

How to Explain the Difference between (γ, e) and $(e, 2e)$ Spectroscopic Factors*

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Abstract

It is shown that the relative line intensity of the main and satellite lines in the atomic shell ionisation spectrum depends significantly on the mechanism responsible for the removal of the electron. This dependence is explained by the influence of many-electron correlations in the initial state of the atom to be ionised, which is considerable when the momentum transferred to the ion is large. This is the case for photoionisation, i.e. the (γ, e) reaction under the condition of large photon energy. On the contrary, in electron momentum spectroscopy, such as the symmetric noncoplanar $(e, 2e)$ reaction, the momentum transferred to the ion is typically small and the initial atomic state correlations are negligible. It follows from this that the spectroscopic factors of the different final states of the ion, as defined in the usual way, can be measured only for the $(e, 2e)$ reaction, whereas a more involved interpretation is necessary for the (γ, e) reaction. Comparison of the calculated spectroscopic factors of Ar II and Xe II 2S ion eigenstates with recent (γ, e) and $(e, 2e)$ experimental data has confirmed this conclusion.

1. Introduction

It is a great pleasure and honour for us to be able to present a paper to this issue dedicated to the sixtieth birthday of Professor McCarthy. His contribution to the problem to be discussed is prominent and extremely essential, forming the basis for a number of theoretical and experimental investigations.

The problem of the difference between the energy separation spectra of the same atomic shell in the (γ, e) and $(e, 2e)$ reactions arises in connection with measurements of the spectroscopic factors of subvalent shells of noble-gas atoms (McCarthy and Weigold 1976). Photoelectron spectroscopy and electron momentum spectroscopy yield different values for the spectroscopic factors of the same final-ion state.

On the other hand, theoretical analysis of the ionisation spectra has shown that the spectroscopic factors of the two reactions should be equal (McCarthy and Weigold 1976). This analysis was based on the assumption of the Hartree–Fock character of the initial state of the target atom. Under this condition, the spectroscopic factor of an arbitrary final state of the ion is defined as the contribution to the state of the Hartree–Fock configuration in the form of a vacancy (hole) in the ‘frozen’ atomic core. The spectroscopic

* Dedicated to Professor Ian McCarthy on the occasion of his sixtieth birthday.

factor defined in this way is a purely structural characteristic of the ion, and should not depend on the ionisation mechanism.

By using a graphical representation of the many-body perturbation theory, Amusia and Kheifets (1985) demonstrated that there is a definite type of correlation diagram that has an appreciable effect on the relative line intensity of separation energy spectra, and that this effect is different for photoionisation and for ionisation by electron impact. Later Kheifets (1985) confirmed this result by the use of the standard configuration interaction technique. It was also shown that the spectroscopic factors of the (γ, e) and $(e, 2e)$ reactions have different physical meanings.

In this paper we present the results of our *ab initio* calculation of the spectroscopic factors and relative line intensities of the Ar 3s subshell ionisation spectra. These results agree well enough with the recent experimental data of Svensson *et al.* (1987) for the (γ, e) reaction, and of McCarthy *et al.* (1989) for the $(e, 2e)$ reaction. For Xe, we have calculated only the ratio of the corresponding line intensities in the (γ, e) and $(e, 2e)$ spectra, which is also in reasonable agreement with the ratio of the (γ, e) experiment of Svensson *et al.* (1988) and the $(e, 2e)$ experiment of Cook *et al.* (1986).

2. Theory

We assume a Hartree-Fock type ground state of the target atom and describe it by the wavefunction $|N, 0\rangle$, which is the antisymmetrised product of N one-electron wavefunctions. The final state of the ion is described by the function $|N-1, \alpha\rangle$, which can be expanded over the Hartree-Fock basis:

$$|N-1, \alpha\rangle = t_i^\alpha \hat{a}_i |N, 0\rangle + \sum_{jlk} t_{jlk}^\alpha \hat{a}_j \hat{a}_l \hat{a}_k^\dagger |N, 0\rangle + \dots, \quad (1)$$

where α is a set of quantum numbers defining the ion state, and \hat{a}_i and \hat{a}_k^\dagger are the second quantisation operators corresponding, respectively, to the annihilation and creation of an electron in a definite Hartree-Fock state. The first term on the right-hand side of (1) is a hole in the frozen atomic core, the second consists of two holes and an excited electron, and so on.

The quantity

$$S_\alpha = |t_i^\alpha|^2 = |\langle N-1, \alpha | \hat{a}_i | N, 0 \rangle|^2 \quad (2)$$

defines the contribution of the pure one-hole state $\hat{a}_i |N, 0\rangle$ to the exact state $|N-1, \alpha\rangle$. It is precisely this quantity that is usually referred to as the spectroscopic factor. In the absence of correlations in the initial state of the atom, it determines the intensity of the corresponding line in the ionisation spectrum.

Indeed, in the case of ionisation of an atom by electron impact, the final-ion state dependent part of the reaction amplitude has the form

$$F_\alpha(\mathbf{q}) = \int d^3r \exp(-i\mathbf{q} \cdot \mathbf{r}) \langle N-1, \alpha | N, 0 \rangle, \quad (3)$$

where \mathbf{q} is the momentum transferred to the ion. Let us substitute the

expansion (1) in (3), and use the obvious relationships

$$\langle N, 0 | \hat{a}_i | N, 0 \rangle = \phi_i(r), \quad \langle N, 0 | \hat{a}_j \hat{a}_l \hat{a}_k^+ | N, 0 \rangle = 0.$$

None of the other terms in (1) will contribute to the overlap integral either. So, the final result is

$$F_\alpha(\mathbf{q}) = t_i^\alpha \phi_i(\mathbf{q}),$$

where $\phi_i(\mathbf{q})$ is the Fourier component of the one-electron wavefunction corresponding to the i th Hartree-Fock orbital. Therefore, the ionisation cross section corresponding to the ion state α is proportional to S_α . An analogous result is valid for photoionisation.

When many-electron correlations are taken into account, the wavefunction of the initial state of the atom can be written in the form

$$|N\rangle = t_0 |N, 0\rangle + \sum_{jlpk} t_{jlpk} \hat{a}_j \hat{a}_l \hat{a}_p^+ \hat{a}_k^+ |N, 0\rangle + \dots \quad (4)$$

The terms omitted from this expansion correspond to the simultaneous creation of two or more electron-hole pairs. The creation of one pair has already been taken into account in the Hartree-Fock approximation.

We shall confine ourselves to first-order perturbation theory in the direct electron interactions. In this approximation, the many-electron wavefunctions (3) and (4) have the form

$$|N\rangle = t_0 \left(|N, 0\rangle + \sum_{jlpk} \frac{\langle pk | \hat{V} | jl \rangle}{\epsilon_p + \epsilon_k - \epsilon_j - \epsilon_l} \hat{a}_j \hat{a}_l \hat{a}_p^+ \hat{a}_k^+ |N, 0\rangle \right), \quad (5)$$

$$|N-1, \alpha\rangle = t_i^\alpha \left(\hat{a}_i |N, 0\rangle + \sum_{jlk} \frac{\langle ik | \hat{V} | jl \rangle}{\epsilon_\alpha - \epsilon_j - \epsilon_l + \epsilon_k} \hat{a}_j \hat{a}_l \hat{a}_k^+ |N, 0\rangle \right). \quad (6)$$

Here we have used the expressions for the coefficients t_i^α and t_{jlpk} , given in March *et al.* (1968), in which ϵ_n , $n = j, l, p, k$ are the energies of the corresponding one-electron Hartree-Fock states $\epsilon_\alpha = E(N) - E(N-1, \alpha)$ is the separation energy, and $\langle pk | \hat{V} | jl \rangle$ is the Coulomb interaction matrix element. The normalisation condition for the wavefunction (6) yields

$$S_\alpha = |t_i^\alpha|^2 = \left(1 + \sum_{jlk} \frac{|\langle ik | \hat{V} | jl \rangle|^2}{(\epsilon_\alpha - \epsilon_j - \epsilon_l + \epsilon_k)^2} \right)^{-1}. \quad (7)$$

We now substitute the wavefunctions (5) and (6) into the formulas for the reaction amplitudes. For ionisation by electron impact, we obtain

$$F_\alpha(\mathbf{q}) = t_0 t_i^\alpha \left(\phi_i(\mathbf{q}) - \sum_{jlpk} \frac{\langle ik | \hat{V} | jl \rangle \langle pk | \hat{V} | jl \rangle^*}{(\epsilon_\alpha - \epsilon_j - \epsilon_l + \epsilon_k)(\epsilon_p + \epsilon_k - \epsilon_j - \epsilon_l)} \phi_p(\mathbf{q}) \right), \quad (8)$$

and, for photoionisation, we have

$$\langle fN-1, \alpha | \sum_{a=1}^N \hat{z}_a | N \rangle = t_0 t_i^\alpha \left(\langle f | \hat{z} | i \rangle \right.$$

$$\left. - \sum_{jlpk} \frac{\langle ik | \hat{V} | j l \rangle \langle p k | \hat{V} | j l \rangle^*}{(\epsilon_\alpha - \epsilon_j - \epsilon_l + \epsilon_k)(\epsilon_p + \epsilon_k - \epsilon_j - \epsilon_l)} \langle f | \hat{z} | p \rangle \right). \quad (9)$$

The squares of the matrix elements (8) and (9) give the relative line intensities in the corresponding ionisation spectra. As compared with the usual spectroscopic factor (2), the squares of (8) and (9) contain an additional term which depends on the final-state energy ϵ_α of the ion. If this term is not small, it may influence the relative line intensity. We shall show now that the relative contribution of this term is quite different in photoionisation and ionisation by electron impact. It is assumed that the energy transferred to the atom is large.

For photoionisation, all the matrix elements containing the outgoing photoelectron wavefunction $|f\rangle$ are small, being integrals of a rapidly oscillating wavefunction. For example, the direct matrix element of the ns

Table 1. Satellite lines intensities of argon and xenon

Main ion configuration	Energy (eV)		Normalised line intensity (%)					
	Exp.	Calc.	(y, e)		(e, 2e)		(y, e)/(e, 2e)	
			Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
<i>Argon</i>	A	C	A	D	B	C	A, B	D, C
3s3p ⁶ 2S _{1/2}	29.24	29.27	100	100	100	100	1	1
3s ² 3p ⁴ (¹ D)3d ² S	38.60	38.63	18.6	18.6	33	36.0	0.56	0.52
4d	41.21	41.14	9.4	8.1	17.0	19.3	0.55	0.41
5d	42.67	42.55	4.1	2.8	9.6	7.6	0.43	0.36
6d	43.43	43.38	1.5	1.3	8.1	6.3	0.25	0.32
7d	44.00	43.87	0.5	0.8				
<i>Xenon</i>	E		E		F		E, F	D, C
5s5p ⁶ 2S _{1/2}	23.40		100		100		1	1
5s ² 5p ⁴ (¹ S)6s ² S	27.35		3.6		31		0.81	0.82
(¹ D)5d ² P	27.82		11.7					
?	28.22		9.8					
?	28.71		13.9					
(¹ D)5d ² S	29.08		22.0		67		0.69	0.78
(¹ D)6d ⁴ P	29.44		10.3					
(³ P)7d ^{4,2} P	30.67		3.1					
(¹ D)6d ² S, ² P	31.44		13.2		28		0.69	0.70
(³ P)8s ⁴ P								
?	31.9		3					
(¹ D)7d ² S, ² P	32.81		5		31		0.23	0.37
(¹ S)7s ² S								
(¹ D)8d ² S, ² P	33.5		2					

A Svensson *et al.* (1987).

B McCarthy *et al.* (1989).

C Calculation including only final state correlations (see text).

D Calculation including both final and initial state correlations (see text).

E Svensson *et al.* (1988).

F Cook *et al.* (1986).

subshell photoionisation is of the order of $(1/\epsilon_f)^{5/2}$ for any n . Using the closure relation and separating higher order terms on the right-hand side of (9), we obtain the following expression for the relative line intensity of the ns -subshell photoionisation spectrum:

$$\tilde{S}_\alpha = S_\alpha [1 + (\epsilon_\alpha - \epsilon_{ns})/\Delta]^2, \quad (10)$$

where ϵ_{ns} is the corresponding Hartree-Fock energy, and Δ is the averaged energy of the two-hole one-electron excitations. It is \tilde{S}_α and not S_α , as assumed earlier, that is the spectroscopic factor measured in photoelectron spectroscopy.

For ionisation by electron impact, under the condition of large momentum transferred to the ion, the situation is just the same as for photoionisation. The Fourier components $\phi_i(\mathbf{q})$ and $\phi_p(\mathbf{q})$ on the right-hand side of (9) contain the small quantity $(1/q)^\beta$, where β depends on the angular momentum of the appropriate one-electron state. As for photoionisation, this smallness leads to (10).

On the contrary, when the transferred momentum is small, another estimation is valid. Under the condition $q \ll 1$, the Fourier components $\phi_i(\mathbf{q})$ and $\phi_p(\mathbf{q})$ reduce to the integrals of appropriate radial wavefunctions. In the case of ns subshell ionisation, it enables us to show that the second term on the right-hand side of (9) gives a small correction of the order of $(1/2n)^2$ to the main first term. It means that the contribution of the initial atomic state many-electron correlations is negligible and the spectroscopic factor is given by the usual formula (2).

3. Numerical Calculation

We have established that the difference between the relative line intensities in the ionisation spectra of the outer ns subshell of noble-gas atoms is due to the difference between the spectroscopic factors \tilde{S}_α and S_α of the (γ, e) and ($e, 2e$) reactions respectively. To confirm this we have performed, according to (7) and (10), a calculation of the spectroscopic factors S_α and \tilde{S}_α for the ground and several excited states of the ArII $2S$ ion. We have taken into account the final-ion state configuration interaction between the $3s3p^6\ ^2S$ and $3s^23p^4(^1D)nd\ ^2S$, $n=3, \dots, 7$, states. Continuum states $3s^23p^4(^1D)\epsilon d\ ^2S$ have also been taken into account. Allowance for the initial atomic state configuration interaction between $3s^23p^6\ ^1S$ and $3s^23p^4nd\ ms$ and $\epsilon s\ ^1S$ states has led to the formula (10) with $\Delta = E_{3s^23p^43d}$. The results of the calculation in the form of normalised line intensities are presented in Table 1 along with the recent experimental results on photoionisation by Svensson *et al.* (1987) and ionisation by electron impact by McCarthy *et al.* (1989).

An analogous calculation for Xe, as it was demonstrated by assignment of experimental lines needs a more extensive basis set for the ion states. In particular, not only 2S , but also 2P and 4P ion states should be taken into account. It requires a relativistic calculation which is beyond our capabilities at present. However, we have compared the ratio of the corresponding line intensities measured in the (γ, e) experiment (Svensson *et al.* 1988) and ($e, 2e$) experiment (Cook *et al.* 1986) with the value $\tilde{S}_\alpha/S_\alpha$ given by expression (10).

In spite of the complex structure of the ion states, we have managed to describe the experimental data rather well using Δ as a fitting parameter. The Δ value obtained turns out to be close to the Hartree-Fock energy of the strongest satellite $5s^25p^4(^1D)5d\ ^2S$.

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