Calculation of $4d - nf$ oscillator strengths in Xe^{q+} ions

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Photoabsorption by the $4d^{10}$ subshell is dominated by the strong $4d \to nf, \varepsilon f$ transition. It possesses a number of interesting features defined largely by the nature of the final state. (The $4d \to np, \varepsilon p$ transition is relatively weak.) For neutral atoms between Pd and Cs the $4d \to nf, \varepsilon f$ strength lies almost entirely in the continuum, forming a broad maximum of ~ 25 Mb about 30 eV above the $4d$ ionization threshold. This feature is caused by a specific double-well shape of the effective potential for the f electrons due to an interplay between the repulsive centrifugal and attractive screened nuclear potentials. The inner well of the potential for these atoms is not deep enough to support a bound state. However, it creates an f-wave resonance. The resonance wavefunction has a strong overlap with the $4d$ subshell, which results in the "giant" resonant maximum in the $4d$ photoabsorption.

The integral oscillator strength of the $4d \to \varepsilon f$ resonance is close to 10 (the number of $4d$ electrons) and accumulates most of the strength of the $4d$ photoabsorption. In order to describe $4d$ photoabsorption theoretically, one needs to use an accurate potential of the f electron. In particular, the strong $4d - nf(\varepsilon f)$ exchange interaction must be included correctly, e.g., by coupling the dipole-excited f electron and $4d$ hole into the ^1P term (in LS scheme) in the Hartree-Fock approximation. Another important effect which is *beyond* any single-particle (e.g., Hartree-Fock) approximation is a collective response of the ten $4d$ electrons to the photon field. This *electron correlation* effect means that an electron can be removed from a many-electron target not only after directly absorbing a photon, but also because of the change in the mean field of the atom in the electromagnetic wave. Such correlation is accounted for by the random phase approximation (RPA), which has been a powerful tool for understanding many features of atomic photoabsorption (see, e.g., Refs. [1, 2]).

Moving from Cs to Ba, La and lanthanides, one observes a rapid and dramatic change in the $4d$ photoabsorption. The $4d$ oscillator strength is shifted from the continuum to the nf and in particular, $4f$ state. This change is driven by the deepening of the f-wave potential. It follows a transformation of the diffuse Rydberg-type $4f$ orbital into a tightly bound valence-type wavefunction with a strong overlap with the $4d$ subshell; the so-called "collapse" of the $4f$ orbital. Accordingly, strong discrete lines become the dominant feature of the $4d$ photoabsorption. A similar effect takes place if an atom with $Z \leq 56$ (e.g., Ba, Cs, Xe or, say, Sn) is ionized. It has been studied widely for a number of ions (see, e.g., Ref. [3] and references therein), including Xe^{+} and Xe^{2+} [4].

The present paper aims to quantify such change in the oscillator strength of the $4d - 4f$ peak in Xe^{4+}, Xe^{5+} and Xe^{6+}, and it is interesting to compare the measured values with the results of calculations. Table I shows the oscillator strengths of $4d - 4f$ and $4d - 5f$ transitions calculated using nonrelativistic HF and random phase approximations for Xe^{6+} through to Xe^{+}. The difference between the results obtained with the length (L) and velocity (V) forms of the dipole operator can be used to gauge the size of electron correlation effects and the uncertainty

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in the calculations.

TABLE I: Oscillator strengths of $4d-4f$ and $4d-5f$ transitions in Xe^{q+} ions. Best predictions are shown in bold face.

Ion	Calc. type	I_{4d} (eV)	ω_{4d-4f} (eV)	f_{4d-4f} L	V	ω_{4d-5f} (eV)	f_{4d-5f} L	V
Xe^{6+}	HF	149.8	102.3	7.39	4.46	118.7	2.88	1.59
	RPA, 1 ch.[a]	–	100.8	6.70	6.37	117.8	1.94	1.86
	RPA, 5 ch.[b]	–	100.7	**6.78**	6.55	117.8	**1.97**	1.88
Xe^{5+}	HF	135.3	99.6	5.95	3.61	112.4	2.66	1.52
	RPA, 1 ch.[a]	–	98.5	5.62	5.22	111.7	2.00	1.87
	RPA, 4 ch.[c]	–	98.2	**5.43**	5.06	111.6	**1.96**	1.84
Xe^{4+}	HF	121.6	96.4	4.28	2.60	105.7	2.10	1.24
	RPA, 1 ch.[a]	–	95.7	**4.24**	3.88	105.2	**1.76**	1.63
Xe^{3+}	HF	108.7	92.7	2.45	1.50	98.6	1.36	0.82
	RPA, 1 ch.[a]	–	92.3	**2.60**	2.35	98.3	**1.30**	1.19
Xe^{2+}	HF	96.7	88.1	0.78	0.49	91.1	0.58	0.35
	RPA, 1 ch.[a]	–	88.0	**0.89**	0.80	91.1	**0.63**	0.57
Xe^{+}	HF	85.6	82.0	0.058	0.035	83.3	0.055	0.033
	RPA, 1 ch.[a]	–	82.0	**0.062**	0.054	83.3	**0.059**	0.052

[a]Calculation includes one channel: $4d \to nf, \varepsilon f$.
[b]Calculation includes five channels: $5s \to np, \varepsilon p$, $4d \to nf, \varepsilon f$, $4d \to np, \varepsilon p$, $4p \to nd, \varepsilon d$, and $4p \to ns, \varepsilon s$.
[c]Calculation includes four channels: $4d \to nf, \varepsilon f$, $4d \to np, \varepsilon p$, $4p \to nd, \varepsilon d$, and $4p \to ns, \varepsilon s$.

The RPA method is fully applicable to (and, hence, more reliable for) systems with closed shells, such as Xe^{6+} $4d^{10}5s^2$, and we examine this ion first. The best HF calculation of the $4d^95s^2nf\ ^1P$ excited states, gives L and V oscillator strengths that are far apart. In contrast, the RPA calculation which includes a single channel, $4d \to nf, \varepsilon f$, brings the L and V results much closer. Note that the correlation contribution is especially large for the oscillator strength in the V-form. RPA corrections also produce a sizeable shift in the transition energies ω_{4d-4f} and ω_{4d-5f}. The $4d \to nf, \varepsilon f$ channel is by far the strongest photoabsorption channel in this photon energy range. Hence, other channels have relatively little influence on the $4d-nf$ oscillator strengths (especially in the L form). Thus, the largest five-channel calculation gives values of $f^{(L)}_{4d-4f}$ and $f^{(L)}_{4d-5f}$ within 1–2% of the one-channel results.

Since the $4d-nf$ transition energies lie above the ionization threshold of the Xe^{6+} ion, the $4d^95s^2nf$ states autoionize into the $4d^{10}5s\varepsilon p$ channel. Figure 1 shows the corresponding photoionization cross section with prominent $4d-nf$ peaks. The autoionizing widths of the $4d-4f$ and $4d-5f$ excitations are 0.277 eV and 0.110 eV, respectively.

RPA can also be applied in a rigorous way to systems with one electron above the closed shells like Xe^{5+} $4d^{10}5s^25p$. However, given the small effect of all channels other than $4d \to nf, \varepsilon f$ on the $4d-nf$ strengths, we estimate these strengths for Xe^{q+} (q = 1–5) from single-channel RPA calculations. The exception is made for Xe^{5+} where a four-channel result is also shown. When applying RPA to open-shell ions, the $5p$ electrons are treated as spectators. Their average field contributes to the potential acting on the f electron and affects the excitation energy, while the important $4d^9nf\,^1P$ coupling is preserved. Calculations show that in Xe^{4+} the energy of the $4d-6p$ excitation is very close to that of the $4d-4f$ line. Although this may result in configuration mixing and a more complicated structure of the line, the total oscillator strength is dominated by the "original" $4d-4f$ strength (in the HF approximation $f^{(L)}_{4d-6p} = 0.17$ and

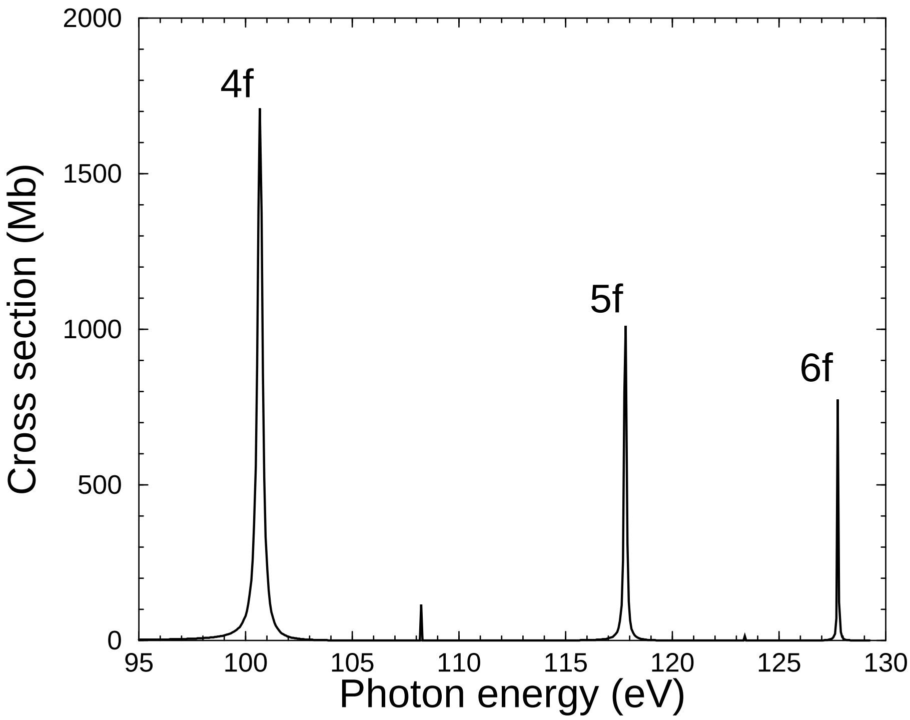

FIG. 1: $5s$ photoionization cross section of Xe^{6+} from the five-channel RPA calculation (L form) including $5s \to np, \varepsilon p$, $4d \to nf, \varepsilon f$, $4d \to np, \varepsilon p$, $4p \to nd, \varepsilon d$, and $4p \to ns, \varepsilon s$.

$f^{(V)}_{4d-6p} = 0.15$).

The calculated oscillator strengths of the $4d-4f$ transition show a near-linear dependence on the charge of the ion between Xe^{+} and Xe^{6+}. For Xe^{6+} both f_{4d-4f} and f_{4d-5f} are in good accord with the measurements. On the other hand, the experiment shows a much more rapid drop of the $4d-4f$ oscillator strength as the ion charge decreases. This discrepancy is not easy to explain, given the good agreement between the RPA calculations and experiment for Xe^{6+} and neutral Xe (where it correctly describes the broad resonance in the continuum).

One possibility is that in the ions with open $5p$ subshell, the $4d-4f$ transition can share its oscillator strength with nearby *satellites*, i.e. other excited states, due to configuration mixing. The ionization cross sections of Xe^{+} and Xe^{2+} [4] give some support for such interpretation. While they do show sharp peaks of the $4d-nf$ lines, these peaks by no means account for the total oscillator strength *below* the $4d$ ionization threshold. A very large portion of this strength takes the form of a background, possibly containing numerous smaller resonances. Given that all other *direct* dipole transitions apart from $4d-nf$ and $4d-np$ are weak in this photon energy range, one may infer that the oscillator strengths of these transitions are redistributed between a large number of satellite lines. However, the present measurements for Xe^{5+} and Xe^{4+} did not reveal any strong additional lines in the neighbourhood of the $4d-4f$ peaks. Hence the discrepancy between experiment and theory remains an open question.

A smaller but nonetheless interesting question is the difference between the simple Breit-Wigner shapes of the $4d-4f$ and $4f-5f$ transitions in RPA and the experimental data. Indeed, Fig. ?? suggests that the $4d-4f$ transition contains contributions of two lines, a stronger one at 97.5 eV, and a weaker one at 98 eV. Likewise, Fig. ?? clearly shows two lines at 115.3 and 116.1 eV, the former probably, with its own internal structure. In principle, such additional structure in the lines could be caused by the spin-orbit splitting of the $4d$ orbital (whose magnitude is equal to 2 eV [5]). To explore this question theoretically, we have performed relativistic Dirac-Fock (DF) and configuration-interaction (CI) calculations of the

TABLE II: Transition energies and oscillator strengths of the $4d-4f$ and $4d-5f$ transitions in Xe^{6+} from the relativistic CI calculations.

Initial state	ω_{4d-4f}	f_{4d-4f}		ω_{4d-5f}	f_{4d-5f}	
	(eV)	L	V	(eV)	L	V
Xe^{6+} $4d^{10}5s^2\ ^1S_0$	100.9	6.9	4.5	117.0	2.8	1.7
Xe^{6+} $4d^{10}5s5p\ ^3P_0$	101.3	6.9	4.5	117.8[a]	2.3	1.4

[a]The $4d-5f$ transition in the metastable ion, Xe^{6+} $5s5p\ ^3P_0$, gives rise to a few satellites, the strongest of which, at 117.0 eV, has the oscillator strengths of 0.19 (L) and 0.11 (V).

relevant transitions. The DF ionization potentials of the two fine-structure components of the $4d$ subshell are: $I_{4d_{5/2}} = 146.6$ eV and $I_{4d_{3/2}} = 148.7$ eV. This splitting, however, turns out to be much smaller than the $4d-4f$ and $4d-5f$ exchange interaction. As a result, both dipole transitions give rise to a single dominant line ($^1P_1$ term), as one would expect in the LS-coupling scheme. The corresponding transition energies and oscillator strengths are reported in table II.

Our CI calculations contained a relatively small number of excited-state configurations $4d^9 5s^2 nf$ ($n = 4, 5, 6, 7$), and we used physical $4f$ and $5f$ DF orbitals, and pseudo-orbitals for $n = 6$, 7 (to take some account of higher n and εf continuum). Important RPA-type correlations remained beyond this CI scheme, which resulted in a marked difference between the L and V results. This difference and the values of f_{4d-4f}, as well as the transition energies, are similar to those obtained in the nonrelativistic HF approximation (Table I). Most importantly, the relativistic calculation confirms that the $4d-4f$ and $4d-5f$ transitions have a simple single-line structure.

However, it is possible that the ion beam contained a fraction of ions in metastable states. The $4d-nf$ lines in the metastable ions can be shifted with respect to their ground-state positions. In principle, the lines can also have a more complicated structure. To investigate this possibility we have calculated the $4d-nf$ excitation energies and oscillator strengths from the lowest metastable state, Xe^{6+} $5s5p\ ^3P_0$ (see Table II). In spite of a larger number of possible final state (due to the open-shell nature of the initial state) we observe that both the $4d-4f$ and $4d-5f$ transitions contain essentially a single strong peak. Their oscillator strengths have changed little, although the main $4d-5f$ line has lost part of its oscillator strengths to a few weaker lines. What is important though, is that the energies of the main $4d-4f$ and $4d-5f$ lines in Xe^{6+} $5s5p\ ^3P_0$ are shifted by 0.4 and 0.8 eV, respectively, relative to the ground-state Xe^{6+}. These shifts are comparable to the spacings between the principal and secondary peaks in Figs. ?? and ??. Therefore, the structure of the $4d-4f$ and $4d-5f$ transitions observed in experiment can be considered as evidence that the Xe^{6+} beam contained about 30% of long-lived metastable states. To test this idea we have constructed the cross section as a sum of Breit-Wigner shapes using the transition energies from Table II, the oscillator strengths from Table I, and the autoionizing widths from the RPA calculation. Assuming that 67% of the ions are in the ground state $5s^2\ ^1S_0$ and 33% are in the $5s5p\ ^3P_0$ state, we obtain the line shapes that are similar to those observed in experiment, see Fig. 2.

The shapes of the cross sections in the $4d-4f$ and $4d-5f$ regions in Xe^{5+} (Fig. ??) also indicate that they consists of a number of individual lines. To analyse this structure, we have performed a relativistic CI calculation of the excited states of Xe^{5+}. We used 32 configurations of the type $4d^9 5s^2 5p\, nf$, with physical orbitals for $n = 4$, 5 and pseudo-orbitals for $n = 6$, 7. The ground state of Xe^{5+} is $4d^{10}5s^2 5p\ ^2P_{1/2}$. There is also a metastable state $4d^{10}5s^2 5p\ ^2P_{3/2}$, lying 1.95 eV above it. The $5^2P_{3/2}$ state decays to the ground state by $M1$ transition, and we have estimated its lifetime to be 7 ms.

CI calculations show that the $4d-4f$ transition in Xe^{5+} $5^2P_{1/2}$ contains two strong lines,

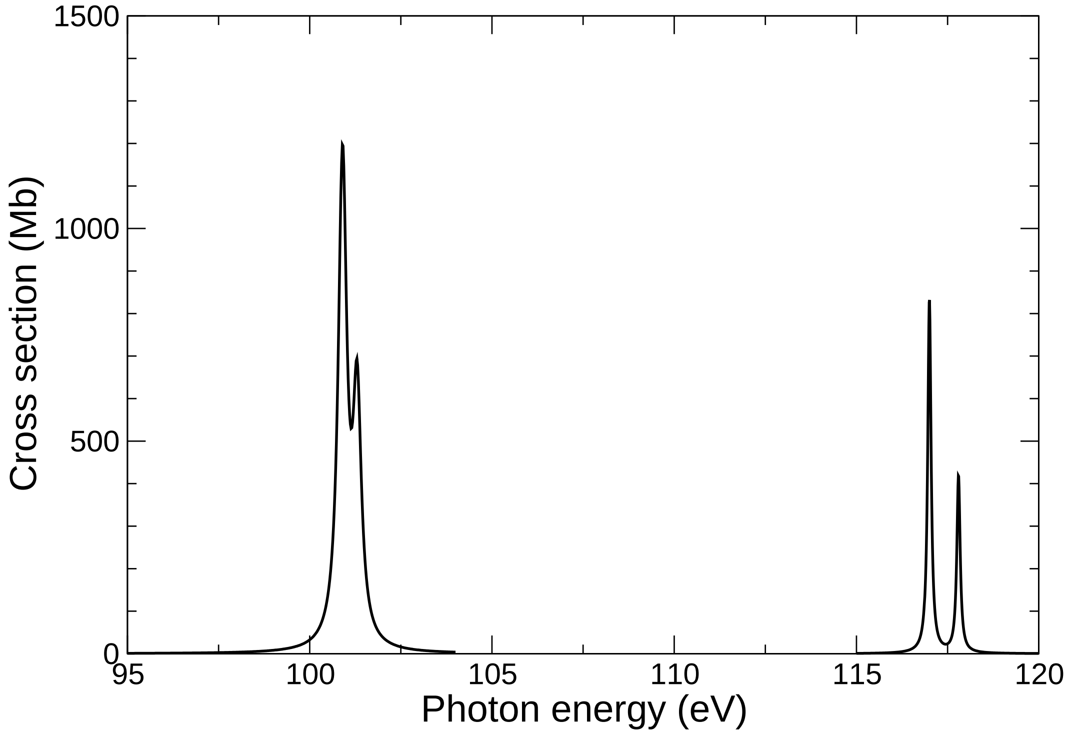

FIG. 2: Xe^{6+} photoionization cross sections in the region of $4d-4f$ and $4d-5f$ transitions calculated for a mixture containing of 67% ground state ions, $5s^2\ ^1S_0$, and 33% metastable ions, $5s5p\ ^3P_0$. See text for details.

while that in Xe^{5+} $5^2P_{3/2}$ contains three strong lines. Their energies and oscillator strengths are shown in Table III. The total oscillator strength of the two lines from the $5^2P_{1/2}$ state is 5.74, while that of the three lines from the $5^2P_{3/2}$ state is 5.84. These numbers are between the HF and RPA values in Table I. The intensities of individual lines in $5^2P_{1/2}$ are in the $2:1$ ratio, while those in $5^2P_{3/2}$ relate as $2:3:1$. This simple picture follows from the fact that the $4d \to 4f$ transition produces a hole-particle excitation $4d^{-1}4f$ with the term $^1P_1$ determined by the $E1$ photon. Its total angular momentum is then coupled with the angular momentum j of the "spectator" $5p$ electron, forming either two $(j = 1/2)$ or three $(j = 3/2)$ states. The resulting intensities are proportinal to the squares of the corresponding Clebsch-Gordan coefficients.

Similarly, there are two strong $4d-5f$ absorption lines in Xe^{5+} $5^2P_{1/2}$. In this case, however, there is an additional weaker line at lower energy due to configuration mixing. The $4d-5f$ transitions from $5^2P_{3/2}$ contains three strong lines with angular momenta $J = \frac{3}{2}$, $\frac{1}{2}$ and $\frac{5}{2}$, which appear in a different order to those of the $4d-4f$ lines. The total oscillator strengths of these groups of lines obtained in CI are 2.28 and 2.35. These numbers are again between the HF and RPA values from Table I.

We can now test the effect of configuration interaction and metastable state on the shape of the line. In Figs. 3 and 4 we show the line shapes obtained by adding the Breit-Wigner contributions of individual transitions from Table III. The width of the individual lines in the $4d-4f$ and $4f-5f$ groups are assumed to be equal to the RPA values of the corresponding autoionizing widths, 0.220 and 0.0893 eV, respectively. We also use the best RPA oscillator strengths from Table I, and distribute the between the lines proportionally to their CI oscillator strengths. The experimental width of the $4d-4f$ maximum is greater than that of either 5^2P_J state. Hence it is likely that the ion beam contains both species. Figure 3 shows that a mixture of 67% of $5^2P_{1/2}$ and 33% of $5^2P_{3/2}$ states results in a line shape similar to that observed in the experiment. The shape of the $4d-5f$ transition contains three clearly separated peaks. Unlike the $4d-5f$ transition in Xe^{6+}, this structure is mostly due to configuration mixing rather than

TABLE III: Transition energies (in eV) and oscillator strengths (in L form) of the strong lines corresponding to the $4d-4f$ and $4d-5f$ transitions in Xe^{5+} $5^2P_{1/2}$ and $5^2P_{3/2}$, from relativistic CI calculations.

Initial state	J	Final state ω	f	Term
$5^2P_{1/2}$	$\frac{3}{2}$	97.64	3.86	$4f$ $^2D_{3/2}$
	$\frac{1}{2}$	97.80	1.88	$4f$ $^2P_{1/2}$
	$\frac{3}{2}$	109.94	0.33	$5f$ —
	$\frac{1}{2}$	110.24	0.80	$5f$ $^2P_{1/2}$
	$\frac{3}{2}$	110.51	1.15	$5f$ $^2D_{3/2}$
$5^2P_{3/2}$	$\frac{3}{2}$	97.85	1.97	$4f$ $^2P_{3/2}$
	$\frac{5}{2}$	97.90	2.93	$4f$ $^2D_{5/2}$
	$\frac{1}{2}$	98.33	0.95	$4f$ $^2S_{1/2}$
	$\frac{1}{2}$	110.54	0.80	$5f$ $^2P_{3/2}$
	$\frac{1}{2}$	110.62	0.40	$5f$ $^2S_{1/2}$
	$\frac{1}{2}$	110.63	1.15	$5f$ $^2D_{5/2}$

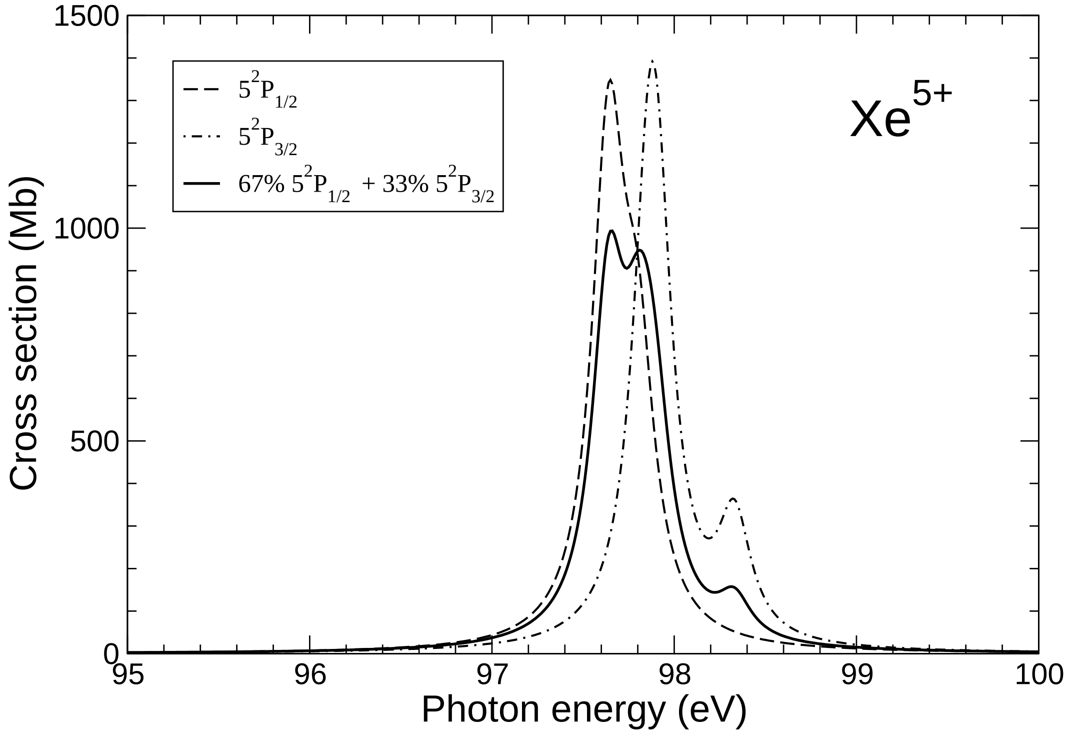

FIG. 3: Xe^{5+} photoionization cross sections in the vicinity of the $4d-4f$ transition calculated for the $5^2P_{1/2}$ and $5^2P_{3/2}$ states, and for a mixture of 67% ground and 33% metastable ions. See text for details.

the effect of metastable species. The latter, though, affects the shape of the main maximum.

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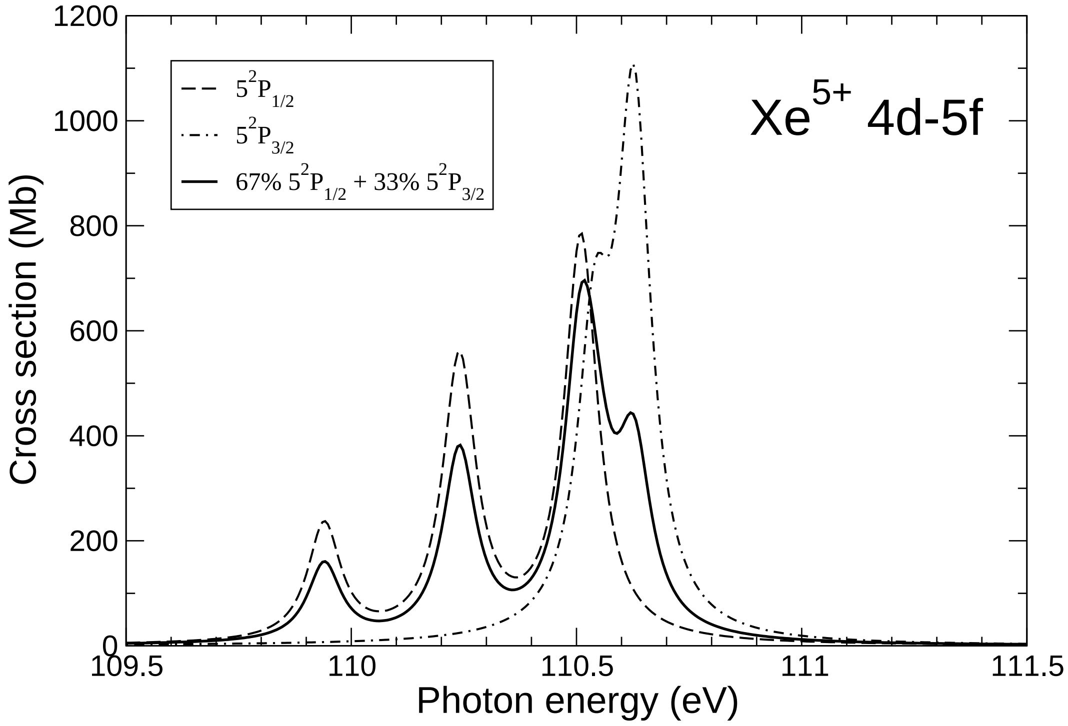

FIG. 4: Xe^{5+} photoionization cross sections in the vicinity of the $4d-5f$ transition calculated for the $5^2P_{1/2}$ and $5^2P_{3/2}$ states, and for a mixture of 67% ground and 33% metastable ions. See text for details.

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