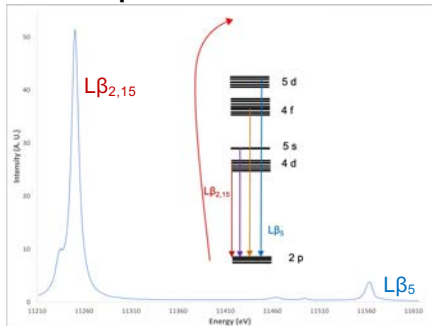


Why XES of platinum compounds

Platinum is a widely used catalyst but is very expensive.

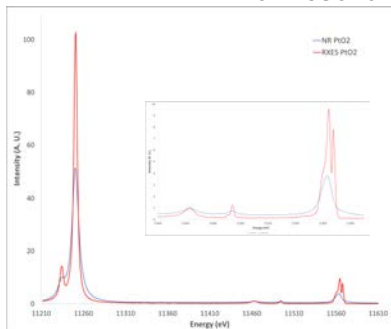
Understanding what makes it so efficient will help design better catalysts.

Methods such as XAS offer insights into the bonding environment of catalytic center, but XES directly probes the valence orbitals, which allows one to better probe the metal-ligand bonding interactions.

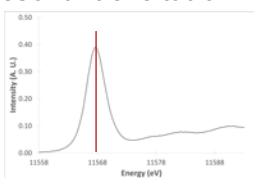


X-ray emission spectrum of platinum oxide

Non resonant vs resonant excitation



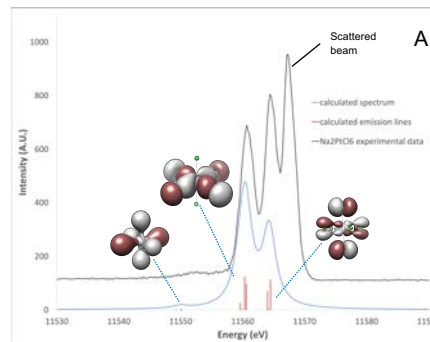
Comparison of the non-resonant x-ray emission spectrum of platinum oxide (blue) with the resonant x-ray emission spectrum of platinum oxide (red)



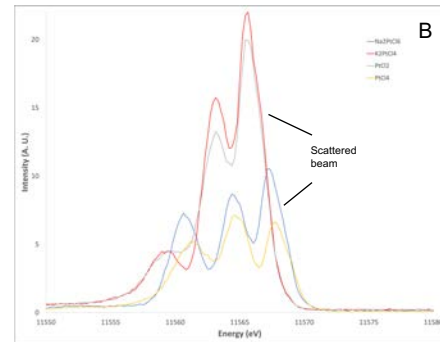
HERFD-XAS spectrum of PtO_2 (black). The energy at the top of the white line is shown in red.

For non resonant data collection, the incident energy is set ~300 eV above the edge. When the energy is set to the top of the white line, resonant emission occurs, increasing the energy resolution and allowing us to distinguish features in the valence-to-core region.

Comparison to calculated emission



Experimental (black) and calculated (blue) emission spectra for Na_2PtCl_6 . Calculated emission lines (red) and representative molecular orbitals are also shown.



Experimental spectra for Na_2PtCl_6 (blue), K_2PtCl_4 (red), PtCl_2 (gray) and PtCl_4 (yellow).

Density functional theory allows us to calculate emission lines, which can help interpret experimental data. The calculations provide insight into which molecular orbitals contribute to the observed emission. Figure A shows the comparison between the experimental and calculated spectra. The highest energy peak in the experimental data is attributed to scattered beam.

When the chemistry varies, the contributions of individual molecular orbitals also varies, as reflected in their spectra (figure B).

Conclusions

Resonant x-ray emission spectroscopy of platinum compounds reveals chemical sensitivity not shown by non-resonant excitation. This sensitivity can be explained by the contributions of different molecular orbitals, as shown with the use of density functional theory.



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