Understanding Molecular Bonding in Vitamin B12 Using X-Ray Spectroscopy

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Background

It is often difficult to accurately describe the electronic configuration of large molecules like cobalamin (Vitamin B12). By defining the electronic and geometric structure of a molecule using X-ray spectroscopy, we can better understand how that molecule behaves. Cobalamin is a molecule of interest because it typically displays dehalogenating properties in the body. By understanding more of how cobalamin analogues operate, it becomes possible to know their chemical properties and reactions.

The Testing Facility

X-ray spectroscopy has been made easier in recent years because of advanced accelerators like the Stanford Linear Accelerator Center (SLAC). All experiments discussed were performed at the Stanford Synchrotron Radiation Lightsource (a circular accelerator).

Figure 1. The Stanford Synchrotron Radiation Lightsource at SLAC.

Methods

XANES Analysis

XANES (X-ray absorption near edge structure) analyzes the near edge region of an absorption curve. The near-edge is the region 10 eV below to 30 eV above the absorption edge, with the absorption edge representing the energy level needed to emit an electron from the core-level of the atom. The XANES region can be further divided into the rising edge and the pre-peak (or pre-edge).

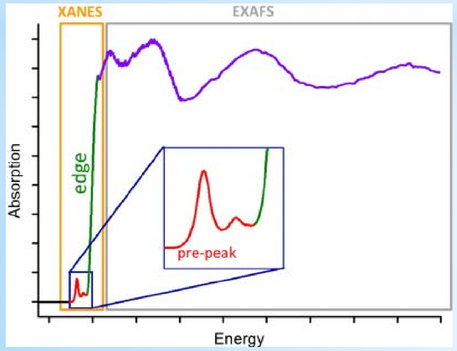

Figure 2. A typical energy spectrum.

Importance of the pre-edge region:
The pre-edge region can give us many details on the ligand binding (what is binding to the metal), spin state (low spin state versus high spin state), and deviation from centrosymmetry of the molecule (determines the three-dimensional shape of the molecule; ex: octahedral in shape). This information can help us determine of the electronic structure and thus electronic interactions of the molecule.

Analysis

Methods for analysis of spectroscopic data involve using programs like Athena and Peak Fit. The purpose of Peak Fit is to find the area under the pre-edge curve and thus determine the energy intensity. Knowing energy intensity will give us information as to how much energy is needed to transition a 1s electron to a d orbital. The pre-edge represents this "forbidden" transition in electron excitation, hence why the intensity of a pre-edge peak is generally very small.

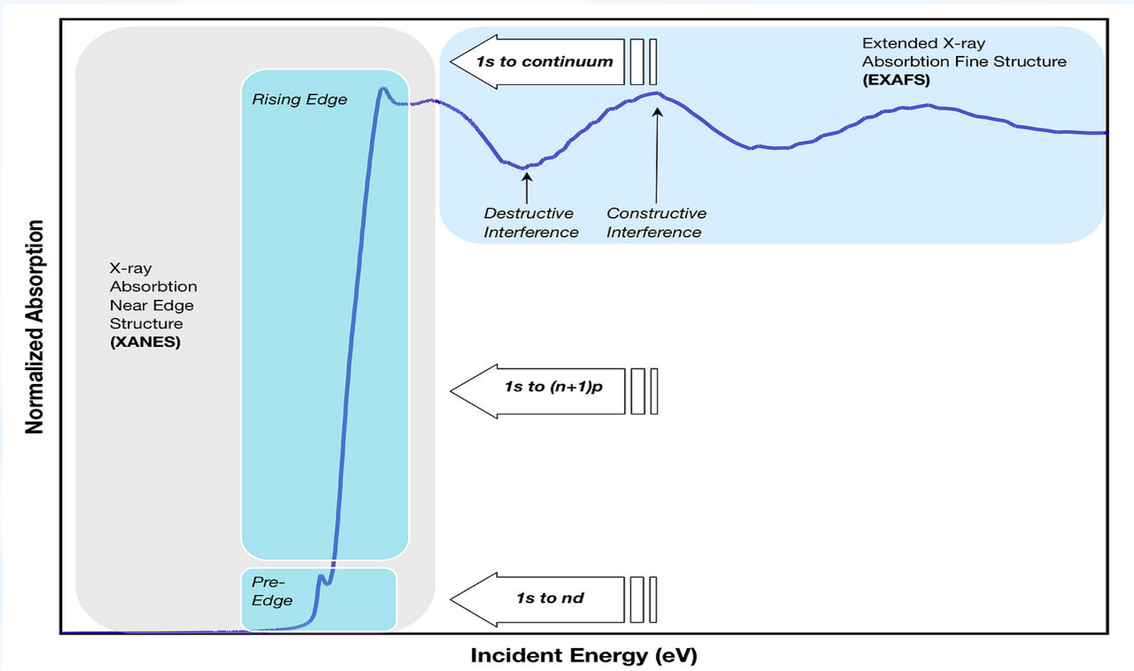

Figure 3. Another diagram detailing the absorption spectrum, with the near-edge structures highlighted. From Chemistry Libre Texts.

Channel Sweeping
Most spectroscopic data is achieved using a 100-element detector. More often than not, some of the channels involved provide errors in data that can skew the entire spectroscopic curve. To make sure the energy absorption curve is accurate, all channels with erred data must be removed before combination of the channels can occur. Channel sweeping involves using programs like Athena to scan the individual channels and individually remove "bad channels".

Results

There is work left to be done at Stanford. Now that the channels have been swept, the remaining channels have been averaged, and the peaks have been "fit" using the Peak Fit software, the area under those peaks must be analyzed for the cobalamin analogues. Studying the area under these peaks can tell us about the oxidation state of the cobalt in the cobalamin analogues, can tell us about the ligand binding to the cobalt, and can help us better understand how this transition metal operates.

Discussion
Overall, the use of X-ray absorption techniques to study the electronic properties of cobalamin analogues could help us determine how cobalt-containing compounds operate. XANES analysis and pre-edge peak-fitting can specifically give us information on the electronic and geometric surroundings of the molecule. Any scientist interested in further defining the electronic environment in their molecule is likely to use an X-ray absorption spectrum and will likely study the near-edge absorption structure.

References

Chemistry LibreTexts. http://chem.libretexts.org/Core/Physical_and_Theoretical_Chemistry/Spectroscopy/X-ray_Spectroscopy/XANES%3A_Theory. Accessed 8 August 2016.

Acknowledgements

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