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A Study of the Interfacial Interaction between Methylene Diphenyl Diisocyanate (MDI) and Metals by XPS and ToF-SIMS

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The Surface Analysis Laboratory

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Adhesion of PU on metals

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Polyurethanes are widely used as adhesives in industry as they show excellent adhesion to metal oxide surfaces.

Often the adhesion is due to intermolecular forces between adherent and substrate: bonds.

The understanding of adhesion phenomena is nowadays investigated by the characterization of the interfacial interaction that occur when the adherent is applied to the substrate.

MDI: a PU monomer

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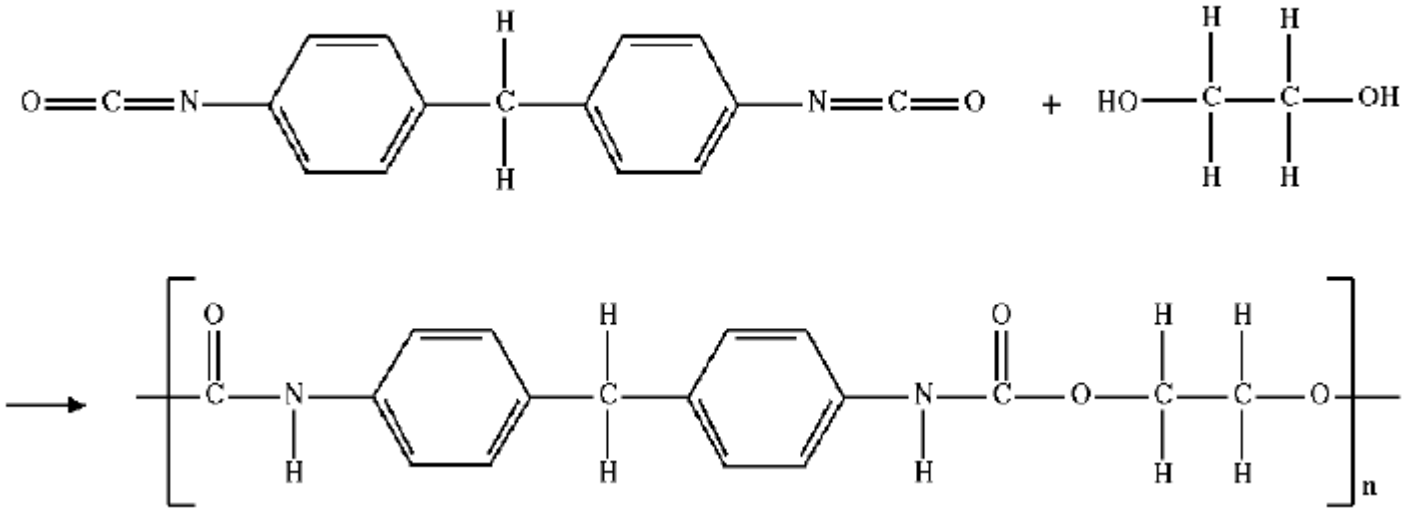

PU polymer chain is formed by urethane linkage. This bond is obtained from the reaction between an hydroxyl group and an isocyanate.

The great majority of di-isocyanate used for the polyaddicion reaction is made by methylene diphenyl diisocyanate: MDI

Project Aim

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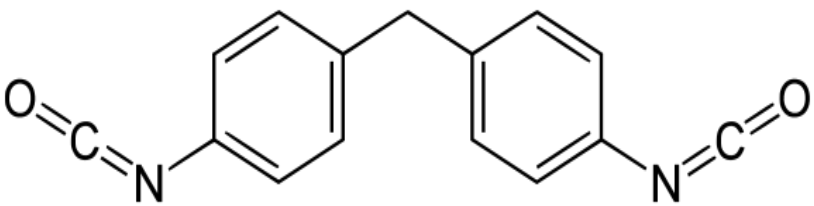
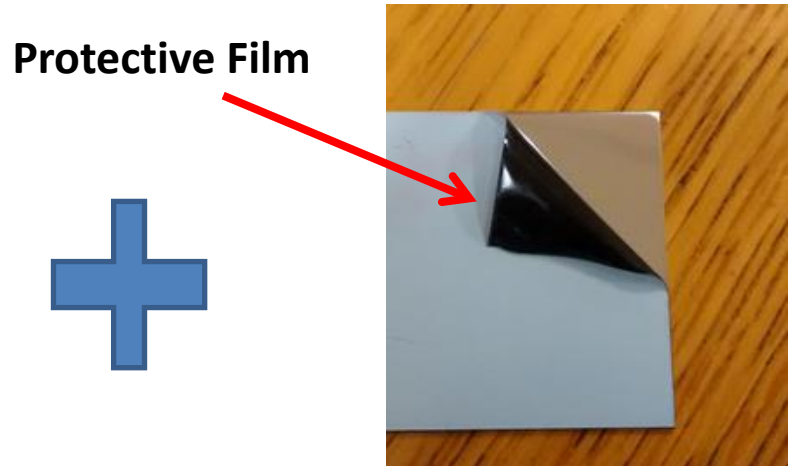
Interface interaction



MDI



In order to understand the adhesion of PU on metal substrates the above interaction was analysed.

- Stainless steel (316L)
- Iron
- Molybdenum
- Nickel
- Chromium

Isocyanate Reactivity

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$$R - NCO + H_2O \rightarrow R - NH - COOH \rightarrow R - NH_2 + CO_2$$

$$R - NCO + R - NH_2 \rightarrow R - NH - CO - NH - R$$

$$R - NCO + R^I - OH \rightarrow R - NHCOOR^I$$

Stainless steel surface is made of metal oxide, metal hydroxide and adsorbed water.

$$R - NCO + M - OH \rightarrow R - NHCOOM$$

MDI/Steel Survey Spectra

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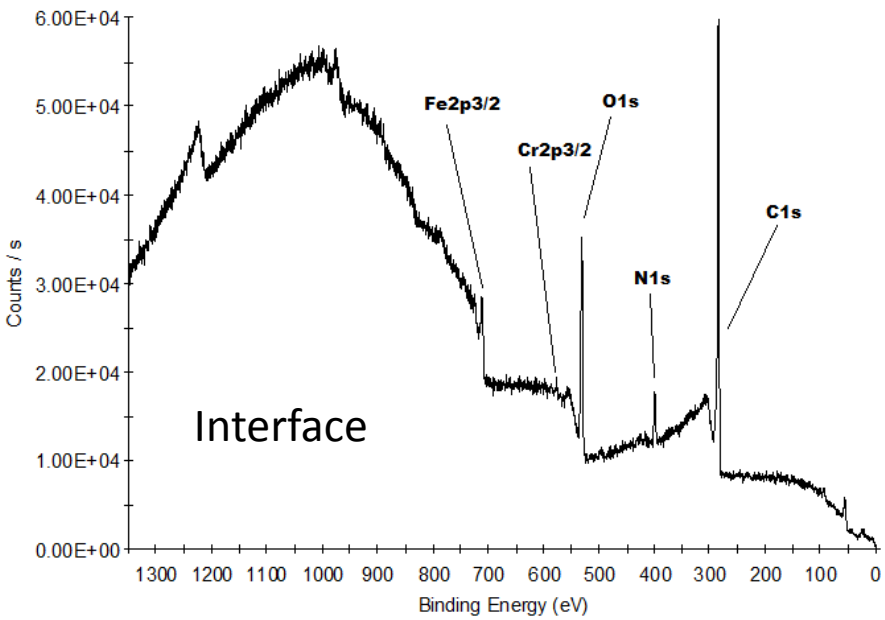
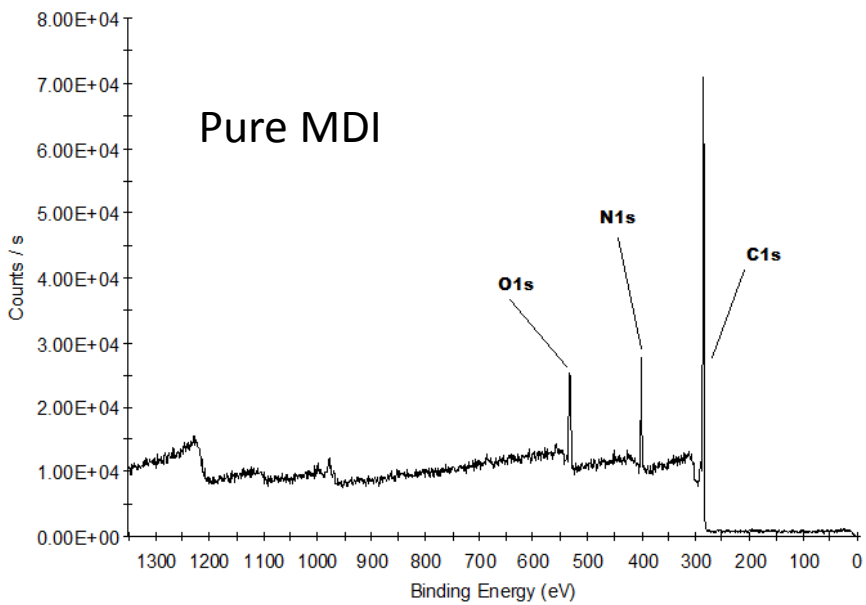
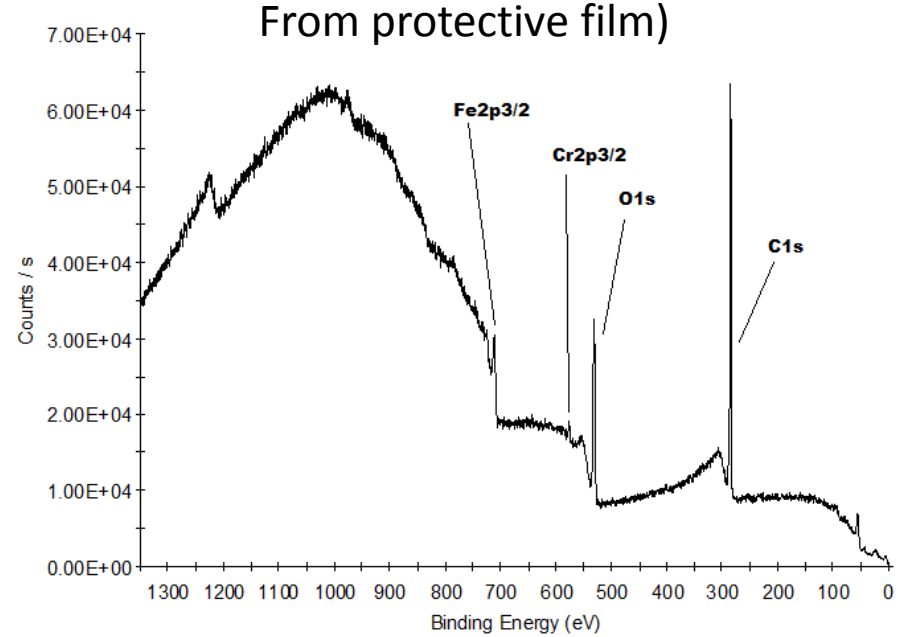


A sample of 3 nm of MDI on stainless steel.



Steel (with carbon contam. From protective film)



C1s High Resolution Spectra

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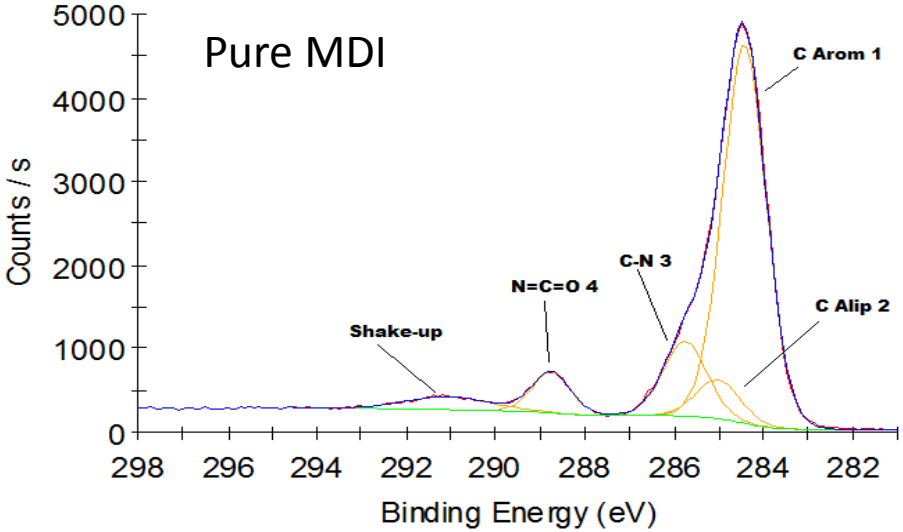

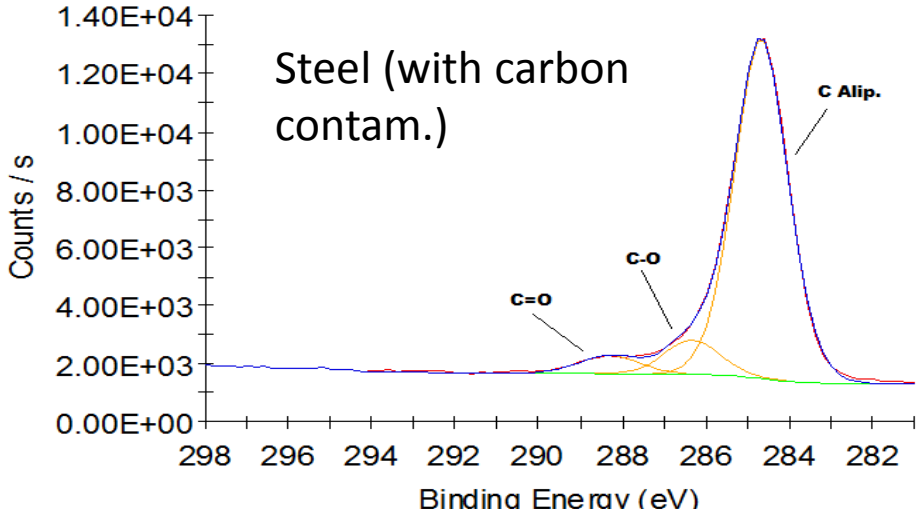

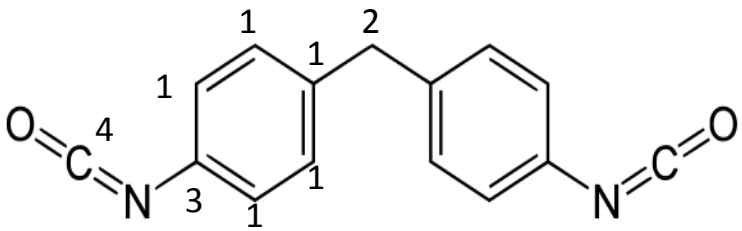

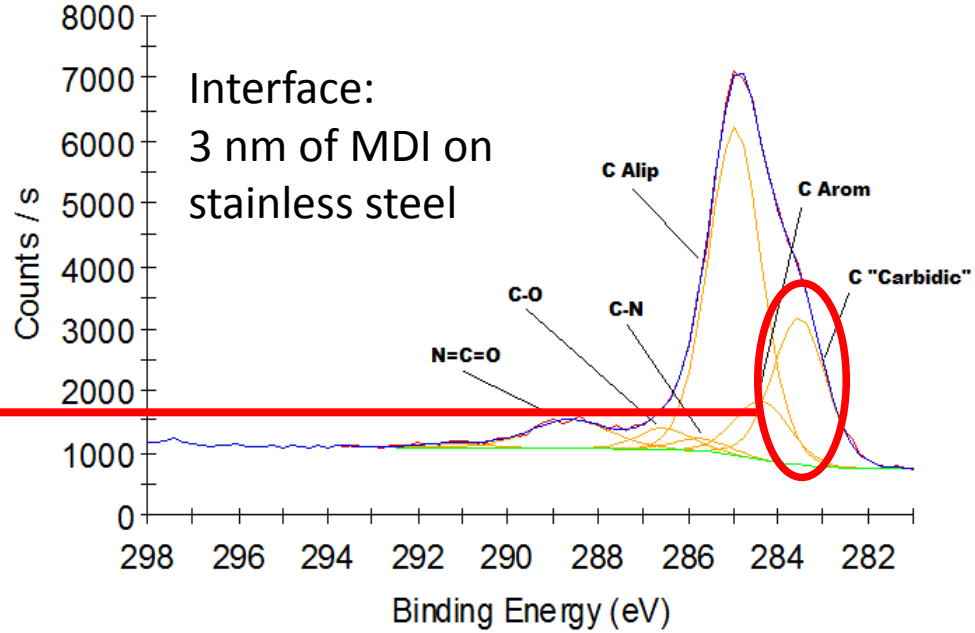

New peak indicates the formation of a M-C bond:

Organometallic complex??

C1s N=C=O Region

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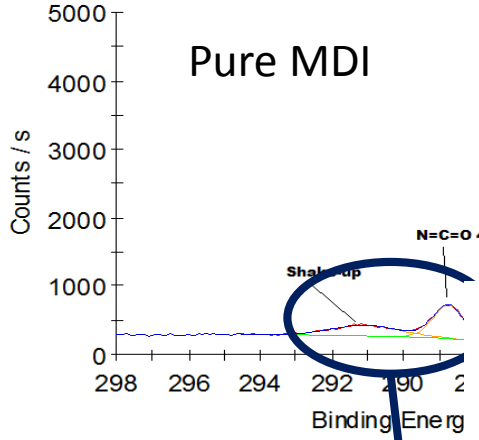

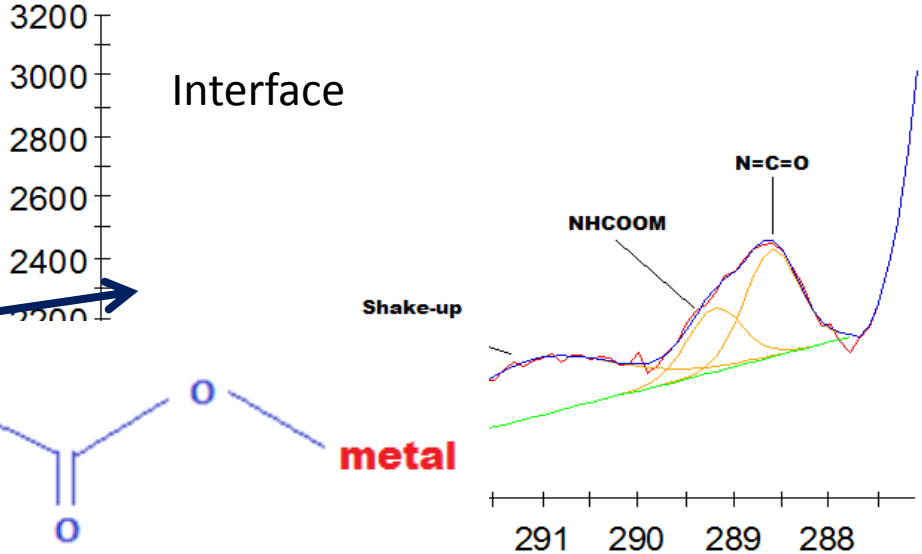

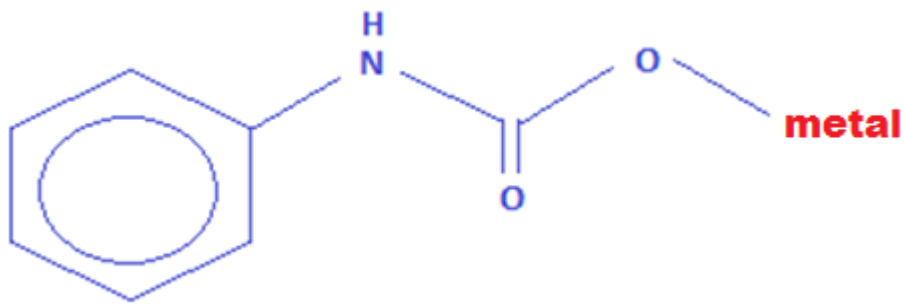

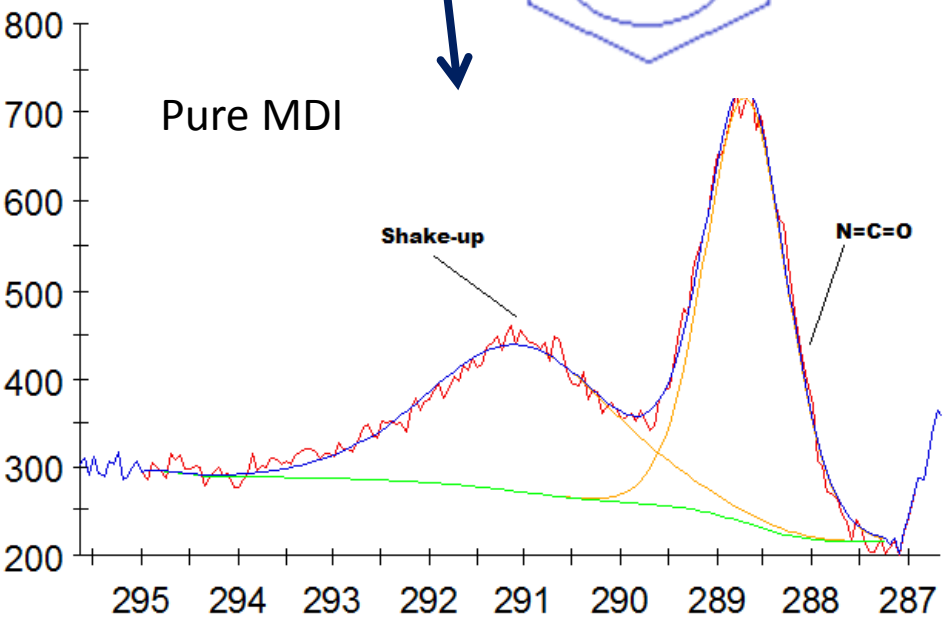

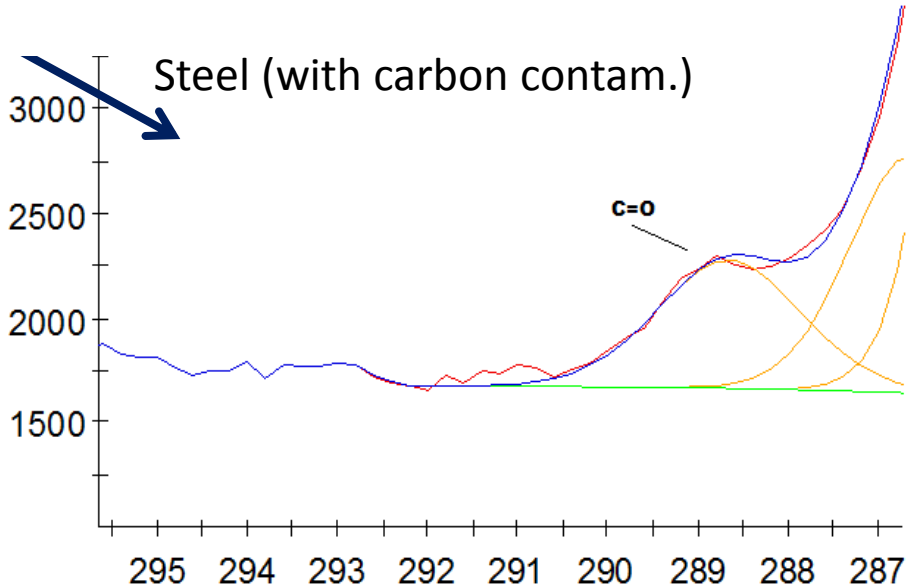

Possible Mechanism of Reaction

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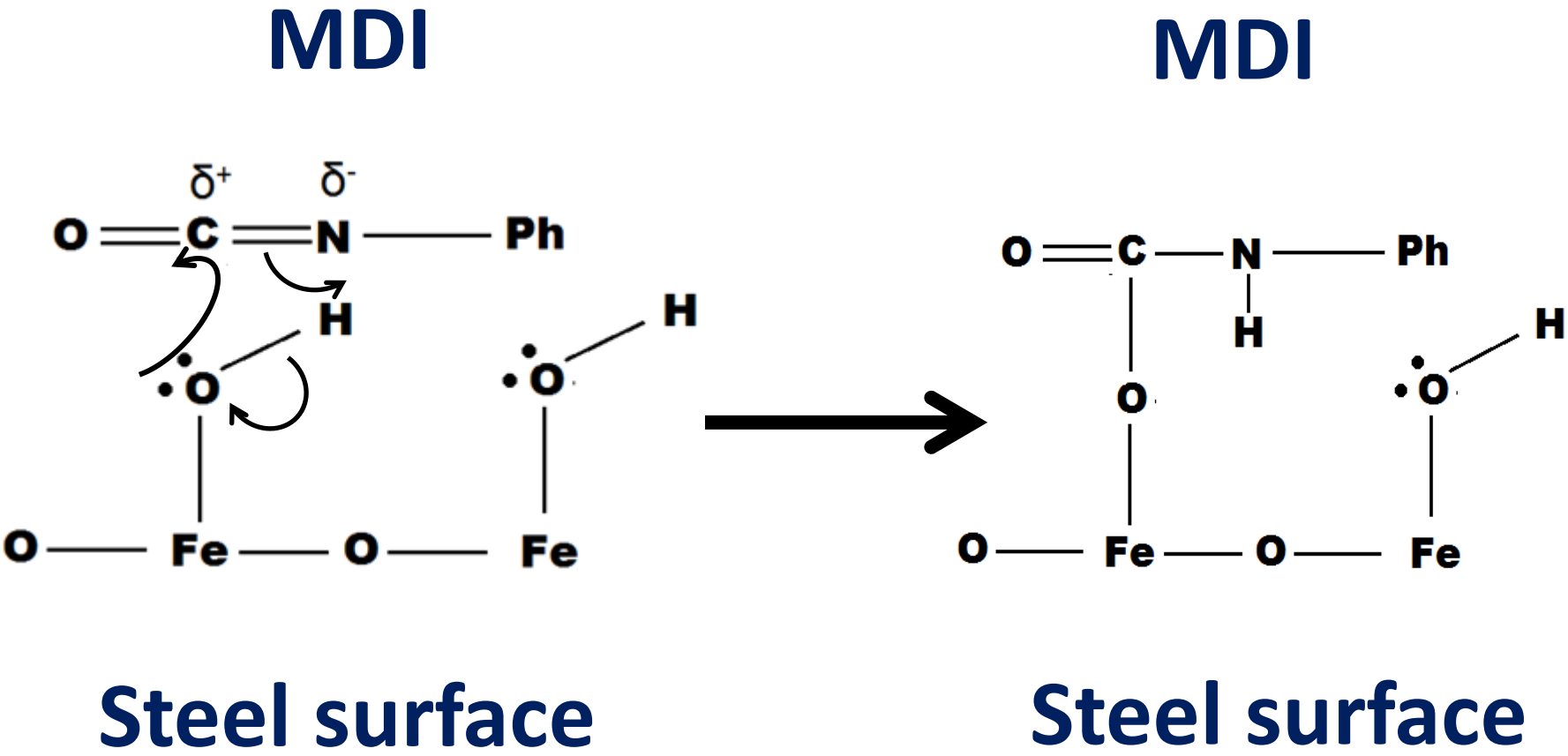

N1s High Resolution Spectra

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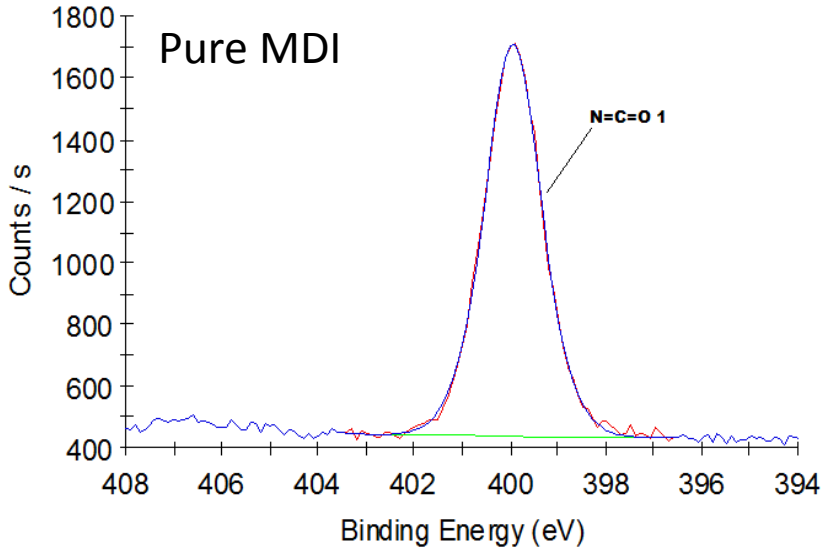

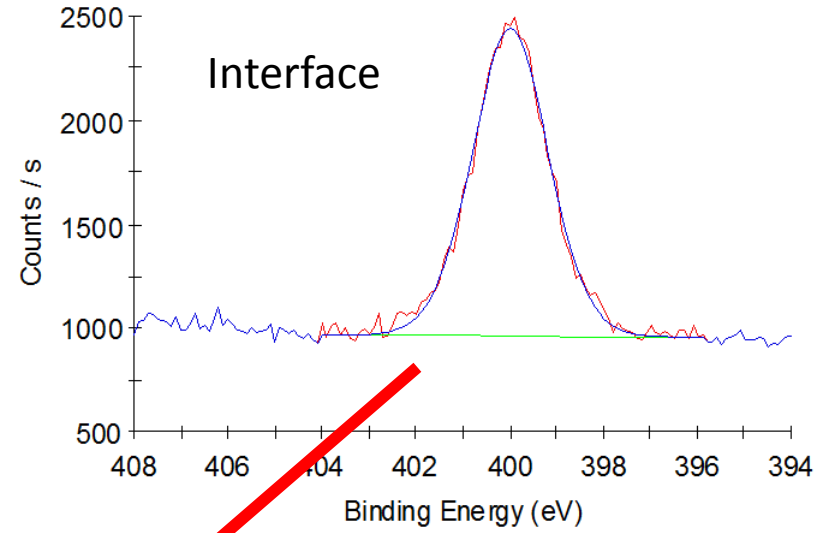

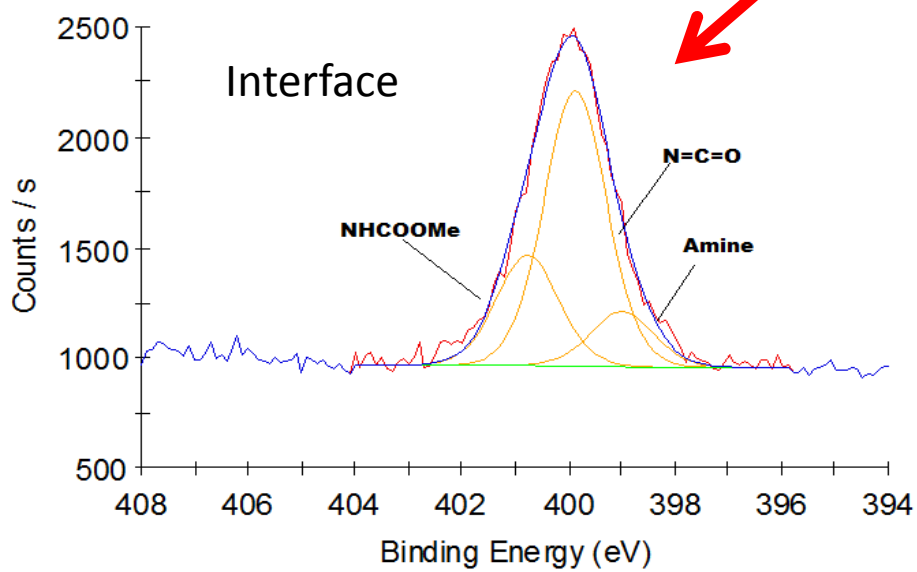

SIMS Negative Spectra

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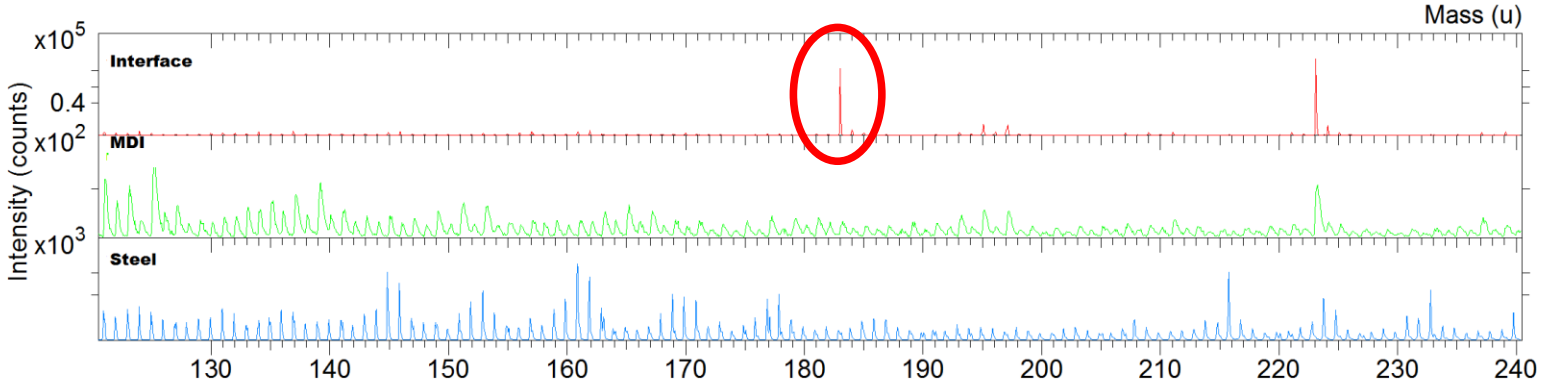

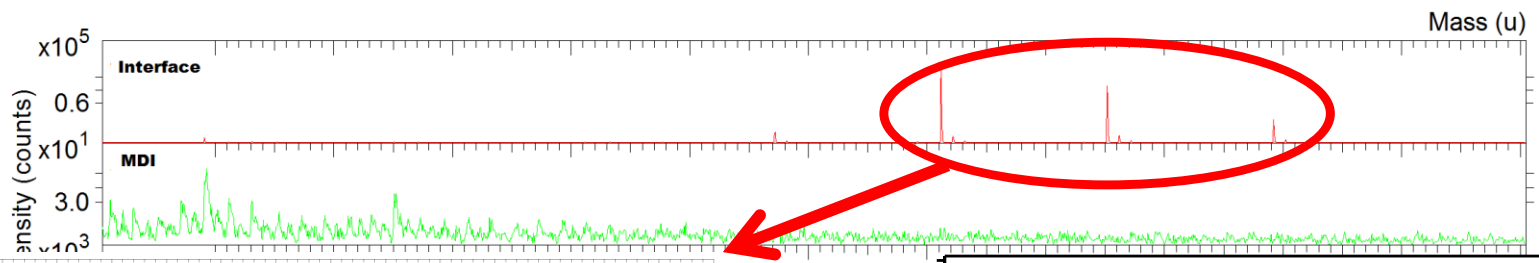

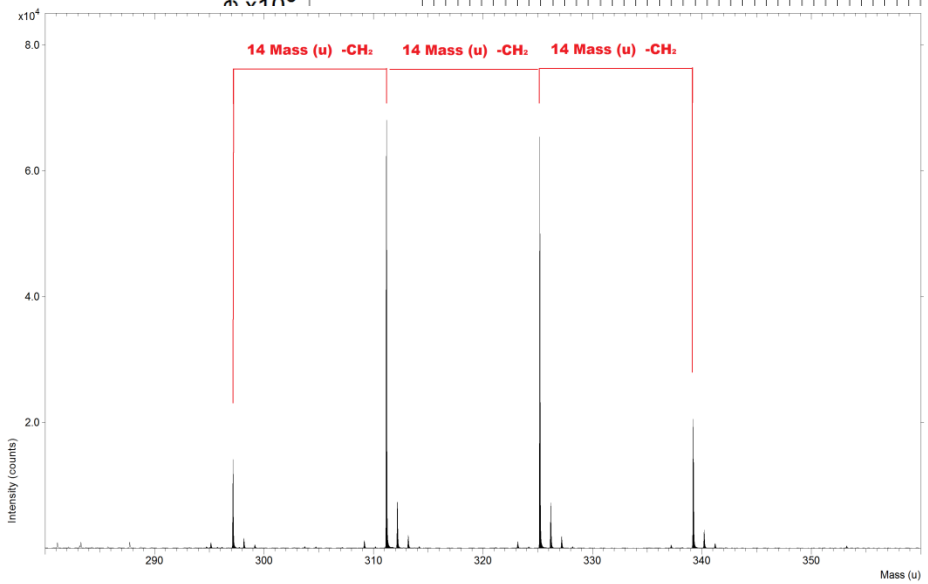

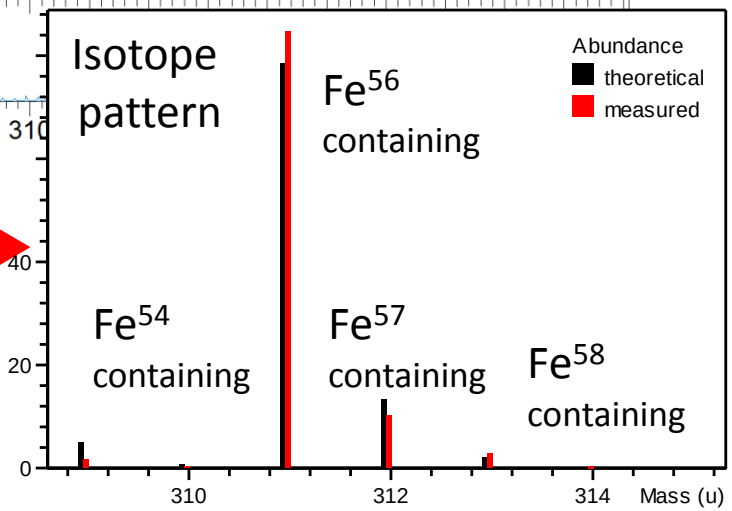

MDI/Fe: C1s

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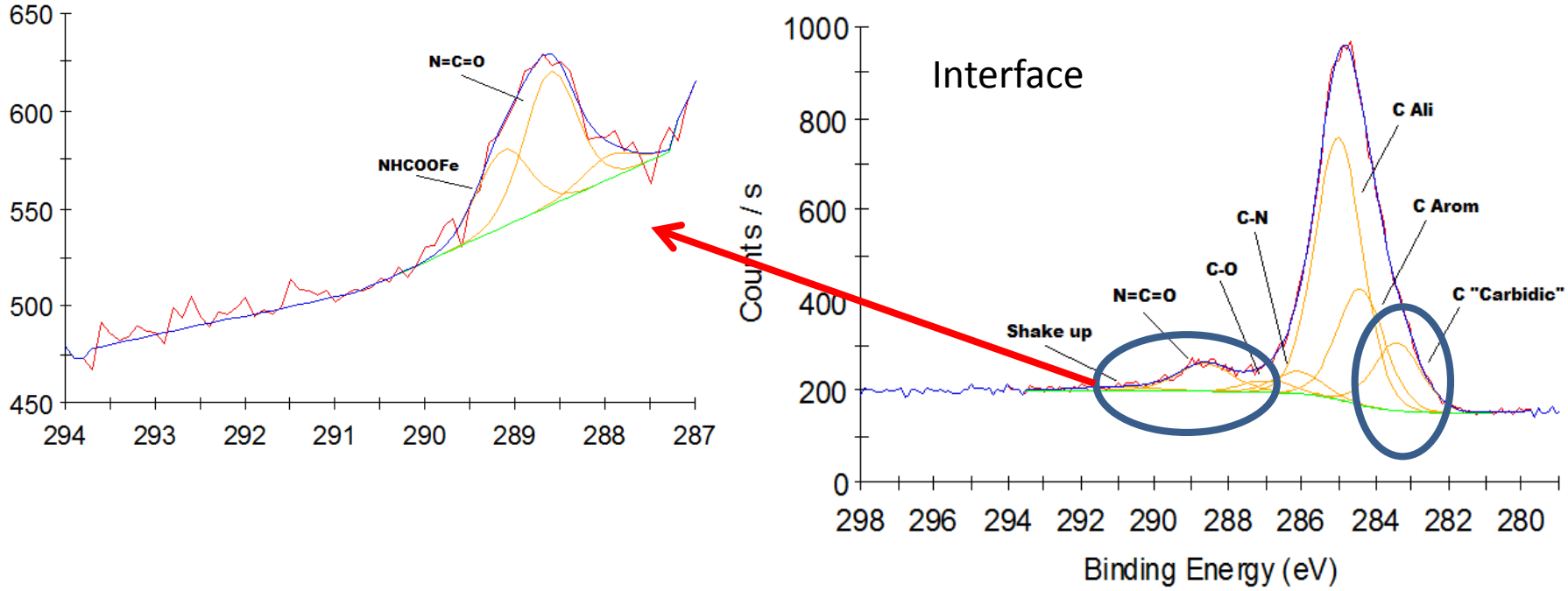

«Carbidic» peak and NHCOOFe peaks present

MDI/Mo: Mo3d

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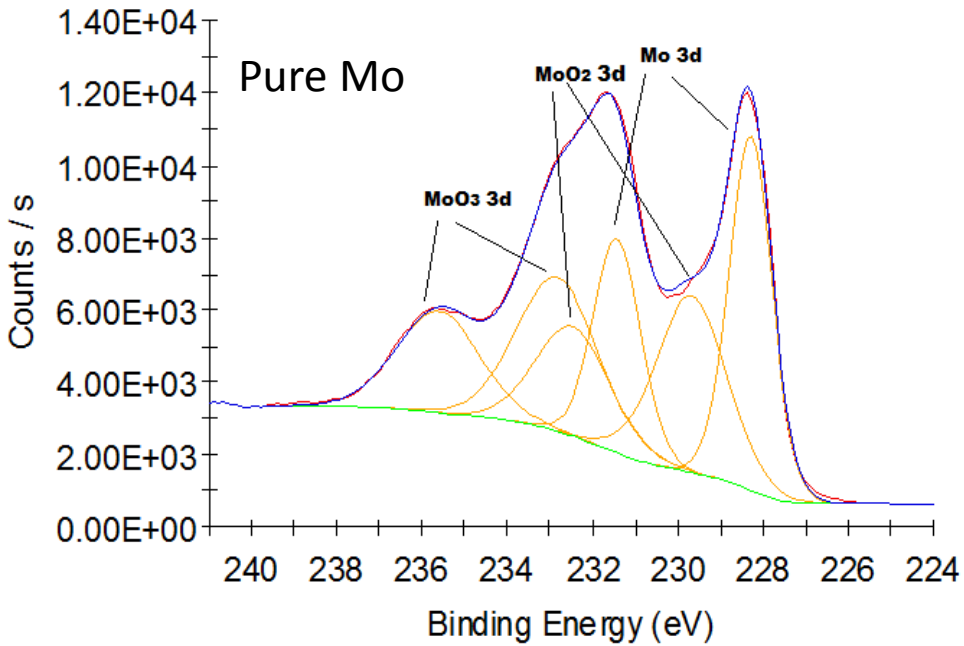

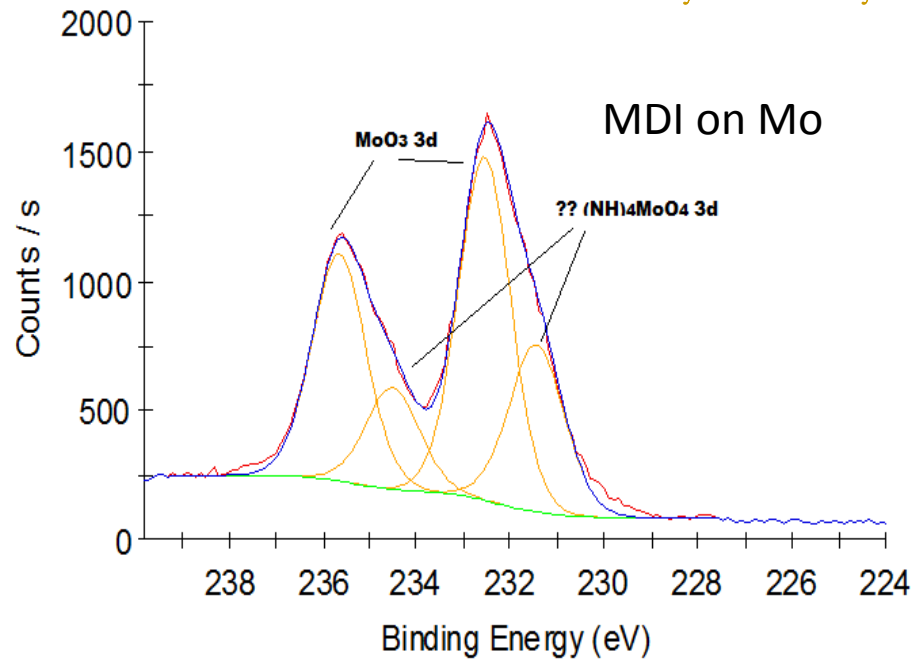

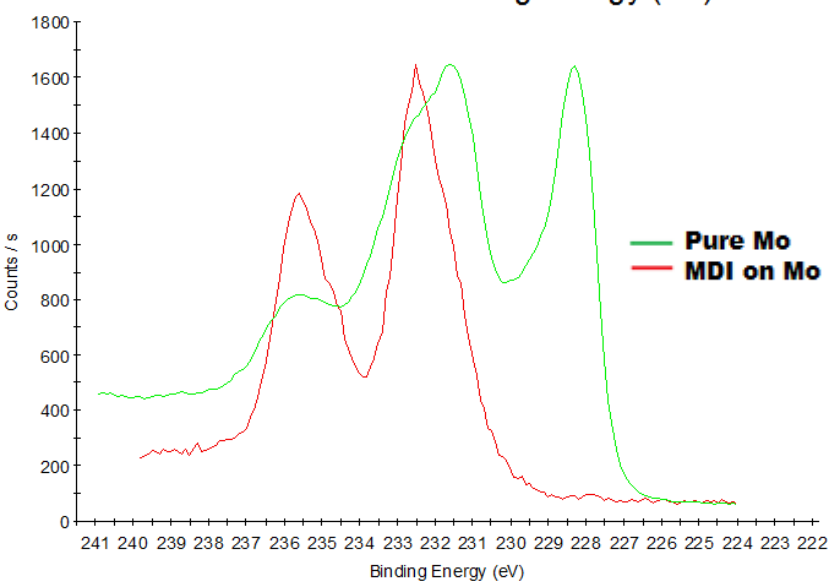

When a thin layer of MDI is applied it is not possible to see metallic Mo and MoO_2 anymore. Most of the peak is due to MoO_3 and a new doublet appears in a position which could be attributed to an interaction with nitrogen.

MDI/Ni: Ni 2p and N1s

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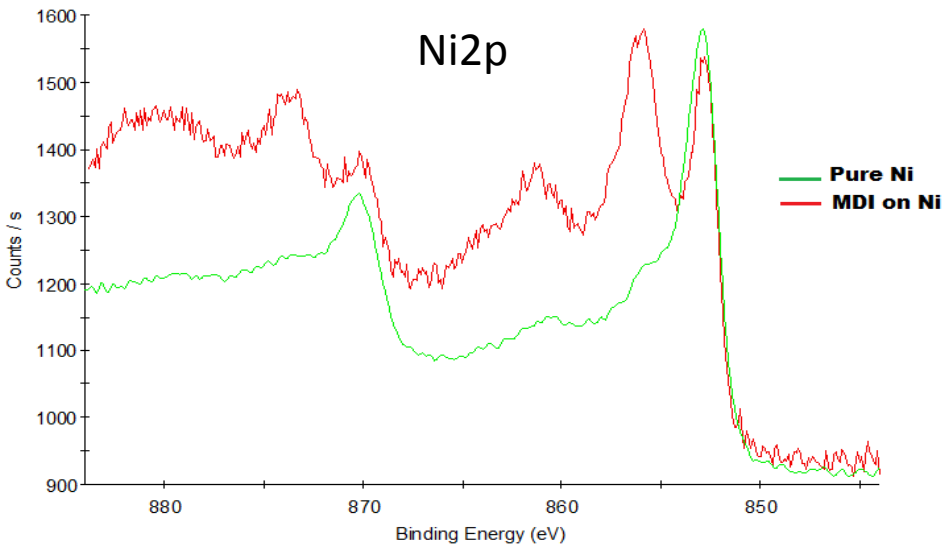

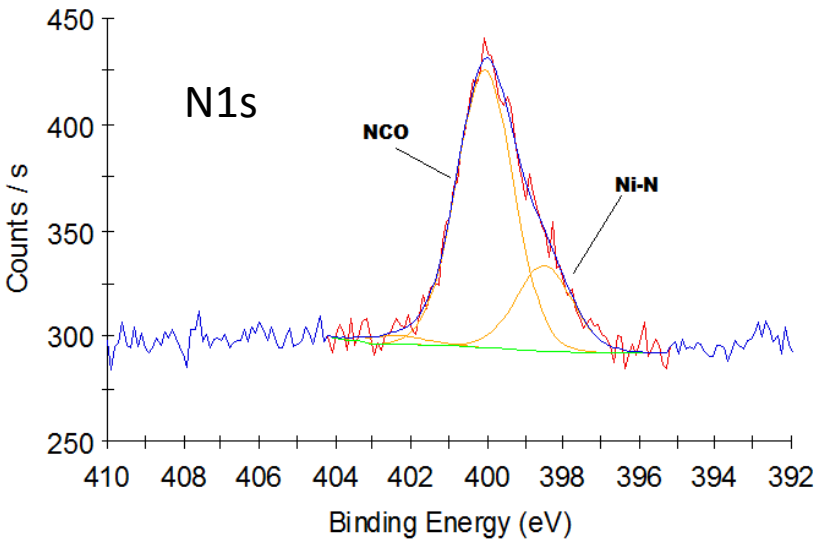

When a thin layer of MDI is applied, a new doublet appears in a position which could be attributed to an interaction with nitrogen. The nitrogen high resolution spectrum confirms the interaction.

MDI/Cr: C1s

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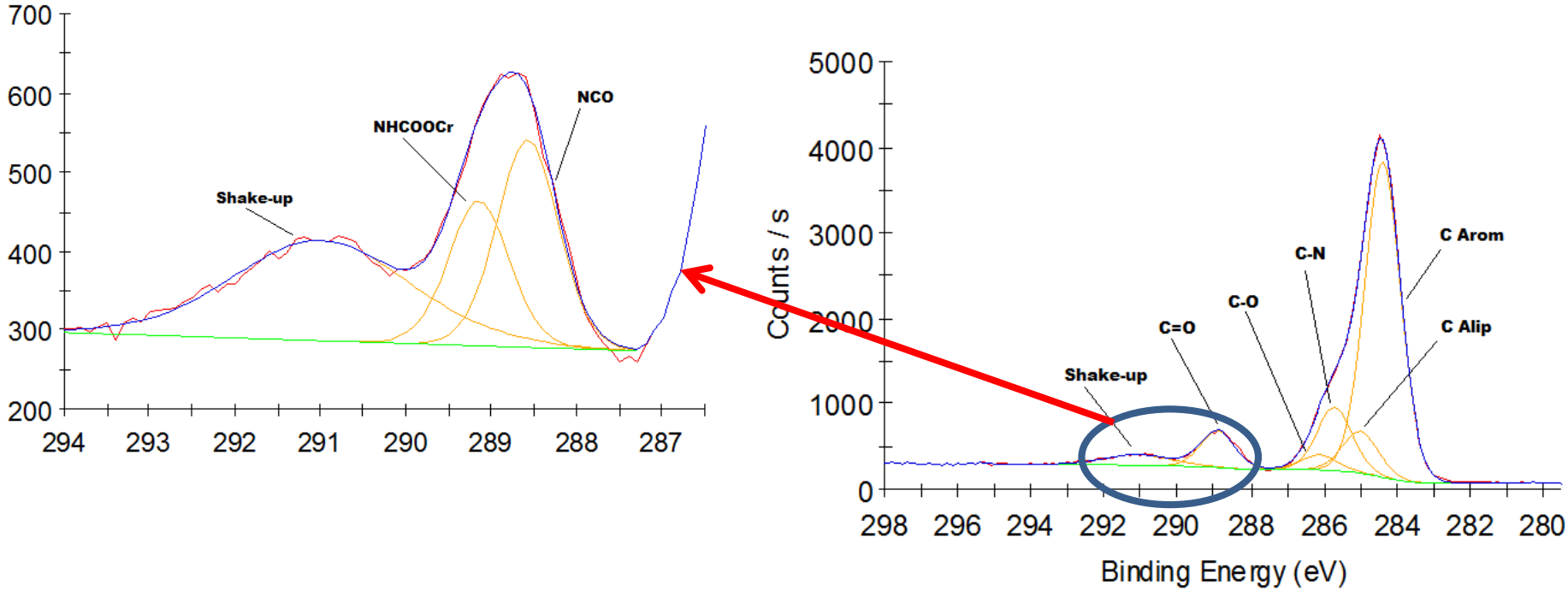

No «carbidic» peak but NHCOOCr peak present

Summary

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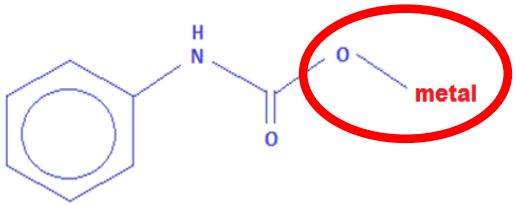
M-C interaction ⟶ Peak at 283.6 eV :

- MDI/Steel and MDI/Fe interfaces

Formation of 

⟶ Peak at 289.2 eV:

- MDI/Steel, MDI/Fe, MDI/Cr interfaces

M-N interaction ⟶ New doublets in the metal peaks:

- MDI/Mo and MDI/Ni interfaces

Conclusions

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- PU is known to show excellent adhesion to metal oxide surfaces.
- PU is formed by polyaddition reaction of MDI with polyols.
- Some adhesive formulations are based on PU monomers, and some prepolymers containing unreacted isocyanate groups.

Conclusions

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- For these kinds of adhesives, the reactions illustrated before between the isocyanate group and the different metals, can partially explain the quality of the adhesion of PUs to metal oxide substrates.

- XPS can be used to differentiate between MDI interaction that are via the C=O or the N=C moieties.

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THANK YOU FOR YOUR ATTENTION!

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