

Is Lifetime-Broadening Free X-Ray Absorption Spectroscopy Really Feasible?

X-ray absorption spectroscopy (XAS) is one of the most powerful and versatile techniques for investigating the composition, structure and electronic structure of matter, and is used not only in physics and chemistry, but now also in a variety of scientific fields such as biology and geology. One of the limiting factors in XAS is the spectral resolution that is restricted by the large natural widths of core-excited states; because of this physical constraint, the details of the core-excited structures are often smeared out of XAS spectra. It has been proposed that lifetime-broadening free XAS can be achieved by scanning over the frequencies of the incoming photons while keeping the emission frequency “fixed at the maximum of the X-ray fluorescence line” [1]. The narrowing of X-ray absorption resonances was experimentally evidenced in previous studies [2,3]. Nowadays, lifetime-broadening free XAS is regarded as a new powerful tool, particularly for studies on the electronic states of solid systems.

In this work, we demonstrate that lifetime vibrational interference (LVI), which arises from a coherent excitation to overlapping intermediate levels, ruins the idea for obtaining XAS in the lifetime-broadening free regime [4]. We have performed an XAS study in the resonant Auger scattering (RAS) mode around the $O1s \rightarrow 2\pi$ resonance of carbon monoxide. The measurement was performed on beamline **BL27SU**. The monochromatized light was introduced into a cell to which CO molecules

were admitted. Emitted electrons were sampled by a hemispherical electron energy analyzer (Gamdata-Scienta SES-2002) placed at right angles with respect to the photon beam. The right panel of Fig. 1 shows the total ion yield curve around the $O1s \rightarrow 2\pi$ resonance, which essentially corresponds to the conventional XAS profile. The resonance exhibits modulations due to the vibrational levels of the core-excited state. We have measured more than one-hundred RAS spectra to the $1\pi^{-1} A^2\Pi$ final state, in this resonance range with a small photon energy step (15 meV). For an effective presentation of the RAS spectra, they were assembled as a two-dimensional (2D) map shown in Fig. 1. The 2D map is formed of diagonal stripes, each of which corresponds to a certain vibrational level of the final ion state. All stripes consist of “hills” of elliptical shape. It may appear, at first sight, that the hilltop positions simply reflect the vibrational progression of the core-excited state seen in the conventional XAS spectrum; however, a closer inspection reveals that the positions of the hilltops slightly deviate from the vibrational progression. The deviations of the resonance energies are essentially due to the LVI effect.

Figure 2(a) shows a lifetime-broadening free XAS spectrum extracted from the 2D map along the vertical axis. The spectrum corresponds to the cut going through the peak position of the global maximum on the 2D map at the kinetic energy of 516.9 eV. This

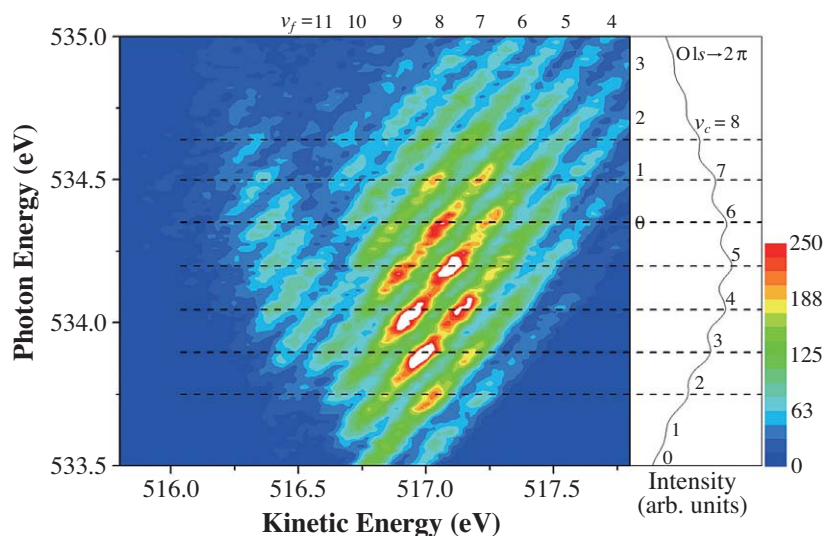


Fig. 1. 2D map of the RAS yields from CO as a function of photon energy and electron kinetic energy, measured around the $O1s \rightarrow 2\pi$ resonance. A total ion yield curve which essentially describes the conventional XAS profile is shown in the right panel.

extraction method follows the idea suggested in [3]. The spectrum shows sharp peaks with widths that are apparently narrower than the natural width of the core-excited state. However, the peak positions of the resonances do not coincide with the vibrational levels of the core-excited state, but instead follow fully the vibrational progression of the final ion state.

Obviously, XAS beyond the natural width is meaningful only if it gives the same positions of the resonances as the conventional XAS. In an effort to overcome the problem in the XAS profile obtained above, a more sophisticated path that follows the local maxima of the “hills” should be adopted in extracting a lifetime broadening XAS spectrum. By such an extraction method, we can obtain narrow XAS resonance by scanning over photon energy in the

vicinity of a hill while keeping kinetic energy fixed at the hilltop. To obtain the rest of the resonances, we must tune the kinetic energy to the corresponding hilltops. Figure 2(b) shows a spectrum thus obtained. The resonance positions seen in the spectrum again disagree with those of the conventional XAS resonances. The peak deviations are due to the LVI.

In conclusion, although the extractions of RAS yields obey the spectral resolution beyond the natural width of the core-excited state, the resonant energies on the extracted XAS spectra deviate from the real resonance energies. The present work demonstrates clearly that interferences arising from coherent core excitation to overlapping electronic/vibrational levels spoil the idea of obtaining XAS spectra in a lifetime-broadening free regime.

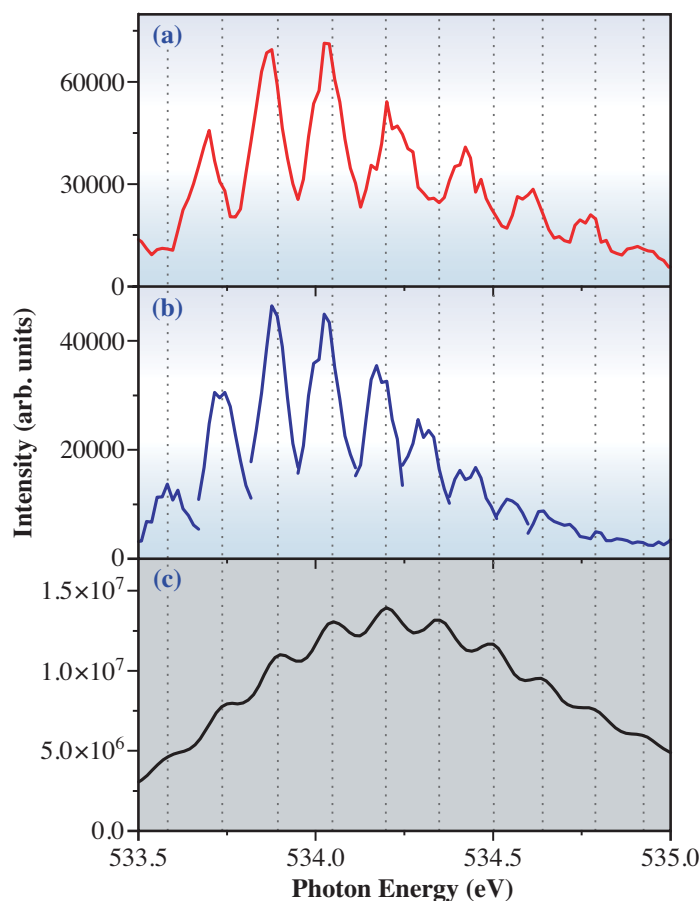


Fig. 2. (a) XAS spectrum extracted along the photon energy axis in the 2D map. (b) XAS spectrum extracted in the way explained in the text. (c) Conventional XAS spectrum.

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References

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