

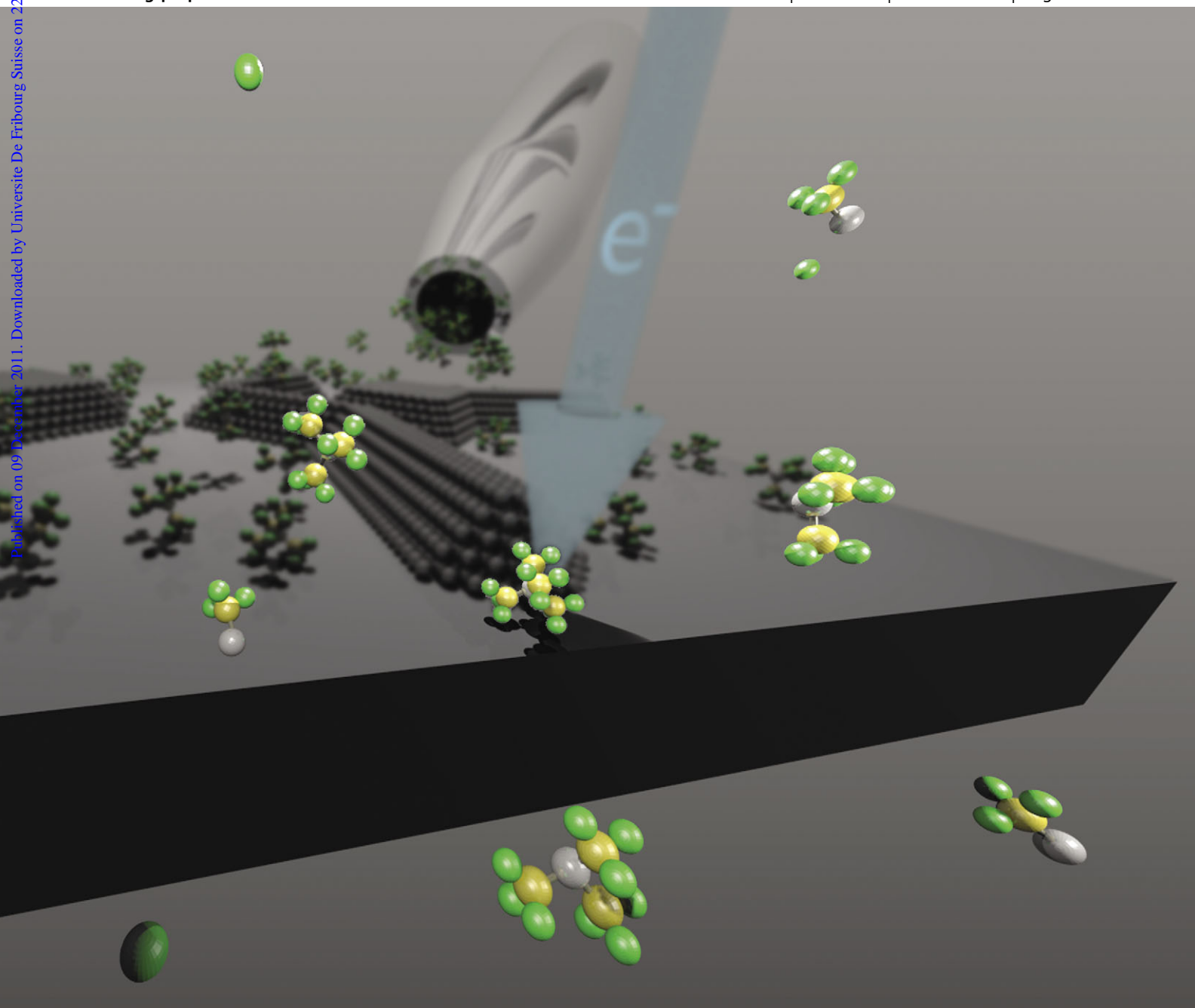
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COVER ARTICLE

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Dissociative electron attachment to Pt(PF₃)₄—a precursor for Focused Electron Beam Induced Processing (FEBIP)

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Experimental absolute cross sections for dissociative electron attachment (DEA) to Pt(PF₃)₄ are presented. Fragment anions resulting from the loss of one, two, three and four PF₃ ligands as well as the Pt(PF₃)F[−] and the F[−] ions were observed. The parent anion Pt(PF₃)₄[−] is too short-lived to be detected. The dominant process is loss of one ligand, with a very large cross section of 20 000 pm²; the other processes are about 200× weaker, with cross sections around 100 pm², the naked Pt[−] anion is formed with a cross section of only 1.8 pm². The resonances responsible for the DEA bands were assigned based on comparison with electron energy-loss spectra and spectra of vibrational excitation by electron impact. Bands around 0.5 eV and 2 eV were assigned to shape resonances with single occupation of virtual orbitals. A DEA band at 5.9 eV was assigned to a core-excited resonance corresponding to an electron very weakly bound to the lowest excited state. An F[−] band at 12.1 eV is assigned to a core excited resonance with a vacancy in an orbital corresponding to the 2nd ionization energy of the PF₃ ligand. Implications of these findings for FEBIP are discussed.

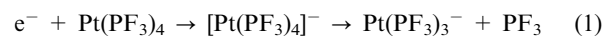
1 Introduction

Focused Electron Beam Induced Processing (FEBIP) is a powerful tool for nanofabrication. It uses a tightly focused electron beam in a modified electron microscope to decompose volatile precursor molecules physisorbed on a surface and converts them into nanosized material.¹ Pt(PF₃)₄ was shown to be a precursor yielding carbon-free platinum nanowires with an order of magnitude improved conductivity when compared to precursors with carbon-containing ligands like MeCpPtMe₃.² A brief review of the subject was given in the recent article of Landheer *et al.*³ Pt(PF₃)₄ is also one of the few gaseous sources of platinum for thermal, photochemical, or plasma-enhanced metallo-organic chemical vapor deposition of platinum metal.⁴

In an attempt to provide information useful for understanding and ideally optimizing the FEBIP process, we already studied several electron-driven processes in Pt(PF₃)₄: elastic scattering (which changes the direction of electron propagation and spreads the electron beam), vibrational excitation (which cools the electrons

and heats the sample) and electronic excitation (which leads to decomposition of the excited precursor into neutral fragments).⁵

This work presents quantitative data (absolute cross sections) for dissociative electron attachment (DEA)—the most important low-energy process because it leads directly to decomposition of the precursor molecules. It is a process where an incident electron with a variable kinetic energy E_i is attached to the target molecule to form a short-lived negative ion, called a resonance, which is then subject to two competing decay channels: dissociation and spontaneous electron detachment.⁶ It can be illustrated, for example, by the loss of one ligand:



Depending on the incident electron energy the short-lived anion [Pt(PF₃)₄][−] may be in its ground or one of the many excited states.

The measurements consist of colliding an electron beam of variable energy with gaseous molecules in a target chamber and accelerating negative ion fragments into a time-of-flight (TOF) mass spectrometer. Our instrument has been optimized for a quantitative detection of fragment anions, that is, for measurement of absolute values of the cross sections.⁷

2 Experimental method

The absolute cross sections were measured with a recently constructed instrument,⁷ operated in the time-of-flight (TOF) mode. In this instrument a short (200 ns) pulse of electrons is sent through a target chamber with a quasistationary sample gas at a temperature of 333 K. An 8 μs long pulse with an amplitude of −300 V, applied to a repeller about 200 ns later, sends the anions into a TOF tube through a slit in the wall of the target chamber. The experiment is repeated at a rate of 20 kHz. The TOF tube consists of a three-cylinder electrostatic lens, which images the ion exit slit onto the MCP detector (anion impact energy 3 keV). The pressure in the collision chamber was measured using a capacitance manometer and was kept typically in the range of (1–6) × 10^{−4} mbar. The electron beam current was typically 20–80 nA (measured without pulsing) and the resolution 200 meV. The absolute calibration was against the 4.4 eV band of O[−] production from CO₂, for which the cross section of 14.0 pm² was used as in our previous work. The setup was repeatedly verified by measuring the DEA cross sections for O[−] formation from N₂O. The error

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of the present absolute measurement (two standard deviations) is estimated to be $\pm 25\%$. The sample was purchased from STREAM Chemicals in a sealed ampule under PF_3 gas. The present instrument does not permit direct *in situ* monitoring of sample purity which was possible in our previous study,⁵ but we used the experience gained there to assure the sample purity in the present study. Specifically, we removed the excess PF_3 by pumping while keeping the test tube at -20°C until a clear pressure drop occurred and then kept the sample at 0°C during the measurements.

3 Results

The mass spectrum in Fig. 1 gives an overview of all the fragments. The major fragments result from loss of one, two and three PF_3 ligands, with a very weak signal due to the naked Pt^- anion (the electron affinity of Pt is 2.12 eV⁸). The $\text{Pt}(\text{PF}_3)\text{F}^-$ fragment with one PF_3 and one F^- ligand is also observed. The parent anion $\text{Pt}(\text{PF}_3)_4^-$ is too short-lived to be detected and the absence of PF_3^- is consistent with the predicted negative electron affinity of PF_3 .⁹

The primary results of this work are the absolute DEA cross sections plotted as a function of electron energy shown in Fig. 2. The values of the peak cross sections are listed in Table 1. The loss of one ligand dominates, with a cross section about a factor of 200 larger than those for the loss of more ligands. The peak cross section for the loss of one ligand, about $20\,000\text{ pm}^2$, is very large when compared to ‘typical’ cross sections like production of O^- from CO_2 (14 pm^2) or from N_2O (860 pm^2).¹⁰ It is comparable to the very large DEA cross sections observed at low energy for multiply halogenated hydrocarbons¹¹ and to the cross section for a loss of one carbonyl group from another FEBIP precursor, $\text{Co}(\text{CO})_3\text{NO}$, which was recently measured to be $40\,000\text{ pm}^2$ by Engmann *et al.*¹² At 0.5 eV it is only a factor of 10 below the $\pi\lambda^2$ limit for s-wave reactive capture cross section. (This limit is given by the DeBroglie wavelength of the incident electron and no cross section can exceed it.¹³) The fact that the loss of a single ligand dominates was also found for $\text{Co}(\text{CO})_3\text{NO}$ by Engmann *et al.* and in earlier (not absolute) DEA studies of metal–organic

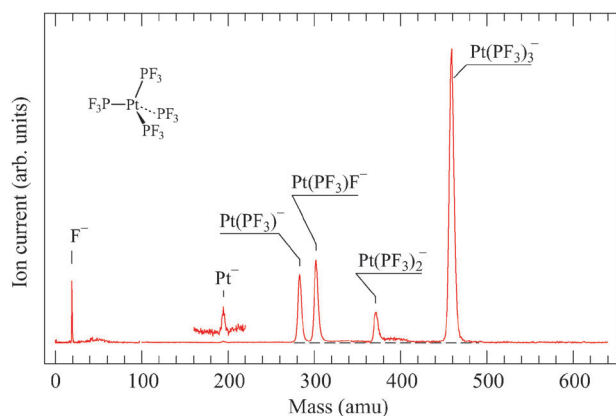


Fig. 1 Negative ion mass spectrum of $\text{Pt}(\text{PF}_3)_4$. Various sections of the mass range were recorded with different electron energies chosen such that all fragments are visible: $\text{Pt}(\text{PF}_3)_3^-$ and $\text{Pt}(\text{PF}_3)_2^-$ at 1 eV, $\text{Pt}(\text{PF}_3)^-$, $\text{Pt}(\text{PF}_3)\text{F}^-$ and Pt^- at 6 eV and F^- at 12 eV.

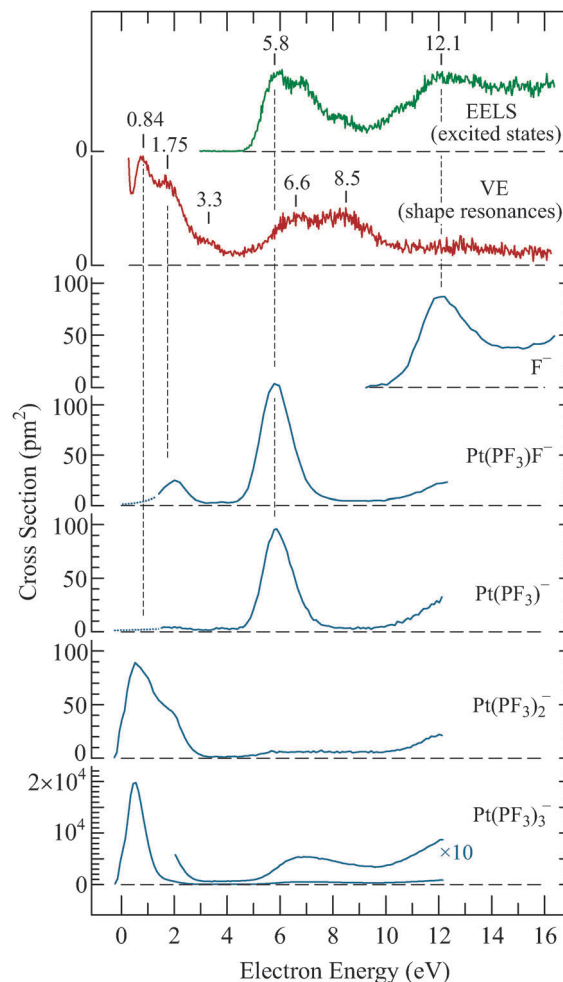


Fig. 2 Cross sections for production of fragment anions shown as a function of electron energy. The top two traces show the electron energy-loss spectrum (recorded at a scattering angle of 180°), that is, the electronically excited states of $\text{Pt}(\text{PF}_3)_4$, and the cross section for vibrational excitation (of the PF_3 deformation mode), indicative of the shape resonances.⁵

Table 1 Peak cross sections (pm^2). Masses are for fragments with the most frequent natural isotope ^{195}Pt

Fragment	Mass/amu	Energy/eV	Cross section
F^-	19	12.0	87
Pt^-	195	6.0	1.8
$\text{Pt}(\text{PF}_3)^-$	283	5.9	96
$\text{Pt}(\text{PF}_3)\text{F}^-$	302	2.1	25
$\text{Pt}(\text{PF}_3)_2^-$	371	0.5	89
$\text{Pt}(\text{PF}_3)_3^-$	459	0.5	19 800

compounds with carbonyl ligands.^{14,15} Pt^- is formed *via* the same 5.9 eV resonance as the $\text{Pt}(\text{PF}_3)^-$ and $\text{Pt}(\text{PF}_3)\text{F}^-$ fragments. Weak signals due to metastable decay were observed.

4 Discussion

We assign the resonances responsible for the individual DEA bands in Fig. 2 by comparing them with the cross sections for

vibrational excitation (VE) and with electron energy-loss spectra (EELS) recorded earlier.⁵ A representative spectrum of each kind is shown on the top of Fig. 2. The vibrational excitation (VE) cross section reveals shape resonances that are states of the transient negative ion whose electron configuration is that of the electronic ground state of the target molecule plus one electron in one of the normally unoccupied orbitals ('one electron resonance'). The VE cross section is, however, normally not sensitive to core excited ('one hole, two electrons') resonances, because their formation—a simultaneous electron capture and electron excitation—is a two-electron process and consequently much less probable than the formation of a shape resonance. Despite this, the core-excited resonances are often very prominent in DEA because of slower autodetachment and thus a more favorable competitiveness of dissociation. In fact, a DEA band which coincides in energy and band shape with the lowest excited (valence) singlet state is found in many molecules.^{16–18} The electron configuration of these resonances is assumed to be that of the excited singlet state plus one electron in a diffuse (spatially large) orbital.

The comparison of the present DEA spectra with the VE cross section indicates that the DEA bands in the 0–3 eV energy range are due to the same shape resonances as those responsible for vibrational excitation. (The exact peak energy of a VE and a DEA band is often not exactly the same even when both are due to the same resonance, because of the dependence of the resonance width on internuclear distances and on energy.) The structure of the Pt(PF₃)F[−] fragment is likely to involve an F[−] bonded directly to Pt; its formation requires breaking of a P–F bond and formation of a F–Pt bond. The higher energy shape resonances seen at 6.6 and 8.5 eV in the VE cross section do not give rise to clearly assignable DEA bands, presumably because of their very large lifetime-related width and thus an unfavorable competition of DEA with autodetachment.

The comparison of the present DEA spectra with the EELS reveals that, like in many molecules, a prominent DEA band is found at the energy of the lowest (singlet) excited state. This band is consequently assigned in line with earlier work^{16–18} to a resonance where an electron is very weakly bound to Pt(PF₃)₄ in its lowest electronically excited state. This state corresponds to the HOMO–LUMO transition and has the configuration (22t₂^{−1}, 23t₂).¹⁹ The configuration of the resonance responsible for the 5.9 eV DEA band could thus be written as (22t₂^{−1}, 23t₂̄) with ̄ being the diffuse orbital. The 22t₂ HOMO orbital is known from photoelectron spectroscopy.²⁰

The 12 eV DEA band in the F[−] yield coincides with the 12.1 eV electronically excited state and is assigned to a high-lying core excited resonance, with a deep-lying hole, an electron in LUMO, and an electron in a diffuse ̄ type orbital. This assignment is supported by the following argument about the excited states of neutral Pt(PF₃)₄. The term energy (difference of energies of the excited state and the cationic state having a hole in the same orbital as the excited state) is about 4 eV for the lowest excited state at 5.8 eV of Pt(PF₃)₄.⁵ If the same term energy is assumed for the 12.1 eV state, then this state converges to an ionization energy of about 16 eV. The photoelectron spectrum of Pt(PF₃)₄ shows a prominent band at 15.87 eV.²⁰ This band occurs at nearly the same energy in free PF₃ and in Pt(PF₃)₄, and is consequently

assigned to ionization from an orbital largely localized on the PF₃ ligands.²⁰ It is thus not surprising that the granddaughter resonance of this state of the cation lies at 12 eV and leads to dissociation of the PF₃ ligand, yielding F[−].

This notion is further consistent with the observations and conclusions of Akbulut *et al.*²¹ who measured the electron stimulated desorption (ESD), that is, the yield of fragment anions resulting from electron impact on PF₃ physisorbed on a Pt surface (1 and 6 monolayers). They observed the yield of F[−] fragments peaking at 11.5 eV, with a band width similar to ours, which most likely involves the same mechanism. The fact that this band is unaffected (except for a 0.5 eV image charge stabilization) when an isolated Pt atom in the present experiment is replaced by a Pt surface in the experiment of Akbulut *et al.* indicates that the resonance is largely localized on the ligand.

Our study, in particular comparison with VE and EEL spectra, permits us to clarify the electronic configuration of the resonances responsible for the individual DEA bands. We have no understanding of the detailed DEA dynamics, however. Detailed theory of DEA to polyatomic molecules is notoriously complicated because of the autodetaching nature of the resonances and at the same time the necessity to include many dimensions of the motion of the nuclei. The present state of the art has been recently demonstrated by the quantitative calculation of DEA cross sections for acetylene^{22,23} and their validation by experiment.⁷ Similarly detailed calculations for Pt(PF₃)₄ would be very interesting and desirable, but appear beyond the capacity of the theory at present.

The present results are linked to the thermal electron attachment studies using a flowing-afterglow Langmuir-probe apparatus by Friedman *et al.*²⁴ The authors observed the Pt(PF₃)₃ fragment with a large rate constant. The activation energy was found to be 0.084 eV—consistent with the present onset at 0–0.1 eV.

The present experiment is also linked to the study of electron-induced reactions of Pt(PF₃)₄ adsorbed on carbon and platinum surfaces by Landheer *et al.*³ They used 500 eV incident electrons in their study, but many of the reactions which they observed could have been caused by much slower backscattered secondary electrons with energies close to those in the present study. They observed that the initial step, obtained with low electron doses, was the loss of one PF₃ ligand, a result reminiscent of the present gas phase observation. A second step, observed at higher dose, involved P–F bond breaking.

5 Conclusions

The present study reveals that Pt(PF₃)₄ is very sensitive to dissociation by slow electrons, with a peak cross section of 20000 pm² at 0.5 eV, and with the loss of one ligand being the dominant channel—a result consistent with the flowing-afterglow study of Friedman *et al.*²⁴ The 0.5 eV band and several higher-lying bands were assigned to specific resonances by comparing them to an electron energy-loss spectrum and the cross section for vibrational excitation.

The relation between the present study and FEBIP is complicated, however, by the role of the substrate and neighboring molecules in the latter and only qualitative conclusions can be made. The large cross section for the loss of one ligand

measured in this study indicates that dissociative electron attachment of slow secondary electrons to $\text{Pt}(\text{PF}_3)_4$ will be important in FEBIP. Only the loss of one ligand has a very large cross section and several consecutive collisions are thus necessary to obtain pure platinum. The platinum-containing fragments revealed in this study are negatively charged and will repulse further electrons. They could be neutralized by losing an electron to the substrate or by electron-induced detachment.

The DEA process requires slow electrons, however. In FEBIP they are the secondary backscattered electrons, and the role of DEA could even be adverse, as has recently been pointed out by Engmann *et al.*¹² because the secondary electrons are not tightly focused and DEA could cause loss of spatial resolution.

Acknowledgements

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