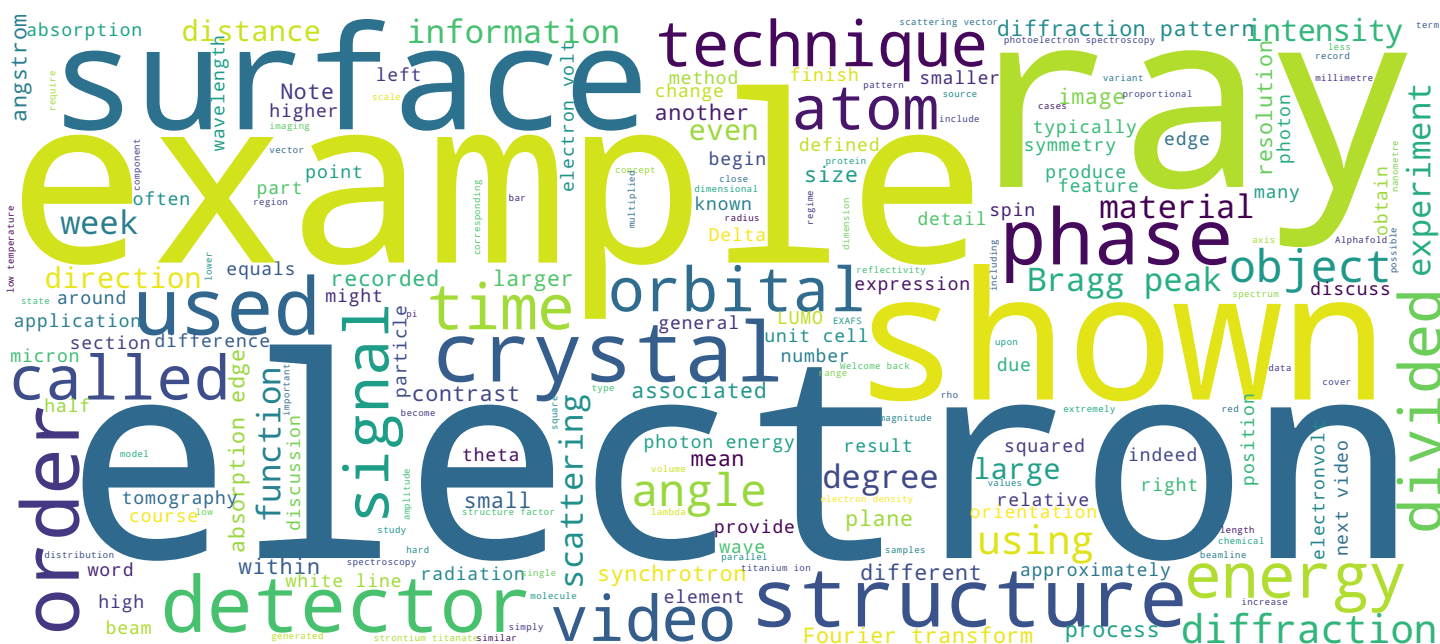


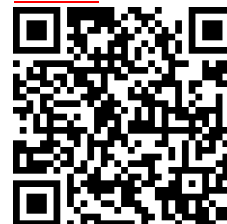
Prof. Philip Willmott



## Search MOOC



## Video



# Contents and objectives of this video



- XANES transitions
  - LUMO
  - Oxidation state
  - Subshell occupation
  - Coordination chemistry
- XANES example – tackling diesel emission

Hello again. In this video, we will consider the information we can extract using XANES and finish with an example of its use in optimising catalytic converters in tackling diesel emissions.

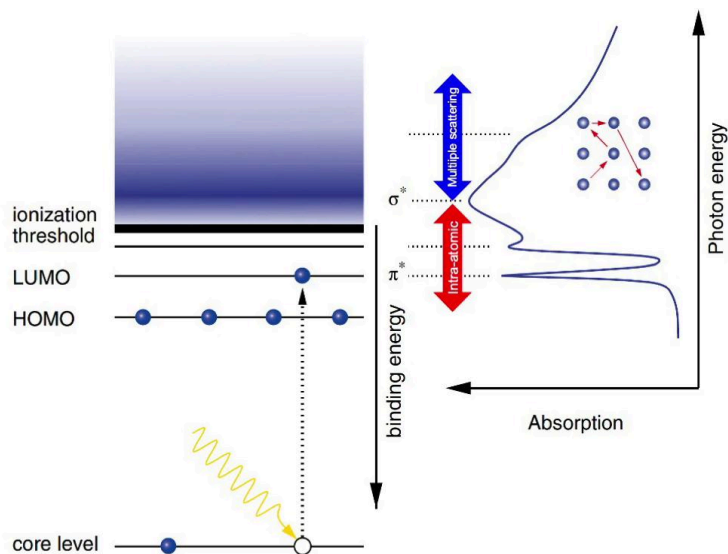
Notes

Summary



0m 05s

# Transitions in XANES



- Core electron promoted to unoccupied excited state (both bound and unbound)
  - “White lines”: unoccupied bound states
  - LUMO
    - e.g.  $\pi^*$ ,  $\sigma^*$
  - Partially empty valence electron shell
    - e.g. 5d shell of noble metals
- KE of promoted electron  $\lesssim 30 - 40$  eV
  - $\lambda_e \gtrsim 2.2$  Å
  - Probes large local region around absorbing atom
  - Multiple elastic-scattering events
    - $\Rightarrow$  difficult to model
- Information about
  - Oxidation state. Shift in edge energy
    - Corresponding but opposite shift in photoelectron energy for a given incident  $h\nu$
  - Coordination chemistry/bond geometry

In all X-ray spectroscopies, a core electron is promoted to an excited and unoccupied state, be it bound or unbound. The white lines mentioned in the previous video are characteristic of the first excited state in energy, or the LUMO, lowest unoccupied molecular orbital. This is typically a pi-star antibonding state, but can also be a sigma-star state.

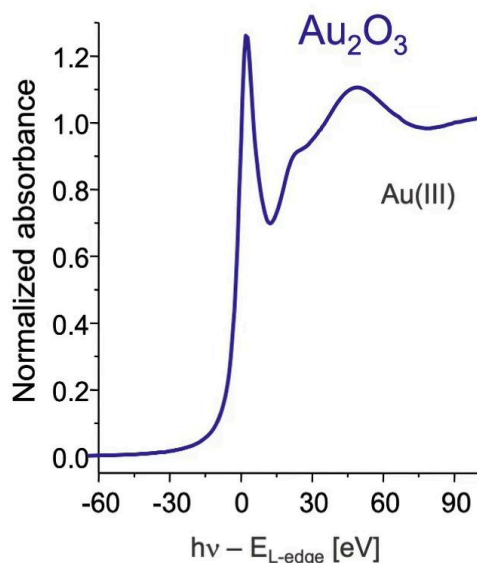
Notes

Summary



0m 19s

# Transitions in XANES



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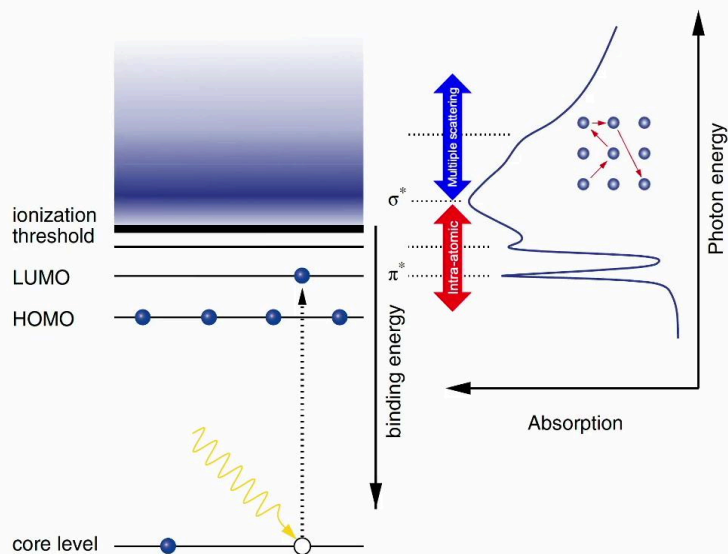
The excited bound state may also be an unoccupied valence electron orbital, such as in the case of the 5D noble metals, provided as an example in the previous video. We see here, for example, that bulk gold has a filled 5d shell and thus no white line resulting from the promotion to an electron to this subshell. In contrast, if one is able to oxidise gold, such as in the exotic compound  $\text{Au}_2\text{O}_3$ , the electrons which are donated to the oxygen atoms originate from the 5d subshell, and as a consequence, this compound does have a pronounced white line. XANES thus provides here information on the oxidation state.

Notes

Summary



# Transitions in XANES



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If the electron is promoted to an unbound state in the continuum, it can have kinetic energies up to 40 electronvolts. This means that in such cases of XANES, the de Broglie wavelength is larger than 2.2 angstroms and can be easily as large as 5 angstroms. This means that XANES probes large local regions containing several atoms and will record multiple elastic scattering events, making XANES rather difficult to model.

Notes

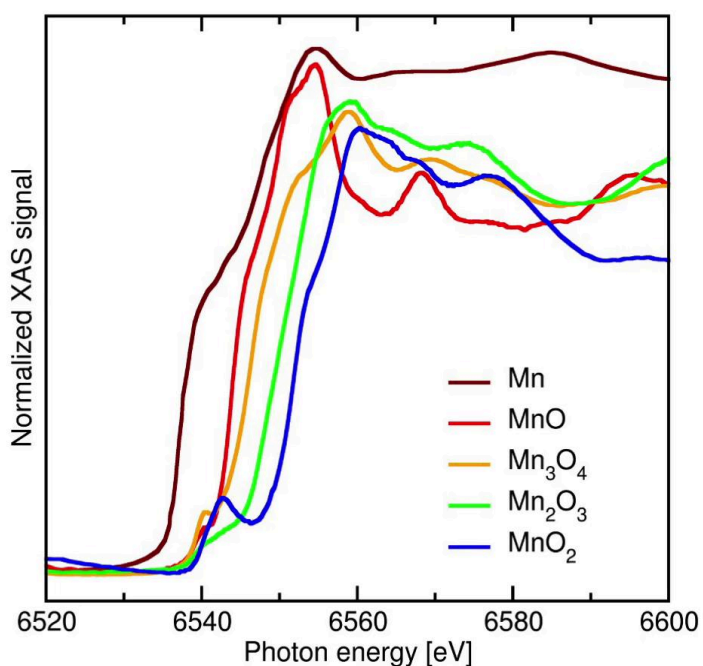
Summary



1m 30s



# Transitions in XANES



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    - $\Rightarrow$  difficult to model
- Information about
  - **Oxidation state. Shift in edge energy**
    - **Corresponding but opposite shift in photoelectron energy for a given incident  $h\nu$**
  - Coordination chemistry/bond geometry

As we have also already seen, the position of the absorption edge depends on the local environment, notably the oxidation state. Note that there is a corresponding but opposite shift in photoelectron energy for a given instant energy  $h\nu$ , as often exploited in ESCA or XPS measurements.

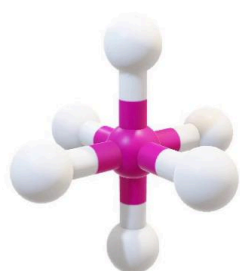
Notes

Summary



2m 03s

# Transitions in XANES



Ti in  $\text{SrTiO}_3$



Ti in  $\text{Ba}_2\text{TiO}_4$

## $\text{TiO}_6$ octahedra in $\text{SrTiO}_3$

- $t_{2g}$ : LUMO with octahedral inversion symmetry
- Cannot be accessed by dipole from 1s core state
- Very weak signal via quadrupole (2-electron) perturbation

## $\text{TiO}_4$ tetrahedra in $\text{Ba}_2\text{TiO}_4$

- $3d^3 4p$  mixed LUMO states
- p-character of these MOs can be accessed from 1s core state via direct dipole perturbation ( $\Delta l = 1$ )

- Core electron promoted to unoccupied excited state (both bound and unbound)
  - "White lines": unoccupied bound states
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  - Oxidation state. Shift in edge energy
    - Corresponding but opposite shift in photoelectron energy for a given incident  $h\nu$
  - **Coordination chemistry/bond geometry**

The symmetry of molecules and motifs in solid-state structures can be probed with XANES, leading to insights into the coordination chemistry and bond geometries. Two examples are shown here for titanium: one in which it resides in an octahedral environment of six oxygen atoms in strontium titanate, and another in which it is bound tetrahedrally to oxygen in a configuration similar to carbon atoms in diamond. The first case has a titanium ion in a position which exhibits octahedral inversion symmetry. The LUMO is a so-called  $t_{2g}$  state. In quantum chemistry, the  $t_{2g}$  state refers to a set of molecular orbitals that arise from the combination of d-orbitals of transition metal atoms. Now remember, d-orbitals have even parity. The term  $t_{2g}$  stands for triply degenerate, which means that there are three degenerate orbitals in this set. The  $t_{2g}$  orbitals are lower in energy than the higher energy set of d-orbitals, known as the  $e_g$  orbitals. The energy difference between the  $t_{2g}$  and  $e_g$  orbitals is called the crystal field splitting energy, which depends on the geometry of the arrangements around the titanium ion. Because the  $t_{2g}$  orbitals have the same symmetry as the 1s core state, it can't be accessed from it.

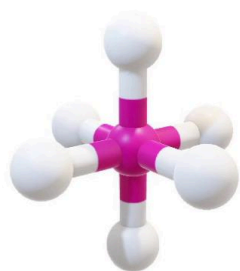
Notes

Summary



2m 24s

# Transitions in XANES



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  - **Coordination chemistry/bond geometry**

There is a weak signal from a quadrupole two-electron perturbation only. Now, in contrast, the titanium ion in the  $\text{Ba}_2\text{TiO}_4$  structure has a LUMO that is a mixture of three d-orbitals and one 4p-orbital. Thanks to the partial p character of this tetrahedral configuration, it can be accessed from the 1s core state via a direct dipole transition.

Notes

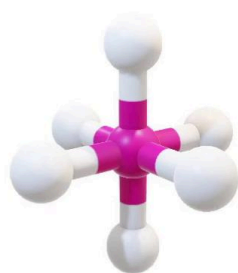
Summary



4m 05s



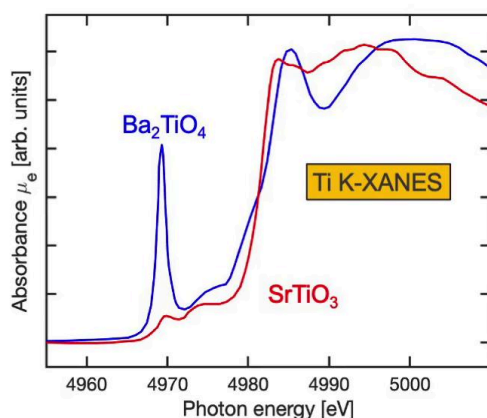
# Transitions in XANES



Ti in  $\text{SrTiO}_3$



Ti in  $\text{Ba}_2\text{TiO}_4$



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  - Oxidation state. Shift in edge energy
    - Corresponding but opposite shift in photoelectron energy for a given incident  $h\nu$
  - **Coordination chemistry/bond geometry**

We see this in the two titanium K-edge XANES spectra for strontium titanate and  $\text{Ba}_2\text{TiO}_4$ , whereby the spectrum for strontium titanate, shown in red, has no or only a very small feature at the absorption edge to the LUMO at 4,970 electron volts, whereas the spectrum for barium titanate has a strong white line as its LUMO.

Notes

Summary



4m 35s

# XANES example – tackling diesel emissions



Wuhan, China, 2016. Creative Commons:  
[http://leipower.lofter.com/post/8b49d\\_cb94873](http://leipower.lofter.com/post/8b49d_cb94873)

- Burning diesel  $\Rightarrow$   $\text{NO}_x$ 
  - Harmful to human health
- Automobile industry
  - Exhaust: catalyst + ammonia ( $\text{NH}_3$ )
  - $\text{NO}_x + \text{NH}_3 \xrightarrow{\text{catalyst}} \text{N}_2 + \text{H}_2\text{O}$
- Selective catalytic reduction system (SCR)
  - Additive “AdBlue” decomposes into  $\text{NH}_3$  in exhaust, which then reacts with  $\text{NO}_x$
  - Up to 90% efficient
  - Efficient only at temperatures  $> 200^\circ\text{C}$
  - Needs ca. 10 minutes after cold; longer on winter days
- Investigate molecular reactions on surface of catalyst using Quick-XANES
  - Optimize temperature/additive provision?

We're going to finish now our discussion of XANES with a recent example of its application that could have a significant impact on environmental damage caused by diesel emission. If the exhaust from diesel engines is not handled properly, significant volumes of  $\text{NO}_x$  are generated, which is very harmful to human, and indeed all animal, health.

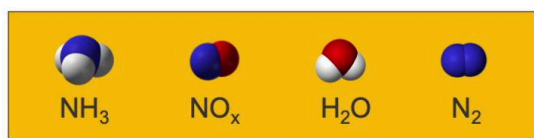
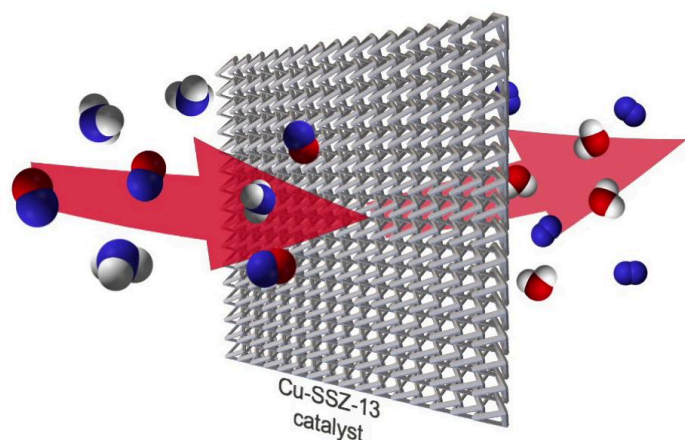
Notes

Summary



5m 02s

# XANES example – tackling diesel emissions



- Burning diesel  $\Rightarrow$  NO<sub>x</sub>
  - Harmful to human health
- Automobile industry
  - Exhaust: catalyst + ammonia (NH<sub>3</sub>)
  - $\text{NO}_x + \text{NH}_3 \xrightarrow{\text{catalyst}} \text{N}_2 + \text{H}_2\text{O}$
- Selective catalytic reduction system (SCR)
  - Additive “AdBlue” decomposes into NH<sub>3</sub> in exhaust, which then reacts with NO<sub>x</sub>
  - Up to 90% efficient
  - Efficient only at temperatures > 200°C
  - Needs ca. 10 minutes after cold; longer on winter days
- Investigate molecular reactions on surface of catalyst using Quick-XANES
  - Optimize temperature/additive provision?

To counter this, the automobile industry came up with a solution to include a catalyst in the exhaust chamber and feed in ammonia to react with the NO<sub>x</sub> to produce harmless nitrogen gas and water vapour. This is known as the selective catalytic reduction system, or SCR. An additive, known under the trademark of AdBlue, is injected into the exhaust where it rapidly decomposes into ammonia before reacting with the NO<sub>x</sub>. Now, the process is up to 90% efficient, but only at temperatures above 200 degrees centigrade. This means that when the car is first turned on, the process is a lot less efficient for the first 10 minutes and can take even longer in cold conditions. Exactly why the process is hindered at low temperatures was not understood, so it was decided to investigate the molecular reactions on the surface of the catalyst using Quick-XANES to see if the process couldn't be tweaked and optimised.

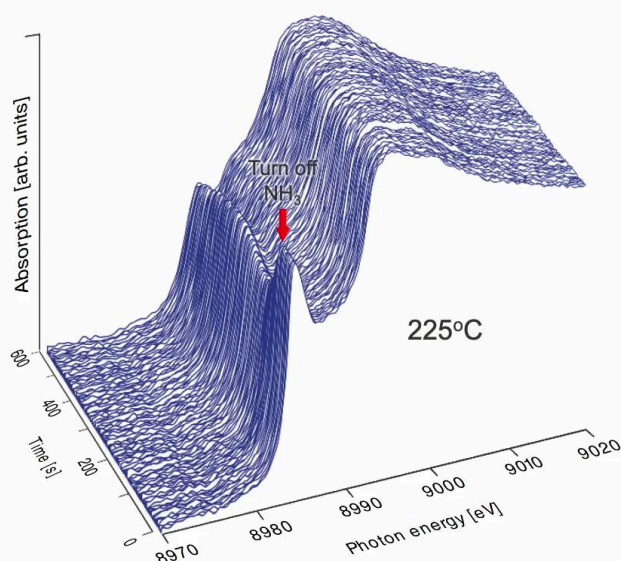
Notes

Summary



5m 26s

# XANES example – tackling diesel emissions



- Operando XAS
  - Cu K-edge spectra @ 8965 – 9035 eV
  - Mass spectrometry of products
- 0.5 s/scan
- Time-resolved response of system to
  - Reactant cut-off
  - Reactant addition
  - Different temperatures: 190, 225, 270°C
- Excess  $\text{NH}_3$  locks Cu into  $\text{Cu}^{\text{I}}(\text{NH}_3)_2$ 
  - Hinders Cu(I) re-oxidation to Cu(II) under SCR conditions
- Mechanistic understanding allows optimization of gas feeding in catalytic converter
  - Modulate  $\text{NH}_3$  feed as function of temperature

The catalyst is known as copper SSZ-13, and is an open zeolite structure with nanopores that facilitate surface reactions on the active copper sites. The study was therefore performed around the copper K-edge at 8,985 electron volts, and complemented by mass spectroscopy of the reaction products. The experiment is capable of recording two scans per second at instantaneous recording rates of approximately 100 electronvolts per second. The time-resolved response of the SCR system was investigated as a function of reactant cutoff and addition and at different temperatures.

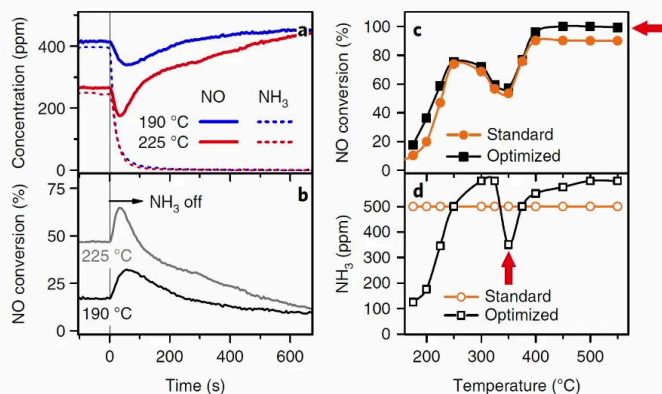
Notes

Summary



6m 32s

# XANES example – tackling diesel emissions



A. Marberger *et al.*, *Nature Catalysis* 1 221 (2018)

- Operando XAS
  - Cu K-edge spectra @ 8965 – 9035 eV
  - Mass spectrometry of products
- 0.5 s/scan
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  - Reactant cut-off
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  - Different temperatures: 190, 225, 270°C
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  - Hinders Cu(I) re-oxidation to Cu(II) under SCR conditions
- Mechanistic understanding allows optimization of gas feeding in catalytic converter
  - Modulate NH<sub>3</sub> feed as function of temperature

At low temperatures, the results demonstrated that the re-oxidation of copper I intermediates to be the rate-limiting step. Moreover, it was discovered that there was an NH<sub>3</sub> inhibiting effect on its cutoff at low temperatures, and identified a fourfold coordinated copper II species as a reactive intermediate during relaxation of this inhibition. At these lower temperatures, excess NH<sub>3</sub> locks the active copper sites into copper I NH<sub>3</sub> 2, hindering the reoxidation from monovalent to divalent copper. A strategy was thus proposed to throttle the NH<sub>3</sub> feed, depending on the current SCR temperature, and in this manner, it should be possible to increase NO<sub>x</sub> conversion from its present value of 90% to essentially 100%. This study thus demonstrated how the application of ultrafast, time-resolved, and operando XANES can suggest new strategies in heterogeneous catalysis under transient conditions. In this illustrative example, a simple temperature probe in the SCR can provide the necessary feedback to the ammonia feed to essentially reduce the NO<sub>x</sub> emissions from 10% to zero.

Notes

Summary



7m 18s



## In the next video...



In the next video, we will look at another variant of XANES called scanning X-ray transmission microscopy.

Notes

Summary



8m 46s