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New determination of the core-level life-time broadenings in mercury

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ABSTRACT

Previously recorded and published photoelectron spectroscopic data for mercury in the gas phase has been reanalyzed. The life-time broadenings have been determined for a large number of core levels. It is then seen that a recent detailed derivation of core-level line-widths based on X-ray emission spectroscopy give life-time widths that are generally too large. The $4d_{3/2}4d_{5/2}$nd Coster–Kronig (CK) transition is also discussed. We find that the additional broadening of the $4d_{3/2}$ level for mercury metal is indeed due to a CK decay, in contrast to recent claims. In atomic mercury, however, the CK process in energetically forbidden. In spite of this we find that the $4d_{3/2}$ level is broadened also in this case. We propose that this is due to a mixing between the $4d_{3/2}$ hole state and discrete $4d_{5/2}$nd states.

1. Introduction

Core and valence electron spectra have been recorded for mercury in the gas phase [1–5], in the solid phase [1] and as a liquid. Data for this element are, however, relatively scarce. Svensson et al. [1] studied already in 1976 all core-levels in mercury down to a binding energy of 1 keV using X-ray Photoelectron Spectroscopy (XPS) with monochromatized Al*K*α X-rays to excite the spectra. Spectra were recorded for free atoms in the gas phase as well as for the metal. This is still the only case where such a comparison has been made for a whole range of electronic levels, including the valence states. This comparison also became the starting point for a thorough theoretical analysis of the fundamental shifts between the free atoms and the metallic solids which was extended to the whole Periodic Table and which led to new insight into the role of metallic screening and the origin of alloy chemical shifts, surface core level shifts, interface core level shifts, etc. [6–8].

Svensson et al. [1] also analysed the intrinsic line widths of the core and valence levels. The inherent width of a core level is determined by the total decay rate of the core ionized state. Under the assumption that the decay continua are structureless the finite life-time produces a Lorentzian contribution to the line shape. The halfwidth Γ of the line can then be expressed as a sum of contributions from all decay processes $\Gamma\Gamma = \sum \Gamma_i$.

The life-time broadenings for mercury [1] were also included in a study of core-level line widths in the whole series of 5d transition elements [9] based on measurements for the elements in the metallic form. In the latter work, trends in the decay rates as function of atomic number were investigated and discussed. The mercury results could then be compared to results for the other metals in the series.

Several of the findings in Refs. [1,9] have more recently been questioned. Maillard et al. [10] have performed a thorough analysis of photo-induced X-ray emission spectra (XES) for liquid mercury. Based on a large number of recordings of spectral line shapes for different transitions they have derived life-time broadenings for essentially all core levels for mercury. They find large differences from the results in Ref. [1], which they attribute to shortcomings in the analysis of the XPS results.

In addition to this, Ohno and van Riessen [11] have questioned the claims in Ref. [9] that there is an NNO Coster–Kronig (CK) process which broadens the 3/2 component of the 4d spin–orbit doublet in the 5d transition metals. The inherent widths of spin–orbit split levels which are not too widely separated are generally the same, since all Γ_i are very similar for the two spin–orbit components. However, in some cases, even at relatively small spin–orbit splittings, there is an excess broadening of the deeper spin–orbit component due to additional decay possibilities for this level. This is due to CK electron emission processes in which a hole in the deeper spin–orbit component can decay into a double-hole state with one hole in the more shallow spin–orbit component and an additional hole in a valence level. In many elements there are CK processes which are allowed in the metallic phase but are absent in the free atoms or in non-conducting compounds [12–14]. This is due to the additional screening of the CK process in the metal. In this way the presence of CK processes can be used to obtain most important information concerning the valence electron structure of

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solids. Ohno and van Riessen [11] made an interesting proposal that the observed additional broadening of the $4d_{3/2}$ levels observed in the 5d series is not necessarily due to a CK process. Instead, they proposed that the difference in line widths is due to different rates of the other decay processes for the two spin–orbit components. This should give a larger broadening of the $4d_{3/2}$ spin orbit component compared to the more shallow $4d_{5/2}$ component due to a larger access energy for in particular the 4d4f4f Super Coster Kronig (SCK) processes. It is known that the rate of such transitions can be very sensitive to the excess energy in the decay process.

2. Results

These more recent claims have prompted us to reconsider the XPS results from Ref. [1]. Since the recording of mercury photoelectron spectra is connected to experimental problems, not the least due to the risk of contamination of the experimental chambers we do not expect many new measurements of this kind to be performed. We have therefore chosen to reanalyze the original gas phase spectra from Ref. [1]. In the original publication the analysis of the spectra was much more primitive than what can be achieved today using modern curve fitting programs. We have now performed a more detailed analysis of the data and new values for the line widths are determined. We will also discuss the specific question of the 4d spectra and the possibility of an NNO CK transition. This is interesting since we can compare data from the free atom and the metal. The CK process should be allowed in the metal but not for the free atom. However, we find that the $4d_{3/2}$ level has an additional broadening in both cases.

In Ref. [1] the line widths were analyzed for the atomic as well as the metallic spectra. For the atomic data an approximate scheme was used to analyze the data in terms of Voigt functions in order to separate the Lorentzian life-time contributions from the Gaussian spectrometer function. For the metal spectra, however, only the total line widths (FWHM), including the spectrometer broadening, were given. For the metal there is in addition an asymmetric broadening due to low energy shakeup processes, leading to more complex total line shapes. However, life-time widths can be extracted with a similar type of precision also for metallic data. In Ref. [9] the 4d and 4f spectra from Ref. [1] were reanalyzed, using numerical fitting procedures, allowing the Lorentzian contributions to be determined.

We have now performed modern numerical fits using Voigt functions to the gas phase spectra. We have used the program package written by Kukk [15]. At first we have determined the spectrometer function by fitting the 5d and 6s outermost levels. Auger decay is energetically not possible for these levels and the optical decay contribution to the line widths is also negligible. In this way the shape of these peaks directly provide the spectrometer function. As seen from Fig. 1 the 5d spectra can be very well fitted by Voigt functions with a Gaussian contribution of 0.72 eV and a Lorentzian contribution of 0.06 eV. The small Lorentzian contribution is not due to life-time broadening. It is most probably required in order to describe the effects of some stray light from the X-ray source, giving some longer tails in the spectrometer function. The total FWHM of the 5d levels was determined to be 0.76 eV and the fitted Voigt parameters were used when determining the life-time widths for all other analyzed lines. The results from this analysis are summarized in Table 1.

In order to estimate the errors we considered the statistical error analysis provided by the fitting program. In addition to this we have made several fits where the Lorentzian with has been artificially varied around the best-fit value in order to determine by eye when the spectral shapes become obviously inconsistent with the data. In this way we have determined more conservative error estimates for the fits. These are the values given in Table 1.

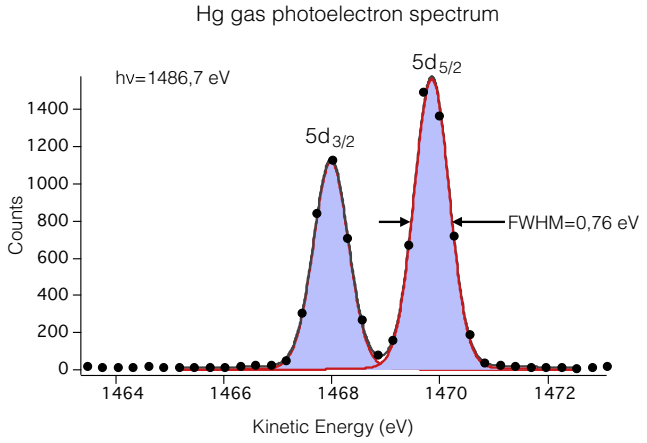

Fig. 1. The 5d photoelectron spectrum of mercury in the gas phase. The lines have negligible life-time widths and can therefore be used to determine the spectrometer function.

Table 1
N and O shell core hole natural linewidths (eV) in atomic mercury.

Core level	Ref. [1] (gas)	This work (gas)	Ref.[9] (solid)	Ref. [10] (liquid)
4s	9.8			8.93(29)
$4p_{1/2}$	8.6	8.3(9)		9.61(55)
$4p_{3/2}$	5.0	5.4(4)		7.22(50)
$4d_{3/2}$	4.3	4.5*	4.09(30)	5.05(17)
$4d_{5/2}$	4.0	4.0(2)	3.74(30)	4.59(15)
$4f_{5/2}$	0.46	0.34(10)	0.32(15)	
$4f_{7/2}$	0.46	0.34(10)	0.32(15)	
5s	–			9.11(41)
$5p_{1/2}$	6.2	5.9(6)**		9.0(8)
$5p_{3/2}$	5.6	5.9(6)**		8.3(7)
$5d_{3/2}$		–		1.6(4)
$5d_{5/2}$		–		1.1(2)

* The derived Lorentzian width is obtained under the assumption that the "$4d_{3/2}$" peak can be described as a single Lorentzian. This is probably not the case, see text.
** The fit is performed under the assumption of identical life-time broadenings for the two spin–orbit components. By fitting the two lines together the background function can be better defined.

As an example of our fitting procedure we show the result for the 4f lines in Fig. 2. The 4f lines have a significantly larger total FWHM (0.96 eV) than the 5d levels and the 6s level, and the result of the fit using Voigt functions can be seen in the figure. The Voigt profiles have Lorentzian contributions of 0.39(6) eV and 0.41(6) eV for the 5/2 and 7/2 components, respectively. The Lorentzian contribution

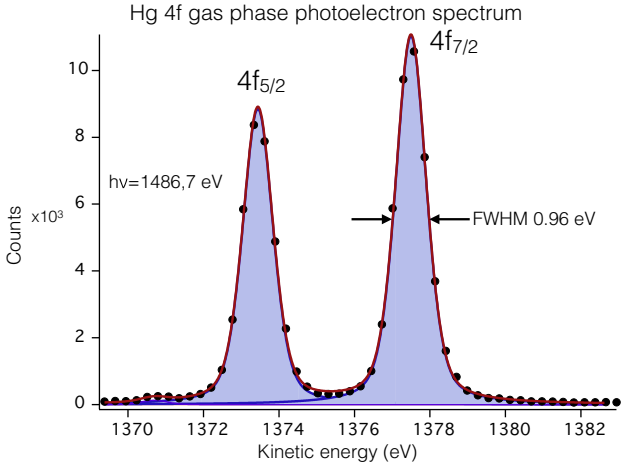

Fig. 2. The gas phase 4f photoelectron spectrum of mercury. An analysis of the Lorentzian contribution gives a life-time broadening of 0.34(9) eV.