results ................................................... 33
   4.1 Cobalt Tricarbonyl Nitrosyl .............................. 34
      4.1.1 Motivation and Previous Work ....................... 34
      4.1.2 Electron Ionization and Dissociative Ionization .... 34
      4.1.3 Dissociative Electron Attachment ..................... 35
4.1.4 A Comparison of Absolute Values for Positive and Negative Ion Formation from [Co(CO)_3NO] and their Implications for FEBID .................................................. 37

4.2 Trimethyl (Methylcyclopentadienyl) Platinum (IV) ........ 40
  4.2.1 Motivation and Previous Work .......................... 40
  4.2.2 Electron Ionization and Dissociative Ionization ....... 40
  4.2.3 Dissociative Electron Attachment ....................... 41
  4.2.4 Implications for FEBID .................................. 44

4.3 Hexafluoroacetylacetone and its Metal Complexes .......... 45
  4.3.1 Motivation and Previous Work ......................... 45
  4.3.2 Ligand Precursor Hexafluoroacetylacetone .......... 46
  4.3.3 Bis-(Hexafluoroacetylacetonate) Palladium (II) .... 48
  4.3.4 Bis-(Hexafluoroacetylacetonate) Copper (II) ....... 50
  4.3.5 Complexing – Going from Hexafluoroacetylacetone to the Chelated Complex ................................ 51
  4.3.6 Implications for FEBID .................................. 51

4.4 Titanium (IV) Iso-Propoxide .............................. 52
  4.4.1 Motivation and Previous Work ......................... 52
  4.4.2 Electron Ionization and Dissociative Ionization .... 53
  4.4.3 Dissociative Electron Attachment ....................... 54
  4.4.4 Implications for FEBID .................................. 55

5 Summary and Outlook ........................................ 57

List of Figures ................................................ 61

List of Tables .................................................. 63

Bibliography .................................................. 65

Included Publications ........................................ 77

I The Role of Dissociative Electron Attachment in Electron Beam Induced Deposition – A Case Study on Cobalt Tricarbonyl Nitrosyl 77

II Die Rolle dissoziativer Elektronenanlagerung in Prozessierungsverfahren mit fokussierten Elektronenstrahlen – eine Fallstudie an Tricarbonyl(nitrosyl)cobalt 79

XII
III Gas Phase Low Energy Electron Induced Decomposition of the Focused Electron Beam Induced Deposition (FEBID) precursor
Trimethyl (Methylcyclopentadienyl) Platinum(IV) (MeCpPtMe$_3$) 81

IV Absolute Cross Sections for Dissociative Electron Attachment and Dissociative Ionization of Cobalt Tricarbonyl Nitrosyl in the Energy Range from 0 eV to 140 eV 83

V Dissociative Electron Attachment to Hexafluoroacetylacetone and its Bidentate Metal Complexes [M(hfac)$_2$], M = Cu, Pd 85
Introduction

Figure 1.1: Schematic pictorial of the FEBID process.

Focused electron beam induced deposition (FEBID) was first observed as an unwelcome contamination side effect in electron microscopy (see, e.g., reference [1]). Yet less than a century later, FEBID has been established as a direct fabrication tool for the deposition of almost arbitrarily shaped nano structures [2]. The basic principle of FEBID is straightforward and is schematically illustrated in figure 1.1. A focused, high energy beam from a scanning- or transmission electron microscope is used to locally dissociate adsorbed precursor molecules, which are continuously replenished by a gas.
injection system. Ideally, a chemically and structurally well defined deposit is left behind while the volatile fragments are pumped away. Contrary to resist based lithography techniques [3], this is a one-step process and almost any desired geometry can in principle be deposited [2]. Furthermore, a large selection of volatile precursor molecules for potential use in FEBID are available, allowing deposition of metallic, semiconducting or insulating nano structures. However, these precursor molecules have originally been designed for thermal decomposition through chemical vapor deposition (CVD) and are not always ideally suited for electron beam induced decomposition.

Notwithstanding its apparent simplicity, the deposit quality obtained through FEBID is subject to several factors, summarized in figure 1.2. Roughly, these can be categorized into substrate-precursor, electron-substrate and electron-precursor interactions [4]. An interplay and interdependence of these factors, even changing over the time of the deposition process, leads to a complex dissociation environment. Thus, for a long time, the search for the “holy grail” [5] of FEBID was limited to em-
1. Introduction

Pirically finding the optimal process parameters for a particular precursor molecule. This empirical approach is reaching its limits and a further advancement of the FEBID technique calls for a more mechanistic understanding of the underlying processes. Some challenges that remain in FEBID are that the lateral resolution of the deposits cannot yet reach the theoretically possible value, and that generally high degrees of contamination are included in the deposited structures. These aspects become particularly important for metallic deposits intended for micro- and nano-engineering, as impurities and geometry can heavily affect properties such as conductivity and magnetization [6,7].

Despite the highly focused primary electron (PE) beam, the width of the actual deposits is generally found to be a multiple of the incident beam diameter [8]. Furthermore, although the current resolution record in FEBID is below one nanometer [9], the holders of this record point out that the deposit size and position varies and are somewhat arbitrary at the nano- and sub-nanometer scale. Additionally, FEBID structures generated from a standard metal organic precursor under high vacuum conditions (HV) generally do not exceed a metal content of 15–75% [2,10]. Higher metal contents can be obtained only at additional instrumental cost in an ultra high vacuum (UHV) environment [11], through post-deposition treatments [7,12] or when autocatalytic [13] or local heating effects [14] dominate the deposition.

The sources of contamination can mostly be narrowed down to the incomplete decomposition of precursor molecules, the co-deposition of already dissociated ligands, and contamination stemming from residual gases. Broadening of the structures, on the other hand, is generally attributed to electron flux outside the focus point of the primary beam due to backscattered electrons (BSEs) and low energy secondary electrons (SEs, E<50 eV as per the usual definition) that are produced through elastic and inelastic scattering of the PE beam from both the deposit and the substrate.

The inelastic scattering of the PEs significantly complicates matters, as electrons with a completely different energy spectrum become available for dissociation of the precursor. Which electrons—PEs, BSEs or SEs—dominate the deposition process in FEBID is still an open question [15–17].

Mostly independent of the incident PE energy, the SE yield peaks at energies <10 eV and their intensities are far from negligible [18,20]. A typical energy spectrum of electrons emitted from the sample surface is shown
1. Introduction

Figure 1.3: A typical energy spectrum of electrons emitted from a sample surface upon irradiation with a focused, high energy primary electron beam (PE); secondary electrons (SE) and backscattered electrons (BSE) are indicated. Adapted from reference [21]. The inset shows an experimentally obtained SE distribution from Ni (111), from 0–50 eV. Adapted from [20] and references therein.

Schematically in figure 1.3, several different dissociation mechanisms can be operative over this broad energy range, i.e., dissociative ionization (DI), dipolar dissociation (DD), neutral dissociation (ND) and dissociative electron attachment (DEA). The threshold for DI, DD and ND is \( \approx 10–15 \text{ eV} \) for most polyatomic molecules. While DI, DD and ND are operative over a broad energy range, their overlap with the expected SE energy distribution, though significant, is restricted to the threshold region of the individual processes. In contrast, DEA can occur at energies close to zero eV with cross sections \( >10^{-12} \text{ cm}^2 \) [22]. While DEA is acknowledged as a possible dissociation mechanism in FEBID [4], only very few studies are available in the literature studying the effect of DEA to FEBID precursors so far [23–26].

Considerable experimental and theoretical work has gone into elucidating the nature of scattering events, and Monte Carlo (MC) simulations have been used to simulate and visualize the process (see for example [8]). In principal, MC calculations can be used to simulate the entire deposition process, as all primary electron trajectories and subsequently generated BSEs and SEs can be traced with their respective energies. An illustrative example of such a trajectory simulation is shown in figure 1.4.

In combination with the energy dependent cross sections of the respective
precursor molecules, MC simulations have the potential to give an accurate prediction of the resulting FEBID deposit. Unfortunately, this approach is currently greatly restricted by the lack of relevant experimental cross sections for FEBID precursor molecules. As a “work-around”, the unknown cross sections are currently replaced by, e.g., adapted cross sections of hydrocarbons [16]. As absolute DEA cross section data for FEBID precursor molecules is even more scarce than DI data, DEA has not yet been explicitly included in such simulations.

The call for a more mechanistic understanding of FEBID has recently motivated several surface science studies on various FEBID precursor molecules, including the compounds trimethyl (methylcyclopentadienyl) platinum (IV) [28–30], tetrakis (trifluorophosphine) platinum (0) [31] and dimethyl (acetylacetonate) gold (III) [32]. In this approach, the precursor molecule is condensed onto a cryostatic substrate. The low temperature fixes the volatile molecules onto the surface and minimizes surface diffusion and local, beam induced, heating effects. The adsorbed precursor molecules are then irradiated with electrons of defined energy, which can be varied from 3–3000 eV. A series of complementary surface science techniques then allows analysis of the deposited film. The oxidation state of the central metal as well as the film composition can be probed by X-ray photoelectron spectroscopy (XPS), while changes in chemical bonding can be monitored with reflection
absorption infrared spectroscopy (RAIRS) or high resolution electron energy loss spectroscopy (HREELS). Finally, the composition of the gas phase species produced during the deposition can be monitored using mass spectrometry (MS). The electron source is variable in both its energy and dose. Data obtained as a function of energy and dose thus not only gives information about the film morphology but also dissociation cross section data of the adsorbed precursor molecule.

The UHV approach addresses important issues such as the film morphology, gas phase reaction products and reaction cross sections for the adsorbed precursor molecule. Some degrees of freedom (figure 1.2) of the FEBID process can be eliminated in this approach, namely surface diffusion and local heating effects, precursor versus electron limited growth and contamination from the background residual gases. However, this approach cannot discern processes induced through PEs from those induced through low energy SEs. Further, it cannot elucidate the processes operating at a molecular level, i.e., differentiate between a DI, DD or DEA mechanism. These are important questions that remain to be answered in FEBID and it becomes clear that complementary approaches are necessary to address those questions.

In order to disentangle the processes occurring on a molecular level from the complex environment generally found in FEBID (see figure 1.2), we have chosen to study the electron-molecule interactions in the gas phase. More specifically, an effusive molecular beam of the FEBID precursor is crossed with an electron beam of well defined energy. The energy of the electron beam can be varied from 0 to 140 eV and thus both negative and positive ion formation as a function of electron energy can be monitored. Apart from identifying the underlying dissociation mechanisms operative at each energy, energy dependent reaction cross sections can be derived in this configuration. These gas phase studies are thus expected to be a valuable first step in rationalizing the electron induced reactions on surfaces and subsequently in FEBID.

This study thus addresses two fundamental questions. First, this work aims at understanding the dissociation processes induced by low energy electrons when interacting with FEBID precursor molecules at the molecular level. This includes both dissociation induced by electron attachment but also by electron impact. Second, it aims at quantifying the effect of DEA versus DI in the secondary electron range through gas phase cross section measurements.
2 Electron-Molecule Interactions

Due to the various scattering events of the PEs, the electron energy range in FEBID available for dissociation of the precursor molecule is quite considerable, spanning the energy range from the PE beam (typically keV) down to almost 0 eV. Depending on its initial velocity, but also the electronic structure of the target, a free electron can interact with molecules in several ways. In particular the electron-molecule interactions can be classified as being either elastic or inelastic processes, depending on whether or not an energy transfer occurs. Elastic scattering proceeds without any energy transfer and thus without excitation of the target molecule, while inelastic scattering of the electron results in excitation of the molecule.

The scattering processes can further be classified according to whether direct or resonant scattering occurs, i.e., with respect to the timescale on which the scattering process takes place. In direct scattering, the electron spends comparable time in the vicinity of the molecule as it would have needed to pass the same distance without the molecule present (a 1 eV electron needs about $5 \times 10^{-16}$ s for a distance of 3 Å). In resonant scattering, the electron is temporarily trapped in the vicinity of the molecule, and the time the electron spends close to the molecule is considerably longer than the direct transit time (from $10^{-14}$ s up to the µs range).

In this work, both positive ion formation through direct EI as well as DEA through resonant electron capture have been investigated and will be presented in more detail. Elastic scattering is not germane with regard to this work and is thus not further discussed.
2. Electron-Molecule Interactions

2.1 Positive Ion Formation through Electron Impact

If an incoming electron transfers an energy amount equal to or exceeding the ionization energy (IE, typically \( \geq 10 \text{ eV} \)) of a molecule, the target may be ionized \[33\]. Direct ionization occurs when the incoming electron directly detaches a bound electron (reaction 2.1) and both electrons leave the molecule with negligible delay. The free electron is in the continuum both before and after the scattering process, and consequently there are no restrictions for the amount of energy being transferred. However, due to the low mass of the electron, rotational or vibrational excitation is in general inefficient and most of the energy is deposited in electronic transitions. In accordance with the Franck-Condon Principle, the ionization is taken to occur through a vertical transition (see also figure 2.1), as the ionization occurs on a timescale that is significantly shorter than the corresponding nuclear motion.

\[
\text{MX} + e^- \rightarrow \text{MX}^+ + 2e^-(2.1)
\]

If the electron transfers sufficient energy, the parent molecule \( \text{MX}^+ \) may undergo dissociative ionization:

\[
\begin{align*}
\text{MX} + e^- & \rightarrow \text{MX}^+ + 2e^- \\
\text{MX}^+ & \rightarrow X^+ + M^+ + \ldots
\end{align*}
\]

or multiple ionization,

\[
\text{MX} + e^- \rightarrow \text{MX}^{n+} + (n+1)e^- . (2.3)
\]

Competing with direct dissociation is an alternate ionization channel termed autoionization (reaction 2.4), where the incident and ejected electron leave the molecule with some time delay. Autoionization occurs as a resonant process where the molecule is first excited to a bound electronic state, but is sufficiently energetic to ionize. Autoionization of the excited parent molecule \( \text{MX}^* \) competes with neutral dissociation (reaction 2.5) and dipolar dissociation (reaction 2.6):

\[
\begin{align*}
\text{MX}^* \rightarrow & \begin{cases} 
\text{MX}^+ + e^- \\
\text{M}^- + X^+ \\
\text{M}^+ + X^- .
\end{cases}
\end{align*}
\]

\[
\begin{align*}
\text{MX}^* \rightarrow & \begin{cases} 
\text{MX}^+ + e^- \\
\text{M}^- + X^+ \\
\text{M}^+ + X^- .
\end{cases}
\end{align*}
\]

\[
\begin{align*}
\text{MX}^* \rightarrow & \begin{cases} 
\text{MX}^+ + e^- \\
\text{M}^- + X^+ \\
\text{M}^+ + X^- .
\end{cases}
\end{align*}
\]
2.1. Positive Ion Formation through Electron Impact

The latter two processes (reactions 2.5 and 2.6) are difficult to detect in standard mass spectrometry, and more elaborate techniques are necessary to identify the product fragments. For instance, ion pairs can in principle be identified by coincidence measurements. Furthermore, neutral reaction products can be ionized and subsequently be detected by standard mass spectrometry through photoionization [34] or electron impact [35], or be identified through more exotic techniques, e.g., by reacting the radical with tellurium to form volatile tellurides [36].

2.1.1 Ionization and Appearance Energies

As briefly mentioned in section 2.1, the ionization of a molecule occurs from within the Franck-Condon region as a vertical transition (see figure 2.1). The probability of a transition from a vibrational level \( v' \) of the neutral to a particular vibrational level \( v'' \) of the ion is given by its Franck-Condon factor (FCF), i.e., the squared norm of the overlap integral of the respective vibrational wavefunctions [37]:

\[
\text{FCF} = |\langle \Psi_{v'} | \Psi_{v''} \rangle|^2, \tag{2.7}
\]

where \( \Psi_{v'} \) is the vibrational wavefunction of the neutral and \( \Psi_{v''} \) the vibrational wavefunction of the ion, respectively. For an ionization event that leaves the internuclear distance unchanged, the transition from \( v' = 0 \) to \( v'' = 0 \) (adiabatic ionization) has the highest FCF. However, removal of an electron through ionization often leads to a weakening of the bond strength in the ion, resulting in a larger bond length. The greater the difference between the ground and excited state geometry, the more likely it is that vibrationally excited states are populated through a vertical transition, assuming that sufficient energy is available.

This makes it difficult, when the aim of the ionization study is determining the ionization energies and appearance energies (AE) of the parent and fragment ions. Here it is important to extract the adiabatic ionization energies, which is not always straightforward, particularly for large polyatomic molecules. One aspect compromising the determination of the true adiabatic energy may be small FCFs, and thus a weak signal at threshold. In crossed beam experiments, this problem is usually treated by scanning the threshold region multiple times until a good signal-to-noise ratio is obtained. The accurate determination of appearance energies is further complicated by the vanishing reaction rates near threshold (figure 2.2).
2. Electron-Molecule Interactions

![Diagram of electron-molecule interactions](image)

**Figure 2.1:** Illustration of the ionization and dissociation process through electron impact; IE Ionization Energy, AE Appearance Energy. Adapted from reference [38].

![Graph of reaction rate vs. electron energy](image)

**Figure 2.2:** General Shape of the reaction rate (log k) as a function of electron energy. Adapted from reference [38].
2.2. Negative Ion Formation through Electron Attachment

The average residence time within the collision region before extraction into the quadrupole mass spectrometer used in this work is on the order of 10 µs. Thus, in order to detect a given dissociation process, a reaction rate on the order of \( k > 10^5 \text{s}^{-1} \) is necessary. As shown in figure 2.2, the rate constant can exceed the critical value \( > 10^5 \text{s}^{-1} \) when sufficient excess energy is available in the system. This, however, leads to an appearance energy exceeding the true value, a phenomenon which is known as the kinetic shift. For instantaneous direct dissociation, this effect is almost negligible. In extreme cases, however, the observed kinetic shift can be \( >30 \text{ eV} \), e.g., for the detection of \( \text{C}_{58}^+/\text{C}_{60} \) [39].

2.1.2 Ionization and Dissociation Cross-Sections

The cross section, \( \sigma \), is the effective area which is directly correlated with the probability of some scattering event, such as ionization or more complex events such as dissociation, occurring. These cross sections are different from the geometrical cross section, where a point like projectile is assumed to hit a solid target, as \( \sigma \) is both energy as well as angle dependent. Nevertheless, \( \sigma \) can be figuratively described as the effective area of the molecule that the electron “sees” and it is expressed in units of area.

For positive (fragment) ion formation from polyatomic molecules, the shape of the energy dependent cross section above threshold is more or less the same for each species. After a steep rise above threshold, the ion yield reaches a maximum at around 70 eV, thereafter gradually decreasing towards higher energies. This is exploited in analytical mass spectrometry, where ionization is generally carried out at 70 eV. The determination of absolute cross sections for (dissociative) ionization is of fundamental importance across disciplines and the procedure for doing so is detailed, along with the approach for derivation of negative ion cross sections for (dissociative) electron attachment, in section 2.3.

2.2 Negative Ion Formation through Electron Attachment

The mechanism for dissociation of molecules through DI and DD has been described earlier in section 2.1. The following sections now describe fragmentation induced through negative ion formation, i.e., dissociative electron attachment (DEA). DEA has been investigated for a plethora of dif-
2. Electron-Molecule Interactions

Different compounds and been the subject of various reviews. The associated phenomena have been extensively described in literature \[37, 40-43\], and thus only a short summary of the formation and relaxation of negative ions is presented here.

2.2.1 Formation and Stability

Whether a molecule can form a thermodynamically stable anion is determined by its electron affinity (EA). The EA is defined as the energy difference between the neutral molecule \(M\) and its anion \(M^-\), in their respective ground state. By convention \[37\], the electron affinity is positive when the ground state of \(M^-\) is more stable and lies below that of the neutral parent, and negative when the ground state energy of the anion is above that of the parent. Thus, for positive electron affinity, a bound state for the extra electron exists.

The formation of the temporary negative ion (TNI) may proceed through several different mechanisms \[40\], with the most common being detailed below.

Whenever an electron is in the vicinity of a molecule, it can polarize it according to its polarizability \(\alpha\), which leads to an induced dipolar attraction \(V_\alpha(r)\):

\[
V_\alpha(r) = -\frac{\alpha}{2r^4}.
\]  

(2.8)

In turn, a repulsive centrifugal potential \(V_\ell(r)\) results from the angular momentum \(\ell\) of the electron:

\[
V_\ell(r) = \frac{\ell(\ell+1)}{2r^2}.
\]  

(2.9)

The effective potential thus has the form:

\[
V(r) = V_\ell(r) + V_\alpha(r) = \frac{\ell(\ell+1)}{2r^2} - \frac{\alpha}{2r^4}.
\]  

(2.10)

In combination with the Coulomb repulsion, the effective potential can be portrayed schematically as shown in figure 2.3. For \(\ell \neq 0\), a centrifugal barrier is formed that can delay or “trap” an electron. The incident electron may be represented as a plane wave that contains all components of angular momentum. If the molecule has an energetically accessible empty orbital characterized by a particular angular momentum \(\ell\), then an electron
2.2. Negative Ion Formation through Electron Attachment

Figure 2.3: Effective potential, including the Coulomb repulsion, of the electron-molecule interactions as a function of their distance (left). The right hand side shows the formation of the potential barrier for electrons with different values of $\ell$. For $\ell = 0$, no potential barrier is formed.

which “fits” [41], i.e., has the same angular momentum and the appropriate energy, may temporarily fill this orbital. In terms of plane waves, this means positive interference within the potential well and thus formation of a resonance. The resonance has a finite lifetime due to the “back tunneling” of the electron through the potential barrier. For angular momentum $\ell = 0$, no such barrier is formed and the electron will leave the vicinity of the molecule without time delay.

When no further changes in the electron configuration are involved, this kind of resonance is termed a one particle (1p) shape resonance, as the electron is trapped by the shape of the potential. Shape resonances lie energetically above the electronic ground state of the neutral and the TNI efficiently decays back to the parent electronic state, often inducing vibrational excitation [41] and resulting in short lifetimes. Typically, shape resonances occur at energies below 4 eV [44], due to the finite height of the potential barrier. Shape resonances are characterized by large attachment cross sections and are thus prominent features in electron transmission spectroscopy [41].

If the energy of the incoming electron is large enough to induce electronic excitation in the parent molecule, a two particle-one hole (2p-1h) resonance can be formed. Also termed core excited resonances, the anion is created with two electrons occupying normally empty molecular orbitals (MOs). Core excited resonances occur at energies close to electronic excitation and usually lead to TNIs that lie energetically above the excited parent state. In this case they are referred to as open channel resonances. A classification of
2. Electron-Molecule Interactions

![Diagram of various resonances]

**Figure 2.4**: Classification of various resonances according to their energy relative to the neutral parent MX. Adapted from reference [37].

The various resonances is given in figure 2.4.

If the energy of the TNI lies below that of the excited neutral, i.e., the electron affinity of the excited neutral is positive, the resonance is referred to as an electron-excited Feshbach or closed channel resonance. As this resonance lies below the the parent excited neutral state, the captured electron has to reabsorb energy before reemission becomes energetically available and thus dissociation is favored.

Finally, at energies close to 0 eV, vibrational [45] or nuclear excited [40] [41] Feshbach resonances may occur through coupling of the kinetic energy of the incoming electron with the molecular motion, resulting in an efficient intramolecular vibrational redistribution. Contrary to what is observed for the electron-excited Feshbach resonance, autodetachment of the extra electron is energetically possible when the vibrational energy is focused into the reaction coordinate from which autodetachment is accessible.

### 2.2.2 Relaxation of the Temporary Negative Ion

The capture of a free electron leads to a metastable, temporary negative ion. Several competitive pathways are available for the decay of the TNI, i.e.,
2.2. Negative Ion Formation through Electron Attachment

autodetachment (AD), radiative cooling (RC) and DEA:

\[
\begin{align*}
MX + e^- & \longrightarrow MX^-(\ast) \\
\tau_{AD} & \rightarrow MX^+(\ast) + e^- \\
\tau_{RC} & \rightarrow MX^- + h\nu \\
\tau_{DEA} & \rightarrow M + X^- .
\end{align*}
\] (2.11) (2.12) (2.13)

The autodetachment lifetime \(\tau_{AD}\) may range from few vibrational periods \((10^{-14} \text{ s})\) in small molecules like \(N_2^-\) [46], to the micro or millisecond scale for large molecules [47]. Typically, these latter anions are observed through narrow resonances close to 0 eV where the dissociation channel is not yet energetically available. A very prominent example of a long lived TNI is \(SF_6\) [47], which is exploited on the industrial scale as a gaseous dielectric medium as well as in our laboratory as calibrant for the electron energy scale.

If the target molecule has a positive electron affinity, the TNI may also relax through radiative cooling, i.e., by emitting a photon (reaction 2.12). However, these radiative processes are considerably slower, with time scales of \(10^{-9}\) to \(10^{-8}\) s [37], and are usually not operative for molecules.

Finally, the time scale for dissociative electron attachment can span a considerable range, depending on the decomposition mechanism. It can vary from \(10^{-14}\) s for direct dissociation from a repulsive state, to microseconds for metastable decay [43]. Nevertheless, two prerequisites exist for whether DEA is an operative channel or not. First, a negatively charged, thermodynamically stable fragment must exist for the respective compound. Second, the dissociative channel leading to this fragment has to be energetically accessible from the TNI.

2.2.3 Dissociative Electron Attachment (DEA)

The DEA process can be illustrated in a simplified two dimensional Born-Oppenheimer potential diagram, as is done in figure 2.5. Strictly speaking this representation is only applicable to diatomic molecules, but it also holds for polyatomic molecules for direct dissociation. In the latter case, the representation is a cut through the potential surfaces of the polyatomic molecule along the relevant reaction coordinate.
2. Electron-Molecule Interactions

Electronic processes occur on shorter timescales than processes involving the nuclei, and thus the electron capture (section 2.2.1) can be represented by a vertical transition from the ground state of MX to some excited state of MX\(^{-}\). This is only possible in the Franck-Condon region, indicated in figure 2.5 by the shaded area. Again, the probability for an electronic transition from the ground to the electronically excited state is given by the Franck-Condon Factor (see section 2.1.1). Once formed, the molecular ion can either dissociate (DEA) or decay back into the (vibrationally excited) parent state through autodetachment of the extra electron. The blue anionic potential curve in figure 2.5 is purely repulsive, and the geometry of the TNI will change towards longer M–X bond lengths. Autodetachment may only occur until the crossing point \(R_c\) of the neutral and anionic potential curve. After that, dissociation is the only remaining relaxation channel. In the case where the anionic curve has a minimum and the excess energy can be efficiently randomized, the parent anion can be observed (see red curve in figure 2.5). For purely repulsive states, only the charged fragment X\(^{-}\) is observable.

The anionic dissociation products are usually observed by mass spectrometry as a function of incident electron energy. The ion yield curve, at least for simple molecules, will show a profile reminiscent of the ground

![Figure 2.5: Potential curve diagram for low-energy electron–molecule collisions with the quasi diatomic molecule MX.](image-url)
state vibrational wave function reflected at the repulsive anionic potential, similar to what is depicted on the left hand side of figure 2.5. The autodetachment lifetime $\tau_{AD}$ of the TNI is related to the finite width $\Gamma_{AD}(r)$ of the potential energy curve through Heisenberg’s uncertainty principle:

$$\Gamma_{AD}(r) \approx \frac{\hbar}{\tau_{AD}}.$$  (2.14)

At shorter intermolecular distance and higher energy, autodetachment often dominates, and the resonance appears shifted to lower energies. The ion yield curves for complex dissociation reactions of polyatomic molecules may deviate substantially from this reflection principle, particularly if competing channels are accessible in the energy window of the TNI. Again the apparent maximum may appear shifted towards lower but also towards higher energies as a result of a non-Gaussian resonance profile. This is precisely what we see in the metastable decay from $[\text{Co(CO)}_3\text{NO}]$, as discussed in articles II and III and later in section 4.1.

The experimentally observed appearance energy of the fragment $X^-$ is given by the general equation:

$$AE(X^-) = \sum_{i=1}^{n} BDE_{i}(\text{educts}) - \sum_{i=1}^{n} BDE_{i}(\text{products}) - EA(X) + E^*,$$  (2.15)

where $BDE_{i}(\text{educts})$ and $BDE_{i}(\text{products})$ are the bond dissociation energies of the respective broken and formed bonds, $EA(X)$ is the electron affinity of the charge retaining fragment $X$ and $E^*$ is the excess energy of the process.

The thermodynamic threshold energy ($E_{th}$) for a given DEA can be approximated by the reaction enthalpy ($\Delta H_{rxn}$) of the relevant reaction. Equation 2.15 thus simplifies to:

$$\Delta H_{rxn} \approx E_{th} = \sum_{i=1}^{n} BDE_{i}(\text{educts}) - \sum_{i=1}^{n} BDE_{i}(\text{products}) - EA(X).$$  (2.16)

The difference between the experimentally obtained AE and the thermodynamic threshold gives $E^*$, which can be either released through translational energy or be transferred into the internal degrees of freedom of the dissociated fragments.
2. Electron-Molecule Interactions

2.3 Cross Sections

The effectiveness, and thus cross section, of a given process as a function of the electron energy, is of fundamental importance for elucidating the contribution of each dissociation pathway in FEBID.

Absolute measurements can be made for both positive and negative ion formation in total ion collection tubes, as demonstrated by, e.g., Rapp, Briglia and Englander-Golden [48, 49] and in a modernized form by Allan and coworkers [50, 51] and Rejoub et al. [52]. The experimental geometry requires passing a collimated electron beam through a gas sample of a certain number density $N$, and subsequent extraction of all ions formed towards an ion collector by an electric field. From the attenuation of the incident beam, the energy dependent absolute scattering cross section $\sigma(E)$ can be evaluated using Beer’s law:

$$I_T = I_0 \cdot \exp(-\sigma(E) \cdot N \cdot l),$$

(2.17)

where $I_T$ and $I_0$ are the transmitted and incident electron currents, and $l$ is the effective electron path length in the target gas. For an ionization event yielding the charged fragment $X$, equation 2.17 can be re-written as:

$$I_0 - I_T = I_X = I_0(1 - \exp(\sigma^{\text{Ion}}_{X}(E) \cdot N \cdot l)),$$

(2.18)

where $I_X$ is the total ion current of fragment $X$ and $\sigma^{\text{Ion}}_{X}(E)$ is the cross section for the ionization event. Under single collision conditions $\sigma^{\text{Ion}}_{X}(E) \cdot N \cdot l \ll 1$, and equation 2.18 can be further simplified through a first order Taylor expansion, i.e.,

$$I_X = I_0 \cdot \sigma^{\text{Ion}}_{X}(E) \cdot N \cdot l.$$  

(2.19)

Thus the cross section for a given ionization process can be expressed by:

$$\sigma^{\text{Ion}}_{X}(E) = \frac{I_X}{I_0 \cdot N \cdot l}.$$  

(2.20)

In the case where multiple ionization and dissociation processes are operative, $\sigma^{\text{Ion}}_{T}(E)$ is the sum of the absolute partial cross sections of the individual fragments $\sigma^{\text{Ion}}_{i}(E)$ i.e.,

$$\sigma^{\text{Ion}}_{T}(E) = \sum_{i=1}^{n} \sigma^{\text{Ion}}_{i}(E).$$  

(2.21)
2.3. Cross Sections

Absolute cross section data for negative ion formation may also be derived from electron attachment rates determined through, e.g., electron swarm techniques [40] 53.

In the case of the swarm technique, a pulsed electron packet is passed through a drift tube containing a non-electron attaching buffer gas of number density $N$ under the influence of a uniform electric field $E$. Accelerated through the electric field but restrained by collisions with the buffer gas, the electrons reach an equilibrium energy distribution $f(v)$ [40]. The latter mainly depends on the ratio of $E/N$, the buffer gas itself and the temperature. Dilute amounts of the reactant gas introduced into the drift tube result in a decrease in the electron pulse intensity at the detector, compared to the buffer gas alone. From the decrease in intensity, the attachment rate constant $k_a$, as a function of $E/N$, can be obtained.

The rate constant $k_a$ and the electron attachment cross section $\sigma_{EA}$ are related by [37] [40]:

$$k_a = \int_0^\infty \sigma_{EA} \cdot v \cdot f(v) \, dv,$$  \hspace{1cm} (2.22)

where $f(v)$ is the normalized velocity distribution of the electrons. Thus, using the mean values, equation 2.22 can be approximated by [37]:

$$k_a = \bar{\sigma} \cdot \bar{v}.$$  \hspace{1cm} (2.23)

It should be noted that swarm experiments, due to the use of a buffer gas, are generally carried out in a high pressure environment, so that collisional induced relaxation of the initially formed TNI may take place [53].

Reliable reference cross sections open up a convenient way of calibrating relative cross sections, obtained through crossed electron-molecular beam configurations, to an absolute scale. This often permits exploitation of the advantages of beam experiments, namely accurate mass separation that allows for identification of the charged species as well as a high sensitivity. In this thesis, absolute cross sections were determined for DEA and DI from the FEBID precursor molecule $[\text{Co(CO)}_3\text{NO}]$. A detailed account of the experimental set-up is given in chapter 3, with a discussion of those results being given in section 4.1 and articles I, II and IV.
2. Electron-Molecule Interactions

2.4 Condensed Phase

An important aspect when considering DEA in FEBID is the transition from the results obtained in the gas phase to molecules adsorbed on a surface. In condensates, the most important effects on the formation and relaxation of the TNI are the polarization interactions of the neutral parent and the TNI with the co-adsorbed molecules, collision induced stabilization, and the energy loss of the incoming electron due to inelastic scattering from surrounding molecules.

The attractive polarization interaction of the surrounding molecules with the neutral precursor and the TNI, generally leads to a stabilization of both the neutral and the TNI. The stabilization effect is more pronounced for the TNI due to the stronger polarization of the surrounding molecules by the negative charge. As the energy of the anionic state is lowered, the critical crossing point $R_c$ is reached in a shorter time period, decreasing the probability for autodetachment and favoring dissociation. The enhancement of DEA through attractive polarization interactions is very well illustrated for the case of C$_6$F$_5$Cl \[43\]. In the gas phase, the core excited open channel resonance decays primarily through autodetachment. In the condensate, the resonance is shifted towards lower energies due to the attractive interaction of the TNI with the surrounding medium. As a consequence, the energy of the TNI becomes lower than that of the associated excited state, increasing the probability for dissociation. If the energy dissipation within the condensate is efficient, i.e., vibrational energy is quenched through intermolecular collisions, the initial TNI may be stabilized against both autodetachment as well as dissociation \[42\] \[43\].

The energy loss of the incident electron through inelastic scattering can occur through resonant and direct scattering. In the resonant process, a higher energy electron is captured forming a short lived core-excited shape resonance. That resonance then quickly decays through autodetachment, but leaves the parent molecule in an excited state. Having lost most of its energy, the electron can then be attached by another molecule within the adsorbate through a low lying resonance and stabilization of the TNI through the surrounding medium, as described above, may become operative. Compared to resonant inelastic scattering, direct scattering is less efficient but still contributes to the overall formation of low energy electrons.

Direct detection of negative fragments from condensates on surfaces through mass spectrometry is only possible for fragments formed with high
2.4. Condensed Phase

enough kinetic energy to overcome the attractive polarization interactions described above \cite{42, 54, 55} and thus escape the condensate. Products that cannot overcome this barrier remain trapped within the condensate, leading to a charging of the film. Such effects can be monitored by electron transmission spectroscopy (ETS) \cite{56}.

Several studies (see for example references \cite{25, 55, 57, 59}) have shown that surface reactions can be induced through an initial DEA process. This includes, for example, the fluorination of hydrogen terminated silicon (111) surfaces through CF$_4$ upon irradiation with low energy electrons: Data obtained from XPS of CF$_4$ adsorbed onto H-terminated Si (111) surfaces, after increasing exposure times (5 eV electrons), indicated a continuous increase in covalently surface bound fluorine \cite{55, 59}. Observation of the overall reaction cross-section as a function of incident electron energy showed a growth rate with a clear maximum just below 6 eV, i.e., an energy range where DEA is the only energetically available dissociation mechanism. Similar observations were made by Olsen and Rowntree \cite{60}, when irradiating self assembled monolayers of alkanethiols with low energy electrons. Here the maximum cross section for DEA to C$_{12}$ chains was found to be at around 10 eV. Finally, Mezhenny et al. \cite{25} monitored the deposition of copper from copper (I) hexafluoroacetylacetonate vinyltrimethylsilane ([(Cu(hfac)(vtms)]) through low energy electrons. The onset for deposition was found to be at 4 ± 0.5 eV and was thus linked to a DEA induced deposition mechanism. More recent surface science results \cite{28, 31}, along with the data presented in this thesis, support DEA as a possible dissociation step in FEBID, as will be detailed in chapter \cite{4}.
3 Experimental Configuration

3.1 General Remarks

During the course of this work, two different crossed beam apparatus were used. All solid samples as well as cobalt tricarbonyl nitrosyl were measured with an apparatus at the laboratory of Prof. Štefan Matejčík at Comenius University (CU), Bratislava, Slovakia. The remaining samples, i.e., hexafluoroacetacetone and titanium iso-propoxide, were investigated with a newly constructed machine in our laboratory at the University of Iceland, Reykjavík, Iceland (UI). The construction of the UI apparatus was not a part of this Ph.D. work, and will be separately presented by Elias H. Bjarnason as a part of his Ph.D. work. The operating principles of both machines are essentially the same. In section 3.2, the general set-up will thus be described along with features specific for each apparatus. Section 3.3 subsequently describes the calibration, measurement and data processing procedures.

3.2 Crossed Beam Setups

3.2.1 The Electron Monochromator

Both the Bratislava and the Reykjavík apparatus are designed to measure the energy dependent positive, as well as negative, ion formation under single collision conditions. An electron beam of narrow energy distribution is crossed with an effusive molecular beam and the generated ions are
3. Experimental Configuration

![Schematic diagram of a crossed electron-molecular beam setup for study of electron impact ionization and electron attachment to gas phase molecules. The trochoidal electron monochromator (TEM), quadrupole mass spectrometer (QMS) and secondary electron multiplier (SEM) are indicated. This setup is mounted in a stainless steel high vacuum chamber, where a base pressure of typically less than $4 \times 10^{-8}$ mbar is achieved.]

extracted into and detected by a quadrupole mass spectrometer (QMS). Depending on the energy of the incident electron beam and the settings of the ion optics and mass spectrometer, either negative or positive ions are detected. A schematic diagram of our crossed beam apparatus is given in figure 3.1. The entire setup is mounted in a stainless steel vacuum chamber with a base pressure of typically less than $4 \times 10^{-8}$ mbar in Reykjavik and $10^{-9}$ mbar (detection limit of the ion gauge) in Bratislava. Further details of the components that comprise the trochoidal electron monochromator (TEM) are given in figure 3.2, while in figure 3.3 details of the apparatus geometry within the HV chamber at CU are shown.

To be able to study energy dependent DEA and to determine accurate appearance energies it is necessary to employ an electron beam with a narrow energy distribution and spatial extend. Furthermore, DEA processes of interest occur already at energies very close to 0 eV. It is thus necessary to work with an electron source that also provides an electron beam with variable energy and with high intensities down to low energies. The trochoidal electron monochromator of Stamatovic and Schulz [61, 62] combines all of these properties, and many groups still use a TEM based on their original design.
3.2. Crossed Beam Setups

The working principles and a schematic diagram of the TEM at UI is given in figure 3.2 and it is similar to the one used at CU (figure 3.3).

The monochromator consists of a hairpin filament (e.g., tungsten) and a set of plates which can be individually tuned for energy selection, collimation and focusing of the electron beam. This is necessary as the filament typically emits electrons with a broad energy distribution. The electrons are further collimated by a homogeneous magnetic field (≈80 Gauss) generated by two Helmholtz coils mounted on the outside of the vacuum system. The monochromator plates are fabricated from either non-magnetic stainless steel (CU) or molybdenum (UI) and are electrically isolated from each other by ruby balls. The monochromator can be heated by halogen lamps mounted close by, to eliminate adsorption of contaminants onto the plates and thus charging effects.

The three plates between the filament (M2–M4) and the deflection region (M5/M6) are drilled off-center, so that the electrons enter the deflection region off axis and are not in direct line of sight of the collision chamber. The deflection region is the heart of the TEM, where the actual velocity selection takes place. The deflection plates are adjusted to generate a weak electric field $\vec{E}$ perpendicular to the incident electron beam and the external magnetic field $\vec{B}$ of the Helmholtz coils (see figure 3.2). As the electrons pass M4, they are accelerated by and along the electric field into the $y$ direction. The combined effect of the electric and magnetic fields forces the electrons onto cycloidal or trochoidal trajectories, depending on their initial velocity.

![Figure 3.2: Schematic diagram of the trochoidal electron monochromator at UI; the QMS is located in the plane of the paper behind the TEM.](image-url)
3. Experimental Configuration

The center of rotation is displaced with a constant velocity \( \vec{v}_x \) according to equation 3.1, effectively dispersing the electrons in \( x \) direction:

\[
\vec{v}_x = \frac{\vec{E} \times \vec{B}}{|\vec{B}|^2}.
\]  

As described above, \( \vec{E} \) is perpendicular to \( \vec{B} \) and the incident electron velocity \( \vec{v}_z \). Thus equation 3.1 simplifies to:

\[
|\vec{v}_x| = \frac{E}{B}.
\]  

The apertures in plates M7–M9, after the deflection region, are drilled in an axial position and are therefore displaced by a certain distance \( \Delta x \) with respect to the apertures in plates M2–M4. Consequently, only electrons of selected velocity, leading to the displacement \( \Delta x \), reach the exit aperture. Plates M7–M9 can then be adjusted to refocus and accelerate/decelerate the velocity selected beam into the collision zone, where the electrons interact with the effusive molecular beam.

The ions formed in the collision region are extracted by a weak electric field on the order of \(< 1 \text{ V/cm} \) (plates C1 and C2, only the extractor is visible in figure 3.2), so as to not disturb the electron beam, and are focused and accelerated into the entrance aperture of a commercial quadrupole mass spectrometer (in the plane of the paper behind the monochromator; Pfeiffer QMA-400 at CU, Hiden EPIC 1000 at UI).

The electrons that are transmitted through the collision region are subsequently focused into a Faraday Cup, by adjusting the voltages on D1–D3. The Faraday Cup serves as an electron beam intensity monitor, as well as an electron trap to avoid the escape of scattered and secondary electrons at the higher beam energies.

3.2.2 The Effusive Molecular Beam

At UI, liquid and gaseous samples are connected to the HV chamber through a conventional stainless steel Swagelok inlet system. The vapor is delivered to the collision region via a capillary, introducing the effusive beam perpendicular to both the electron beam and the quadrupole entrance aperture (similar to the configuration at CU, see figure 3.3). The operating
3.3 Calibration Procedures and Data Processing

3.3.1 Energy Scales and Electron Energy Resolution

The electron energy for negative ion formation is calibrated using the well characterized \( SF_6^-/SF_6 \) formation at close to 0 eV. The full-width-at-half-maximum (FWHM) of this resonance was shown to be <1 meV \([63]\) and thus the width of the observed peak is only determined by the energy resolution of the incident electron beam. A typical ion yield curve of \( SF_6^- \), the corresponding electron current measured at the collector and the first derivative of the electron current, as a function of energy, is shown in figure 3.4.
3. Experimental Configuration

![Graph](image)

**Figure 3.4:** Ion yield curve of $\text{SF}_6^-$ formation (top) and the corresponding electron current with its derivative (bottom), as a function of incident electron energy.

Energy resolution at CU was usually in the range of 140–180 meV and is similar for the apparatus at UI.

The energy resolution for positive ion detection is obtained as described above, in negative ion mode with $\text{SF}_6$ as the calibrant. The energy scale, on the other hand, is calibrated using the first ionization energy of argon at 15.759 eV [64]. Due to the finite energy spread of our electron beam, the true onset of the ion yield is convoluted with the energy distribution of the incident electron beam. To evaluate the true appearance energy, a fitting procedure detailed in equations 3.3 to 3.5 [65] was used. More specifically, a Wannier type model of the cross section dependence as a function of electron energy ($\sigma(E)$) was fitted to the experimental data,

\[
\sigma(E) = b \quad \text{for } E \leq IE_1 \tag{3.3}
\]
\[
\sigma(E) = b + a_1(E - IE_1)^{d_1} \quad \text{for } IE_1 < E \leq IE_2 \tag{3.4}
\]
\[
\sigma(E) = b + a_1(E - IE_1)^{d_1} + a_2(E - IE_2)^{d_2} \ldots \quad \text{for } IE_2 < E \tag{3.5}
\]
3.3. Calibration Procedures and Data Processing

Here \( b \) is the background signal from the detector, \( a_i \) is a scaling factor, \( IE_i \) the ionization energy and \( d_i \) an adjustable exponential factor. The fitting procedure further involves a convolution of the expected cross section dependency with the electron energy distribution function, which is assumed to be Gaussian, and which allows accounting for the energy spread of the incident electron beam. This procedure was also applied for determining the ionization and appearance energies of \([\text{Co(CO)}_3\text{NO}]^+\) and its cationic fragments in [66].

3.3.2 Determination of Absolute Cross Sections

In the present work, absolute EI and DI, as well as DEA, cross sections for the compound \([\text{Co(CO)}_3\text{NO}]\) were determined by comparison of the respective relative yields to that of a suitable reference compound.

For negative ion formation, the \( \text{SF}_5^-/\text{SF}_6 \) formation with a peak cross section of \( 0.810 \times 10^{-20} \text{ m}^2 \) [22] was used to calibrate the partial cross sections to an absolute scale. For positive ion formation, the relative \( \text{Ar}^+/\text{Ar} \) yield curve was scaled to best represent the absolute curve published by Rejoub et al. [52] and then used to derive absolute values for \([\text{Co(CO)}_3\text{NO}]^+\) and its fragments. The absolute cross section of the fragment \( X_i \), \( \sigma_{\text{abs}}(X_i) \), can thus be estimated by:

\[
\sigma_{\text{abs}}(X_i) = \frac{p(\text{Standard})}{p(X_i)} \cdot \frac{\sigma_{\text{rel}}(X_i)}{\sigma_{\text{rel}}(\text{Standard})} \cdot \sigma_{\text{abs}}(\text{Standard}) , \quad (3.6)
\]

where \( \sigma_{\text{rel}} \) is the relative ion yield and \( p \) the pressure determined by the absolute pressure gauge. For this approximation to be valid, all remaining parameters have to either remain constant or be corrected for, i.e., temperature, electron current and, most importantly, the transmission through the mass spectrometer.

The inlet system at CU described in section 3.2.2 allows for very accurate monitoring of the pressure during the course of an experiment and even during prolonged scans the deviations were \( \leq 3\% \). Furthermore, the temperature of the chamber was monitored with a thermocouple and was constant at 302 K throughout the present measurements.

A characteristic electron current curve for the TEM at CU, in the energy range from 0 to 10 eV, was shown in figure 3.4. In the energy range from 0.2 to 10 eV, the current was constant to within \( \pm 7\% \). The cross section
3. Experimental Configuration

of the calibrant, i.e., SF$_5^-$ formation from SF$_6$, has its maximum at about 0.55 eV \cite{22} and thus falls within that range. Consequently, the DEA cross sections above 0.2 eV should not be influenced significantly by any current fluctuations in the electron beam. Below 0.2 eV, close to 0 eV, the electron current is up to 50% lower than the plateau value found for the higher energies. This may lead to an underestimation of the cross sections for fragments formed at these very low energies. In the higher energy range, relevant for the determination of the positive ion formation, the electron current drops gradually by about 10%, (at the plateau, in the range of about 50 to 140 eV), but current fluctuations are found to be <±3% in this energy range.

The present setup is operated in continuous mode and the ion extraction field is kept below 1 V/cm to minimize its effect on the electron beam. This can result in a reduced extraction efficiency for fragment ions that are formed with higher kinetic energy release (KER) than the thermal Ar$^+$ and SF$_5^-$ \cite{17} ions used for calibration. For [Co(CO)$_3$NO], no direct information on the KER in EI and DI is available in the literature. However, based on the work of Fieber-Erdmann \textit{et al.} \cite{67} and Sztaray and Baer \cite{68}, it is estimated that in these processes the KER does not exceed 100 meV.

In DEA to [Co(CO)$_3$NO], the KER is expected to be even lower due to the high mass of the detected negative ions. The lighter anions are predominantly formed through metastable decay and the multiple ligands lost are expected to carry off most of the translational energy. This is supported by the fact that the total excess energy for each fragment, at the peak position of the ion yield, does generally not exceed 1 eV. The only exceptions are [CoCO]$^-$ and Co$^-$, which are formed through a higher lying resonance peaked at 6 eV \cite{69, 70}. In those cases, the KER might be higher.

The potential effect of the KER on the draw-out efficiency was estimated by simulating the extraction efficiency for individual fragments, with different KER, using the commercial program SIMION (8.0) \cite{71} and the actual geometry and extraction fields of the collision/extraction region at CU. In the energy range from 50 to 100 meV, the extraction efficiency is found to be reduced by about 30%–60% with respect to the thermal calibrant ions.

The transmission of ions through a QMS can be very dependent on their m/z ratio, and can cause a significant discrimination against higher masses \cite{72}. To be able to quantify this effect and correct the absolute cross sections for it, the relative ion yields were measured for N$_2^+/N_2$, Ar$^+/Ar$, and...
3.3. Calibration Procedures and Data Processing

Figure 3.5: Transmission response through the QMS as a function of the m/z ratio. A linear fit to the data is also shown.

Kr⁺/Kr and Xe⁺/Xe, for which the absolute partial cross sections are well established [52, 73]. The transmission data shown in figure 3.5 are extrapolated to m/z 145 and, as further extrapolation leads to negative values, the same correction factor is used for m/z 145 and 173.

For the negative ions the transmission through the QMS was optimized with respect to the SF₆⁻ signal. The mass difference between the SF₅⁻ calibrant and the fragments from [Co(CO)₃NO] is much smaller in this case, and thus the DEA cross sections were not corrected with respect to mass discrimination.

Based on the discussion above, the EI, DI and DEA cross sections of [Co(CO)₃NO], presented in section 4.1 and articles I, II and IV are estimated to be accurate to within a factor of two.
A general overview of low energy electron-molecule interactions, along with the instrumentation to study those processes, has been given in chapters 2 and 3. The aim of this chapter is to now present and summarize the main results obtained for FEBID relevant molecules studied during the course of this Ph.D. project, and to put them into context with the works of others in the field. A detailed discussion can be found in the publications on which this summary is based. They are appended to this thesis and listed on pages IX.

Section 4.1 gives a brief account of DEA, EI and DI of the precursor molecule cobalt tricarbonyl nitrosyl, based on articles I, II and IV. Section 4.2 summarizes results obtained for the compound trimethyl (methylcyclopentadienyl) platinum (IV), based on article III. Selected results from DEA studies of the hexafluoroacetylacetonate complexes bis-(hexafluoroacetylacetonate) palladium (II) and bis-(hexafluoroacetylacetonate) copper (II), as well as the ligand precursor, hexafluoroacetylacetone, are presented in section 4.3 and are further detailed in manuscript V. Finally, a brief discussion on the precursor molecule titanium (IV) iso-propoxide is given in section 4.4.
4. Results

4.1 Low Energy Electron Interactions with Cobalt Tricarbonyl Nitrosyl – An Absolute Study

4.1.1 Motivation and Previous Work

Very pure deposits in FEBID have been obtained with the precursor molecule [Co$_2$(CO)$_8$] [14]. While an excellent cobalt source, this particular precursor molecule exhibits poor stability under both vacuum and air, potentially leading to polymerization reactions and pressure build up in the precursor reservoir [10]. Recent research has thus focused on [Co(CO)$_3$NO] as an alternative candidate for electron beam induced Co deposition [10, 74]. Without post-deposition treatment, the deposited structures are reported to have a cobalt content of roughly 49%. The highest contaminant is determined to be oxygen ($\approx$27%), followed by nitrogen ($\approx$14%) and carbon ($\approx$10%). This is reminiscent of what is observed in surface science studies of [Co(CO)$_3$NO] adsorbed onto a substrate, and irradiated with 500 eV electrons [75]. The main desorbing species was observed to be carbon monoxide. Corroborating XPS data indicates that multiple CO ligands are dissociated, explaining the fairly low carbon content of the FEBID structures compared to the original precursor stoichiometry. The nitrosyl ligand, on the other hand, undergoes deposition rather than desorption, reflected in the higher nitrogen content of the FEBID structures.

The compound [Co(CO)$_3$NO)] combines two favorable properties that made it viable to normalize the relative ion yield curves to an absolute scale. First, it is a high vapor pressure liquid at room temperature, that allows for easy transfer into the HV apparatus without the risk of condensation in the inlet system or Baratron. Second, its metal center is a single isotope metal, i.e., its only stable isotope is $^{59}$Co, and thus no overlap between masses exists apart from minor contributions from $^{18}$O.

4.1.2 Electron Ionization and Dissociative Ionization

The ionization and dissociative ionization appearance energies of [Co(CO)$_3$NO], for all observed singly charged ions, lie well below 50 eV, as was determined by Opitz [76] and Sztaray and Baer [68] and as has been reinvestigated by Papp et al. [69]. DEA is not operative at energies >15 eV, and thus fragmentation induced through electron impact is the dominating
4.1. Cobalt Tricarbonyl Nitrosyl

![Graph showing partial absolute cross sections for cobalt containing positive fragment ions as a function of incident electron energy.](image)

**Figure 4.1:** Partial absolute cross sections for the cobalt containing positive fragment ions, as a function of the incident electron energy. Figure taken from reference [70]. Copyright © American Institute of Physics 2013.

dissociation pathway above 15 eV. To be able to quantify the effect DEA has in comparison to EI and DI, it is essential to know the cross sections for positive (fragment) ion formation. Those were investigated in article [IV]. Figure 4.1 shows the absolute values determined for [Co(CO)$_3$NO]$^+$ and its fragments, from threshold to about 140 eV (the maximum impact energy of the current setup at CU). A comparison of the values determined at 70 eV with the respective maximum cross sections obtained for DEA is given in table 4.1.

### 4.1.3 Dissociative Electron Attachment

The DEA ion yield curves for anionic fragments of [Co(CO)$_3$NO] are shown in figure 4.2. The DEA fragmentation observed can be briefly summarized as follows: The initial step at low energies is the formation of a single-particle shape-resonance, which peaks at around 0.5 eV and decays by loss of one CO ligand, portrayed in figure 4.2a. The contribution at about 2 eV is tentatively assigned to a low-lying core-excited resonance, resulting in the initial NO loss shown in figure 4.2d. This resonance is correlated with the HOMO-LUMO transition observed at 3.3 eV in the UV/Vis absorption spectrum [78, 79]. Due to the competition of dissociation of the TNI with autodetachment of the extra electron, the ion yield appears shifted towards lower electron energies. The occupation of a previously empty MO causes both NO as well as CO loss through direct dissociation and the shape of the respective ion yields, [Co(CO)$_3$]$^-$ and [Co(CO)$_2$NO]$^-$, reflect the formation and survival probability of the underlying TNI. At increasing ener-
Figure 4.2: DEA cross sections for the individual fragment formation from $[\text{Co(CO)}_3\text{NO}]$, as a function of incident electron energy. The inset in panel d is offset for clarity. The Gaussian-type fit functions indicate the two contributions to the ion yield of $[\text{CoCO}]^-$ in panel f. Figure adapted from references [69, 77].
4.1. Cobalt Tricarbonyl Nitrosyl

gies, further dissociation is then governed by a redistribution of the excess energy within the remaining anion fragment, leading to statistical dissociation. The fragment \([\text{Co(CO)}_3\text{NO}]^-\) can also be formed through a higher lying core-excited resonance with significantly lower intensity (see inset in figure 4.2d). Nevertheless, this resonance contributes significantly to the \([\text{CoCO}]^-\) ion yield, as indicated by the dashed and dotted lines in figure 4.2, and the formation of the bare metal anion, \(\text{Co}^-\) (figure 4.2c).

The consecutive loss of CO ligands from metal carbonyls upon DEA appears to be a fragmentation pathway inherent to carbonyls, irrespective of the central metal atom. This behavior has already been observed by Compton and Stockdale in their early study of iron pentacarbonyl and nickel tetracarbonyl [23], and has recently been observed by Wnorowski et al. for tungsten hexacarbonyl [80].

Estimates of the absolute DEA cross sections are summarized along with the electron impact and dissociative ionization cross sections in table 4.1.

4.1.4 A Comparison of Absolute Values for Positive and Negative Ion Formation from \([\text{Co(CO)}_3\text{NO}]\) and their Implications for FEBID

The main fragment observed through DEA to \([\text{Co(CO)}_3\text{NO}]\) is \([\text{Co(CO)}_2\text{NO}]^-\), with an estimated cross section of \(4.1 \times 10^{-16} \text{ cm}^2\). The corresponding DI cross section for formation of \([\text{Co(CO)}_2\text{NO}]^+\), on the other hand, is on the order of \(1.1 \times 10^{-16} \text{ cm}^2\) (at 70 eV). On the low mass side of the observed mass spectrum, \(\text{Co}^+\) is formed with a cross section exceeding \(4.6 \times 10^{-16} \text{ cm}^2\), while the formation of the bare \(\text{Co}^-\) ion in DEA is observed with a cross section of less than \(0.01 \times 10^{-16} \text{ cm}^2\). The formation of the fragment \([\text{Co(CO)}_3]\) is only observed through DEA, with an approximate cross section of \(0.45 \times 10^{-16} \text{ cm}^2\). The parent as well as the only fragment where inter-ligand fragmentation is observed, i.e., \(\text{CoC}\), are products that are only discernible through EI and DI, with respective cross sections of \(0.61 \times 10^{-16} \text{ cm}^2\) and \(0.37 \times 10^{-16} \text{ cm}^2\).

The partial cross sections for the individual ionization and fragmentation channels are heavily dependent on the incident electron energy. This is particularly obvious for the DEA channels, portrayed in figure 4.2, but also holds true for the EI and DI channels close to threshold as seen in figure 4.1. At 0 eV \([\text{Co(CO)}_2\text{NO}]^-\) is formed almost exclusively, but at close to 2 eV
4. Results

Figure 4.3: Combined total cross sections for DEA (red) and DI (blue) of [Co(CO)$_3$NO] at $E \leq 50$ eV (panel a), shown on a logarithmic scale. Also included are the normalized secondary electron (SE) yields determined by simulation (long dashed) and experiment (short dashed). The normalized effective damage yield as a function of incident electron energy is shown in panel b. Figure taken from reference [70]. Copyright ©American Institute of Physics 2013.

incident electron energy, the cross section for the formation of this fragment is already close to zero. By 7 eV, the only DEA fragments detected are [CoCO]$^-$ and Co$^-$. At slightly higher energies, DEA is no longer operative and DI becomes energetically accessible, quickly dominating the total cross section.

The energy distribution of the PEs, BSEs and SEs in FEBID is going to determine which dissociation channels are in fact relevant in the deposition process. The PE and BSE energies are usually on the order of several keV and so are outside the capability of our instrumental setup. However, al-
4.1. Cobalt Tricarbonyl Nitrosyl

Table 4.1: Comparison between the positive and negative fragment ion absolute cross sections. The positive ion cross sections were measured at 70 eV, while the negative ion cross sections are reported at whatever energy their maximum value occurred at. Table adapted from reference [70]. Copyright ©American Institute of Physics 2013.

<table>
<thead>
<tr>
<th>fragment</th>
<th>m/z</th>
<th>$\sigma_{\text{DEA}}^{\text{max}}(X^-)/10^{-16}$ cm$^2$</th>
<th>$\sigma_{70\text{eV}}^{\text{EI/DI}}(X^+)/10^{-16}$ cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>59</td>
<td>&lt; 0.01</td>
<td>4.64</td>
</tr>
<tr>
<td>CoC</td>
<td>71</td>
<td>—</td>
<td>0.37</td>
</tr>
<tr>
<td>CoCO</td>
<td>87</td>
<td>0.03</td>
<td>2.77</td>
</tr>
<tr>
<td>CoNO</td>
<td>89</td>
<td>0.02</td>
<td>0.16</td>
</tr>
<tr>
<td>Co(CO)$_2$</td>
<td>115</td>
<td>0.2</td>
<td>0.53</td>
</tr>
<tr>
<td>COCONO</td>
<td>117</td>
<td>0.2</td>
<td>0.17</td>
</tr>
<tr>
<td>CO(CO)$_3$</td>
<td>143</td>
<td>0.45</td>
<td>—</td>
</tr>
<tr>
<td>CO(CO)$_2$NO</td>
<td>145</td>
<td>4.1</td>
<td>1.13</td>
</tr>
<tr>
<td>CO(CO)$_3$NO</td>
<td>173</td>
<td>—</td>
<td>0.61</td>
</tr>
</tbody>
</table>

most independent of the incident electron energies, the primary electrons generate a SE energy distribution similar to the one shown in figure 4.3a (dashed lines) when impinging on a substrate. The overlap with the DEA total cross section (red curve) at low energies is significant, while the tail of the SE distribution still has significant overlap with the DI total cross section (blue curve). The effective damage yield obtained by multiplying the respective cross sections with the experimental SE yield from Ni (111), shown in figure 4.3b, illustrates how the energy distribution of the SE may favor one dissociation channel over another. The resulting maximum effective damage yield for DEA is thus about twice that of DI, while the integral damage yield is about sixfold for EI and DI compared to DEA, in the energy range from threshold to 50 eV.

From the gas phase studies presented here (articles I, II and IV) it can be concluded that the effect of DEA compared to EI and DI is not negligible in the energy range of the SEs generated in FEBID. The incomplete decomposition through DEA may contribute significantly to the inclusion of non-metallic contaminations in FEBID structures. DI, on the other hand, is an efficient process for Co$^+$ formation and is thus more likely to be responsible for Co deposition. As the primary electron beam induces a considerable flux of SEs outside the focal point of the beam, this is likely to also contribute to the broadening of the deposit.
4. Results

4.2 Low Energy Electron Interactions with Trimethyl (Methylcyclopentadienyl) Platinum (IV)

4.2.1 Motivation and Previous Work

[Chemical structure]

Figure 4.4: Trimethyl (methylcyclopentadienyl) platinum (IV), [MeCpPtMe₃].

Selective platinum deposition is useful for purposes in both catalysis as well as micro-/nano-engineering. Consequently, the platinum containing precursor molecule trimethyl (methylcyclopentadienyl) platinum (IV), [MeCpPtMe₃] (figure 4.4), has been extensively studied with respect to finding the optimal FEBID process parameters that yield maximum platinum content in the deposited structures (see, e.g., references [7, 12, 81]). The fact that FEBID, lacking post processing treatment of the deposit, yields mostly structures with a high carbon content has sparked interest in obtaining a more mechanistic insight, which was to some extent provided by a surface science approach [28, 29, 82]. Briefly, [MeCpPtMe₃] adsorbed onto a gold substrate was irradiated with 500 eV electrons. The gas phase reaction products were monitored by mass spectrometry, while the nonvolatile products left on the surface were analyzed by XPS and RAIRS. The residue was identified as platinum encapsulated in a carbonaceous matrix, with a Pt:C stoichiometry of 1:8, i.e., one carbon less than the original precursor molecule. Identification of methane in the gas phase led to the conclusion that scission of one Pt–CH₃ bond was the main dissociation step involved, yet the mechanism that induces the dissociation remained unclear.

4.2.2 Electron Ionization and Dissociative Ionization

The mass spectrum resulting from electron impact ionization of gas phase [MeCpPtMe₃] at 100 eV impact energy is shown in figure 4.5a. Figures 4.5b, c and d show an expanded view of the mass ranges 0–85 u, 180–250 u and 250–330 u, respectively. While fragmentation through DI is abundant, pure
4.2. Trimethyl (Methylcyclopentadienyl) Platinum (IV)

Figure 4.5: Dissociative ionization of [MeCpPtMe$_3$] at 100 eV; subfigures show an expansion of the spectrum for the mass ranges 0–85 u (b), 180–250 u (c) and 250–330 u (d). Figure taken from reference [77]. Copyright ©The Royal Society of Chemistry 2012.

Pt$^+$ is discernible with only weak intensity. In light of later discussion, it should be noted here that the formation of fragments induced through single ligand loss, i.e., the methyl radical (m/z 15) and [MeCpPtMe$_2$]$^+$ (peaks centered around m/z 301), is also negligible. The dominant DI fragments observed can be assigned to the loss of two and three methyl groups along with hydrogen, i.e., [MeCpPtMe]$^+$ centered around m/z 288 and [MeCpPt]$^+$ centered around m/z 272.

4.2.3 Dissociative Electron Attachment

Different to DI, the dominant fragment observed in DEA to [MeCpPtMe$_3$] appears at m/z 304 (for the most abundant platinum isotope, $^{195}$Pt) and is assigned to the loss of one methyl radical from the parent, i.e., to the frag-
4. Results

Figure 4.6: Relative DEA ion yields for individual fragment formation from [MeCpPtMe₃], as a function of incident electron energy. Figure adapted from reference [77]. Copyright ©The Royal Society of Chemistry 2012.

Fragment [MeCpPtMe₂]⁻, see figure 4.6. It is formed through a low energy shape resonance with an onset close to 0 eV, a maximum close to 0.5 eV and through a minor contribution between 6 and 8 eV. The only other fragment formed through the 0 eV resonance is [MeCpPtMe₃-CH₃CH₂]⁻ (main peak m/z 290, bottom left panel of figure 4.7), albeit with significantly lower intensity. At slightly higher energies, with a threshold of about 2 eV and a peak maximum at 2.3 eV, a fragment consistent with the loss of two methyl groups and one hydrogen atom (main peak m/z 288, also figure 4.7), becomes discernible. Considering the thermodynamics and the low AE, the neutral products probably combine to form methane and one methyl radical.

Due to the natural isotope distribution of Pt (¹⁹⁰Pt 0.01%, ¹⁹²Pt 0.8%, ¹⁹⁴Pt 33%, ¹⁹⁵Pt 34%, ¹⁹⁶Pt 25%, ¹⁹⁸Pt 7.2% [83]), the two different fragments, [MeCpPtMe₃-CH₃CH₂]⁻ and [MeCpPtMe₃-CH₄-CH₃]⁻, contribute to the same m/z ratio. A correct assignment was possible by recording the ion yields with high mass resolution for the m/z ratios 287 and 291, respectively, i.e., at the low and high m/z ratio of the respective isotope distributions.

The remaining fragments are formed through a core excited shape resonance close to 4 eV. The assignment of the m/z ratios 210, 195 and 79 is fairly straightforward from their stoichiometry and the observed isotope
4.2. Trimethyl (Methylcyclopentadienyl) Platinum (IV)

Figure 4.7: Separation of the ion yields of [MeCpPtMe₃–CH₃CH₂]⁻ (main peak m/z 290) and [MeCpPtMe₃–CH₃–CH₄]⁻ (main peak m/z 288) through selection of isotopic peaks where their overlap is minimized. Figure taken from reference [77]. Copyright ©The Royal Society of Chemistry 2012.

ratios. They are attributed to [PtCH₃]⁻, the bare platinum anion, Pt⁻, and the methylcyclopentadienyl anion, MeCp⁻, respectively. For the formation of m/z ratios 272 and 224, on the other hand, a loss of 47 u and 95 u is necessary. These fragments must thus be formed through a partial loss of the MeCp unit (m/z 272) and the loss of the MeCp unit, a methyl group and a hydrogen (m/z 224). From the thermochemical point of view, the formation of all these fragments is likely to be accompanied by new bond formation, fueling the extensive fragmentation.

The high yield for the scission of the Pt–CH₃ bond can be qualitatively explained as follows: The η⁵-bound MeCp ring shares six electrons with the central platinum atom, while the σ-bonded methyl group shares only two.
4. Results

At close to zero eV incident electron energy, the attachment of an electron into the LUMO is therefore more likely to weaken the Pt–CH$_3$ bond for dissociation rather than the Pt–Cp bond.

4.2.4 Implications for FEBID

The dominant fragmentation channel observed in DEA from [MeCpPtMe$_3$] is the homolytic scission of a single Pt–CH$_3$ bond, yielding the negative ion fragment [MeCpPtMe$_2$]$^-$. The dominant fragmentation channel observed for EI and DI, on the other hand, is the loss of two and three methyl groups along with hydrogen. For both processes the formation of the bare Pt ion, stripped of all ligands, is only a minor channel and a partial decomposition of the precursor dominates.

In the photolytic decomposition of [CpPtMe$_3$], studied in various organic solvents, illumination by a 300/350 nm (4.1/3.5 eV) light source yielded mainly methane, along with small amounts of ethane and ethene [84]. The dissociation was shown to result from homolytic bond rupture and subsequent reaction with neighboring (solvent) molecules. Thus, in the surface science study discussed in section 4.2.1 it can also be assumed that an intermolecular reaction leads to the formation of methane. Under single collision conditions, where the present DEA studies were performed, only intramolecular abstraction of hydrogen can lead to the formation of methane and the loss of a methyl radical dominates.

In the light of recent results from the surface science study by Wnuk et al. [28] and van Dorp et al. [29] (section 4.2.1), it appears that a DEA rather than a DI mechanism is operative as the initial bond breaking step. This is similar to what is observed in recent studies on the carbon free platinum containing precursor tetrakis trifluorophosphine platinum, [Pt(PF$_3$)$_4$] [85 86]. Gas phase DEA studies show the main dissociation channel to be the loss of one PF$_3$ ligand, with a peak cross section of about $2 \times 10^{-16}$ cm$^2$ at 0.5 eV. Analogous to the gas phase studies, the decomposition of adsorbed [Pt(PF$_3$)$_4$] proceeds initially through the cleavage of a single Pt–PF$_3$ bond [31]. Subsequent electron induced reactions of the surface bound species results exclusively in the scission of P–F bonds.
4.3 Dissociative Electron Attachment to Hexafluoroacetylacetone and its Bidentate Metal Complexes

4.3.1 Motivation and Previous Work

![Figure 4.8: General structure of the metal (II) hexafluoroacetylacetonate complexes, [M(hfac)$_2$]. In this work, M = Cu, Pd.]

Aectylacetonates (acac) are a versatile class of compounds that can complex almost any metal in the periodic table of elements. They are found to be fairly stable and generally have sufficient vapor pressure for deposition techniques requiring volatile metal sources [87]. Chemical substitution of the methyl groups allows direct modification of the physical and chemical properties of the acac ligand, and fluorination to hexafluoroacetylacetonate (hfac) has shown to increase the volatility of these metal complexes even further [87].

From a fundamental standpoint, this class of compounds is interesting for two different reasons. First, it is possible to study the ligand precursor hexafluoroacetylacetone (Hhfac) and to establish all its viable dissociation pathways. Comparison to the metal complex then allows us to evaluate what role ligand based orbitals play in the dissociation of these complexes. Second, by varying the central metal atom, it can be evaluated how the dissociation pattern depends on the central metal itself.

A brief account [82] on the electron induced decomposition of adsorbed bis-(hexafluoroacetylacetonate) copper (II) ([Cu(hfac)$_2$]) under UHV conditions reveals the release of CO into the gas phase upon decomposition of the precursor. Changes in the adsorbate layer further indicated loss of fluorine. No further mechanistic, electron induced, decomposition studies of adsorbed [Cu(hfac)$_2$] or bis-(hexafluoroacetylacetonate) palladium (II) ([Pd(hfac)$_2$]) have been published and thus, for the later discussion in section 4.3.6 studies on hexafluoroacetylacetonate Cu (I) vinyltrimethylsilane
4. Results

([Cu(hfac)(vtms)]) \[25\], a compound of similar ligand architecture, are consulted for comparison with the gas phase studies.

FEBID of copper from [Cu(hfac)\_2], with 25 keV electrons \[88\], results in an insulating deposit with a copper content of about 14%. The main contaminants are carbon (75%) and oxygen (5%), while no significant amounts of fluorine are detected.

4.3.2 Ligand Precursor Hexafluoroacetylacetone

The extensive fragmentation of the parent compound Hhfac, which takes place upon attaching a low energy electron, is pictured in figure 4.9.

Prominent fragments are discernible at mass to charge ratios (m/z) 207, 188, 171, 168, 143, 137, 94 and 69. Less intense fragments are also found at m/z 140, 113 and 39. In most cases, the identification of the neutral counterparts is straightforward. The mass peak at 207 u is assigned to [M-H]\(^-\), i.e., the loss of one hydrogen atom from the parent molecule (M). At m/z 188, a loss of 20 u points towards formation of HF. Correspondingly, the formation of m/z 168 requires 40 u, indicating a loss of two HF molecules. HF loss is also anticipated to play a role in the formation of the fragments m/z 171, 143, 140 and 94: For C\(_5\)F\(_5\)O\(^-\) formation at m/z 171, further loss of OH is anticipated, while for the formation of C\(_4\)F\(_5\) (m/z 143), the additional formation of neutral CO and OH may lead to the detected mass. The formation of C\(_4\)F\(_4\)O\(^-\) at m/z 140 may either be due to the loss of two HF molecules and one CO molecule, or the loss of molecular hydrogen and difluoroformaldehyde. Formation of C\(_3\)HF\(_3\), m/z 94, may proceed via subsequent loss of COF\(_2\) and CO. For the fragment C\(_4\)O\(_2\)F\(_5\), m/z 137, loss of molecular hydrogen and a CF\(_3\) radical are assumed. CF\(_3\) is detected at m/z 69, while HF\(_2\) is detected at m/z 39. For the mass fragment at m/z 113, i.e., C\(_3\)HF\(_4\), no straightforward stochiometry results for the neutral counterparts.

The loss of one hydrogen atom from the parent to form [M-H]\(^-\) (m/z 207) proceeds through a sharp and narrow contribution at 0 eV threshold (figure 4.9), peaking at slightly above 0 eV. Additional, broader, contributions are also discernible at 1.0, 3.0 and 5.4 eV. Using the bond dissociation value calculated for the enol form of Hhfac, i.e., BDE(O–H) = 4.3 eV \[59\], and 0 eV as the threshold for [M-H]\(^-\) formation, a lower bound of 4.3 eV can be deduced for the EA of (hfac).
Figure 4.9: DEA ion yield curves, as a function of incident electron energy, for the ligand precursor hexafluoroacetylacetone.
4. Results

The loss of HF yielding [M-HF]− at m/z 188 proceeds through a fairly narrow channel, with a threshold of 0 eV and a maximum just slightly above 0 eV. The loss of HF from Hhfac has previously been observed by Basset and Whittle [90], in a photolysis study using incident wavelengths of ≥235 nm. The efficient, DEA induced loss of HF close to 0 eV has also been described by Ómarsson et al. [91] for the compounds pentafluorotoluene, pentafluoroaniline and pentafluorophenol. The very low reaction threshold and considerably higher cross sections they observed in DEA were ascribed to the energy released through the HF formation (about 5.9 eV [83]). In the present DEA study, about half of the observed negative fragments are formed through concomitant HF loss and its formation can thus be seen as the driving force for the formation of those fragments. This is supported by recent studies carried out in our laboratory on the unfluorinated analogue acetylacetone, from which only weak DEA induced dissociation can be observed.

4.3.3 Bis-(Hexafluoroacetylacetonate) Palladium (II)

Two prominent anions are formed upon low energy electron attachment to [Pd(hfac)2], i.e., the parent anion [Pd(hfac)2]− (m/z 520) and the free ligand base (hfac)− (m/z 207) (see figure 4.10). Further low intensity fragments include [Pd(hfac)CF3]− (m/z 382), (hfac-CF2)− (m/z 157), (hfac-H-CF3)− (m/z 137), CF3− (m/z 69) and F− (m/z 19). While dissociation of both ligands through a DEA mechanism appears energetically possible [92], no bare metal anion was detected to support the possibility of complete dissociation. The ion yield of the parent anion, [Pd(hfac)2]−, is characterized by two distinct peaks. The higher intensity peak has its maximum at 0 eV, while a smaller contribution peaks at approximately 0.7 eV. The detection of the parent anion at such high energies is quite unusual and points towards an efficient redistribution of energy within the molecule. The bidentate nature of the (hfac) ligand may work in favor of this randomization of energy, as anions where the ligand is only partially dissociated (monodentate) will still be detected as [M]−. Alternatively, the binding mode of (hfac) may change in a way that involves the binding of the γ-carbon atom of the ligand to the central metal atom, which has been observed for diketonate complexes of platinum [93].

The dissociation of (hfac)−/[Pd(hfac)2] proceeds through four individual resonances, similar to what has been observed for the formation of (hfac)−/Hhfac. The peak maxima of (hfac)−/[Pd(hfac)2] appear at higher
energies, i.e., at 1.3, 2.4, 3.9 and 6.4 eV. It can thus be concluded that the ligand based unoccupied molecular orbitals associated with the resonances are destabilized through complexation. A minor competing channel is the formation of [Pd(hfac)CF₃]⁻ (m/z 382). The formation of this fragment requires the migration of one CF₃ moiety to the central metal atom, and the subsequent release of the Pd–CF₃ bond energy may aid in the dissociation of the neutral (hfac-CF₃) fragment. The remaining metal-free fragments, i.e. (hfac-CF₂)⁻ (m/z 157), (hfac-H-CF₃)⁻ (m/z 137), CF₃⁻ (m/z 69) and F⁻ (m/z 19), probably result from complex metastable decay of (hfac)⁻. From those fragments (hfac-H-CF₃)⁻ is observed with the highest intensity, and its formation may be favored by the formation of trifluoromethane.

Figure 4.10: Ion yield curves for dissociative and non-dissociative electron attachment to [Pd(hfac)₂], as a function of incident electron energy.
4. Results

4.3.4 Bis-(Hexafluoroacetylacetonate) Copper (II)

Only weak fragmentation is observed from electron attachment to \([\text{Cu(hfac)}_2]\), with the respective ion yield curves portrayed in figure 4.11. The dominant anion observed is attributed to the parent anion \([\text{Cu(hfac)}_2]^-\) at m/z 477 (main isotope peak). The only dissociation products identified are the free ligand base (hfac)$^-$ at m/z 207 and (hfac-H-CF$_3$)$^-\) at m/z 137. Again, no bare metal anion was detected.

The formation of the parent anion proceeds through a narrow contribution peaking at 0 eV and a very weak shoulder at around 0.5 eV. Again, efficient randomization of the excess energy or change of the binding motive, possibly including a geometry change from a square planar to tetrahedral conformation, is believed to stabilize the parent anion. Nevertheless, loss of (hfac)$^-$ is observed at 0 eV as well as from contributions peaking at 1.3, 2.9 and 6.4 eV. Finally, (hfac-H-CF$_3$)$^-\) formation is observed through a broad contribution peaking at around 6 eV.

Figure 4.11: Ion yield curves for dissociative and non-dissociative electron attachment to \([\text{Cu(hfac)}_2]\), as a function of incident electron energy.
4.3.5 Complexing – Going from Hexafluoroacetylacetone to the Chelated Complex

While a rich fragmentation pattern is discernible from electron attachment to the ligand precursor Hhfac, the fragmentation of the bis-hexafluoroacetylacetonate complexes is fairly restricted. Most of the high intensity channels that proceed with concomitant HF loss observed for Hhfac are not observed for the metal complexes. In fact, HF loss from the metal complexes is not discernible at all, and it thus appears that substitution of the enol-hydrogen by the central metal atom suppresses HF formation.

From comparison of the various ion yields of \((\text{hfac})^-\), i.e., \((\text{hfac})^- / \text{Hhfac}\), \((\text{hfac})^- / [\text{Pd(\text{hfac})_2}]\) and \((\text{hfac})^- / [\text{Cu(\text{hfac})_2}]\), it becomes clear that i) the ligand based orbitals involved in formation of the underlying resonances are significantly influenced by complexation and ii) mixing with metal based orbitals occurs, as the shape and position of the ion yield curves are strongly influenced by the central metal atom. The importance of the central metal atom is also manifested in the formation of the parent anion. While non-dissociative electron attachment is only weakly pronounced for \([\text{Pd(\text{hfac})_2}]\), \([\text{Cu(\text{hfac})_2}]^-\) formation dominates over DEA to \([\text{Cu(\text{hfac})_2}]\). Thus, while the main fragments formed from the metal complexes are the same, their energy dependence and intensity vary on a case to case basis.

4.3.6 Implications for FEBID

Mezhenny et al. [25] have studied the decomposition of \([\text{Cu(\text{hfac})(\text{vtms})}]\), adsorbed onto a Si(111)-(7x7) surface, with low energy electrons in the range 2–27 eV. Contrary to what is observed for the same precursor as well as \([\text{Cu(\text{hfac})_2}]\) at 25 keV impact energies (section 4.3.1), this study showed considerable fluorine contamination. The authors derived a threshold for deposit growth of 4.0±0.5 eV [25] and thus inferred a DEA induced growth. A notable difference between the high [88] and low [25] electron energy dissociation study of adsorbed Cu(hfac)(vtms) is the absence, and presence, of fluorine contamination in the deposit. A possible explanation for this observation may be an initial, low-energy electron supported dissociation of the hfac ligand, fixing the ligand as well as the remaining molecule at the surface. Metastable decay is likely to be quenched and further removal of fluorine from the surface bound intermediate is likely to proceed through
4. Results

further electron irradiation, leading to C–F bond cleavage.

While CO formation was observed from DEA to the ligand precursor Hhfac, no such liberation was discernible from DEA to the metal hexafluoroacetylacetonates. The formation of CO⁺ or complimentary fragments is also negligible in DI of HFAc and its hexafluoroacetylacetonates and thus surface effects seem to play a large role in CO evolution.

4.4 Low Energy Electron Interactions with Titanium (IV) Iso-Propoxide

4.4.1 Motivation and Previous Work

As was the case for the hexafluoroacetylacetonate complexes presented in sections 4.3.3 and 4.3.4, titanium (IV) iso-propoxide, TIPO (see figure 4.12), is a common precursor for CVD, used for deposition of TiO₂ films (see, for example, references [94, 95]). With respect to FEBID, TIPO has found practical application as a negative type, electron beam resist for semiconductor etching [96, 97]. During the development of the latter, it was noted that the deposition of the precursor occurs with unusually high cross sections, i.e., on the order of 1.5×10⁻¹⁴ cm² [96]. Furthermore, it was observed that the deposit composition is dependent on the total electron exposure, i.e., the carbon contamination increased with higher exposure rates. The authors [96] ascribed this behavior to a higher cross section for TiO–C bond rupture compared to C–H bond cleavage. The rupture of the TiO–C bonds is believed to lead to volatile hydrocarbon species that are removed from the film through desorption, while the C–H cleavage leads to a nonvolatile carbon deposit. With increasing electron exposure, the C–H cleavage may
become more relevant, resulting in the higher carbon content \[96\]. Finally, the authors noted that titanium oxide growth occurred in between electron beam exposed areas. This in turn was attributed to decomposition induced through low energy secondary electrons or backscattered primary electrons \[96, 98\].

Unfortunately, Mitchell and Hu do not quantify the chemical composition of the deposits. A fairly recent study by Schirmer et al. \[99\] estimated the composition of their structures deposited from TIPO at 15–30 at.% carbon, \(\approx 30\) at.% titanium and \(\approx 50\) at.% oxygen. In agreement with Mitchell and Hu \[96, 98\], they noted that the carbon content is dependent on the lithographic parameters as well as whether surface or volume sensitive techniques, i.e., Auger electron spectroscopy (AES) or energy dispersive x-ray spectroscopy (EDX) is used for composition analysis. Nevertheless, considering a C:Ti:O ratio of 12:1:4 in the original precursor molecule, the removal of the carbon based ligands is remarkably efficient when compared to, e.g., electron induced decomposition of [MeCpPtMe\(_3\)] (section 4.2).

The implicated change in the cross section may be due to a change in the reaction mechanism, i.e., a DEA versus a DI mechanism. This idea therefore prompted us to investigate whether DEA or DI are efficient mechanisms for TIPO decomposition, with those results being discussed below.

### 4.4.2 Electron Ionization and Dissociative Ionization

Abundant fragmentation of the parent compound is discernible in the mass spectrum, resulting from electron impact at an incident energy of \(E = 90\) eV, as shown as the top left panel in Figure 4.13. The spectrum is dominated by the loss of one \(\text{CH}_3\) group from the parent at \(m/z\ 269\). Further ligand loss leads to the mass-to-charge-ratios 225 (loss of \(-\text{OC}_3\text{H}_7\)), 223, 211, 181, 167, 139, 135, 125, 122, 121, 108, 81 (\(\text{TiO}_2\text{H}^+\)) and 64 (\(\text{TiO}^+\)). A more detailed assignment is hindered by the sheer number of hydrogen atoms in the precursor, and the close mass of carbon and oxygen. Metal free, ligand based fragments can be observed at \(m/z\ 45, 43, 41, 27\) and 15. The parent less one hydrogen atom, [M-H]\(^+\), is also observable with weak intensity at \(m/z\ 283\), while bare titanium (main isotope \(m/z\ 48\)) is not detected.
4. Results

Figure 4.13: Results of our EI and DI experiments at 90 eV (a), and our DEA (b, c, d) results from titanium iso-propoxide.

4.4.3 Dissociative Electron Attachment

Figure 4.13 also portrays a negative ion mass spectrum made up of several negative ion scans recorded at energies from 0–10 eV (see figure 4.13b). The only significant masses originating from TIPO are m/z 241 and m/z 199, two fragments barely observable in the positive ion mass spectrum. The signals at m/z 35 and 37 are due to chlorine contamination from the synthesis of TIPO. The fragment $[\text{TiO}_4(\text{C}_3\text{H}_7)_3]^-$ at m/z 241 may be formed via a low lying shape resonance with a maximum at 0.1 eV and a broad, presumably core excited, resonance peaking at 8.8 eV, inducing the cleavage of one TiO–C bond. The fragment $[\text{TiO}_4(\text{C}_3\text{H}_7)_2\text{H}]^-$ at m/z 199, on the other hand, is exclusively formed through the high energy resonance, resulting in cleavage of two Ti–O bonds with subsequent migration of one hydrogen atom to the charge retaining fragment. The respective ion yields are portrayed in figure 4.13c and d.
4.4.4 Implications for FEBID

The DEA ion yields presented in this section were recorded at the same pressure as the EI and DI yields, with identical (yet reversed) settings on the extraction and ion optic lenses. Although this permits only a rough comparison, it appears that the DEA induced bond cleavage is a very inefficient process in the gas phase compared to dissociation induced through direct electron impact. On the other hand, while fragmentation from DI is abundant, the main fragments observed still contain considerable amounts of carbon. Thus, no direct parallels can yet be drawn between the composition of the FEBID deposits and the gas phase fragmentation patterns observed.

As the FEBID experiments of Mitchell et al. [96,98] were carried out at a substrate temperature of <-20°C, local heating can likely be ruled out to have an effect on the deposit composition. The carbon content (even at elevated exposure) in FEBID structures is lower than what might be expected on the basis of the gas phase studies. It is thus reasonable to assume that multiple electron-molecules collisions result in volatile species, effectively reducing the carbon content to the observed values (see section 4.4.1). Competing reactions operative after the initial bond cleavage, similar to what is observed for the dissociation of trifluorophosphane and fluorine from [Pt(PF₃)₄] [31], may then be responsible for the increased carbon content at higher exposure.
5

Summary and Outlook

The work presented in this thesis focused on the gas phase interactions of low energy electrons with precursor molecules relevant for FEBID. Motivated by the characteristic SE distribution found in FEBID, particular emphasis was placed on the role of DEA at energies below 15 eV as well as EI and DI at energies above threshold.

For \([\text{Co(CO)}_3\text{NO}]\), the absolute DEA, EI and DI cross sections were determined in the electron energy range from 0 to 140 eV. The dominant DEA channel was found to be the loss of a single carbonyl group. Further fragmentation is an order of magnitude less intense and the formation of the bare \(\text{Co}^-\) anion is practically insignificant. In contrast, the dominant DI fragment was the \(\text{Co}^+\) cation.

For the compound \([\text{MeCpPtMe}_3]\), a DEA pattern similar to \([\text{Co(CO)}_3\text{NO}]\) was observed. The loss of one methyl radical is the dominant dissociation pathway for the TNI, and further ligand loss down to bare \(\text{Pt}^-\) occurs only with significantly lower intensity. DI at 100 eV results mainly in the loss of two or three methyl groups, while bare \(\text{Pt}^+\) is hardly discernible.

DEA from \([\text{TiO}_4(\text{C}_3\text{H}_7)_4]\) yielded only two detectable fragments of low intensity, i.e., the parent less one or two hydrocarbon ligand moieties. Fragmentation induced through electron impact, on the other hand, was abundant and efficient, yielding both \(\text{TiO}^+\) as well as \(\text{TiO}_2\text{H}^+\).

Finally, the picture changes slightly on going from monodentate to bidentate binding motives. Dissociation of a single ligand remains a viable relaxation pathway for the TNI, yet non-dissociative electron attachment be-
5. Summary and Outlook

comes a competitive channel for [Pd(hfac)$_2$] and the dominant channel for [Cu(hfac)$_2$].

As a result of the work presented here, several qualitative conclusions can be drawn. For almost all the precursor molecules, the dissociation of a single ligand was the predominant dissociation pathway in DEA. The only exception we found was [Cu(hfac)$_2$], which predominantly forms the parent anion. Dissociation to the bare metal ion, on the other hand, was either inefficient ([Co(CO)$_3$NO] and [MeCpPtMe$_3$]) or was not discernible at all ([Cu(hfac)$_2$], [Pd(hfac)$_2$] and TIPO). For DI, no such direct trends could be observed. While Co$^+$ was the dominant fragment observed from DI of [Co(CO)$_3$NO], Pt$^+$ formation from [MeCpPtMe$_3$] was extremely inefficient and only partial fragmentation dominated. For the compound TIPO, where DEA does not play a significant role, DI resulted in the desired TiO$_x$ species but also in the loss of only a single CH$_3$ moiety. Abundant, incomplete dissociation, but also efficient Pd$^+$ formation was also observed for DI of [Pd(hfac)$_2$]. The fragmentation pattern observed through DEA and DI was thus largely dependent on the molecule itself, and no general predictions can yet be made from this limited set of molecules.

A more quantitative picture regarding the role of DEA and DI induced through low energy SEs, came from our gas phase absolute cross section measurements of [Co(CO)$_3$NO]. The DEA induced single bond cleavage was shown to occur with similar peak magnitude cross sections as the dominant DI channel, i.e., Co$^+$ formation, and to overlap “favorably” with the expected SE yield in FEBID. Thus, unless significant quenching occurs at the surface, DEA induced through low energy SEs might significantly influence the composition of the deposited FEBID structures. The absolute cross section for positive ion formation, on the other hand, still overlapped significantly with the tail of the SE yield and so is expected to also contribute substantially to the deposition process. As the DEA induced decomposition was predominantly incomplete, <15 eV electrons are expected to mainly contribute to the inclusion of non-metallic contaminants, while DI is expected to be responsible for more or less pure cobalt deposition.

Studies on the adsorbed precursor exposed to 500 eV electrons [75], showed the main desorbing fragment to be CO. Whether this dissociation was induced through DEA or DI is difficult to judge, and electron energy dependent studies including the very low energy regime <15 eV as carried out by e.g., Olsen and Rowntree [60], Di et al. [59] or Bass and Sanche [55] would be helpful to gain further insight.
Support for DEA being an operative dissociation channel in FEBID came from comparing the gas phase DEA and DI ion yields from [MeCpPtMe₃], to an earlier study on adsorbed [MeCpPtMe₃] when exposed to 500 eV electrons [28]. The composition of the deposit implied that DEA rather than DI may be the initial step in the dissociation of this common precursor. Further electron irradiation is then expected to lead to the final composition of the deposited film. Similar conclusions can be drawn for the carbon free precursor [Pt(PF₃)₄], studied by Landheer et al. [31] and Allan et al. [85, 86]. Again the irradiation experiments of the adsorbed precursor were carried out with fairly high incident electron energies so that irradiation at electron energies <15 eV may be beneficial for establishing the operative mechanisms.

The gas phase studies presented in this thesis lay the fundamental groundwork to identify and understand the underlying processes operative in FEBID. They demonstrated that both DEA as well as DI can be expected to contribute significantly to the deposit composition observed in FEBID. However, this work also demonstrated that gas phase studies alone do not suffice to gain a detailed understanding of the FEBID process as a whole and that collaborative research effort across disciplines is necessary in order to promote such an understanding.

For future studies it would be desirable to not only combine insights gained from gas phase and surface science studies, but to also have information on the effect of aggregation on the dissociation mechanisms observed in the gas phase. A first step into this direction may be the study of FEBID precursor molecules in (seeded) cluster beams. This still allows the use of mass spectrometric methods, with the added benefit of being able to observe whether collisional relaxation or scavenging effects influence the DEA and DI behavior. Surface effects may then be investigated separately through electron transmission (ETS), electron induced desorption (EDS) or high resolution electron energy loss (HREELS) spectroscopy of precursor molecules deposited on inert gas buffer layers or directly onto a cryogenic substrate.

Even the relatively small selection of FEBID precursor molecules covered in this work, demonstrated that the composition of the FEBID deposit was largely dependent on the molecular structure of the precursor. It is thus necessary to deepen our understanding of how certain metal-ligand architectures are affected by DEA and DI, respectively. A detailed understanding of the precursor chemistry may then lead to precursor molecules designed specifically for FEBID, with the aim of improving the deposited structures.
# List of Figures

1.1 Schematic pictorial of the FEBID process .......................... 1  
1.2 Factors influencing the FEBID process ............................. 2  
1.3 A typical energy spectrum of electrons emitted from a sample surface upon irradiation with a focused, high energy primary electron beam ........................................ 4  
1.4 An illustrative example of a BSE trajectory simulation from nickel ........................................... 5  

2.1 Illustration of the ionization and dissociation process through electron impact ........................................ 10  
2.2 General Shape of the reaction rate \( \log k \) as a function of electron energy ........................................ 10  
2.3 Effective potential, including the Coulomb repulsion, of the electron-molecule interactions as a function of their distance. Also shown is the formation of the potential barrier with different values of \( \ell \) ........................................ 13  
2.4 Classification of various resonances according to their energy relative to the neutral parent MX ........................................ 14  
2.5 Potential curve diagram for low-energy electron–molecule collisions with the quasi diatomic molecule MX ........................................ 16  

3.1 Schematic diagram of a crossed electron-molecular beam setup ........................................ 24  
3.2 Schematic diagram of the trochoidal electron monochromator at UI ........................................ 25  
3.3 Details of the apparatus geometry within the HV chamber at CU ........................................ 27  
3.4 Ion yield curve of \( \text{SF}_6^- \) formation and the corresponding electron current with its derivative, as a function of incident electron energy ........................................ 28  
3.5 Transmission response through the QMS as a function of the \( m/z \) ratio. A linear fit to the data is also shown ........................................ 31
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1</td>
<td>Partial absolute cross sections for the cobalt containing positive fragment ions.</td>
</tr>
<tr>
<td>4.2</td>
<td>DEA cross sections for the individual fragment formation from [Co(CO)$_3$NO], as a function of incident electron energy.</td>
</tr>
<tr>
<td>4.3</td>
<td>Combined total cross sections for DEA and DI of [Co(CO)$_3$NO] at $E \leq 50$ eV. Also shown are the normalized secondary electron (SE) yields, both calculated and measured as well as the normalized effective damage yield.</td>
</tr>
<tr>
<td>4.4</td>
<td>Trimethyl (methylcyclopentadienyl) platinum (IV), [MeCpPtMe$_3$].</td>
</tr>
<tr>
<td>4.5</td>
<td>Dissociative ionization of [MeCpPtMe$_3$] at 100 eV.</td>
</tr>
<tr>
<td>4.6</td>
<td>Relative DEA ion yields for individual fragment formation from [MeCpPtMe$_3$], as a function of incident electron energy.</td>
</tr>
<tr>
<td>4.7</td>
<td>Separation of the ion yields of [MeCpPtMe$_3$-CH$_3$CH$_2$]$^-$ (main peak m/z 290) and [MeCpPtMe$_3$-CH$_3$CH$_4$]$^-$ (main peak m/z 288) through selection of isotopic peaks where their overlap is minimized.</td>
</tr>
<tr>
<td>4.8</td>
<td>General structure of the metal (II) hexafluoroacetylacetonate complexes, [M(hfac)$_2$]. In this work, M = Cu, Pd.</td>
</tr>
<tr>
<td>4.9</td>
<td>DEA ion yield curves, as a function of incident electron energy, for the ligand precursor hexafluoroacetylacetone.</td>
</tr>
<tr>
<td>4.10</td>
<td>Ion yield curves for dissociative and non-dissociative electron attachment to [Pd(hfac)$_2$], as a function of incident electron energy.</td>
</tr>
<tr>
<td>4.11</td>
<td>Ion yield curves for dissociative and non-dissociative electron attachment to [Cu(hfac)$_2$], as a function of incident electron energy.</td>
</tr>
<tr>
<td>4.12</td>
<td>Titanium (IV) iso-propoxide, TIPO.</td>
</tr>
<tr>
<td>4.13</td>
<td>Results of our EI and DI experiments at 90 eV, and our DEA results to titanium (IV) iso-propoxide.</td>
</tr>
</tbody>
</table>
# List of Tables

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1</td>
<td>Comparison between the positive and negative fragment ion absolute cross sections.</td>
<td>39</td>
</tr>
</tbody>
</table>
Bibliography


Bibliography


Included Publications
Article 1

The Role of Dissociative Electron Attachment in Electron Beam Induced Deposition – A Case Study on Cobalt Tricarbonyl Nitrosyl

Sarah Engmann, Michal Stano, Štefan Matejčík and Oddur Ingólfsson


DOI:10.1002/anie.201103234

Copyright © 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. All rights reserved.

Sarah Engmann actively participated in developing the research concept and carried out the measurements in collaboration with Michal Stano. Sarah took an active part in the data analysis and interpretation. She wrote the first draft of the manuscript and contributed to editing until publication of the final version.
Die Rolle dissoziativer Elektronenanlagerung in Prozessierungsverfahren mit fokussierten Elektronenstrahlen – eine Fallstudie an Tricarbonyl(nitrosyl)cobalt

Sarah Engmann, Michal Stano, Štefan Matejčík and Oddur Ingólfsson


DOI:10.1002/ange.201103234

Copyright © 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. All rights reserved.

Sarah Engmann actively participated in developing the research concept and carried out the measurements in collaboration with Michal Stano. Sarah took an active part in the data analysis and interpretation. She wrote the first draft of the manuscript and contributed to editing until publication of the final version. Sarah also translated the final version into German.
Gas Phase Low Energy Electron Induced Decomposition of the Focused Electron Beam Induced Deposition (FEBID) precursor Trimethyl (Methyl-cyclopentadienyl) Platinum(IV) (MeCpPtMe$_3$)

Sarah Engmann, Michal Stano, Štefan Matejčík and Oddur Ingólfssson


DOI:10.1039/c2cp42637d

Copyright ©The Royal Society of Chemistry 2012
All rights reserved.

Sarah Engmann actively participated in developing the research concept and carried out the measurements in collaboration with Michal Stano. Sarah took over a major part in the data analysis and contributed to their interpretation. She independently wrote the first draft of the manuscript and contributed to editing until publication of the final version.
Absolute Cross Sections for Dissociative Electron Attachment and Dissociative Ionization of Cobalt Tricarbonyl Nitrosyl in the Energy Range from 0 eV to 140 eV

Sarah Engmann, Michal Stano, Peter Papp, Michael J. Brunger, Štefan Matejčík and Oddur Ingólfsson


DOI:10.1063/1.4776756

Copyright ©American Institute of Physics 2013
All rights reserved.

Sarah Engmann actively participated in developing the research concept and carried out most of the measurements in collaboration with Michal Stano. Sarah contributed to the data analysis and their interpretation. She independently wrote the first draft of the manuscript and contributed to editing until publication of the final version.
Dissociative Electron Attachment to Hexafluoroacetylacetone and its Bidentate Metal Complexes \([M(hfac)_2], M = \text{Cu, Pd}\)

Sarah Engmann, Bennedikt Ómarsson, Michal Lacko, Michal Stano, Štefan Matejčík and Oddur Ingólfsson


Sarah Engmann developed the main research concept and carried out most of the measurements in collaboration with Michal Stano. Sarah took over the data analysis and the major part of their interpretation. She independently wrote the first draft of the manuscript.
Dissociative Electron Attachment to Hexafluoroacetylacetone and its Bidentate Metal Complexes M(hfac)₂; M = Cu, Pd

Sarah Engmann¹, Benedikt Ómarsson¹, Michal Lacko², Michal Stano², Stefan Matejcík²*, Oddur Ingólfsson¹*

¹Department of Chemistry and Science Institute, University of Iceland, Dunhagi 3, 107 Reykjavík, Iceland
²Department of Experimental Physics, Faculty of Mathematics, Physics and Informatics, Comenius University, Mlynska dolina F2, 84248 Bratislava, Slovakia

Beta-diketones are a versatile class of compounds that can complex almost any metal in the periodic table of elements. Their metal complexes are found to be fairly stable and generally have sufficient vapor pressure for deposition techniques requiring volatile metal sources. Motivated by the potential role of low energy electrons in focused electron beam induced deposition (FEBID), we have carried out a crossed electron-/molecular beam study on the dissociative and non-dissociative electron attachment (DEA, NDEA) to hexafluoroacetylacetone (HFAc) and its bidentate metal complexes, bis-hexafluoroacetylacetonate copper(II), Cu(hfac)₂, and bis-hexafluoroacetylacetonate palladium(II), Pd(hfac)₂. The relative ion yield curves for the native precursor to the ligand as well as its stable, 16 valence electron Pd(II) complex and open shell, 17 valence electron Cu(II) complex, are presented and compared. For HFAc, the loss of HF leads to the dominant anion observed, and while NDEA is only weakly pronounced for Pd(hfac)₂ and loss of hfac⁻ is the main dissociation channel, [Cu(hfac)₂]⁻ formation from Cu(hfac)₂ dominates. A comparison of the ion yield curves and the associated resonances give insight into the role of the ligand in the attachment process and highlights the influence of the central metal atom.

* Authors to whom correspondence should be addressed: odduring@hi.is and stefan.matejci@fmph.uniba.sk
I. INTRODUCTION

Beta diketones exist in a keto/enol equilibrium where the enol form is typically the more stable conformation. An internal O–H···O hydrogen bridge, resulting in a six-membered cyclic structure, stabilizes the enol conformer. Figure 1 shows the keto–enol tautomerization reaction for the case of hexafluoroacetylacetone (HFAc)\(^1\).

![Figure 1. The keto-enol equilibrium of hexafluoroacetylacetone. Typically, the enol form is the more stable configuration due to the stabilizing effect of the internal O-H···O hydrogen bridge.](image)

This equilibrium has been studied through gas phase electron- and single crystal X-ray diffraction\(^1, 2\) experiments as well as through temperature dependent UV absorption spectroscopy\(^3\). The latter showed that at room temperature, the unfluorinated analogue acetylacetone (ACAc), mainly exists as the enol tautomer (>95\%)\(^3\). These experimental findings have since also been supported for HFAc by various DFT calculations, placing the energy of the most stable keto isomer 0.3-0.4 eV above the most stable enol isomer (C\(_s\) symmetry)\(^2, 4, 5\). Deprotonation of the enol form of the β-diketone leads to a very stable anion, as the extra electron is delocalized in the π system of the molecule (Figure 2).

![Figure 2. Stabilization of the hexafluoroacetylacetonate anion through delocalization of the electron.](image)
As a complexed ligand, the β-diketonate is in general bidentate, bracketing the central metal through two M–O bonds, resulting in either square planar M(hfac)$_2$ or octahedral M(hfac)$_3$ complexes. Exceptions, i.e., M–C bonding, are known for a few Pt complexes$^6$.

Acetylacetonate, one of the smaller representatives of this class, is a common ligand in CVD and LCVD precursor molecules (see, for example references$^7, 8$). This class of compounds is fairly stable and generally has sufficient vapor pressure for deposition techniques requiring volatile metal sources. Chemical substitution of the methyl groups allows direct modification of the physical and chemical properties of the acetylacetonate ligand, and fluorination has shown to increase the volatility of these metal complexes$^9$.

As electronic devices have been scaled down and become more complex, lower substrate temperatures and more localized deposition techniques have become necessary. One promising evolving technique to meet this demand is focused electron beam induced deposition (FEBID), where the precursor molecule is locally dissociated using a highly focused, high-energy electron beam (for a review on the subject, see references$^{10, 11}$). One of the many factors that play a role in this electron induced deposition process is the generation of low-energy (secondary) electrons (LESEs) during the irradiation of the substrate with the high-energy electron beam. The generated SEs typically have an energy distribution that peaks below 10 eV, and thus below the typical ionization energy of most molecules. The only efficient fragmentation mechanism available at such energies is dissociative electron attachment (DEA). This is a process that typically leads to incomplete dissociation of the precursor molecules and is thus believed to contribute significantly to co-deposition of ligands (and partly fragmented ligands). Furthermore, due to the high flux of LESEs outside the focal point of the primary electron beam, DEA is also likely to contribute significantly to the broadening of the deposited structures$^{12, 13}$. Additionally, several gas phase studies have demonstrated high DEA cross sections for precursor molecules used in FEBID$^{14-16}$. Together
with surface science studies, more reminiscent of the actual FEBID process parameters, these constitute an important aid in elucidating the mechanisms operative in FEBID\textsuperscript{13, 16-18}, and may eventually help in addressing adverse effects such as insufficient purity of the deposits and broadening of structures beyond the resolution of the primary electron beam.

In this contribution we present a comparative gas phase DEA (and NDEA) study on the free ligand precursor; hexafluoroacetylacetone (HFac), the open shell copper complex; bis-hexafluoracetylacetonate copper(II), Cu(hfac)$_2$, and the Pd complex; bis-hexafluoracetylacetonate palladium(II), Pd(hfac)$_2$, in the energy range 0-15 eV. While Pd(hfac)$_2$ is a 16 valence electron (VE) complex and thus, as a square planar complex, has the most stable electron configuration, Cu(hfac)$_2$ has 17 VEs and is thus, in its square planar geometry, expected to have an unpaired electron in the destabilized $d_{xy}$ orbital\textsuperscript{19}. We note that the classical textbook crystal field theory actually predicts this to be the $d_{x^2-y^2}$ orbital. The results are discussed in this context and in relation to the role of the ligand in the respective DEA processes as well as in context to available data, relevant to the performance of Pd(hfac)$_2$ and Cu(hfac)$_2$ in FEBID.

II. EXPERIMENTAL METHODS

The experiments were carried out with two different machines. The free ligand was measured with a newly constructed crossed molecular-/electron beam apparatus at the University of Iceland (UI) in Reykjavik and the metal hexafluoroacetylacetonates were measured with a crossed molecular-/electron beam apparatus at the Comenius University (CU) in Bratislava. The working principle of both machines is similar and both have been described elsewhere\textsuperscript{20, 21}. In both experiments, the electron beam was generated by a trochoidal electron monochromator (FWHM ~130-180 meV)\textsuperscript{22}, and the electron energy scale was calibrated with respect to the 0 eV resonance of SF$_6$/SF$_6$ prior to each measurement. At the UI, the molecular beam was generated by gas effusion from a stainless steel capillary
fitted to the collision region. The liquid sample was connected to the capillary through a conventional inlet system which was kept at 60°C throughout the measurements to avoid condensation. The sample is expected to have equilibrated at this temperature before entering the collision region. The vacuum chamber was maintained at a constant temperature of 120°C. At the CU, the low vapor pressure solid samples were mounted directly inside the vacuum chamber and thus a sufficient pressure to run the experiments was reached (~2.5 x 10⁻⁷ mbar uncorrected pressure reading on a cold cathode gauge at 29°C). In both experiments, fragment ions were extracted by a weak electric field and selected by a quadrupole mass analyzer. Energy dependent detection of the ion current was carried out in single counting mode.

Bis-hexafluorooacetylacetonate palladium(II) and anhydrous bis-hexafluoroacetylacetonate copper(II) were purchased from Strem Chemicals with a stated purity of 98 and 99.99%, respectively. Hexafluoroacetylacetone was purchased from Sigma Aldrich with a stated purity of 98%. All compounds were used as received.

III. RESULTS AND DISCUSSION

A. Hexafluoroacetylacetone

Figure 3 shows (a) the positive ion and (b) the negative (DEA) mass spectra of hexafluoroacetylacetone (HFAc). The positive spectrum was recorded at a fixed energy of 65 eV while the DEA spectrum is a stick mass spectrum generated from the maximum ion yield for each observed fragment from 0-15 eV. In the positive spectrum, the most prominent peaks correspond to single bond dissociations leading to CF₃⁺ (m/z 69) and the complimentary fragment [M – CF₃]⁺ (m/z 139) while the parent cation, HFAc⁺, is only weakly discernible at m/z 208. The DEA mass spectrum, on the other hand, shows a large number of fragments, the two dominating contributions corresponding to [M – HF]⁻ (m/z 188) and [M – H]⁻ (m/z 207). In addition to these, we also observe C₅F₅O⁻ (m/z 171), [M –
2HF$^-$ (m/z 168), [M – HF – CO – OH]$^-$ (m/z 143), [M – 2HF – CO]$^-$ (m/z 140), [M – CF$_3$ – H$_2$]$^-$ (m/z 137), C$_3$HF$_4^-$ (m/z 113), CF$_3$CCH$^-$ (m/z 94), CF$_3^-$ (m/z 69) HF$_2^-$ (m/z 38), F$^-$ (m/z 19), OH$^-$ (m/z 17) and O$^-$ (m/z 16). In this contribution, however, we limit our discussion to fragments relevant for comparison with DEA to the metal complexes, i.e., fragments that are either observed in DEA to the complexed metals or are relevant in the discussion of their attachment profiles. A more thorough discussion of DEA to HFAc in comparison with trifluoroacetylacetone and the native acetylacetone is in preparation and will be presented elsewhere.

Figure 3. a) Positive and b) negative ion mass spectrum of hexafluoroacetylacetone. The positive spectrum is recorded at a fixed energy of 65 eV. The negative spectrum is a stick mass spectrum showing the maximum ion yield for each observed fragment from 0-15 eV on a log10 scale.

Figure 4 shows ion yield curves for [M – H]$^-$ (m/z 207), [M – HF]$^-$ (m/z 188), C$_4$F$_5$O$^-$ (m/z 171), CF$_3$CCH$^-$ (m/z 94) and CF$_3^-$ (m/z 69), resulting from DEA to HFAc in the energy range 0-15 eV. The main contributions observed are through resonances at 0, 1.0 and 3.0 eV incident electron energy but lower yields are also observed through resonances at 5.4, 7.0 and...
10 eV. Based on the low energy we attribute the contributions close to 0 and 1.0 eV to shape resonances formed by electron capture into the $\pi^*$ LUMO of HFAc, and a higher lying virtual orbital, respectively. From the reaction channels observed it seems clear that these states couple efficiently with the vibrational degrees of freedom promoting the corresponding reactions. The yield at 3.0 eV, on the other hand, correlates well with an optically forbidden $n$-$\pi^*$ transition at 2.65 eV, predicted by modified CNDO-CI calculations$^{23}$, and is thus likely to result from a core-excited (two particle one hole) resonance associated with this transition.

The resonances at 5.4 eV and between 7.0 and 10 eV we attribute to three, or more, core-excited resonances corresponding to e.g., $\pi$-$\pi^*$, $\pi$-$\sigma^*$ and $n$-$\sigma^*$ excitations appearing in the near and vacuum UV spectrum of HFAc in this energy range$^{23}$.

Figure 4. Ion yield curves for dissociative electron attachment to Hexafluoroacetylacetone (HFAc), as a function of incident electron energy.
For the sake of clarity it is noted here that while the neutral molecule; hexafluoracetylacetone is abbreviated as HFAc, the ligand, which corresponds to the deprotonated HFAc molecule; \([M – H]^–\), is conventionally abbreviated as hfac in metal-complex chemistry (with lower case letters). We adhere to this convention, except that here the free ligand dissociated from the respective metal complexes is signified as hfac\(^–\) to clearly state the charge state of this fragment. Note again that this is the same anion as \([M – H]^–\) from HFAc.

Hydrogen loss from HFAc (Figure 4a) upon electron attachment is observed through the first 4 resonances, discussed here above, with the highest cross section at 0 eV. This is not surprising as the resulting anion; \([M – H]^–\), is highly stabilized through the mesomeric effect (see figure 2). The electron affinity (EA) of the dehydrogenated HFAc radical can be estimated from the thermochemical threshold for the formation of the \([M – H]^–\) fragment from HFAc. The threshold for a given DEA reaction is acquired by subtracting the EA of the charge carrier from the bond dissociation energy (BDE) of the dissociated bond:

\[
E_{\text{a}}(X) = \text{BDE}(M–X) – \text{EA}(X). \tag{1}
\]

Thus, at an appearance energy of 0 eV, the EA(X) must be \(\geq\) BDE(M–X) for the process to be thermochemically accessible. Correspondingly, with an O–H bond energy of 4.3 eV\(^5\), we derive a lower limit of 4.3 eV for the EA of the dehydrogenated HFAc radical. This value is very high and is in fact considerably above the highest atomic EAs. However, considering the high intensity of this fragment at 0 eV we find it very unlikely that this contribution is due to hot band transitions or other “artifacts”. This is further supported by preliminary calculations we have conducted at the B3LYP/TZVP level, where we find the EA of the radical to be 4.1 eV.

Despite the apparent high EA of the dehydrogenated HFAc radical, the most efficient channel observed in DEA to HFAc leads to \([M – HF]^–\) \((m/z 188)\) formation (Figure 4b).
Furthermore, the HF formation proceeds exclusively through a fairly narrow channel peaking slightly above 0 eV. A similar channel has been observed in photolysis of HFAc\textsuperscript{24} where it was shown that the photon induced loss of HF leads to rearrangement forming the five-membered ring depicted in figure 5. Such efficient DEA induced loss of HF has been studied extensively in the model compounds pentafluoro-toluene (PFT), \(-\text{aniline (PFA)}\) and \(-\text{phenol (PFP)}\)\textsuperscript{25, 26}. For PFA and PFP, the low appearance energy and high cross sections for the formation of \([M – HF]^{-}\) are rationalized by the energy release through the HF formation (about 5.9 eV\textsuperscript{27}). There, the proposed prerequisite for the reaction was the presence of a X–H···F intramolecular hydrogen bond (X = O or N). Similarly, in HFAc, the capture of an electron may lead to sufficient weakening of the O–H···O hydrogen bond, allowing rotation around the C–C bond and the formation of an O–H···F hydrogen bond. Hence, promoting HF formation as proposed in conjunction with the above mentioned photolysis study\textsuperscript{4, 24} (Fig. 5).

\[
\begin{array}{c}
\text{1} \quad \text{2} \quad \text{3}
\end{array}
\]

*Figure 5. Proposed reaction pathway for the HF formation from HFAc through photolysis or DEA. Adapted from ref\textsuperscript{24}.*

This mechanism is also supported by preliminary calculations we have conducted at the B3LYP/TZVP level which show that the energy difference at room temperature between the neutral enol 1 and the anionic equivalent to the intermediate 2, promoting HF formation (Fig. 5), is 1.13 eV in favor of the latter. Hence, if the EA of HFAc is larger than the rotational barrier associated with the required conformational change, this reaction can proceed already at 0 eV incident electron energy.

The ion yield curve of C\textsubscript{3}HF\textsubscript{3}\textsuperscript{–} ([HFAc – C\textsubscript{2}O\textsubscript{2}F\textsubscript{3}H] m/z 94) shown in figure 4d, strongly resembles that of \([M – H]^{-}\) apart from the fact that no contribution is observed above 4 eV.
Judging from the mass of the negative fragment and the derived stoichiometry, several combinations of neutral fragments accommodating the dissociation process are possible. Currently we cannot offer any comprehensive picture of this complicated reaction channel, however, based on the low threshold observed, and in analogy to the aforementioned photolysis study of Basset and Whittle\textsuperscript{24}, we find it likely that this reaction is associated with considerable rearrangement and new bond formations. These possibly include the formation of HF, CO and CF\textsubscript{2}O, as was observed in the photolysis study by Basset and Whittle\textsuperscript{24}, and probably involves the negatively charged analogue of the intermediate five membered ring portrayed in figure 5. It is worth mentioning here, that photolysis and the DEA process are analogous in the sense that an electronic excitation from a binding MO (e.g. HOMO) to an antibonding MO (e.g. LUMO) in the photolysis is comparable to the occupation of the same antibonding MO in DEA.

Unlike the fragments discussed above, C\textsubscript{4}F\textsubscript{3}O\textsuperscript{−} (m/z 171) and CF\textsubscript{3}\textsuperscript{−} (m/z 69), shown in figure 4c and e, respectively, are exclusively formed through the higher energy core-excited resonances. While C\textsubscript{4}F\textsubscript{3}O\textsuperscript{−} is formed in a fairly narrow range between 5 and 8 eV, CF\textsubscript{3}\textsuperscript{−} is observed through a broad but structured contribution stretching from 3-14 eV. Using a CH\textsubscript{3}–CF\textsubscript{3} bond energy of 4.45 eV\textsuperscript{27} as an approximate for the R–CF\textsubscript{3} bond energy and the EA of CF\textsubscript{3} (1.81 eV\textsuperscript{28}), equation 1 predicts this dissociation channel to be thermochemically accessible above 2.6 eV. Hence, a direct dissociation leading to CF\textsubscript{3}\textsuperscript{−} is thermochemically accessible over the entire energy where this fragment is observed. The formation of C\textsubscript{4}F\textsubscript{3}O\textsuperscript{−} however, is likely to result from rearrangement and new bond formation. A probable path for this reaction is the loss of an OH radical along with HF. Again, this is supported by the observation of OH in photolysis of HF\textsubscript{Ac} at 266 nm (4.6 eV)\textsuperscript{29}, which corresponds well with the assignment of the π-π* transition in the vacuum UV spectrum.
B. Bis-hexafluoroacetylacetonate- palladium(II) and copper(II)

Figure 6. a) Positive ion mass spectrum of Pd(hfac)$_2$ at an incident electron energy of 100 eV. b) DEA mass spectrum showing the maximum ion yield for each observed fragment from 0-13 eV on a log10 scale.

Figure 6 shows; a) the positive ion mass spectrum and b) the DEA mass spectrum of bis-hexafluoroacetylacetonate palladium(II), Pd(hfac)$_2$. The positive ion mass spectrum was recorded at 100 eV electron impact energy, while the DEA mass spectrum is a stick spectrum composed of the maximum yield of negative ion fragments formed in the energy range 0-13 eV. The positive spectrum is mostly dominated by the Pd$^+$ ion (m/z 106) but further prominent fragments include CF$_3^+$ (m/z 69), [Pd(hfac-CF$_3$)]$^+$ (m/z 244) and [Pd(hfac)]$^+$ (m/z 313). The parent cation, [Pd(hfac)$_2$]$^+$, is discernible at m/z 520 with weak intensity. The most prominent anion in the negative DEA mass spectrum is the free ligand base hfac$^-$ (m/z 207), but also the parent anion; [Pd(hfac)$_2$]$^-$ (m/z 520) is observed, though with considerably lower intensity. Further low intensity fragments observed are [Pd(hfac)CF$_3$]$^-$ (m/z 382), (hfac –
CF$_2$\(^-\) (m/z 157), \((\text{hfac} - H - \text{CF}_3)\)\(^-\) (m/z 137), CF$_3$\(^-\) (m/z 69) and F\(^-\) (m/z 19). In \([\text{Pd(hfac)}_2]\), however, only the parent ion is observed through the 0 eV resonance.

Figure 7. Ions yield curves for dissociative and non-dissociative electron attachment to \(\text{Pd(hfac)}_2\), as a function of incident electron energy.
The DEA and NDEA ion yield curves for Pd(hfac)₂ are shown in figure 7. The resonance profile for Pd(hfac)₂ bears a close resemblance to that of HFAc, showing contributions through resonances located at 0, 1.35, 2.4, 3.9 eV and from 6-12 eV. We attribute the 0 eV contribution in the ion yield from Pd(hfac)₂ to a shape resonance formed by electron attachment to either the π* ligand based LUMO, or the destabilized d₆₋₃₀(dₓ²−y² as predicted by crystal field theory) of this square planar complex. Hence, the 16 VE configuration, as is the case for Pd(hfac)₂, is the most stable electron configuration for such square planar complexes and the additional electron is expected to destabilize the complex. The contribution centered around 1.35 eV is attributed to a higher lying shape resonance. The resonance yielding contributions around 2.4 eV, as well as the higher lying resonances observed from Pd(hfac)₂, on the other hand, correlate well with transitions observed in the gas phase absorption spectrum of Pd(hfac)₂. This spectrum has not been published explicitly, but has been reported to strongly resemble that of Pt(hfac)₂, with the exception of slightly higher extinction coefficients and a blue shift of the observed absorption bands of about 25 nm. Absorption-peak maxima for the Pd(hfac)₂ compound should thus appear at 190 nm (6.5 eV), 230 nm (5.4 eV), 295 nm (4.2 eV) with a shoulder at 313 nm (4.0 eV), 390 nm (3.2 eV) and lower intensity peaks at around 475 nm (2.6 eV) and 540 nm (2.3 eV). Following the assignment made by Rebers et al. for Pt(hfac)₂, the lowest energy transitions, around 2.3-2.6 eV, are tentatively assigned to (metal based) ligand field excited states, while the absorption around 3.2 eV is attributed to ligand-to-metal charge transfer; these transitions correlate well with the contribution at around 2.4 eV in the hfac⁻ ion yield from Pd(hfac)₂. Consequently, even at low incident electron energies, various electronic transitions in the parent can be excited, leading to potentially repulsive states. Higher energy absorption bands in the UV/VIS spectrum of the complex at around 4-6.5 eV are likely to be rooted in ligand...
based \( \pi-\pi^* \), \( \pi-\sigma^* \) and \( n-\sigma^* \) transitions, as discussed above for HFAc\(^{23}\). These also correlate well with the contributions observed in the DEA ion yield curves.

In addition to the 0 eV contribution to the ion yield of the parent anion, \([\text{Pd(hfac)}_2]^-\) (figure 7a), a smaller but distinct contribution is also observed at approximately 0.7 eV. We attribute this to a contribution from the lower energy flank of the 1.3 eV shape resonance, however, efficient redistribution of energy within the molecule is clearly necessary for the stabilization of the parent anion at this high energy. Stabilization of the parent anion at such high energies is quite remarkable, although not unique to this particular case (see references\(^{34-36}\)). Furthermore, the bidentate nature of the hfac ligand may work favorably here, as anions where either, or both, ligands are only partially dissociated (monodentate) will still be detected as the parent anion \([\text{Pd(hfac)}_2]^-\). Furthermore, the bonding of hfac may even rearrange towards a complex-ligand binding known for \( \beta \)-diketonate complexes of Pt\(^6\) where the central carbon atom, instead of the two oxygen atoms, is bound to the metal.

The negatively charged ligand hfac\(^-\) is the most intense fragment observed from Pd(hfac\(_2\))\(^2\) (Fig. 7c) Similar to the hydrogen loss from HFAc, this channel is observed through four (or more) individual resonances in Pd(hfac\(_2\)). Hence, through the higher energy shape resonance at 1.3 eV and the core-excited resonances at 2.4, 3.9 and 6.5 eV. Taking the EA of hfac to be 4.3 eV as derived above and the Pd–O bond energy of 1.5 eV\(^{37}\), equation 1 gives a thermochemical threshold of \(-1.3\) eV. Unlike HFAc, however, this channel is not observed through the 0 eV resonance, although the resonance is sufficiently long-lived for the parent anion to be detected in our experiments. In fact, no dissociation is observed at this energy.

Beside the molecular ion and the hfac\(^-\) anion also Pd(hfac)CF\(_3\)\(^-\) (m/z 382) is formed at low incident electron energies (Fig. 7b). This fragment, whose formation requires the migration of one CF\(_3\) unit from the ligand to the central metal atom, is formed through the higher energy shape resonance at 1.3 eV and the first core-excited resonance at 2.4 eV.
The remaining fragments \([\text{hfac} – H – CF_3]^-\), \([\text{hfac} – CF_2]^-\), \(CF_3^-\) and \(F^-\) (Fig. 7d, e, f and g) all constitute ligand fragmentation and are explicitly formed through higher lying core-excited resonances, i.e., above 4 eV. From these, the fragments \(CF_3^-\) and \(F^-\) are also observed, with a comparable ion yield profile, from DEA to HFAC, and the energy dependence of the \([\text{hfac} – H – CF_3]^-\) formation resembles strongly that of \([\text{HFAC} – 2H – CF_3]^-\) from HFAC (not shown here). These fragmentation products are thus most likely predominantly formed through ligand based transitions and \([\text{HFAC} – H – CF_3]^-\) may involve the formation of trifluoromethane (CF3H). Given the high energy of the respective resonances and the absence of any complementary, Pd containing fragments, these are likely to be associated with ligand loss prior to, or concomitant to, the fragmentation.

Figure 8 shows a stick spectrum of the negative fragment ions formed in DEA to bis-hexafluoroacetylacetone copper(II), Cu(hfac)2, from 0-9 eV incident electron energy, constructed in the same way as the Pd(hfac)2 DEA mass spectrum. The positive ion mass spectrum, recorded at 70 eV, is reported in the literature38, and the dominating positive ion fragments correspond the loss of one CF3 moiety (m/z 408), \([\text{Cu(hfac)}CF_3]^+\) (m/z 339), \([\text{Cu(CF}_3)_2]^+\) (m/z 201) and \(CF_3^+\) (m/z 69), while \(Cu^+\) (m/z 63) and the parent ion \([\text{Cu(hfac)}_2]^+\) (m/z 477) are observed with slightly lower intensity (about 1/3 compared to the other ions). From DEA to Cu(hfac)2, on the other hand, only three (fragment) masses are observed. These
correspond to the parent anion [Cu(hfac)₂]⁻ (m/z 477), the free ligand hfac⁻ (m/z 207) and the ligand fragment (hfac – H – CF₃⁻) (m/z 137). The corresponding fragments are also observed in DEA to the Pd complex. Figure 9 shows the ion yield curves from DEA to bis-hexafluoroacetylacetonate copper(II). Although the complex does not exhibit as rich a fragmentation pattern as Pd(hfac)₂, the resonance profile is the same and we therefore refer to our discussion on Pd(hfac)₂, in assigning the resonances. The absorption spectrum of Cu(hfac)₂ in trichloromethane, however, exhibits three distinct bands. A metal based ligand field band at 690 nm (1.80 eV), a maximum around 300 nm (4.1 eV) and another around 240 nm (5.2 eV)³⁹. Contributions from the core-excited resonance corresponding to the lowest energy transition are thus expected to overlap with the higher energy shape resonance.

![Figure 9. Ions yield curves for dissociative and non-dissociative electron attachment to Cu(hfac)₂, as a function of incident electron energy.](image)

As discussed above, the splitting of the metal d orbitals causes significant destabilization of the metal dₓᵧ (dₓ₂₋ᵧ₂ crystal field) orbital in square planar complexes, and thus 16 VE is favorable over 18 VE. Nevertheless, for the 17 VE neutral Cu(II)(hfac)₂ complex, where the unpaired electron is expected to reside in the destabilized dₓᵧ orbital, a square planar
configurations is adopted\textsuperscript{40}. For 18 VE Cu(I) complexes, on the other hand, a tetrahedral configuration is preferable. In this context, reversible configuration “redox-switching” of Cu(I)/Cu(II) complexes on a SiO\textsubscript{2} substrate has recently been demonstrated \textsuperscript{41}. Similarly, upon attachment of the extra electron to Cu(II)(hfac)\textsubscript{2}, the Cu(II) central metal atom is formally reduced to Cu(I). We thus infer an analogous isomerization of [Cu(I)(hfac)\textsubscript{2}], from square-planar to tetrahedral configuration, upon capture of the 0 eV electron, and thus efficient delay in autodetachment.

This is well reflected in the ion yield curve of [Cu(hfac)\textsubscript{2}]\textsuperscript{−} (figure 9a), which exhibits a high cross section through the 0 eV shape resonance. Similar to Pd(hfac)\textsubscript{2}, a small contribution to the parent-ion curve is also observed through the higher energy shape resonance, appearing as a shoulder at about 0.5 eV. In [Cu(hfac)\textsubscript{2}]\textsuperscript{−} this contribution is likely to be due to stabilization through isomerization from square-planar to tetrahedral configuration, however, similar to Pd(hfac)\textsubscript{2}, stabilization through a partial dissociation of the ligands cannot be excluded (see discussion above).

The loss of hfac\textsuperscript{−} from the copper complex is observed through similar channels as in the Pd compound, as well as through a contribution from the 0 eV shape resonance. The average Cu–O bond energy in Cu(hfac)\textsubscript{2} has been determined to be 1.7±0.1 eV\textsuperscript{42}. Consequently, about 3.4 eV are needed to dissociate the intact ligand. Using the approximate value of 4.3 eV for the EA of hfac derived above, the formation of hfac\textsuperscript{−} is exothermic by about 0.9 eV. Though the 0 eV contribution is significant, it is weak compared to the higher energy hfac\textsuperscript{−} contributions, and especially in comparison to the [Cu(hfac)\textsubscript{2}]\textsuperscript{−} parent ion signal, which in turn indicates that this channel is inefficient in Cu(hfac)\textsubscript{2} (as well as in Pd(hfac)\textsubscript{2}).

Finally, the formation of [hfac – H – CF\textsubscript{3}]\textsuperscript{−} is observed through a core-excited resonances between 3 and 9 eV, i.e., through a similar dissociation channel as discussed above for Pd(hfac)\textsubscript{2}. 

103
Compared to the rich fragmentation pattern observed for HFAc, the fragmentation pattern for the bis-hexafluoroacetylacetonate complexes is fairly straightforward. Most of the high intensity channels observed for HFAc are not observed in the metal complexes. This is most likely due to the absence of one of the hydrogen atoms, blocking the HF formation associated with the most intense fragmentation channels in HFAc. Any other, internal, ligand fragmentation from the metal complexes also occurs with very low intensity. As no isolated metal anion was observed from either complex, it is difficult to judge whether only one or both of the hfac ligands can be dissociated through DEA. The average metal–ligand bond energy in the copper complex is 1.7 eV as mentioned above, and the EA of copper is 1.2 eV\textsuperscript{43}. The thermochemical threshold for the formation of Cu\textsuperscript{+} is therefore 5.6 eV. Similarly, the average Pd–O bond energy derived for bis-acetylacetonate palladium(II) is 1.5±0.2 eV\textsuperscript{37} and the EA of palladium is 0.56 eV\textsuperscript{44}. The threshold for Pd\textsuperscript{+} formation in DEA to Pd(hfac)\textsubscript{2} is thus approximately 5.4 eV. Compared to hfac, the EA of Cu and Pd are rather low and although the thermochemical threshold for the formation of the negative metal ions is below the higher lying core excited resonances, the formation of the charged ligand is energetically more favorable.

IV. COMPARISON WITH EARLIER WORK AND RELEVANCE FOR FOCUSED ELECTRON BEAM INDUCED DEPOSITION

While no studies on the composition of FEBID deposits are available in the literature for Pd(hfac)\textsubscript{2}, the composition of copper deposits from Cu(hfac)\textsubscript{2} on a SiO\textsubscript{2} surface has been reported for room temperature deposition with 25 keV electrons\textsuperscript{45}. The resulting structures were found to be insulating, with a copper content of about 14%. The main contaminants were determined to be carbon (75%) and oxygen (5%), while no significant amount of fluorine was detected. From mechanistic CVD studies of Cu(hfac)\textsubscript{2} on Ag surfaces\textsuperscript{46}, it is known that the hfac ligands remains adsorbed on the surface after thermally induced
V. Article 5

dissociation from the metal central atom. Unless a proton source is available to generate volatile HFAc, the adsorbed ligand will undergo further, thermal induced decomposition. Similar behavior was observed for Pd(hfac)$_2$, which dissociatively chemisorbs on copper surfaces at temperatures as low as 120 K. Annealing to temperatures $>$ 373 K then results in decomposition of the hfac moiety, leading to surface bound carbon, oxygen and fluorine containing species, which finally desorb as CF$_3$CO, CF$_3$CO$_2$, and CO at temperatures exceeding 500 K. However, Cu(hfac)$_2$ adsorbs intact onto Pd, indicating that the decomposition also depends on the metal and surface relative redox potentials. It should, however, be mentioned in this context that in the growth of three dimensional structures the deposit itself becomes the substrate early on in the deposition process.

A brief account on the electron induced decomposition of adsorbed Cu(hfac)$_2$ under UHV conditions revealed the release of CO into the gas phase upon decomposition of the precursor. Changes in the adsorbate layer further indicated loss of fluorine. No further mechanistic, electron induced, decomposition studies of adsorbed Cu(hfac)$_2$ or Pd(hfac)$_2$ have been published and thus the study on hexafluoroacetylacetonate Cu(I) vinyltrimethylsilane (Cu(hfac)(vtms))$^{49}$, a compound of similar ligand architecture, is consulted for comparison with the gas phase studies.

Mezhenny et al.$^{49}$ have studied room temperature decomposition of Cu(hfac)(vtms) adsorbed on a Si(111)-(7x7) surface with low energy electrons in the range 2-27 eV. Contrary to results from high-energy impact experiments at 25 keV with the same precursor (and also Cu(hfac)$_2$)$^{42}$, this study showed considerable fluorine contamination. The authors derived a threshold for deposition of 4.0 ± 0.5 eV and thus infer a DEA induced growth.

A notable difference between the high$^{45}$ and low$^{40}$ electron energy dissociation study of adsorbed Cu(hfac)(vtms) is the absence, and presence, of fluorine contamination in the deposit. A possible explanation for this observation may be an initial, low-energy electron...
supported dissociation of the hfac ligand, fixing the ligand as well as the remaining molecule at the surface. Metastable decay is likely to be quenched and further removal of fluorine from the surface bound intermediate is likely to proceed through further electron irradiation leading to C–F bond cleavage. It is interesting to note that in the gas phase, C–F bond cleavage is observed with only low intensity through both DEA and DI. The loss of CF₃, on the other hand, is observed through both DI as well as DEA. This proposed dissociation scheme is similar to what is observed in the low energy electron-induced decomposition of adsorbed Pt(PF₃)₄, where an initial loss of PF₃ results in surface bound Pt(PF₃)₃ species. Subsequent electron irradiation then leads exclusively to P–F bond cleavage and release of fluorine into the gas phase. Alternatively, in light of the above mentioned CVD studies⁴⁷, local heating effects may also play a role, as irradiation of an insulating substrate with 25 keV electrons is bound to locally increase the temperature, and thus liberate surface bound species.

While CO loss from HFAC is presumed to occur concomitant to the loss of other neutral products, such as HF and CF₂O, e.g., in the formation of C₃HF₃, no such liberation was discernible upon DEA to the metal hexafluoroacetylacetones. The formation of CO⁺ or complimentary fragments is also negligible in DI of HFAc and its hexafluoroacetylacetones and thus surface effects seem to play a large role in CO evolution.

V. CONCLUSION

In this study we have presented DEA and DI studies of hexafluoroacetylacetone and two of its metal complexes, i.e., Cu(hfac)₂ and Pd(hfac)₂. The abundant fragmentation of HFAC induced through DEA is found to be fueled by HF formation, a dissociation mechanism that is not available in the complexed ligand. Consequently, these channels are quenched in the metal complexes, and the main ions formed upon electron attachment to these are the parent ion and the intact ligand hfac⁻. While dissociation of both ligands through DEA appears
thermochemically possible through the higher lying core excited resonances, no isolated metal anions were detected. In contrast, DI of Pd(hfac)$_2$ yields the bare metal cation as the main fragment and Cu$^+$ from Cu(hfac)$_2$ is formed with appreciable intensity$^{38}$.

A comparison of the obtained gas phase results with the deposit composition obtained in FEBID is complicated by other effects that may influence the deposition process. This includes adsorption behavior, i.e., molecular physisorption vs. dissociative chemisorption and locally induced heating effects, which can change the reaction mechanism from an electron induced to a thermally induced dissociation (or a combination thereof). It is thus clear that the predictive nature of the gas phase studies is limited to the initial deposition step, and though these may dictate subsequent electron and surface induced reactions, more detailed mechanistic surface studies of these effects are necessary to explain and/or predict the final composition of the deposits.

ACKNOWLEDGMENTS

This work was supported by the Icelandic Center for Research (RANNIS) and the Slovak Research and Development Agency, project Nr. APVV-0733-11, project VEGA 1/0379/11 and is also the result of the project implementation: 26240120012, 26240120026 and 2622020004, supported by the Research & Development Operational Programme funded by the ERDF. S.E. gratefully acknowledges funding for the visit to Bratislava by ECCL (COST Action CM0601) and a PhD grant from the research fund of the University of Iceland.
REFERENCES


