Beamline-induced chromium structure in carbon K-edge absorption spectra

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Abstract

We show that Cr subcoatings in beamline optical elements can introduce an additional structure in C K-edge X-ray absorption measurements, which somewhat resembles the well-known losses produced by carbon contamination. The photon throughput variations induced by Cr and C require different treatments when correcting absorption spectra. The potential difficulties in unravelling the two effects could be avoided with efficient filtration of higher-order light. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

In soft X-ray absorption studies, especially in the case of heterogeneous compounds and adsorbates, one commonly encounters the problem of photon intensity variations and background structure [1]. These intensity changes are well known to often be particularly strong at the carbon K-edge and they have been ascribed to absorption by carbon contaminants found on the optical elements of the beamline [2,3]. They introduce a characteristic double-loss structure in the absorption spectra. Often a correction procedure suggested in [1] is followed, i.e., the original spectrum is divided by a reference spectrum which is supposed to contain the photon intensity variations only. In addition, a considerable amount of effort has been put into finding methods to clean the optical elements from the contamination [4–10], though often with limited success.

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Another double-loss structure in the mono-chromator transmission function is often observed at photon energies between 570 and 585 eV due to chromium 2p absorption [11]. Chromium has traditionally been used as a subcoating in mirrors and gratings below the final gold, platinum or rhodium coating. Peatman [11] argues that "the radiation penetrates the top coating and is absorbed by the elements of the subcoating, producing dips in the spectrum". We present a case in which carbon contamination plays a minor role only and the instrumental structure found in the C 1s X-ray absorption spectra is caused by the chromium absorption dips due to a large component of second-order light.

2. Experimental

The experiments were conducted at beamline D1011 [12,13] at Max-lab, Lund, Sweden, which is a bending magnet beamline equipped with a modified SX-700 monochromator. The beamline was formerly operated as beamline 22 at the 550 MeV MAX-I ring. It was moved to the 1.5 GeV MAX-II ring in 2000 and has been in operation there for approximately one year. The critical energy of the bending magnet source lies at around 2.2 keV [14] compared to 308 eV at the old location [12].

We conducted X-ray absorption spectroscopy (XAS) and X-ray photoemission spectroscopy (XPS) measurements on a rutile $TiO_2(1\,1\,0)$ sample. The X-ray absorption spectra where recorded with the monochromator set to the C K-edge and Cr L-edge regions. The detector was in partial-yield mode with a retardation voltage of −220 V (C K-edge) and −430 V (Cr L-edge). Two different samples were used, the clean surface on the one hand, and a monolayer of benzoic acid (C_6H_5-COOH) on $TiO_2(1\,1\,0)$ on the other, resulting in a well-defined C 1s line similar to the one in [15]. The clean sample had been sputtered and annealed until no carbon signal was discernible in XPS. Neither sample contained any other elements that could give rise to any absorption structure for the relevant photon energies.

3. Experimental results

In Fig. 1 the C 1s X-ray absorption spectrum of a monolayer of benzoic acid on $TiO_2(1\,1\,0)$ is shown as the uppermost curve. A comparison with C 1s and N 1s measurements on similar hydro-carbons [15,16] makes it apparent that the spectrum incorporates structure produced by photon intensity variations. We monitored these variations by taking the spectrum of the clean crystal, also shown. For reasons discussed below we did not divide the original spectrum by that of the clean crystal, as usually is done for normalisation purposes [1], but subtracted it, which resulted in the difference spectrum displayed.

In Fig. 2 we show three different clean crystal spectra in the carbon K-edge region measured at the same beamline, though the two lower spectra were taken before the move from MAX-I to MAX-II, and the top one afterwards. The two lower curves show the typical beamline carbon contamination structure, and an advancing de-
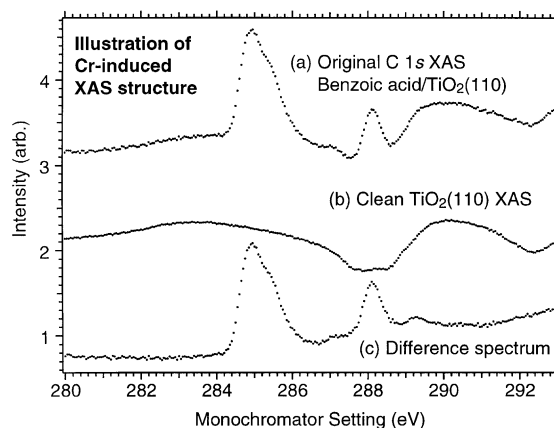

Fig. 1. Absorption spectra of the indicated samples. Spectrum (b) was taken as measure of the photon intensity variations. As explained in detail below, the observed structure in the clean crystal spectrum can nearly completely be ascribed to variations in the second-order background, and not to first-order light changes. Therefore we subtracted (b) from (a) rather than dividing it out as recommended in [1]. For that purpose curve (b) was scaled as to match the background-induced fine structure in (a). The resulting curve (c), which has slightly been shifted downwards, shows clearly that structure was both introduced as well as hidden in the original curve by the photon intensity variations.
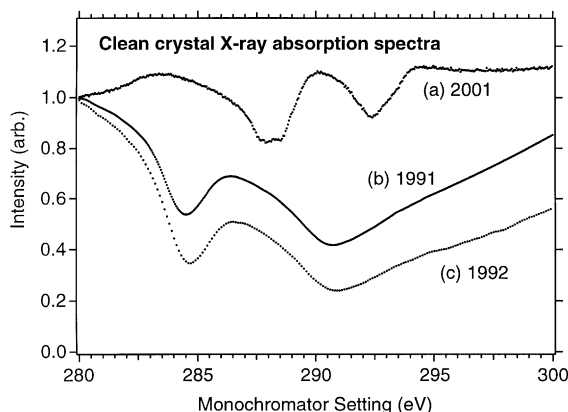
Fig. 2. Clean crystal absorption spectra in the C 1s region, taken in the indicated years, measured on samples that do not contain any structure in the photon region used. The two lower curves (b) and (c) show a typical carbon contamination structure, while (a), taken after the beamline relocation, contains two loss structures that are due to chromium structure in the second-order light background, but virtually no carbon contamination structure. There is an additional peak at around 283.5 eV. Measurements not presented here show that it is induced by second-order light, and we speculate that it is due to substrate oxygen absorption.

gradation with time is suggested. The most recent spectrum has changed drastically. One observes two losses which at first glance could be interpreted as the typical carbon structures. However, the dips have absolute and relative positions, as well as relative intensities, that are not consistent with this interpretation as being due to optical element carbon contamination.

In Fig. 3 we show that this new structure is induced by beamline Cr absorption. Curve (a) (displayed against the top axis) corresponds to the Cr 2p edge region. The two (inverse) features at 576 and 585 eV, respectively, are transmission losses due to Cr $2p_{3/2}$ and $2p_{1/2}$ absorption at mirrors and/or the grating, which can easily be checked by comparison to Cr 2p X-ray absorption spectra [17]. The middle curve (b) (displayed versus the bottom axis) is the clean crystal curve from Fig. 2. Here, the two dips of the Cr spectrum appear at half the original photon energy in the carbon K-edge region. They stem from the second-order light background generally found in soft X-ray absorption measurements. The finding is confirmed in a direct measurement of the second-
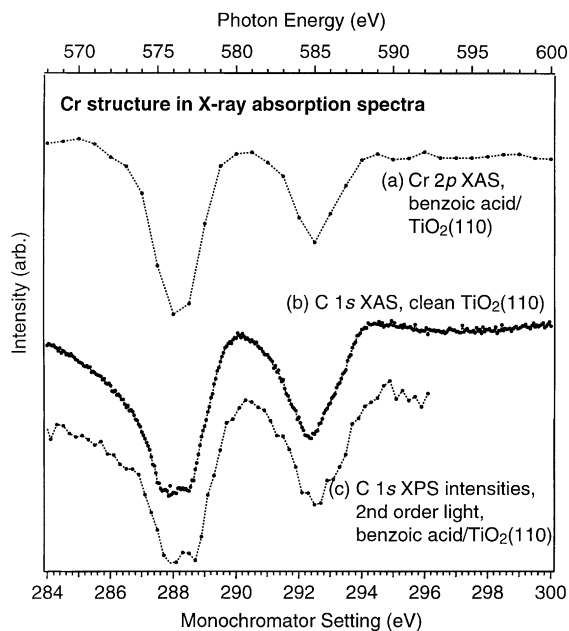

Fig. 3. (a) and (b) Absorption spectra from the indicated samples. (a) was acquired in partial-yield mode (−430 V retardation voltage) with monochromator settings suitable for Cr 2p absorption (top axis). It shows the typical Cr 2p absorption structure [17]. The same structure can be found in (b) at half the photon energy (bottom axis). Here the monochromator was set to energies at the C K-edge, and the retardation voltage to −220 V. Spectrum (c) displays C 1s intensities excited by second-order light versus the monochromator settings (bottom axis) in the C 1s region, see e.g. [18]. As the C 1s cross-section varies slowly for the relevant photon energies (568–594 eV), it is a direct measure of the second-order light intensity. The spectra have not been calibrated, which results in a small shift.

order intensity presented in curve (c). The spectrum was obtained by recording a series of C 1s photoemission spectra excited by second-order light for nominal photon energies between 284 and 292 eV for the benzoic acid/TiO$_2$(1 1 0) sample. The intensities of these second-order C 1s lines were integrated and displayed versus the nominal photon energy, i.e. each data point corresponds to one C 1s photoemission spectrum. This second-order structure has been observable before although it did not emerge this clearly in the carbon K-edge X-ray absorption spectra. In Fig. 4 the second-order C 1s curve from Fig. 2 is compared to a similar spectrum measured on a thick film of C$_{60}$ [18] at the same beamline in 1992, i.e. before
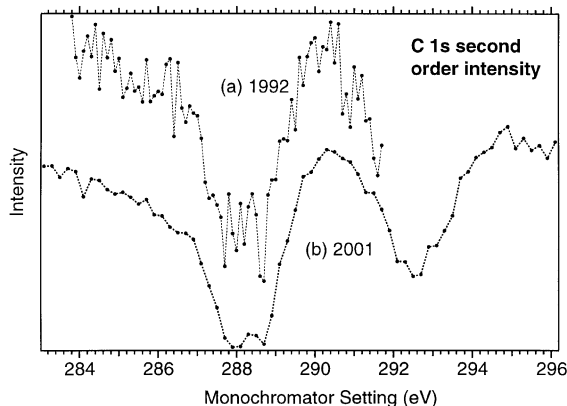
Fig. 4. Comparison of the second-order photon intensities for cases (a) and (c) in Fig. 2. The curves were recorded as described in the text of Fig. 3. *Y*-scaling and offset of both curves are arbitrary and chosen for the purpose of an easy comparison. Clearly, the second-order light is affected by Cr absorption in both cases, although this is much less obvious in case (c) of Fig. 2.

the move to MAX-II. Clearly, the structures are identical and can be related to the Cr absorption. However, in the most recent measurements at beamline D1011 the Cr structure is much stronger than the one introduced by the C contamination, as seen in Fig. 2.

4. Discussion

We have thus established that the Cr sublayers frequently found in beamline optical elements can introduce unwanted structure in carbon K-edge absorption spectra. This has implications for the background treatment in C 1s absorption spectra, as well as for the planning and construction of beamlines in the soft X-ray regime. The problem could be expected to be severe for bending magnet beamlines similar to D1011, with a critical energy (2.2 keV) quite far above the carbon threshold, leading to a high share of second-order light in the monochromator transmission. For insertion device beamlines with their lower share of second-order light this can be of less importance. The present results make clear that one should determine the relative shares of first and second-order

light in order to conclusively decide on the importance of the second-order background.

Quite generally, second-order backgrounds have been neglected in the practical recipes for background corrections. This is defensible if the amount of second-order light is low. As we have seen here this condition is not necessarily fulfilled and thus can imply the second issue of a structured background in the data. Another example can be found in Fig. 5.23(c) of [1]. Obviously, the Cr-induced throughput minima occur in that spectrum together with the structure from carbon contamination.

A proper background treatment in the general case is illustrated in Fig. 5. It would involve a separation into first- and second-order components. The second-order part should be removed (as done in Fig. 1), and the first-order contribution should be divided by a reference spectrum containing the first-order structure only. However, it is non-trivial to obtain such a first-order reference spectrum. The procedure described applies also in the case of a flat second-order background because only the first-order part has to be corrected for the first-order transmission function. In all common electron yield approaches to the measurement of a first-order reference spectrum (involving, for example, gold meshes, gas cells, or the clean surfaces), background electrons excited by second-order light are recorded, falsifying the result. The subtraction of the second-order part, the form of which in principle can be reliably measured by monitoring a direct photoemission peak excited by second-order light, can be much easier as presented for our data in Fig. 1. Here we were able to estimate its amount by comparing the fine structure in the spectra. However, we cannot exclude here either that carbon contaminant structure affects the final result. In general, there is of course also the concern of substrate structure in the case of monolayer measurements, which we do not take into account here.

Interestingly, we observed a very similar background behaviour at undulator beamline I511 at MAX-lab when the undulator is in taper mode [19]. In this case the observed Cr dips were by about 50% larger than the carbon contamination ones.
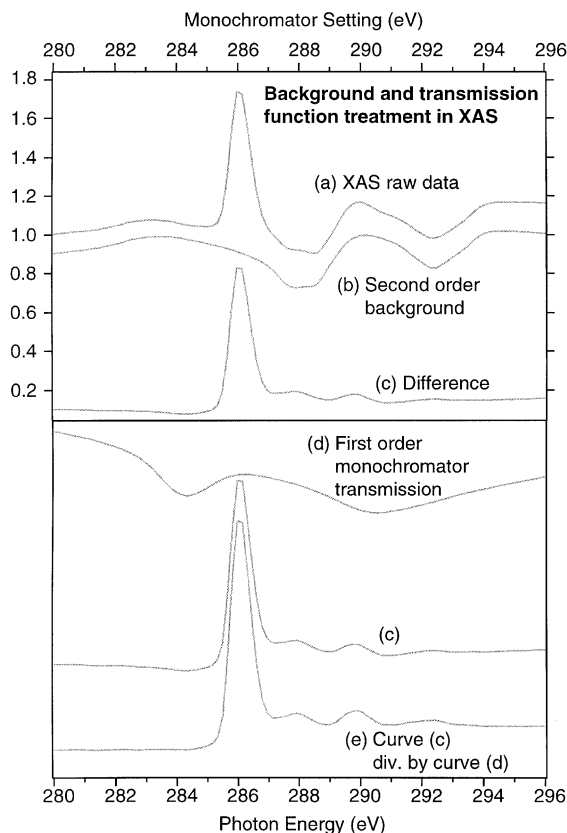
Fig. 5. Schematic of a proper background and photon intensity treatment of X-ray absorption spectra. (a) represents the measured curve containing a large contribution of second-order background (b). In addition, it contains a first-order background observed as difference between the two curves. The second-order background has to be subtracted which results in curve (c). First then one can correct for the changes in the first-order photon intensity. This is illustrated in the lower panel, where the curves have been shifted in the *y*-direction in order not to overlap. Spectrum (d) represents the monochromator transmission function, i.e. it monitors the changes in first-order photon intensity. (c) has to be divided by the transmission function in order to give the desired spectrum of the sample only. The first-order light background could contain further structure due to substrate variations which we have not taken into account here.

It is clear that there are no trivial solutions to the problem presented here. Instrumental measures could comprise for example the introduction of filters for higher-order light and the renunciation of optical elements with Cr subcoatings. The latter alternative seems to become feasible as some manufactures have developed gratings and mirrors without a Cr binding layer [11]. The introduction of filters has the advantage of a general lowering of higher-order backgrounds. This is very desirable as even structureless higher-order backgrounds falsify any first-order transmission correction using the standard method [1].

5. Conclusions

We have shown here that background structure in C 1s X-ray absorption studies can stem from Cr absorption in the beamline, in addition to the well-known structure produced by carbon contamination. The structure is observed in the portion of the spectrum attributable to second-order light and has been observed at both a bending magnet and an undulator beamline. Our results emphasize that the presence of second-order light greatly complicates the analysis of C 1s X-ray absorption spectra. A proper analysis would have to identify and distinguish first, second, and perhaps even higher-order background contributions, so that these can be treated separately and correctly. It seems to be advisable to seek instrumental solutions to the reported problem, such as the introduction of higher-order filters.

References

[1] J. Stöhr, NEXAFS Spectroscopy, Springer, Berlin, 1992 (Chapter 5.5).
[2] J. Stöhr, L. Johansson, I. Lindau, P. Pianetta, Phys. Rev. B 20 (1979) 664.
[3] D. Denley, P. Perfetti, R.S. Williams, D.A. Shirley, J. Stöhr, Phys. Rev. B 21 (1980) 2267.
[4] W.R. McKinney, P.Z. Takacs, Nucl. Instr. and Meth. 195 (1982) 371.

 [5] T. Koide, S. Sato, T. Shidara, M. Niwano, M. Yanagihara, A. Yamada, A. Fujimori, A. Mikuni, H. Kato, T. Miyahara, Nucl. Instr. and Meth. A 246 (1986) 215.

 [6] E.D. Johnson, S.L. Hulbert, R.F. Garrett, G.P. Williams, M.L. Knotek, Rev. Sci. Instrum. 58 (1987) 1042.

 [7] E.D. Johnson, R.F. Garrett, Nucl. Instr. and Meth. A 266 (1988) 381.

 [8] R.A. Rosenberg, D.B. Crossley, Nucl. Instr. and Meth. A 266 (1988) 386.

 [9] T. Koide, T. Shidara, M. Yanagihara, S. Sato, Appl. Opt. 27 (1988) 4305.

[10] B.R. Müller, J. Feldhaus, F. Schäfers, F. Eggenstein, Rev. Sci. Instrum. 63 (1992) 1428.

[11] W.B. Peatman, Gratings, Mirrors and Slits, Gordon and Breach, Reading, 1997.

[12] R. Nyholm, S. Svensson, J. Nordgren, A. Flodström, Nucl. Instr. and Meth. A 246 (1986) 267.

[13] J.N. Andersen, O. Björneholm, A. Sandell, R. Nyholm, J. Forsell, L. Thånell, A. Nilsson, N. Mårtensson, Synchr. Rad. News 4 (4) (1991) 15.

[14] Å. Andersson, M. Eriksson, L.-J. Lindgren, P. Röjsel, S. Werin, Nucl. Instr. and Meth. A 343 (1994) 644.

[15] M. Zharnikov, M. Neuber, Surf. Sci. 464 (2000) 8.

[16] P. Persson, S. Lunell, P.A. Brühwiler, J. Schnadt, S. Södergren, J.N. O'Shea, O. Karis, H. Siegbahn, N. Mårtensson, M. Bässler, L. Patthey, J. Chem. Phys. 112 (2000) 3945.

[17] Y. Ito, T. Tochio, A.M. Vlaicu, D. Ohsawa, T. Mukoyama, Y. Muramatsu, R.C.C. Perera, M.M. Grush, T.A. Callcott, E. Sherman, J. Electron Spectros. Relat. Phenom. 101–103 (1999) 851.

[18] P.A. Brühwiler, A.J. Maxwell, A. Nilsson, R.L. Whetten, N. Mårtensson, Chem. Phys. Lett. 193 (1992) 311.

[19] J. Schiessling et al., Unpublished.