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DOUBLE EXCITATION SATELLITES OF IODINE : THEORETICAL STUDY

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Résumé - Une étude théorique des spectres de photoélectrons 5p et 5s de l'iode atomique ($Z = 53$) pour des énergies de photons au dessous des seuils d'ionisation 4d est présentée dans le but de mettre en évidence l'origine d'un grand nombre de raies s'étalant sur un large domaine d'énergies (environ 20 eV) et de leur amplification pour l'énergie excitatrice de la transition $4d^{10}5s^25p \rightarrow 4d^95s^25p$ ($h\nu = 46.2$ eV). Elle montre que d'importants effets d'interaction de configurations font prédominer les satellites de double excitation (configuration $5s^25p^35d$) sur les raies parentes (configuration $5s^15p^5$) et que leur amplification à l'énergie 46.2 eV provient des grandes valeurs des taux de désexcitation AUGER dans les voies satellites.

Abstract - A theoretical study of 5p and 5s photoelectron spectra of iodine ($Z = 53$) for photon energies below the 4d ionisation thresholds is presented within the purpose of pointing out the origin of numerous lines spreading over a large energy range (about 20 eV) and of their enhancement when exciting the transition $4d^{10}5s^25p \rightarrow 4d^95s^25p$ ($h\nu = 46.2$ eV). It shows that important configuration interaction effects make the double excitation satellites (configuration $5s^25p^35d$) predominant over the parent lines (configuration $5s^15p^5$) and that their enhancement is coming from the large Auger decay rates of this excited state into the satellite channels.

1 - INTRODUCTION

Complex satellite structure has been observed in high-resolution photoelectron, X-ray emission and Auger electron spectra of many atomic systems. It is now widely recognised that much of this structure originates from electron correlation effects including relaxation effects associated with the initial and final states of the atomic system. A photoelectron spectrum from atoms excited by monochromatic radiation usually reveals a number of intense lines corresponding to the one-electron picture accompanied by sets of less intense peaks, the so-called satellite lines. These transitions correspond to cases in which the ion has been left in an excited state. For closed-shell atoms all satellite lines are an indication of the breakdown of the one-electron frozen structure model and thus a manifestation of electron correlation effects.

Among the closed-shell atoms, the rare gases have certainly been the most studied systems, and in order to understand the nature of the excitation processes leading to photoelectron satellites, a comprehensive experimental study of these lines for Ar, Kr and Xe has been achieved as soon as 1974 /1/ by photoelectron spectroscopy, as a function of the orbital in which photoelectron ejection occurs. Its results concerned photoionization in both inner (core) and outer (valence) shells; for the first ones, the results are consistent with the behaviour expected from electron shake-up whereas in the second case, the electron shake-up probability is strongly influenced by electron correlation and in addition, there also may arise excited states, which involve two-electron excitation in conformity with configuration-interaction states.

Many other experimental works have been devoted to satellite lines in rare gases and only a few are mentioned here /2, 3, 4, 5, 6/ in so far as the

present paper is devoted to iodine for which photoelectronspectra have been obtained for the first time and very recently / 7/ using synchrotron radiation. Indeed, the situation of iodine ($Z = 53$) just before xenon in the periodic table allows to hope profitable comparisons with results obtained for xenon a few years ago, using both Auger spectroscopy / 8, 9, 10 / and photoelectron spectroscopy after exciting resonances below inner shell thresholds / 11, 12, 13, 14 /. The availability of a strong tunable light source like synchrotron radiation has made possible investigations of the Auger decay of resonant states located below inner-shell thresholds of atoms and reference 11/ reports the first photoemission experiments relative to Auger decay after excitation of xenon to the $4d^9 5s^2 5p^6 ({}^2D_{5/2}) 6p$ and to the $4d^9 5s^2 5p^6 ({}^2D_{3/2}) 6p$ resonance states at 65 and 67 eV, respectively, and after excitation of krypton to the $3d^9 4s^2 4p^6 ({}^2D_{5/2}) 5p$ and $3d^9 4s^2 4p^6 ({}^2D_{3/2}) 5p$ states at 91.2 and 92.4 eV, respectively. Later on, other experiments have been achieved with better resolution, but the same major conclusions / 12, 13, 14 /. Such investigations have considerable relevance for a detailed knowledge of the mechanism of deexcitation of certain resonance excitations and also towards a better understanding of correlation effects in excited atoms. As a consequence, it was of great interest to extend the previous studies relative to rare gases to open-shell atoms whose first core excited states correspond to the filling of this outermost open sub-shell: within this purpose, photoabsorption, photoelectron and ejected electron spectra of atomic 3d transition metals and rare-earths have been obtained /15/ in the energy range of the strong $3p \rightarrow 3d$ and $4d \rightarrow 4f, 5f$ excitations, leading to a discussion of the Z-dependence of the strength, shape and decay channels of the giant resonances. Another example of such an excitation below the inner 3p thresholds is given by copper for which both experimental /16/ and theoretical /17/ studies of resonant satellites driven by the super-Coster-Kronig decay of the resonant excitation $3p^6 3d^{10} 4s^2 \rightarrow 3p^5 3d^{10} 4s^2 {}^2P$ have been achieved.

The present theoretical study aims to focus on the various paths of decay of both excitations $4d^{10} 5s^2 5p^5 ({}^2P_{3/2}) \rightarrow 4d^9 5s^2 5p^6 ({}^2D_{5/2}, {}^2D_{3/2})$ observed /7/ recently for atomic I through photoelectron spectra, produced by laser induced dissociation of molecular iodine and excited with synchrotron radiation in the region below the 4d ionisation thresholds.

2 - THEORETICAL PROBLEMS RELATIVE TO PHOTOELECTRON SPECTRA OF IODINE

Let us recall first the major experimental results displayed in /7/ :

1°) a constant energy spectrum (CES) of iodine shows that the spectrum below the 4d ionisation thresholds is dominated by two strong resonances which are assigned to the transitions mentioned above:

The position of these two lines, respectively 46.2eV and 47.9eV, is in relative good agreement with previous absorption measurements of Pettini et al./18/.

For both ${}^2P_{3/2} \rightarrow {}^2D_{5/2}$ and ${}^2P_{3/2} \rightarrow {}^2D_{3/2}$ transitions, I have calculated the factor $R_{line} [S L J, S' L' J']$ containing the whole dependence of the electric dipole matrix element on J, J' and the spin. The relative strengths of the lines within a multiplet are given by R_{line}^2 whose values for both transitions are:

$$R_{line}^2 [1/2 \ 1 \ 3/2, 1/2 \ 2 \ 5/2] = 1.2$$

$$R_{line}^2 [1/2 \ 1 \ 3/2, 1/2 \ 2 \ 3/2] = 0.13$$

Their ratio close to 9 is in good agreement with the experimental ratio (about 10) which means that the ratio of absorption intensities is geometrical and independent on the background cross section whose contributions are coming from direct ionisation into $5p^{-1}$ and $5s^{-1}$ channels. This work will be devoted to the decay and relaxation processes of the major resonance located at 46.2 eV, the other one having the same behaviour, although the corresponding experimental spectra display a weaker enhancement of lines at 47.9 eV.

2°) both photoelectron spectra recorded off ($h\nu = 45.5$ eV) and on ($h\nu = 46.2$ eV) the major resonance ($2^2P_{3/2} \rightarrow 2^2D_{5/2}$) display numerous lines whose enhancement is evident only for the second spectrum. A first glance allows to distinguish 3 regions along the binding energies axis. Whereas the 10-15 eV binding energy interval corresponds without ambiguity to the various $5p^{-1}$ channels [$3P$, $1D$ and $1S$ terms of the $5p^4$ configuration], the 20-30 eV interval is too broad to be assigned to $5s^{-1}$ lines (since a relaxed single configuration Hartree-Fock calculation relative to both $3P$ and $1P$ terms of the $5s5p^5$ configuration locates the corresponding lines respectively at 22.4 and 27.2 eV, i.e. within a 4.8 eV interval). Beyond 30 eV, isolated lines overlapping a broad continuum let us think to increasing shake-off processes, as soon as the double ionisation first threshold ($5p^3$ configuration) is reached, i.e. around 29.5 eV. These features are clearly displayed in Figure 1 /7/ :

Fig.1 - Experimental photoelectron spectra /7/ recorded on [46.2 eV] and off [45.5 eV] resonance. Assignment of peaks labelled 1 to 11 is explained in section 3. Shaded area indicates the double ionisation limit $5p^3$.

Coming back to the 10-15 eV binding energy interval and the $3P$, $1D$ and $1S$ lines of the final ionic states ($5p^4$ configuration), it is remarkable to notice that both spectra [off and on resonance] display branching ratio values different from one another and from those observed and calculated at $h\nu = 21.2$ eV par Berkowitz et al. /19/. This feature is easily understood if we refer to our previous theoretical work /20/ relative to the determination of both partial and total $5p$, $5s$ and $4d$ cross sections of atomic iodine, using several sophisticated theoretical models, and which allows to point out that the energy range considered here corresponds to the Cooper minimum region for both $5p$ and $5s$ photoionisation processes. In other words, whereas at 21.2 eV, a geometrical but non statistical branching ratio interprets correctly the experimental spectra, further on below the $4d$ ionisation thresholds, a different position of the Cooper minimum according to the channel considered has to be taken into account to explain the different values of the branching ratio on the off-resonance spectrum. As for the on-resonance spectrum, the enhancement factors are the major points of this paper and their determination will be made explicit in the next section when pointing out the origin of extra lines usually identified as satellite lines.

Because of the similarity of configurations for the resonant excited state of iodine and the $4d$ ionised state of xenon, we can mention now some similar configurations participating to both types of core hole relaxation. In iodine, we could remark above that they are singly-ionised configurations whereas in xenon, they correspond to doubly-ionised states, in agreement with a normal $4d$ Auger spectrum for xenon likely to be compared to the resonant Auger spectrum of I.

Both excitation (or ionisation) and decay main processes may be described in L-S coupling as follows:

Excitation or ionisation :

According to this scheme, the on-resonance photoelectron spectrum of iodine at 46.2 eV should have similarities with the 4d normal Auger spectrum of xenon, recorded previously / 8, 9, 10/ and on the contrary, be very different from the resonant Auger spectra mentioned in the Introduction /11, 12, 13, 14/ and relative to the decay of Rydberg states located below an inner-shell threshold. My calculations reported below are necessary to understand these similarities and differences, but their major purpose lies in pointing out the origin of extra decay channels which are not accounted for by processes D1, D2 and D3.

3 - THEORETICAL CALCULATIONS AND RESULTS

In a previous theoretical paper /21/, using the multichannel scattering formalism, I have established general formulae giving the resonant cross sections in the various decay channels for an excited state located below an inner shell threshold. The parametrisation of the general formula giving the photoemission cross section σ_μ in a μ channel, in the vicinity of the resonance is written in terms of Fano's parameters/22/ well known in photoabsorption: q the profile index and ξ_0 the energy parameter such as $\frac{1}{\xi_0} = \frac{\Gamma_t}{2(E - E_r)}$

Γ_t being the total linewidth and E_r the position of the resonant state.

$$\sigma_\mu = |Q_\mu^0|^2 \left[1 + \alpha^2 \frac{q^2 + 1}{\xi_0^2 + 1} + 2\alpha \frac{\xi q - 1}{\xi_0^2 + 1} \right] \quad (1)$$

In this formula Q_μ^0 represents the non resonant background cross section and $\alpha(\mu E)$ parameter characteristic of each channel defines the fraction of the dipole amplitude Q_μ^0 that passes through the eigenchannel $|1E\rangle$ which involves the whole interaction with the resonance, and satisfies the relation:

$$\alpha(\mu E) Q_\mu^0 = \frac{\sqrt{\Gamma_\mu}}{\sqrt{\Gamma_t}} \langle 1E | Q | 0 \rangle \quad (2)$$

$$\text{with } \Gamma_\mu \text{ such as : } \Gamma_t = \sum_\mu \Gamma_\mu \quad (3)$$

$$\text{and } \langle 1E | Q | 0 \rangle = \frac{1}{\sqrt{\Gamma_t}} \sqrt{\Gamma_\mu} Q_\mu^0 \quad (4)$$

Expression (4) provides with the relation between the resonant dipole matrix element and the various non resonant background matrix elements in each physical channel μ . In (1) simplifications of the formula may occur if Q_μ^0 is ≈ 0 or very weak since in this latter case, the predominant term in (1) is the enhancement factor $(q^2 + 1)/(\xi_0^2 + 1)$, q very large leading to a nearly Lorentzian profile in the channel considered, similarly to an Auger decay channel. The corresponding formula giving the cross section becomes:

$$\sigma_\mu = \frac{\Gamma_\mu}{\Gamma_t} \langle 1E | Q | 0 \rangle^2 \frac{q^2 + 1}{\xi_0^2 + 1} \quad (5)$$

From (5) we infer a very simple expression for the branching ratio relative to two decay channels μ_1 and μ_2 under the form of the ratio of corresponding partial linewidths:

$$\frac{\sigma_{\mu_1}}{\sigma_{\mu_2}} = \frac{\Gamma_{\mu_1}}{\Gamma_{\mu_2}} \quad (6)$$

Because of very small cross sections in the decay channels relative to processes D1, D2 and D3, as emphasized in the previous theoretical work /20/ the on resonance spectrum in Figure 1 should display lines whose branching ratios satisfy both (5) and (6) whereas the interpretation of the off-resonance spectrum should require the determination of the various non resonant background cross sections in order to account for the variation of intensities of lines with the energy of the ejected electron ξ .

As a consequence, in a first step, my calculations have been focused on the various Auger decay rates $4d \rightarrow 5p, 5p [N_5 O_{23} O_{23}]$, $4d \rightarrow 5s, 5p [N_5 O_1 O_{23}]$ and $4d \rightarrow 5s, 5s [N_5 O_1 O_1]$ involved in processes E, D1, D2 and D3 explicitied above.

The determination of these Auger rates Γ_A has been achieved in L-S coupling for each final term A of the configurations above by summing the contributions relative to each channel μ considered. Each contribution is expressed as a linear combination of direct and exchange matrix elements whose radial part is defined below, using the following notations:

$n_1 l_1$ (4d here) represents the initial hole,

ξl_2 refers to the Auger hole in the continuum,

whereas $n_3 l_3$ and $n_4 l_4$ describe both electrons participating to the Auger process, i.e. filling the holes;

$$\Gamma_A = \sum_{\mu} T_{\mu A}^2 \quad [n_1 l_1 \rightarrow n_3 l_3, n_4 l_4] \quad (7)$$

$$\text{where: } T_{\mu A} = \langle \Phi [n_1 l_1, \xi l_2, L'S'J'M'] \left| \frac{2}{r_{12}} \right| \Phi [n_3 l_3, n_4 l_4, LSJM] \rangle \quad (8)$$

Let us remark that for the same A term, the various μ differ by l_2 only.

The wavefunctions introduced in (7) and (8) are Hartree-Fock ones [single configuration] relative to the final ionic state of I^+ . The matrix element in (8) is written in L-S coupling as follows:

$$T_{\mu A} = (-1)^{L+1/2} \sum_k [A_k R_k(3,4,1,2) + B_k R_k(4,3,1,2)] \delta_{MM'} \delta_{SS'} \delta_{LL'} \delta_{JJ'} \quad (9)$$

A_k and B_k in (9) are angular parts expressed in terms of 3j and 6j symbols, and the generalised Slater integrals R_k are given by:

$$R_k(3,4,1,2) = \iint P_{n_3 l_3}(i) P_{n_4 l_4}(j) \frac{2r_i^k}{r_{ij}^{k+1}} P_{n_1 l_1}(i) P_{\xi l_2}(j) dr_i dr_j \quad (10)$$

The exchange integral is deduced from the direct one above by exchanging $n_3 l_3$ and $n_4 l_4$. For a more compact notation, we will refer to $D(k, l_2)$ for R_k in (10) and to $E(k, l_2)$ for the corresponding exchange integral. Within these approximations I have calculated Γ_A relative to the final 6 terms: $3P$, $1D$ and $1S$ of $5s^2 5p^4$, $3P$ and $1P$ of $5s 5p^5$ and $1S$ of $5s^2 5p^6$. The corresponding results are reported in Table 1 which mentions in addition to the corresponding binding energies the relative intensities. Despite a slight energy shift due to the mono configuration Hartree-Fock approximation, it is remarkable to notice that the first 3 values reproduce pretty well the relative intensities of the experimental spectrum in the 10-15 eV energy range. The $1D$ contribution is the dominant one and both $1D$ and $1S$ rates are more important than the $3P$ one leading to the conclusion that the branching ratio values at 46.2 eV are quite different from the branching ratios measured and calculated by Berkowitz et al./19/ at 21.2 eV; this result emphasizes the enhancement factors which characterize the resonant behaviour of the relaxation channels when $h\nu = 46.2$ eV.

Table 1 - Theoretical binding energies, expressions of the absolute intensity and relative intensities of the various lines corresponding to the final ionic states A of 3 configurations : $5p^4$, $5s5p^5$ and $5s^05p^6$

Final ionic state A	Binding Energy(eV)	Absolute intensity Γ_A	Relative intensity
3P	10.7	$\frac{81}{25} - [D(1,2) - D(3,2)]^2$	100
1D $5p^4$	12.2	$\frac{21}{25} - [D(1,2) + \frac{3}{7}D(3,2)]^2$ $+ \frac{6}{5}[D(1,0)]^2 + \frac{108}{35}[D(3,4)]^2$	217
1S	14.5	$\frac{3}{25}[2D(1,2) + 3D(3,2)]^2$	127
3P $5s5p^5$	22.4	$1.8[D(2,1) - E(1,1)]^2 + 2.7[D(2,3) - E(3,3)]^2$	6
1P $5s5p^5$	27.2	$0.6[D(2,1) + E(1,1)]^2 + 0.9[D(2,3) + E(3,3)]^2$	295
1S $5s^05p^6$	32.5	$[D(2,2)]^2$	251

In Table 1, the formulae which give the absolute intensities Γ_A are fundamental to explain the predominance of the singlets over the triplets. Indeed, a minus sign is between the two different integrals for the triplets whereas we find a plus sign in the singlet formulae. Noticing that both integrals have the same sign, it is nevertheless quite remarkable to point out that despite larger angular coefficients for the triplets than for the singlets, the latter ones are still greater. However, in case of 1D of the $5p^4$ configuration, because of the conservation of angular momentum rule, several values of l_2 [0, 2 and 4] bring their contribution, whereas only $l_2 = 2$ for both 1S and 3P . Anyway, the enormous difference between the 3P and 1P of the $5s5p^5$ configuration as the last column of Table 1 emphasizes it let us think that extra effects likely to modify the distribution of intensities should be considered in order to account for the experimental spectra. Moreover, the energy position of these levels distant of about 4 eV in the Hartree-Fock approximation [single configuration] is not in agreement with the intense resonant lines displayed in Figure 1 by the on-resonance spectrum and spreading over 8 eV [between 20 and 28 eV]. That is why I have resumed the description of the residual ionic states in this region by taking into account the strong interaction with the satellite configurations $5s^25p^5d$, $5s^25p^36s$... This important effect has been emphasized for the normal 4d Auger spectrum of xenon /8, 10, 12/ which involves the same initial ionised configuration as the excited iodine $4d^95s^25p^6$ and the necessity of taking into account configuration interactions with the parent $5s5p^5$ configuration has been emphasized by several authors /23, 24, 25/ who tried to interpret some discrepancies between experimental spectra for xenon and relativistic random phase approximation [RRPA] calculations /26/ which neglect all correlation effects involving two-electron excitations.

That is why I have performed configuration interaction calculations within the multiconfiguration Hartree-Fock approximation /27/ for both 3P and 1P by optimizing a 5d correlation orbital and determining the mixing coefficients C_i of the 3 configurations in both developments:

$$\begin{aligned}
 &C_1[5s5p^5 \ ^3P] + C_2[5s^25p^3(^3P)\bar{5d} \ ^3P] + C_3[5s^25p^3(^1D)\bar{5d} \ ^3P] \\
 &C_4[5s5p^5 \ ^1P] + C_5[5s^25p^3(^3P)\bar{5d} \ ^1P] + C_6[5s^25p^3(^1D)\bar{5d} \ ^1P]
 \end{aligned}
 \quad (11)$$

As shown previously by Hansen /28/, the multiconfiguration Hartree-Fock approximation (MCHF) using one basis state to represent the effect of the d series can reproduce the result of an elaborate series perturbation calculation. Thus, the 5d orbital in [11] is a correlation orbital which represents the whole d series and has little resemblance to a Rydberg orbital being located much closer to the nucleus.

My calculations used the 3 basis functions $5s5p^5$, $5s^25p^3(^3P)5d$ and $5s^25p^3(^2D)5d$, the 5s and 5p orbitals being constrained to be the same for the 3 basis functions. Due to Brillouin's theorem, as explained by Froese-Fischer/27/, the 5d orbital function represents contributions from both the bound and continuum members of the d series. Using the Froese-Fischer code /29/, I have determined the lowest eigenvalues for both 3P and 1P in developments [11] by optimizing the 5d orbital. Then, by diagonalizing both 3X3 matrices, I have determined four higher eigenvalues, corresponding to 2 triplets and 2 singlets. Whereas the lowest eigenvalues correctly represent the $5s5p^5$ states of ionized iodine, the others describe roughly the importance of physical excited states $5s^25p^3(^3P)5d$ and $5s^25p^3(^2D)5d$, since the 5d orbital is a correlation one. However, because the most important configuration interaction effects between the parent $5s5p^5$ configuration and the double excitation channel lie in the double excited satellites represented by both states : $5s^25p^3(^3P)5d$ and $5s^25p^3(^2D)5d$

we can consider that both weights and eigenvalues resulting from the minimisation followed by a diagonalization explained above are a pretty good first approximation which we can improve by scaling the Slater integrals. The scaling factor is chosen within the purpose of decreasing the spreading energy interval (over 11 eV in my calculations) for the 6 lines up to the experimental value (about 8 eV). Using a scaling factor value of 0.65, and keeping the same values for the weights, the 6 theoretical lines corresponding to 3 3P and 3 1P reproduce pretty well the major features of the resonant experimental spectrum over the 20-28 eV energy interval.

Table 2 below displays these theoretical results by providing us for each final ionic state, the corresponding binding energy, the kinetic energy of the Auger electron, the relative intensities of the lines and the respective weights of the parent configuration [$5s5p^5$] and of each satellite state.

Table 2 - Theoretical results corresponding to the binding energy E_B [in eV] and the kinetic energy [in Ryd.] of the ejected Auger electron for each final ionic state, the relative intensities of the various lines and the respective weights of both parent and satellite configuration. Let us recall the notation: P is the parent $5s5p^5$ configuration whereas S_1 and S_2 are respectively the satellite ones $5s^25p^3(^3P)5d$ and $5s^25p^3(^2D)5d$.

Final Ionic states	E_B (eV)	ξ_A (Ryd.)	P	$S_1(^3P)$	$S_2(^3P)$	$S_1(^1P)$	$S_2(^1P)$	Relative Intensity
3P	20.1	1.92	0.710	0.080	0.211			4
1P	21.6	1.81	0.332			0.073	0.595	16
3P	24.2	1.62	0.002	0.785	0.213			0
3P	26.1	1.475	0.28	0.135	0.576			2
1P	26.2	1.46	0.331			0.2885	0.381	34
1P	27.4	1.38	0.337			0.6385	0.024	44

Several important quantitative results are summarized in Table 2 and illustrate 4 major conclusions of this theoretical study of the double excitation satellites in iodine:

1°) Only the first 3P line has an important parent character (weight > 0.7). It

corresponds to the lowest calculated binding energy state and is likely to account for lines 1 and 2 in Figure 1.

2°) The $1P$ three lines share the contribution of the parent configuration with almost equal weight, the first one taking predominant contribution from the S_2 satellite $[5s^2 5p^3 ({}^2D) 5d]$ configuration] whereas the S_1 satellite $[5s^2 5p^3 ({}^2P) 5d]$ configuration] is stronger for the third line, the second one taking nearly equivalent contributions from the parent configuration and both satellites. Because of the existence of 3 major lines [referenced as 3, 7 and 9 in Figure 1] in both on and off resonance spectra of figure 1, I think that we may tentatively assign lines 3, 7 and 9 to these three $1P$ calculated states in so far as static correlation effects introduced via the configuration interaction mentioned above account for the position and the composition of final ionic states which are the most likely to correspond to intense lines since in absence of initial correlation effects, only the $5s5p^5$ ionic configuration is involved in the dipole matrix element. This point will be emphasized in the fourth conclusion below.

3°) Moreover, the important spreading of the 6 lines in my calculations (about 8 eV after scaling the energy Slater integrals) allows to point out not only the static correlation effects due to different weights for the various configurations, but also dynamic correlation effects via the variation of the Auger decay rate with the kinetic energy ξ_A of the Auger electron. Indeed, as mentioned above, not only the $3P$ and $1P_A$ contributions display a very different variation, the first one always smaller than the second one, but the variation of $\Gamma_A ({}^1P)$ increases dramatically when ξ_A decreases, i.e. the binding energy E_B is increasing. In Table 2 which displays the variation of both the binding energy and the kinetic energy of the Auger electron, as well as the relative intensities of the various lines, we can point out the increasing of $1P$ intensities as long as E_B is increasing, despite the predominance of the satellite configurations weights over those of the parent one.

4°) Coming back to the approximation which consists in describing the initial excited state by the $4d^9 5s^2 5p^6$ configuration only, the contribution to the various dipole matrix elements as well as the various decay matrix elements Γ_A

may come from the parent final ionic configuration only. As a consequence, the configuration interaction effects between the parent configuration and the satellite ones allow to push down the various levels, and to locate them in good agreement with experimental results but does not bring extra intensity to the lines if corresponding configuration interactions are not introduced in the description of the initial states, both the ground state and the excited one.

Indeed, it is clear and evident that introducing the following configurations in the description of the ground state of iodine :

$$4d^{10} 5s^2 5p^5 + 4d^{10} 5s^2 5p^3 5d^2 + 4d^{10} 5s^2 5p^3 6s^2 + 4d^{10} 5s^2 5p^3 6d^2 + \dots \quad ({}^2P)$$

leads to describe the initial excited state located at 46.2 eV by a linear combination of the various configurations below:

$$4d^9 5s^2 5p^6 + 4d^9 5s^2 5p^4 5d^2 + 4d^9 5s^2 5p^4 6s^2 + 4d^9 5s^2 5p^4 6d^2 + \dots \quad ({}^2D)$$

The Auger decay of states thus represented involves the two electron satellite configurations discussed above and let us think that a part of the contribution from the parent configurations could be redistributed over the other configurations of the development above, leading to extra contributions to the intensities whose importance is not yet known. Further theoretical work within the framework of a more rigorous study including both static and dynamic correlation effects should take into account these extra contributions in order to improve the theory-experiment agreement.

4 - CONCLUSIONS

The theoretical work presented in this paper has shown the existence of important two electron satellites in the 5s photoelectron spectrum of iodine, spread over about 8 eV and whose intensity is greatly enhanced at the 46.2 eV energy which corresponds to the $2P \rightarrow 2D$ transition from the $2p$ to the $2d$ subshell:

This transition in iodine gives rise to an absorption resonance which decays into many channels, including $5p^{-1}$ ones, by contrast to the case of rare gases when Rydberg states located below the 4d thresholds are excited. Whereas lower binding energies correspond to direct 5p ionisation channels [final ionic configuration $5s^2 5p^4$] with predominant Auger decay rates for singlet states, increasing binding energies opens new decay channels which cannot be described correctly by a single final ionic configuration $5s 5p^5$. Strong configuration interactions with two-electron excitation satellite configurations involving 5d 6s, 6p and 6d orbitals leads to numerous extra lines spread over about 10eV. As a consequence, the position of the resonant lines in the corresponding channels is determined by the respective weights of both parent and satellite configurations. However, the determination of their intensity would require extra calculations relative to the weights of the corresponding configurations in the excited initial state, as explained at the end of section 3, and to the corresponding Auger decay rates into the satellite channels. Using here less elaborated approximations, I have nevertheless pointed out that introducing only satellite configurations in the final ionic state is successful to explain the existence of 3 small lines assigned as 3P (lines 1, 4 and 5 in fig.1) and 3 major ones which share with equal parts the total Auger rate in the parent $5s 5p^5$ (1P) channels. Because of the most important weights for the double excitation satellite configurations $5s^2 5p^3(^2P)5d$ and $5s^2 5p^3(^2D)5d$ these major lines can be considered as 5d satellite lines and take the place of parent ones, although the major contribution to the intensity seems to come from singly ionised configurations; this point should deserve further attention and later development. Moreover, the large spreading of these lines emphasizes dynamical correlation effects due to the large variation of the Auger decay rates when the energy of the Auger electron decreases, i.e. the binding energy of the residual ionic states increases. An increased intensity of the lines located further in energy is observed also in the normal Auger 4d spectrum of xenon /8, 9, 10/. However, because the final ionic states refer to a doubly-ionised atom in xenon, instead of a singly-charged ion in iodine, both results are not quantitatively similar in so far as this difference leads to a different sharing of the parent intensity between the various satellites.

In addition to the 5 lines mentioned above and labelled 1, 2, 3, 7 and 9 in the resonant experimental spectrum /7/, some extra lines whose intensity is much weaker have been observed. Most ones correspond probably to shake-up $5s 5p$ np satellites and 6s or 6d double excitation satellites but a few ones may also have their origin in spin-orbit effects, which increase the intensity of triplet states on one hand and mix both 3P and 1P issued from each core term 2P and 2D of $5p^3$ on the other hand. This core spin-orbit splitting is probably the origin of both lines 6 and 8 which accompany lines 7 and 9 respectively, as well as of a certain enhancement of lines 4 and 5.

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