Line sharpening effect due to PCI in Ar LMM Auger spectra: experimental and theoretical results

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LETTER TO THE EDITOR

Line sharpening effect due to PCI in Ar LMM Auger spectra: experimental and theoretical results

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Abstract. High-resolution argon LMM Auger spectra excited by electrons at two different excess energies (2750 and 30 eV) above the L_3 level in Ar are presented. Due to post-collision interaction (PCI) the low-energy excited spectrum reveals a line sharpening effect of the low-energy sides of the peaks which are sharper than the corresponding Lorentzian. An extra structure at the high-energy side of the $L_2M_{2,3}M_{2,3}$ ($^1D_2$) peak and an edge at 209 eV are observed. These are interpreted to be caused by electron shake down from the electron continuum to ionic Rydberg states. A new semiclassical theory for PCI in photoexcited Auger spectra is outlined. The theory leads to simple analytical expressions which reproduce the experimental Auger line shapes both at low and at high excess energies.

In the study of energy levels in atoms, ions and molecules different excitation processes are used, e.g. photon, electron or ion excitation. The subsequent de-excitation of the excited states can take place by emission of a charged particle. This is the case in Auger decay and in autoionisation. If at the time of such an emission more charged particles are present besides the ion and the emitted particle these three or more particles may interact. This interaction is called post-collision interaction (PCI).

In Auger decay the effect of PCI generally manifests itself as an energy shift as well as a modified and broadened peak profile. Since the PCI is dependent on the number of charged particles with which the interaction occurs, the PCI in Auger decay will be dependent on the excitation process. The strength of the interaction is inversely proportional to the distance between the charged particles at the time of emission of the Auger electron. This distance is a function of the excess energy at the excitation, E_1, that is the difference between the excitation energy and the binding energy of the core electron level involved in the primary excitation. In photon-excited Auger spectra, the shift is a direct function of the excess energy, while in electron-excited spectra there is an additional dependence on how the excess energy is distributed between the two electrons. Even at high excess energies one of the electrons is likely to be rather low in energy. Hence, electron-excited spectra show a more pronounced PCI effect than photon-excited spectra at the same excess energy.

The PCI process has been studied widely, first in ion scattering experiments e.g. by Barker and Berry (1966) and by Gerber *et al* (1972) and later in electron scattering experiments by Smith *et al* (1974), Hicks *et al* (1974), Spence (1975), Fryar and McConkey (1976) and by Baxter *et al* (1979).

Recently, PCI has been given a great deal of attention in Auger decay experiments. Photoexcited Auger electron studies with synchrotron radiation have been reported

by Schmidt *et al* (1977, 1981), Hanashiro *et al* (1979), Bahl *et al* (1979) and Chiang *et al* (1980). Auger decay following electron excitation has been studied by Ohtani *et al* (1976), Hink *et al* (1979), Suzuki *et al* (1979), Huster (1980), DuBois and Rødbro (1980) and Huster and Mehlhorn (1982).

Various theoretical treatments for PCI in Auger decay have been presented. A semiclassical theory which results in a simple analytical expression for the PCI function has been developed by Niehaus (1977). Based on the classical Barker–Berry theory Huster derived the same analytical expression (Huster 1980). More rigorous quantum mechanical models which include the PCI effect have been proposed by Nienhuis and Heideman (1975), Wendin (1978), Amusia *et al* (1977, 1980), Amusia (1980), Åberg (1980) and by van der Water *et al* (1981). In autoionisation the 'shake-down' model of King *et al* (1975), Read (1975, 1977) and Read and Comer (1980) has been able to reproduce the complex lineshapes.

In this letter we report new features in the argon LMM Auger electron spectrum with electron excitation at energies near the $L_{2,3}$ ionisation threshold. These results are the first reported from a new high-resolution electron spectrometer built in Uppsala (Gelius *et al* 1974, 1982).

The electron spectrometer contains a number of excitation sources. A high-power monochromatised x-ray source, a UV source with a toroidal grating and an electron gun for Auger excitation. In this study we used the electron gun to focus an electron beam into a carbon-coated gas cell. The pressure in the gas cell was kept at about 1 Pa. Electrons scattered or emitted in a small solid angle at 105° to the primary beam are preretarded and focused onto the entrance slit of the energy analyser using an electrostatic lens. The electrons are energy analysed in a hemispherical electrostatic analyser with multichannel electron detection and recorded using a video camera connected to a multiprocessor computer (Basilier 1980).

The electron analyser with a radius of 36 cm was operated in a constant-resolution mode (20 eV analyser energy). The theoretical resolution of the analyser (at 20 eV analyser energy and 0.3 mm slit width) is better than 0.02 eV. However, charging effects in the gas cell have limited the experimental resolution to about 0.06 eV in this study.

Calibration of the Ar LMM PCI energy shifts was made against the Kr $M_5N_{2,3}N_{2,3}$ ($^1S_0$) Auger line. For the energy shift of the peak position, $\Delta\varepsilon$, we use the functional form (Huster and Mehlhorn 1982)

$$\Delta\varepsilon = c\Gamma E_1^{\alpha}$$

where E_1 is the excess energy and Γ^{-1} is the natural lifetime of the primary ionised state. c and α are constants independent of the element used.

The energy difference between the Ar $L_3M_{2,3}M_{2,3}$ ($^1D_2$) line and the Kr Auger line used can thus be written as

$$\Delta(E_1^{\mathrm{Ar}}) = c[\Gamma_{\mathrm{Ar}}(E_1^{\mathrm{Ar}})^{\alpha} - \Gamma_{\mathrm{Kr}}(E_1^{\mathrm{Ar}} + \Delta E_{\mathrm{B}})^{\alpha}] + \Delta_0$$

where ΔE_{B} is the electron binding energy difference between the Ar L_3 level and the Kr M_5 level, i.e. 154.8 eV. Δ_0 denotes the Auger energy difference between these lines at infinite excess energy, i.e. with no PCI.

The constants c, α and Δ_0 were determined by a least-squares fit of 36 experimental energy differences, $\Delta(E_1^{\mathrm{Ar}})$, with excess energies E_1 for Ar L_3 varying between 5 and 4750 eV (Helenelund *et al* 1982). We use $\Gamma_{\mathrm{Ar}} = 0.12$ eV (Nordgren *et al* 1979) and $\Gamma_{\mathrm{Kr}} = 0.090$ eV (McGuire 1972). The value of Γ_{Kr} is not critical. The optimal values

of the constants were found to be $c = 4.9$, $\alpha = -0.37$ and $\Delta_0 = 152.16$ eV. Our values of c and α differ somewhat from the values of Huster and Mehlhorn (1982) who obtained $c = 5.3$ and $\alpha = -0.45$. However, their treatment of the relative shift implies that the point at $E_1 = 1500$ eV is given infinite statistical weight, and their values of c and α therefore depend critically on this single point.

The above value for Δ_0 can be used to obtain the electron binding energy for the krypton M_5 level. The Ar $L_3M_{2,3}M_{2,3}$ ($^1S_0$) nominal Auger energy, i.e. without PCI, can be evaluated from accurate optical data for Ar (Nordgren *et al* 1979, Bashkin and Stoner 1978) to 203.502 eV. This value and the value of Δ_0 gives the Kr $M_5N_{2,3}N_{2,3}$ ($^1S_0$) nominal Auger energy of 51.34 eV. Combined with optical data for the Kr Auger final state which lies 42.461 eV above the ground state (Moore 1949, Minnhagen *et al* 1969), the value of the Kr M_5 level is thus determined to be 93.80 eV. This value is in excellent agreement with the values of Johansson *et al* (1973) (93.80 eV) and King *et al* (1977) (93.788 eV). A more detailed study of the energy shift as a function of the excess energy will be presented in a forthcoming work (Helenelund *et al* 1982).

Auger electron spectra from argon recorded at two different electron impact energies (3 keV and 280 eV) are shown in figure 1. The upper spectrum shows that the lines are asymmetric due to the PCI effect even at this high energy. This is a

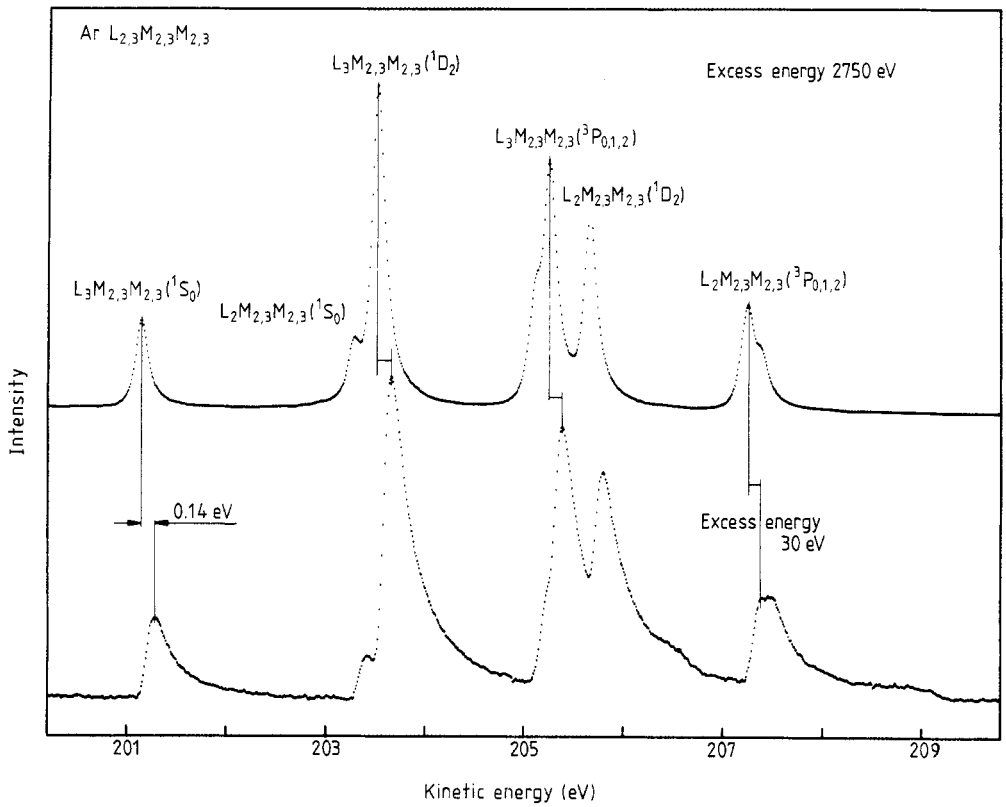

Figure 1. Argon $L_{2,3}M_{2,3}M_{2,3}$ Auger spectra, electron excited at two different excess energies. The prominent change of the shape of the spectra is caused by PCI.

consequence of the energy distribution between the two initial electrons which is U shaped, thus having a high probability for one electron to be low in energy. The lower spectrum clearly shows the asymmetry of the peaks resulting from the more pronounced PCI at this low energy.

The different shapes of the Ar $L_3M_{2,3}M_{2,3}$ ($^1S_0$) peak at the two different excess energies are shown in greater detail in figure 2. A Voigt function is included for comparison. At high excitation energy the shape is mainly due to Lorentzian lifetime broadening and instrumental broadening, the asymmetry resulting from a small PCI contribution.

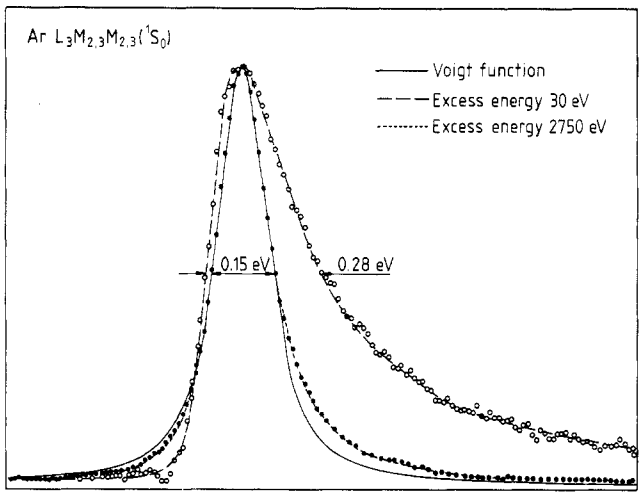

Figure 2. Argon $L_3M_{2,3}M_{2,3}{}^1S_0$ Auger peak at two different excess energies. A Voigt function ($\Gamma = 0.12$ eV and $\sigma = 0.06$ eV) is included for comparison. The peaks have been shifted so that their peak positions coincide. Note that the steep low-energy side of the 30 eV excess energy peak is steeper than the Voigt function.

In the low-energy excited spectrum the peak is steep on the left side, which is considerably sharper than the Voigt function and even sharper than a Lorentzian with the natural half width (Γ_{Ar}). The same effect can also be observed in the other peaks in figure 1. This line sharpening effect on the low-energy side of the peaks can be seen as an effect of 'time selection' in PCI.

Qualitatively, this effect can be explained by a simple model. Auger electrons contributing to the intensity on the steep low-energy side have acquired a smaller energy shift from the PCI interaction than most of the electrons. This means that for these events the Coulomb interaction between the ion and the (two) slow electron(s) at the time of the Auger decay was smaller than the Coulomb interaction on the average. In other words, the slow electron(s) must have moved away an extra long distance from the ion when the Auger decay took place. However, the excess energy is the same for all Auger transitions. Hence, these Auger transitions must have occurred after an extra long time, i.e. the corresponding primary ions must have been extra long lived. This is also seen from the semiclassical theory by Niehaus in which the PCI energy is directly related to the decay time (Niehaus 1977, Huster 1980). The decay time on the steep low-energy side is by this theory found to vary typically

between about $10\,\tau_0$ (at 1% of the peak intensity) and $2\,\tau_0$ (near the peak), being about $4\,\tau_0$ at half the peak height. τ_0 is the natural lifetime of the primary hole state.

It is a well known phenomenon in physics, and fully in line with the uncertainty principle, that for extra long-lived states the line width will be smaller than the natural line width for that state (Denis and Désesquelles 1979). Therefore, one should expect that the low-energy side of the Auger lines actually are sharper than the Lorentzian distribution with the natural line width. By the same arguments the opposite must be true for the high-energy side of the Auger lines. These PCI effects become strikingly significant for low excess energies. It is interesting to note that by the PCI effect it is thus in effect possible to make a kind of time-selective study on a time scale as short as 10^{-15} to 10^{-16} s which is a typical lifetime of the core hole states. The effect of 'time selection' in PCI has been discussed earlier in connection with the sharp structures observed in autoionisation spectra of argon by Wilden *et al* (1978). Line sharpening in autoionisation spectra has also been commented on by Read and Comer (1980), Amusia (1980) and by Amusia *et al* (1980).

Previous experimental results on PCI in Auger spectra have been compared with the analytical expressions for the PCI line shape obtained by Niehaus (1977). However, in this context it has been noticed that these analytical expressions are incorrect at high excess energies since, in the high-energy limit, the Niehaus expressions result in a delta function instead of a Lorentz function with the proper natural line width. To obtain agreement with the experimental results for high excess energies the Niehaus PCI function must be convoluted with a Lorentzian. It is then questionable whether this should not be done for all excess energies in order to treat the theory consistently. The sharp low-energy edge obtained by the Niehaus expressions at low excess energies would then disappear. Previous experimental results did not fully contradict such a treatment although a somwhat better agreement was found when no convolution with a Lorentzian was made (Huster 1980, Huster and Mehlhorn 1982).

The present experimental results indicate than an improved PCI theory is required to account for the line sharpening effect in a proper way. We have developed an alternative semiclassical model for PCI in Auger decay following photoionisation (Helenelund *et al* 1982). WKB wavefunctions are used to describe the slow receding electron, before and after the Auger decay. The transition amplitude can then be expressed as a one-particle overlap integral. The new theory describes the line shape continuously from low to high excess energies. With this theory the correct steep left side of the peaks at low excess energies is well described and the proper Lorentzian shape is obtained in the high-energy limit.

The following expression is obtained for the Auger decay transition probability, $P(\varepsilon)$, including PCI:

$$P(\varepsilon) = g(\varepsilon)\exp[2\sqrt{2}\,\mathrm{Im}(I1 - I2)]$$

where $g(\varepsilon) = c[\varepsilon^2 + (\Gamma/2)^2]^{-1}[(E_1+\varepsilon)^2+\Gamma^2]^{-1/4}$

$$I1 = I_1(E_a) - I_1(z^*) \qquad \text{and} \qquad I2 = I_2(E_a) - I_2(z^*).$$

In this expression, c is a constant, $z^* = \varepsilon + \frac{1}{2}\mathrm{i}\Gamma$ and $E_a = 1/\delta$, where δ can be taken to be the expectation value $\langle r\rangle$ of the orbital to be ionised.

$I_1(z)$ and $I_2(z)$ are given by

$$I_1(z) = \frac{(E_1+\frac{1}{2}\mathrm{i}\Gamma+z)^{1/2}}{z} - \frac{1}{2(E_1+\frac{1}{2}\mathrm{i}\Gamma)^{1/2}}\ln\frac{(E_1+\frac{1}{2}\mathrm{i}\Gamma+z)^{1/2}-(E_1+\frac{1}{2}\mathrm{i}\Gamma)^{1/2}}{(E_1+\frac{1}{2}\mathrm{i}\Gamma+z)^{1/2}+(E_1+\frac{1}{2}\mathrm{i}\Gamma)^{1/2}}$$

and

$$I_2(z)=\frac{(E_1-\varepsilon+2z)^{1/2}}{z}-\frac{1}{(E_1-\varepsilon)^{1/2}}\ln\frac{(E_1-\varepsilon+2z)^{1/2}-(E_1-\varepsilon)^{1/2}}{(E_1-\varepsilon+2z)^{1/2}+(E_1-\varepsilon)^{1/2}}.$$

This theory gives the same energy shift of the peak position as the Niehaus theory, except for negative values of the excess energy where the Niehaus theory has a singularity and gives different peak profiles.

In figure 3 the experimental Ar $L_3M_{2,3}M_{2,3}$ ($^1S_0$) peak obtained at 30 eV excess energy is compared with a line calculated according to our theory. The excess energy of the theoretical line was chosen to best reproduce the experimental line shape and was found to be 3 eV. However, the theoretical shift at this excess energy is only 0.12 eV whereas the experimental shift is 0.17 eV. To faciliate the comparison of the line shapes the theoretical energy scale in figure 3 was therefore shifted.

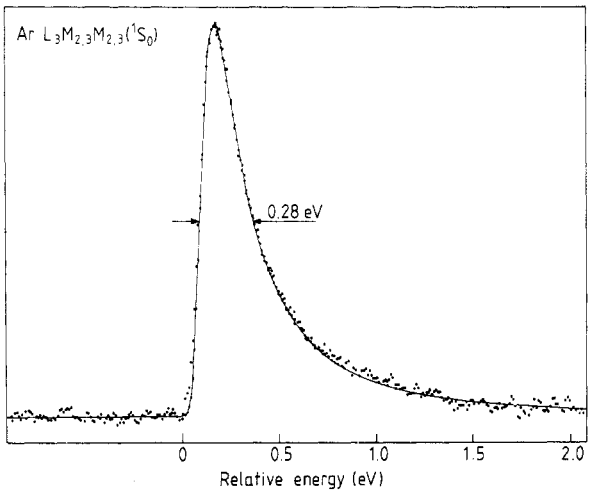

Figure 3. Comparison between the theoretical and experimental line shapes. The theoretical PCI function has an excess energy, $E_1^{h\nu}=3$ eV. The experimental electron-excited peak was obtained at 30 eV excess energy.

The argument for choosing a smaller excess energy for the theoretical photoexcited spectrum is the above mentioned U-shaped energy distribution between the two electrons in the case of electron excitation. This causes the energy shift and peak profile to be most influenced by the low-energy electron. On the other hand, accounting for the complete energy distribution by merely selecting a single energy value is a crude approximation. Therefore, one can hardly expect to obtain an optimal line shape and correct energy shift simultaneously.

The structure at 206.4 eV in the low-energy excited spectrum in figure 1, is probably due to the one of the two outgoing electrons which is trapped in a shakedown process in a Rydberg state. This will give a noncontinuous sharing of the excess energy between the two electrons and will favour certain energy shifts. As one electron is trapped and the final product is a singly ionised atom the effect can also be seen as an autoionising effect with an excited final state. It is probably not caused by an interference effect due to coherent mixing of Auger transitions from two closely spaced

core hole states as discussed for the Mg $L_2M_1M_1$ ($^1S_0$) line by Niehaus (1977). The reason for this is that we observe a similar structure in the Ne KLL ($^1D_2$) Auger spectrum where such interference effects cannot occur since there is only one initial core hole state.

On the high-energy side of the spectrum in figure 1 (at 209 eV), we observe an edge which we tentatively explain as an effect of autoionisation. This edge becomes even more pronounced at lower excess energies (Helenelund *et al* 1982).

We want to thank Professor Mehlhorn for interesting discussions and communications during the early course of this work.

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