



	Experiment title: X-ray Raman scattering study of linear and branched alcohols	Experiment number: HE-2736
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Report:

Alcohols are a fundamentally important class of organic liquids, which in their many forms are widely used: as solvents, biofuels (e.g. methanol, ethanol), intermediates in chemical synthesis (e.g. butanol), and in solvent extraction (e.g. octanol). Each alcohol's specific properties derive from the intermolecular interactions. Ultimately, the determining factor is the electronic structure, both at the polar OH group and at the carbon chain. These kind of properties can be very efficiently studied via x-ray absorption spectroscopy (XAS). However, the oxygen and carbon *K* edges in pure liquid alcohols have been studied very little, as liquids are mostly incompatible with the vacuum requirements of soft x-ray absorption experiments. X-ray Raman scattering (XRS) has recently become a very important complementary tool to study the x-ray absorption fine structure of low-*Z* elements. There are two key advantages to use XRS for liquids: XRS is a true bulk probe, and its momentum transfer dependence provides additional symmetry information.

We have performed a systematic near-edge XRS study on a series of linear (methanol, ethanol, 1-propanol, 1-butanol) and branched (2-propanol, 2-butanol, isobutanol) alcohols at the oxygen *K* edge. The measurements were performed utilizing the new multianalyzer spectrometer at ID16, in which the scattered radiation is focused on a 2D photon-counting Maxipix detector by 9 spherically bent Si(110) crystal analyzers. The samples were contained in a peristaltic-pump-based flow setup, which produced a 2-mm diameter liquid jet from a stainless steel nozzle.

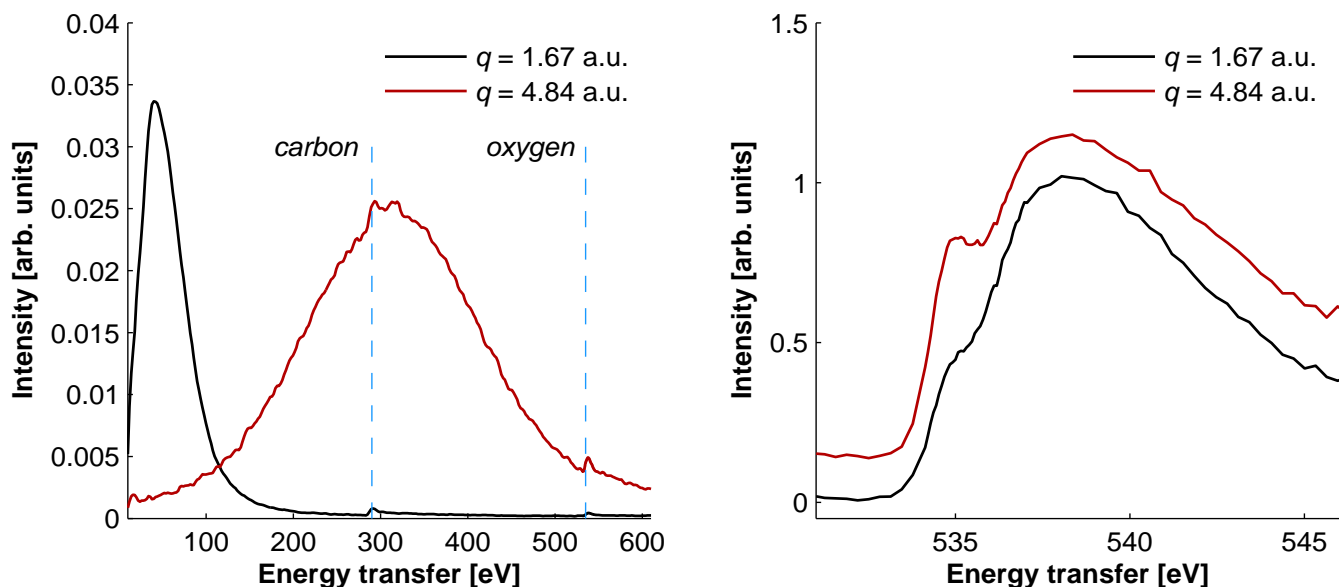


Figure 1. (a) (Left) The inelastic scattering spectra of methanol for low momentum transfer q (black) and high q (red). The carbon and oxygen K edges are marked with vertical lines. (b) (Right) The oxygen near K -edge spectra of methanol for low q (black) and high q (red, offset vertically). In both cases, the pre-edge background has been removed. The total measurement times were 7 h.

The incoming radiation was monochromatized with a double-crystal Si(111) monochromator followed by a Si(440) channel-cut. The beam was focused into a $150(\text{H}) \times 50(\text{V}) \mu\text{m}^2$ spot by a Rh-coated toroidal mirror. Spectra were gathered scanning the incident energy while analyzing the scattered radiation using the Si(660) reflection near backscattering, giving an elastic energy $E_0 = 9.68 \text{ keV}$ and energy resolution of $\Delta E = 0.5 \text{ eV}$ (FWHM). For each sample, spectra were measured at both low momentum transfer q (scattering angle $2\theta = 35^\circ$, $q = 1.67 \pm 0.40 \text{ a.u.}$) and high q ($2\theta = 130^\circ$, $q = 4.84 \pm 0.17 \text{ a.u.}$), where the scatter in q is due to the different scattering angles of the individual analyzers.

Figure 1(a) shows the inelastic scattering spectra of methanol for both low q and high q . For analysis of the near-edge features, the inelastic scattering background from other electrons was removed from each analyzer signal before summing them to obtain the final result, shown in Figure 1(b). The increase in q is clearly seen to enhance the near-edge spectral features. The O K -edge signal gets progressively weaker for alcohols of longer chain length due to the simultaneous decrease in oxygen number density and increase in the dynamic structure factor due to electrons from other atoms (mainly carbon), both effects that are unavoidable. This limited the current study to include alcohols only up to butanol. A detailed analysis of the series is underway, and the resulting data will be compared with calculations using a novel theoretical scheme [1].

[1] A. Sakko, M. Hakala, J. A. Soininen, and K. Hämäläinen. Density functional study of x-ray Raman scattering from aromatic hydrocarbons and polyfluorene. *Phys. Rev. B* **76**, 205115 (2007)