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Fourier analysis and a bright light: advancing catalysis research through frequency analysis.

Think about cars. The exhaust from cars is dangerous to both human health and the climate, due to greenhouse gases such as carbon dioxide (CO2), carbon monoxide (CO), methane (CH4), and other products of incomplete combustion. Of these, CO is highly toxic, while CH4 is much worse for the climate than CO2.

The process through which such compounds can be turned into CO2 is called catalysis (think of a catalytic converter). A catalyst is a substance which can help a chemical reaction occur or speed it up, but which does not itself get used up in the reaction. Traditionally, in automobiles, noble metals (e.g. Rhodium) are used to help convert CO (and other gases) into CO2. Even though they work well, the precise mechanism through which these metals act as catalysts is not fully understood, and further study of this mechanism is likely to help researchers and engineers design more efficient and cheaper catalysts. During catalysis, the noble metal surface can develop various structures on its surface, due to CO and oxygen (O2) "sticking" (adsorbing onto) to the surface. One avenue of research is finding out whether these intermediate structures can enhance or frustrate the surface's ability to act as a catalyst.

Now, some things about X-ray photoelectron spectroscopy (XPS). Atoms are composed of nuclei, with protons and neutrons inside of them, and a "shell" of electrons. These electrons are bound to the nucleus, and they require a certain amount of energy, called the binding energy, to become detached from it. Each type of atom has specific binding energies, and these can be used to "fingerprint" it. Atoms in a certain state have a slightly modified fingerprint, and this can be used to, say, distinguish carbon in CO from carbon in CO2, and even figure out if a molecule is "stuck" to a surface. By bombarding atoms with photons (light), we can obtain this "fingerprint". My research focuses on trying to figure out how the structures that form on a Platinum surface during the oxidation of CO into CO2 can impede or help the reaction along. We can force structures which form on top of the Platinum surface to oscillate continuously, therefore changing the "fingerprint" we see using XPS. If we do this periodically (with a given rhythm), the surface structure will change periodically as well. The question is: how does this help?

Think about water droplets hitting the ground in a noisy room. It is easy to pick out the rhythm (frequency) of the water droplets' impact, despite the noise. Even though they are quiet, you can still distinguish them, and you can even get an intuitive sense of how loud they are. Now consider a second, larger flow of water, hitting the ground a bit faster. You will hear both sets of droplets. This is true of XPS signal as well. If it changes a bit with a certain frequency, we will be able to distinguish this by a so-called Fourier Transformation of the signal. This is a mathematical trick which takes signal that varies in time and shows what frequencies it changes at. This method has several advantages, but the main ones are that it is very sensitive, so it can be used to detect very small changes in signal, and therefore even shows us changes on small areas of the surface, and that it is also time-sensitive. For instance, if CO sticks to the

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surface while O2 “unsticks” (desorbs) from it, we will be able to see this. Similarly, if both stick to the surface at the same time, we will see that as well.
My work focuses on applying Fourier Transformations to XPS spectra taken while the catalytic surface oscillates between several structural states. This is a new idea developed recently by Jan Knudsen, and it has not yet been applied to the oxidation of CO on Platinum. Moreover, I have applied the method to electrons with very low binding energies, which is a new approach that has not been tried before. I demonstrated that it is possible to relate the information we get from high binding energy electrons with information we get from electrons with low binding energies. The key idea here is that electrons with low binding energies carry information about the so-called electronic structure of the catalytic surface, while high binding energy electrons are more suited to providing information about which molecules are stuck to the surface. The overarching goal is to see how these sets of electrons relate to each other and to the catalytic activity of the surface.

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