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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 is 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.

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 AlK 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 $\Gamma = \sum \Gamma_i$.

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] and [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 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.

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 E. 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

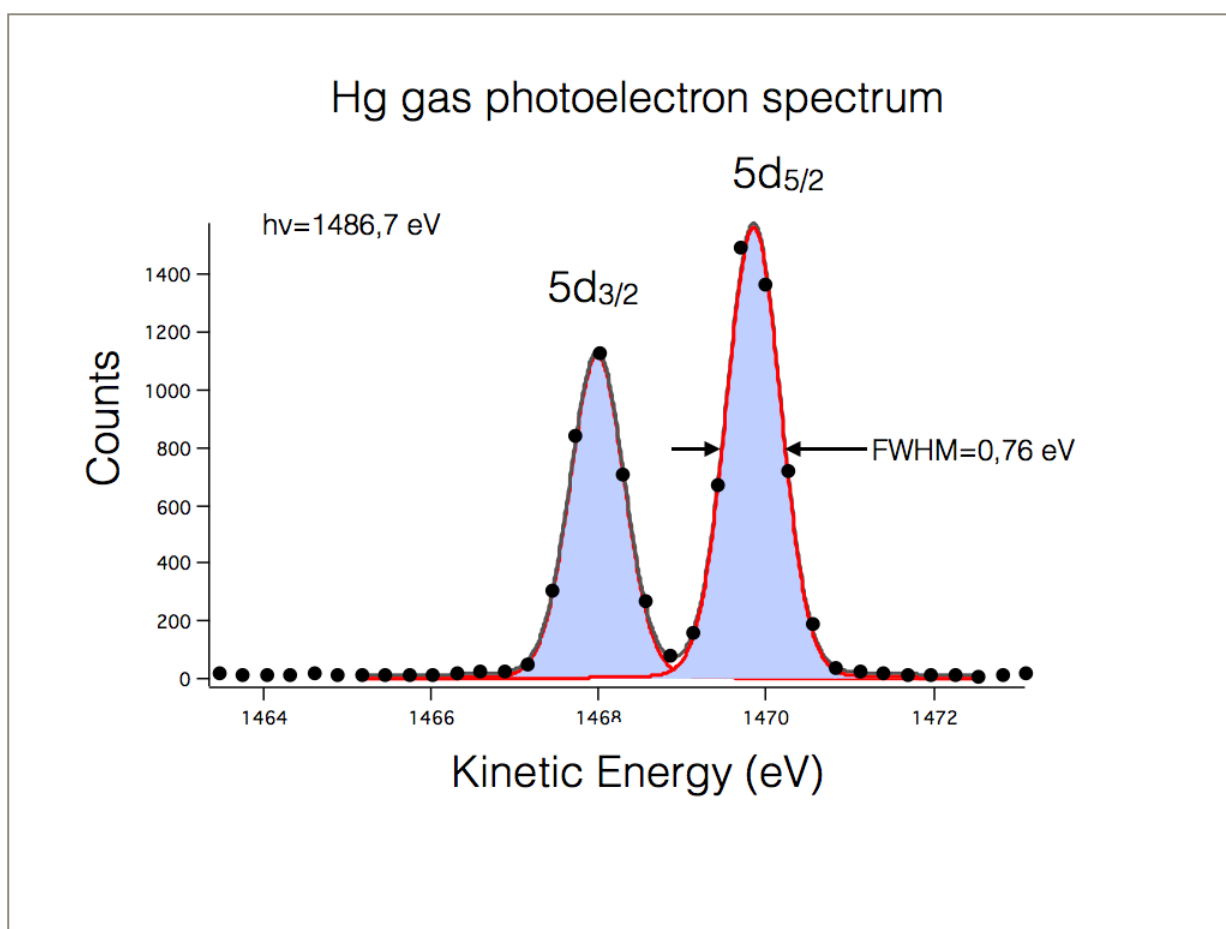


Fig1. The 4d photoelectron spectrum of mercury in the gas phase. The lines have negligible life-time widths and can therefore be used to determine the spectrometer function.

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.

As an example of our fitting procedure we show the result for the 4f lines in Fig. 2. The 4f lines

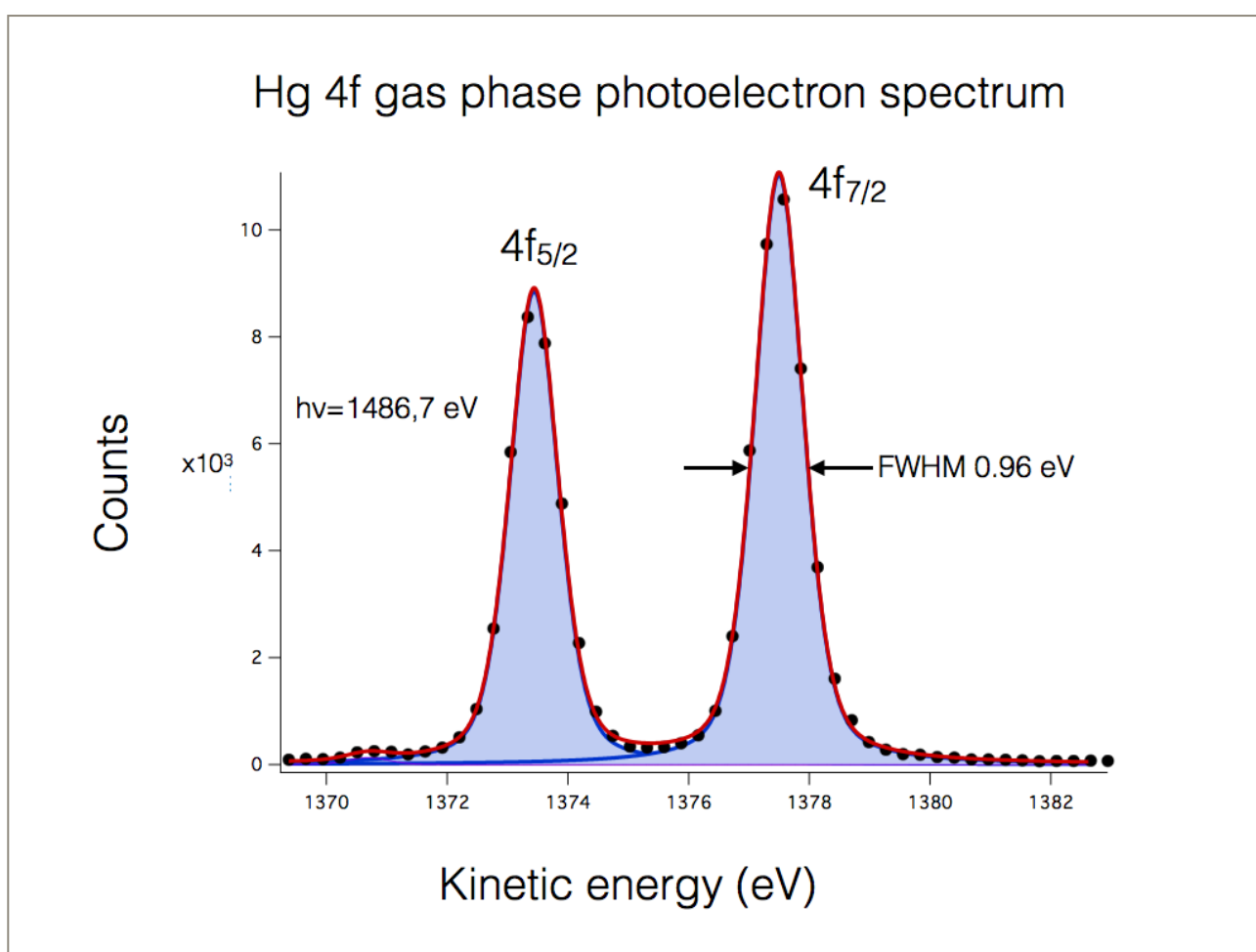


Fig. 2 The gas phase 4f photoelectron spectrum of mercury. An analysis of the Lorentzian contribution gives a life-time broadening of 0.34(9) eV.

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 to the spectrometer function is 0.06 eV, and since the widths add when Lorentzian functions are convoluted, this gives a life-time width of 0.34 eV(9) for the 4f levels. First

of all we note that this agrees well with the fitted solid phase data (0.32 eV)[9]. It is slightly larger than the value 0.24 eV of ref. [2] based on the line width of the Auger lines. However, we find that the two values agree, considering the respective error bars.

We have reanalyzed all the electron spectra from the 4s to the 6s sub-shells. Most vacancies in these shells have very short life-times, giving broad, almost completely Lorentzian line profiles. As an example we show in Fig. 3 the $4p_{3/2}$ photoelectron line. The line is almost perfectly Lorentzian and the error in the fits originates mostly from the difficulty in accurately knowing the background. For these broad lines there will be an overlap with inelastic loss and shakeup features. We have used very wide (typically 30 eV or more) Gaussians for modeling the background. By using different assumptions in the fits and by comparing the results we have estimated the errors, and adopted a conservative attitude.

In Table 1 we summarize our newly determined life-time broadenings for the mercury levels from 4s to 6s. First of all we note that the newly obtained values are quite similar to the ones reported in Ref.[1], showing the accuracy of the original approximate fitting scheme. In Table 1 we have also included the values for those core levels for metallic mercury that were previously reanalyzed in Ref. [9]. Also in this case we give rather conservative error bars. A comparison between the atomic and metallic data for the 4d and 4f levels shows that there are no significant solid effects to the life-time broadenings.

Discussion

In Table 1 the redetermined XPS values are compared to the recent results for liquid mercury based on XES [10]. In this investigation they have studied a large number of X-ray transitions. Each fundamental X-ray transition has an intrinsic Lorentzian width given by the sum of the widths of the initial and final hole states. By studying and analyzing a large number of spectra they obtain a set of equations for the line widths. From this set of data, the widths of the individual core levels were determined using a least-square fit method. In this way, Maillard et al.[10] derived life-time broadenings for essentially all core levels from 1s to 5s. From the least-square fitting procedure they could furthermore obtain estimates of the error bars. They also reported values for the 5p and 5d levels. In this case, however, the widths are obtained only from one X-ray transition for each level.

It is clear that the XES results for most of the core levels are significantly different from the XPS results, well outside what is consistent with the respective error bars. Most of the widths obtained in Ref.[10] are significantly larger than our values. When this difference was discussed in Ref.[10] it was attributed to shortcomings in the analysis of the XPS results [1]. On the contrary we can now

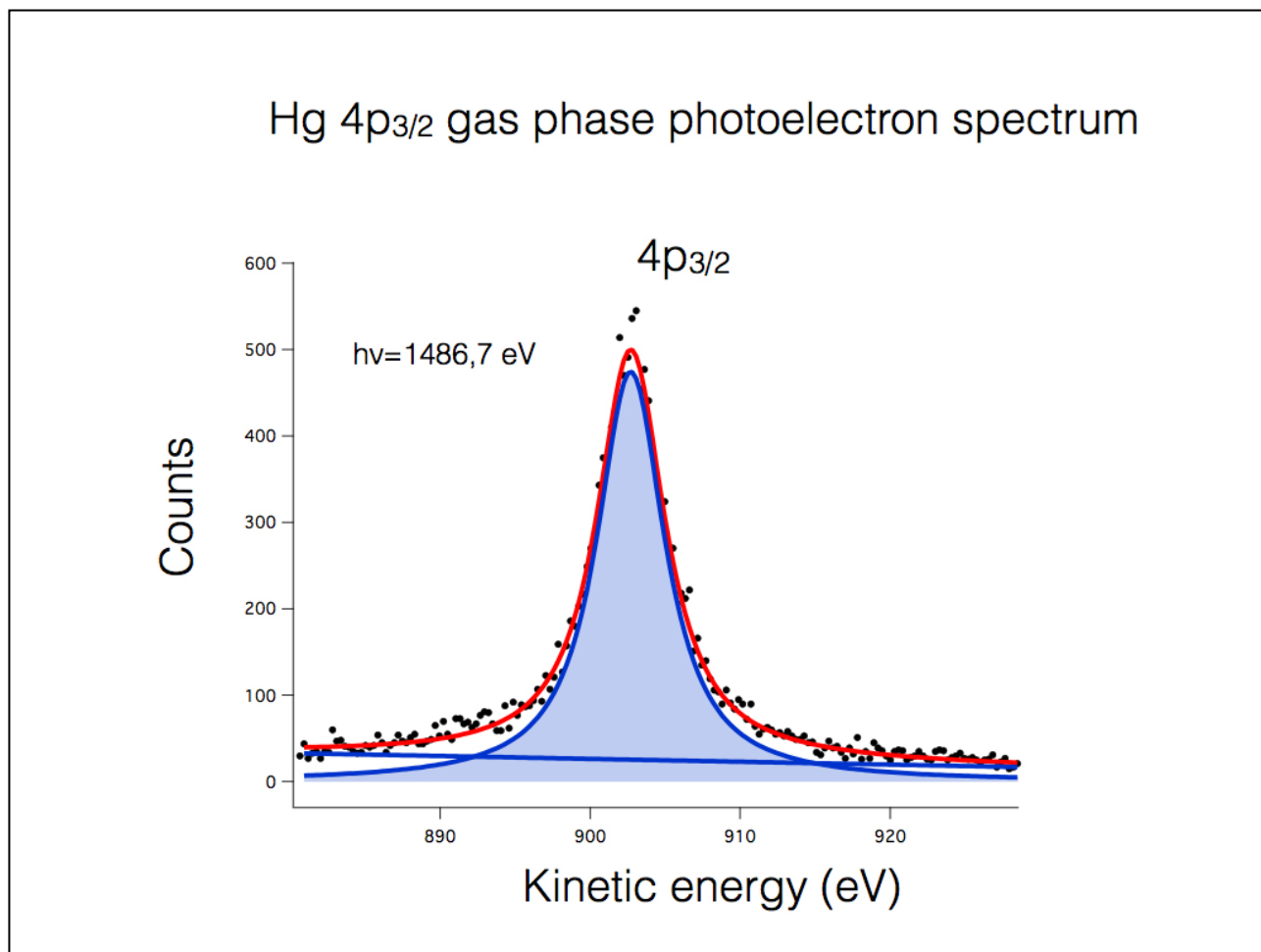


Fig. 3. The 4p_{3/2} photoelectron spectrum of mercury in the gas phase mercury

establish that already the previous XPS results were quite accurate, and furthermore we have now derived improved values. The analysis of highly resolved atomic XPS spectra is straightforward, especially for a closed-shell atom like mercury, and can be done with high accuracy. Since intrinsically very narrow valence levels can be studied, the spectrometer resolution function can furthermore be accurately determined. Our presented error bars can therefore be considered as rather safe estimates. The conclusion from this comparison is that a large part of the discrepancy must be traced back to the X-ray emission data. There must be other sources of errors which are not accounted for by this analysis.

The 5d levels represent a special case. First of all we note that the life-time broadenings are very small. These valence levels are, however, modified in the condensed phases. In Ref. [1] the valence electron spectra for the solid and the atom were compared. It is then seen that the 5d levels are broadened as a result of the metallic bonding. Due to the large spin-orbit coupling and the relatively weak bonding we observe a valence band spectrum with two structures with a separation approximately corresponding to the atomic 5d spin-orbit splitting. To the extent that we

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)

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

*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.

can make this decomposition it is clear that the "5d_{5/2}" part of the spectrum is broader than the "5d_{3/2}" component. Similar widths should be expected for the liquid. On the contrary, Maillard et al.[10], find that the "5d_{3/2}" component is broader. In this comparison, however, one should be aware of the fact that XPS and XES probe the valence electronic structure in different ways. XES give symmetry projected data due to the dipole selection rules, whereas XPS provides total density of

states results, although modified due to ionization cross-sections, which can be quite different for different sub-bands and orbital symmetries.

Next we turn to the special case of the 4d spin-orbit doublet. In the metal it has been found that the 4d_{3/2} component is about 0.35 eV broader than the 4d_{5/2} component and that the additional broadening can be well described by an additional Lorentzian contribution [9]. The same type of

broadening was seen for most of the elements in the 5d transition series and it was interpreted in terms of a $4d_{3/2}4d_{5/2}5d$ CK process. This process is allowed for all metals in the 5d transition series until the 5d shell becomes core-like and when its binding energy becomes too large compared to the 4d spin-orbit splitting. In the case of mercury the 4d spin-orbit splitting is 19.4 eV [1]. The energy to ionize a 5d electron in the presence of a 4d core hole in mercury metal can be rather accurately estimated from the 5d ionization energy in the Z+1-element, Tl, which is 12.5 eV [16]. From this comparison it is seen that the CK process is energetically allowed. With the same type of argument we find that the process becomes energetically forbidden around Pb and Bi in the Periodic Table. In order to evaluate the closing of the CK channel in detail one would also need to consider the role of multiplet splitting of the $4d5d$ double hole state, which will yield a range of energies for the possible CK final states. It is, however, clear from the measurements that the widths of the 4d spin-orbit components become similar for these elements [9].

For atomic mercury we can estimate the energy of the CK process in the same way using the (Z+1) equivalent core approximation. A valence ionization of a core ionized $4d^95d^{10}6s^2$ mercury atom is then substituted by the corresponding ionization in $Tl^+(5d^{10}6s^2)$. The second ionization energy of Tl is 20.4 eV[17]. It then takes another 8.3 eV to reach the $Tl(5d^96s^2)$ state. The energy for a 5d ionization is therefore, $20.4+8.3=28.7$ eV, which is larger than the 4d spin-orbit splitting. Hence, the CK process is forbidden in the atom. It is therefore rather remarkable that the 4d photoelectron spectrum for atomic Hg shows the same kind of broadening effect as the metal, see Fig. 4. This may seem to support the alternative interpretation of the additional $4d_{3/2}$ broadening provided by Ohno and van Riessen [11] in terms of different SCK decay rates for the $4d_{3/2}$ and $4d_{5/2}$ components. However, as will be shown below, the observed broadening for the atom is perfectly consistent with the CK interpretation.

Already the results in Ref. [9] for the metals gave strong support for the CK interpretation. Firstly, we note the disappearance of the additional $4d_{3/2}$ broadening for the high-Z elements where the CK channel becomes energetically forbidden. Secondly, we find that the observed broadening corresponds very well to calculated transition rates, as discussed in Ref.[9].

The gas phase 4d spectrum of mercury is shown in Fig. 4. If we simply make a fit to the spectrum with two spin-orbit split Voigt functions we find an additional Lorentzian broadening of 0.5 eV for the $4d_{3/2}$ level. This value is included in Table 1. However, there is additional structure in the spectrum. First of all we need to consider the possibility of overlapping energy loss features and shakeup states. The shakeup spectrum of mercury has been studied experimentally for the 4f levels [1]. The shakeup spectrum is due to valence electron excitations in the presence of a core-hole.

We have made a numerical fit using a number of discrete lines, all having the same width as the $4d_{5/2}$ line. The result from this fit is shown in Fig. 4. The small structures we discern by eye are numbered 1-5. The small peaks have intensities relative to the "main" lines that suggest that they may originate from inelastic scattering or monopole shakeup processes. Structure 1 is found at 6,3 eV from the $4d_{5/2}$ peak, corresponding to 6s-6p inelastic scattering processes. Structure 2 is located at 13.3 eV from the $4d_{5/2}$ peak, suggesting a 6s-7s monopole shakeup process. Structure 4 could be a similar shakeup process related to the $4d_{3/2}$ peak. Structures 3 and 5 may be due to shakeup processes close to the shake-off threshold, related to the $4d_{5/2}$ and $4d_{3/2}$ main lines, respectively. The central part of the " $4d_{3/2}$ " peak, however, is broader than the $4d_{5/2}$ peak. The broadening gives in this fit rise to two shifted peaks of about the same intensity.

The analysis of the 4f shakeup spectrum in Ref. [1] shows that there are $4d_{5/2}5dnd$ states in the region of the $4d_{3/2}$ peak. These states will have $J=5/2$ symmetry. However, this implies that there are also such states of $J=3/2$ total symmetry in the same energy region. When the energies of different excited states of the same symmetry match, the interaction between them might cause the single particle model to break down [18]. In ionization spectra from the inner valence electron region (20-40 eV) such energy matchings are frequent and complex spectral shapes are often seen in the spectra. In the core electron region on the other hand, this is rather unusual due to the large energy separation between different core levels. However, in a few cases very strong Configuration Interaction (CI)-resonances have been seen also in core level spectra. For the elements around Xe in the Periodic Table there is a very strong interaction between 4p and $4d^2nl$ states [19, 20]. This occurs for the elements in which the 4p $4d^2$ Super Coster Kronig (SCK) decay process has just been closed. A similar energy matching between the 3p single and $3d^2$ double hole states occurs in the elements around Kr which also leads to complex spectral line shapes. Due to the SCK character of these interactions they give rise to very strong mixing effects. We interpret the broadening of the $4d_{3/2}$ peak as due to such CI effects. Some of the discrete structures in the $4d_{3/2}$ region may have such a contribution as well.

In order to test this interpretation for the $4d_{3/2}$ line shape we have also performed preliminary multiconfigurational Dirac-Fock calculations using the program of Grant et al. [21] in which we let the $4d_{3/2}$ hole state interact with $4d_{5/2}5d6d$ states with $J=3/2$ symmetry. From this we see that the spectral intensity is distributed over a number of states in the $4d_{3/2}$ region. In fact, this calculation describes the main $4d_{3/2}$ line in terms of two closely spaced features of approximately equal intensity and a number of smaller peaks in a range of a few eV from the main feature. We have not brought the theoretical analysis further than that and we just note that these calculations

support our interpretation for the modified line shape. A more detailed analysis would require the inclusion of further states and is completely outside the scope of this work.

The solid phase $4d_{3/2}$ spectrum can be described in a similar Configuration Interaction (CI) picture. In this case the $4d_{3/2}$ hole state interacts with the CK decay continuum corresponding to a free electron above the Fermi level of the metal. This continuum is expected to be rather flat and the interaction therefore simply leads to an additional Lorentzian broadening. In the atom there are instead a number of similar $4d_{5/2}$ derived states, although in this case discrete states, which interact with the $4d_{3/2}$ hole state. The fact that this leads to a broadening of the spectrum also in the atomic case shows that this type of interaction is significant, giving additional support for the interpretation

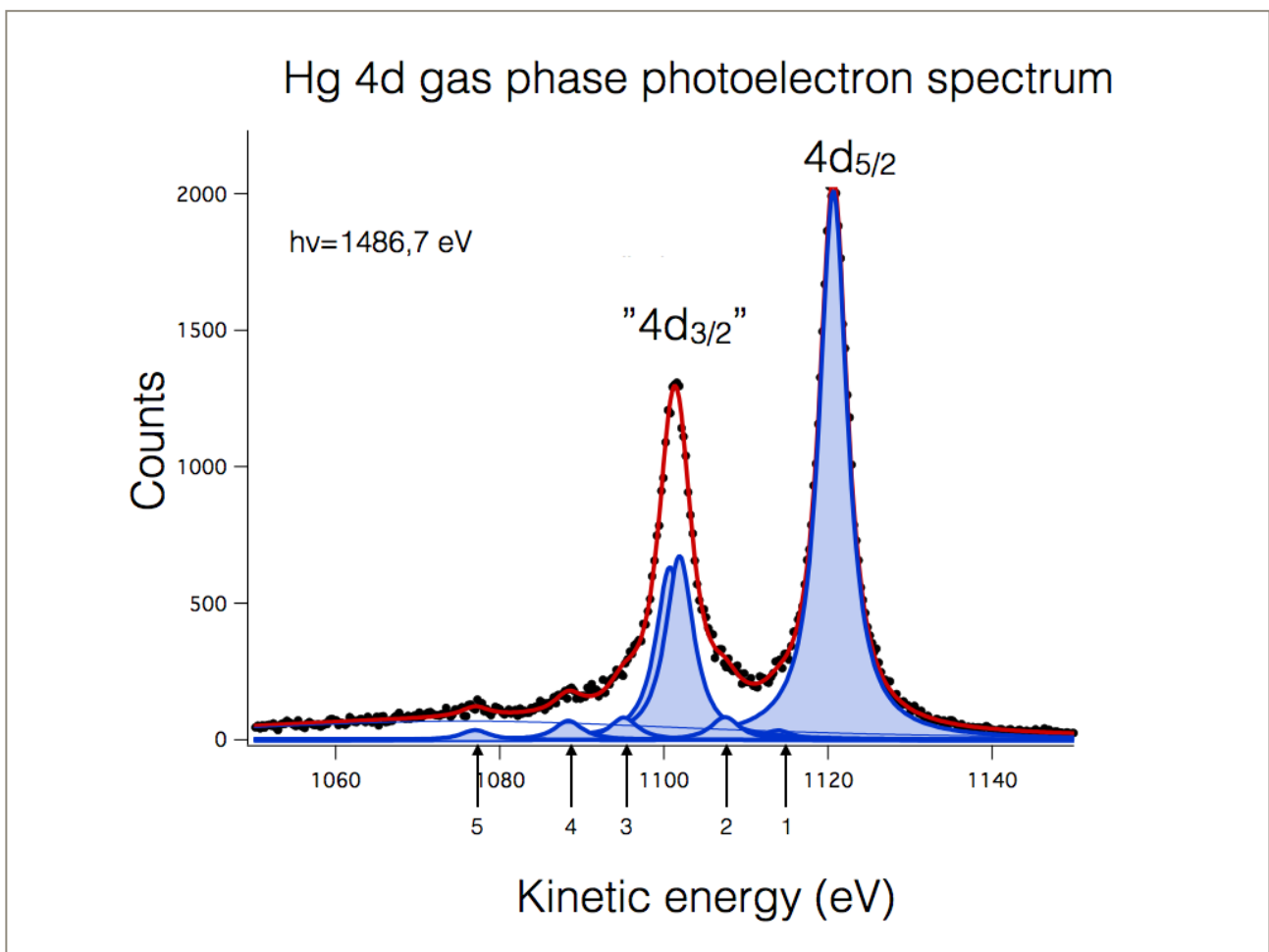


Figure 4. The 4d photoelectron spectrum of Hg. The fitting is made using Voigt functions with the same profile as the $4d_{5/2}$ peak. See text.

of the metal spectra in terms of a CK process.

Conclusions

In conclusion we find that XPS provides accurate life-time broadenings for the core levels of mercury. A comparison between the atomic and metallic data shows that any solid state effects for the life-time widths are very small. It has recently been claimed that an analysis of a large number of X-ray emission spectra provides superior estimates of the life-time widths. We have shown that this is not the case. Instead there must be additional effects, not accounted for in this analysis, which lead to uncertainties in the determined line widths. We also find clear evidence that the additional broadening of the $4d_{3/2}$ spin-orbit component compared to $4d_{5/2}$ is due to processes of Coster-Kronig type. This is in contrast to more recent claims that this should instead be due to different $4d4f4f$ SCK transition rates for the two spin-orbit split components. In atomic mercury we find a similar broadening of the $4d_{3/2}$ level as for the metal, in spite of the fact that the CK process in this case is energetically forbidden. We interpret this as due to configuration interaction between the $4d_{3/2}$ hole state and $4d_{5/2}5dnd$ states.

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