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X-ray absorption in atomic potassium

Jana Padežnik Gomilšek ^{a,*}, Alojz Kodre ^{b,c}, Iztok Arčon ^{c,d}, Vincenc Nemanič ^c

^a *University of Maribor, Faculty for Mechanical Engineering, Smetanova 17, SI-2000 Maribor, Slovenia*

^b *University of Ljubljana, Faculty of Mathematics and Physics, Jadranska 19, SI-1000 Ljubljana, Slovenia*

^c *Jozef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia*

^d *University of Nova Gorica, Vipavska 13, SI-5000 Nova Gorica, Slovenia*

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Abstract

A new high-temperature absorption cell for potassium vapor is described. X-ray absorption coefficient of atomic potassium is determined in the energy interval of 600 eV above the K edge where thresholds for simultaneous excitations of 1s and outer electrons, down to [1s2p] excitation, appear. The result represents also the atomic absorption background for XAFS (X-ray absorption fine structure) structure analysis. The K ionization energy in the potassium vapor is determined and compared with theoretical data and with the value for the metal.

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1. Introduction

X-ray absorption of pure elements, revealing the minute details of the absorption edge profile and of the multielectron excitations in the near-edge energy region, provides a thorough check of the theoretical models of the atomic system [1]. The absorption coefficient in this region is modified also by the scattering of the photoelectron on the atomic surroundings (XAFS = X-ray absorption fine structure). To avoid the interference with XAFS, atomic absorption is measured on a free-atom sample of the element. The appropriate density for absorption spectroscopy in the vicinity of K and L edges is in the mg/cm² range. In noble gases this corresponds to a few centimeters of gas at ambient pressure, so that a relatively simple experimental setup can be used: nevertheless, a wealth of data on the effects of electron correlation has been gained in these experiments [2]. For most other elements, however, the required density

of the free-atoms is very difficult to prepare and maintain. High-temperature cells have been employed for the purpose for volatile metals [3–9]. The range of application of the cells depends critically on the material for the windows: it must withstand the elevated temperature, the pressure difference and the chemically aggressive vapor, at a minimum attenuation of the X-ray beam. The problem is aggravated in the low-energy region (<5 keV) where only thin organic or beryllium foils can be used.

X-ray atomic absorption of potassium in the vicinity of K edge was first measured in 1998 [3] in a cell of heat-pipe design: stainless-steel mesh lining the inner wall acted as a wick enabling the circulation of the hot potassium vapor, while a stream of cool helium gas protected kapton windows. Within the 2 h period of stable operation of the cell the region of 60 eV above the edge could be investigated, so that only the edge profile and the closest group of multielectron excitation could be reported.

To extend the study to the entire region of multielectron excitations, so that an exact atomic absorption background for XAFS analysis would be available, a new type of

* Corresponding author. Tel.: +386 2 220 7821; fax: +386 2 220 7990.
E-mail address: jana.padeznik@uni-mb.si (J.P. Gomilšek).

potassium cell has been developed, together with an oven with a protecting atmosphere.

2. Experiment

To ensure a longer operation time, a cell with a static confinement of the vapor is constructed. The stainless-steel cell with a length of 120 mm and diameter of 10 mm is equipped with 50 μm thick beryllium windows, transmitting more than 50% of the beam at 3.8 keV photon energy, and resistant to the aggressive potassium vapor at 650 °C. The essential technological novelty is a vacuum-tight brazing of the Be foil to the stainless steel with silver foil in high vacuum [10]. It is essential that the flanges holding the Be windows and the body of the cell to which the flanges are welded are annealed in hydrogen to remove the adsorbates and the oxide layer prior to the brazing. The cell was filled with 7 mg of potassium metal and He gas up to 300 mbar. In the experiment, the cold-sealed and welded cell was heated in a tubular oven equipped with 5 μm thick aluminum windows and filled with protective He gas (Fig. 1).

The absorption spectrum was measured at the E4 station of Hasylab, which provided a focused beam from Au-coated mirror and a Si(111) double-crystal monochromator. Higher harmonic components of the beam were effectively eliminated by a plane Au-coated mirror and by detuning the monochromator crystal using a stabilization feedback control. The intensity of the beam was measured by three consecutive ionization detectors, filled with 180 mbar N_2 , 66 mbar Ar and 126 mbar Ar. The absorption cell was placed between the front pair of the detectors. The absolute energy calibration was provided by a simultaneous absorption scan of the L_2 edge of a 1 μm thick silver foil inserted between the posterior pair of the detectors. The energy region from 100 eV below the K edge to 600 eV above was scanned with the step of 0.25 eV, appropriate for the lifetime width of the $\text{K}[1s]$ state of 0.74 eV

[11] and the energy resolution of the monochromator of ~ 1 eV. Several scans of the region were taken to check the reproducibility of the experiment and to improve the signal-to noise ratio of the data by superposition of the scans.

For comparison, the absorption was also measured on a sample of metallic potassium. Several approaches to prepare a layer of metal close to the optimum thickness of ~ 15 μm were employed: most involved pressing a speck of the metal between two kapton foils in a drop of paraffin oil to seal off the air. Regularly, the layers were either too thick or developed pinholes. The best result was obtained by kneading some boron nitride powder into the potassium, so that the metal was effectively diluted.

EXAFS spectra of the solution of K_2CO_3 in a liquid-absorption cell and KMnO_4 and KCl powders on adhesive tape were recorded for a demonstration of the true atomic absorption background.

3. Results and discussion

In Fig. 2, the new data are compared to those of the previous experiment. The operating parameters of the beam-line were not exactly reproduced in the new experiment, so that the resulting noise level of 2×10^{-3} was somewhat higher than in the previous experiment, and the energy resolution slightly lower. Nevertheless, all the spectral details of the old data were clearly reproduced. The entire span of the new data is shown in Fig. 3. Since the K edge profile and the closest group [1s3s,p] of multielectron excitations have already been comprehensively analyzed [4], the following discussion will be limited to the novel elements in the data: the absolute energy calibration and the deep double excitation [1s2p].

The absolute energy scale is set by the L_2 edge in the spectrum of metallic silver: in this work, the position of the L_2 inflection point is adopted at 3525.5(3) eV, the mean of the new NIST values 3525.83(15) eV and 3525.24(26) eV

Fig. 1. Potassium vapor experiment: 1 – stainless steel tube, 2 – beryllium window, 3 – filling tube, welded, 4 – potassium sample in He atmosphere, 5 – stand, 6 – oven, 7 – end flange, 8 – aluminum window, 9 – O-ring, 10 – helium inlet, 11 – oven coil, 12 – synchrotron radiation beam.

Fig. 2. The normalized K-shell photoabsorption of potassium vapor and potassium metal in a boron nitride matrix. The energies of the potassium K ionization threshold and single- and double-electron resonant transitions are marked. In the inset, the position of the inflection point at Ag L₂ edge used for energy calibration, is marked with a vertical line.

Fig. 3. K-shell photoabsorption of potassium vapor with the power-law asymptote and the exponential model.

[12] for the L₂ ionization threshold energy, obtained by two independent experimental techniques. The uncertainty in the position of the characteristic points in the potassium spectrum, relative to the Ag L₂ inflection point, is less than 0.6 eV. After the decomposition of the potassium edge profile into a set of resonances and an edge, as in the previous analysis [4], the energy of the potassium K ionization threshold is found at 3614.7(6) eV, in a fair agreement with the NIST theoretical value of 3616.22(12) eV. The inflection point of the potassium metal is then at 3609.0(10) eV close to the tabulated NIST values 3607.81(16) eV and 3608.49(16) eV.

Asymptotically, the cross section follows a power law E^{-7} . A steeper slope immediately above the edge, attributed to core relaxation and post-collision interaction (Fig. 3) can be, in the lack of a definite theoretical expression, approximately described by an exponential decay

[5]. With this model (inset of Fig. 3), the 1s3p feature at ~3635 eV is properly recognized as an absorption edge with a subsequent double-ionization change of slope.

The 1s2p absorption edge, analogous to a weak spectral feature discovered so far only in the absorption of the neighbor element argon, can be discerned above the noise level at ~3960 eV (Fig. 4) with the relative amplitude estimated as $3(1) \times 10^{-3}$ of the K-edge jump. The edge is less than 10 eV from the lowermost [1s2p] sublevel of Hartree–Fock calculation [13].

The atomic absorption spectrum of potassium can be used as the atomic background in EXAFS analysis of potassium compounds as shown in Fig. 5: the atomic absorption is shown as the natural middle line of EXAFS oscillations of K₂CO₃ solution and KCl and KMnO₄ salts. The practical use of the exact background against the conventional XAFS practice of spline background has been argued for weak EXAFS signals [14].

Fig. 4. Potassium 1s2p double excitations with Hartree–Fock theoretical predictions of the onsets of double excitation, ionization–excitation and double ionization.

Fig. 5. Potassium vapor absorption as the atomic absorption background for EXAFS spectra of K⁺ ion in solid KMnO₄ and KCl, and in water solution of K₂CO₃.

4. Conclusions

The new potassium-vapor cell for the X-ray absorption spectroscopy poses no limits to the duration of the experiment, so that the entire EXAFS spectral region can be investigated, with the possibility of superposing a number of consecutive scans to suppress the noise level. The latter feature is demonstrated by the isolation of the extremely weak 1s2p multielectron excitation in the potassium absorption spectrum. The spectrum is also shown in the role of the EXAFS atomic background. Its application is not limited to the analysis of potassium compounds. Since potassium is one of the lightest elements for which the standard EXAFS analysis is amenable, its atomic background may be essential in construction of interpolated backgrounds for the entire group of light elements.

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