Influence of the Energy of the Incident Photon on Satellite Intensities in Photoelectron Spectra of the Rare Gases

Henk Smid and Jørgen E. Hansen
Zeeman Laboratory, University of Amsterdam, NL-1018 TV Amsterdam, The Netherlands

(Received 30 January 1984)

The influence of the energy of the incident photon on the statellite structure associated with ionization in the outer *s* shell of the heavier rare gases is calculated. When the photon energy decreases from 200 to 50 eV, an increase in satellite intensity of about 30% is predicted for Ar. This prediction agrees, within the experimental accuracy, with recent observations. Similar behavior is predicted for Kr and Xe.

PACS numbers: 32.80.Fb

Measurements of satellite structures have contributed significantly to the understanding of correlation effects in atoms. The strong satellite lines associated with ionization in the outer *s* shell of the heavier rare gases have been the subject of many investigations.[1] This satellite structure has its origin in the interaction between $nsnp^6\,{}^2S$ and the $ns^2np^4({}^1D)\,md/\epsilon d\,{}^2S$ series.

Additional interest in this interaction has arisen recently as a result of measurements of the angular asymmetry factor β for the *main* ns^{-1} line in Xe.[2,3] It was found that relativistic random-phase–approximation (RRPA) calculations,[4] which have been very successful in predicting partial photoionization cross sections for the rare gases, are less successful in predicting β in the region of the "Cooper minimum" for *ns* ionization. The RRPA does not include the above mentioned interaction and this has been proposed[5] as a possible explanation. The proposal has not been supported by actual calculations and in fact the recent relativistic time-dependent local-density–approximation calculations by Parpia and Johnson,[6] which do not include the interaction either, are seemingly in good agreement with the observed variation of β in the Cooper minimum.

The situation for the ns^{-1} *satellites,* which is the subject of the present Letter, is better understood. In both photoelectron and $(e,2e)$ spectroscopy it has been assumed that the relative strengths of the satellites are proportional to the admixture of $|nsnp^6\,{}^2S\rangle$ in the different final states. However, these two types of experiments give different results[1] and the disagreement has been attributed[7] to the neglect of the influence of the energy of the photon on the satellite intensities in photoelectron spectroscopy. It has recently been shown[1,8] that *ab initio* calculations of $|nsnp^6\,{}^2S\rangle$ admixtures are in good agreement with measurements based on photoelectron satellite intensities without the photon energy dependence taken into account *provided* that the interaction with the continuum part of the *d* series is included. To be certain that this agreement is not accidental it is necessary to have an estimate of the satellite intensities as a function of the photon energy.

We report here the first theoretical estimate of the energy dependence of the ns^{-1} satellite intensities in Ar, Kr, and Xe. Calculations of photoionization with excitation[9] have been reported previously for He[10] and Ne.[11] However, the satellite structures in Ar, Kr, and Xe, which are much stronger, have a different origin. Figure 1(a) gives the main contribution to the satellite spectra in Ar, Kr, and Xe. Here the configuration interaction in the final state involves the core hole. Figure 1(b) gives, according to Ref. 11, the main contributions to 1*s* photoionization of Ne accompanied by excitation of a 2*p* electron. This diagram can be interpreted as representing an internal inelastic-scattering process in which the photoelectron excites a 2*p* electron on its way out. In He, this process is the only possible type of configuration interaction in the final state. The cross section for the process shown in Fig. 1(b) depends on the energy of the continuum electron via the dipole as well as the Coulomb interaction in contrast to the process represented by Fig. 1(a) for which only the dipole interaction depends directly on the energy of the continuum electron. The interaction represented by Fig. 1(a) is very strong in

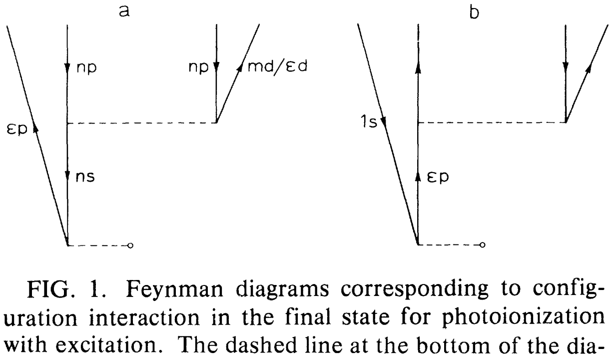

FIG. 1. Feynman diagrams corresponding to configuration interaction in the final state for photoionization with excitation. The dashed line at the bottom of the diagram represents the dipole interaction.

Ar, Kr, and Xe and cannot be determined by use of second-order perturbation theory. In this paper we use a nonperturbative approach[8] to determine the Coulomb-interaction part of Fig. 1(a) in combination with the lowest-order approximation for the dipole-interaction part. In this approximation the dependence of the satellite intensity on the photon energy is through the dipole matrix element $\langle \epsilon p|r|ns\rangle$ which depends on the final ionic state via the energy ϵ of the free electron.

We have calculated the dipole-length and velocity matrix elements for a number of electron energies in Ar, Kr, and Xe in a single-configuration Hartree-Fock (HF) approximation. The calculations for the $nsnp^6\epsilon p\ ^1P$ states were carried out with a frozen $nsnp^6$ HF core with the computer program of Chernysheva, Cherepkov, and Radojevič.[12] To check the continuity of the results across threshold, dipole matrix elements for bound np states were also determined. The squared dipole-length matrix elements $D(\epsilon) = |\langle \epsilon p|r|ns\rangle|^2$ are shown in Fig. 2. The results in the dipole-velocity approximation are similar except for a distinct maximum in $D(\epsilon)$ in this approximation which in all three atoms occurs about 10 eV above threshold. In the dipole-length approximation a maximum closer to threshold is visible in Fig. 2 for Ar and Kr. For energies larger than 300 eV the length and velocity results differ by less than 10%. Near threshold, there are differences of up to a factor of 3, the dipole velocity values being the smaller. These differences have, as we will see, a small effect on the *relative* satellite intensities.

Since $\epsilon = h\nu - E_{\text{binding}}$, the energy dependence of the satellite intensities is determined by the variation in $D(\epsilon)$ over the limited energy range covering the main line and the satellites. For the ns^{-1} satellites this is the distance between the $nsnp^6\,^2S$ term and the $ns^2np^4(^1D)$ limit (16 eV in Ar). Since $D(\epsilon)$ increases with decreasing ϵ, at least down to 10 eV, the satellites, having the smaller values of ϵ, are predicted to be stronger, relative to the main line, near threshold than in the high-energy limit. The same behavior was predicted for He (Ref. 10) and Ne (Ref. 11) although the mechanisms are different. For Ar, the results in Fig. 2 give an increase in satellite intensity of 20% to 30% (10% to 20% in the velocity formulation) for photon energies around 150 eV and 30% to 50% (20% to 30% in the velocity formulation) for photon energies around 60 eV where the effect has a maximum.

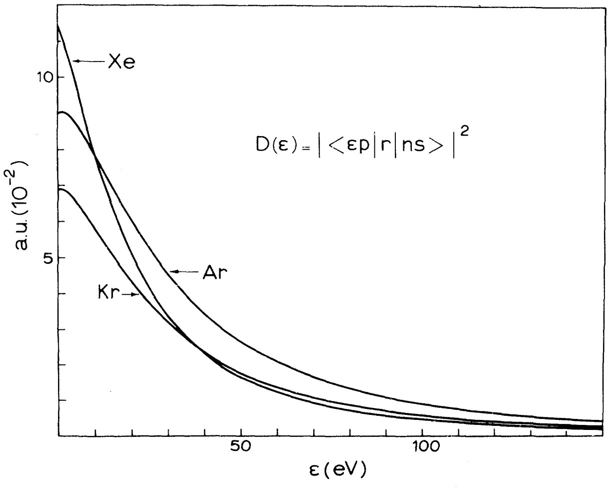

FIG. 2. Squared dipole-length matrix elements $|\langle \epsilon p|r|ns\rangle|^2$ as a function of the energy ϵ of the free electron for Ar, Kr, and Xe.

In Table I we give the calculated satellite intensities for Ar in the dipole-length and velocity approximations at a number of photon energies for which measured[13,14] satellite intensities exist. Both theoretical and experimental values are normalized to an intensity of 100 for the main line. The theoretical values for high photon energy are taken from Ref. 8. The small increase in satellite intensities predicted at low photon energy is in agreement with the recent experiments[13,14] although the variation is of the same size as the experimental accuracy. (We note that Adam *et al.*[14] considered the measured satellite intensities to be independent of the photon energy.) The quantitative agreement at 151, 77.2, and 58.3 eV is very good (Table I) and in fact better than that obtained if the photon energy dependence is neglected. The agreement at high energy is worse but it is difficult to ascribe the differences between the measurements at 1487 and 1254 eV to the differences in photon energy and the accuracy of these measurements might have been overestimated.

For photon energies less than 50 eV the calculations predict a decrease in the satellite intensities. There is an indication of such an effect in the experimental data since the satellite corresponding to the $5d$ final state was not observed by Adam *et al.*[14] at 58.3 and 43 eV. To decide whether this effect is real, better calculations are required. Although it seems certain that the contribution to the satellite cross section calculated here is the most important one, the RRPA calculations[4] for the main lines show that, particularly in the Cooper minimum, correlation between inner shells can influence the cross sections significantly. Therefore our results very close to threshold are at best approximate given that "post-collision" effects must be con-

TABLE I. Observed and calculated photoelectron satellite intensities for the satellites associated with ionization of a $3s$ electron in Ar. For the method of calculation see the text. Both dipole length (len.) and dipole velocity (vel.) values are given.

				Photon energy (eV)								
				151			77.2			58.3		
	1487[b]	1254[b]	1487,1254		Calc.			Calc.			Calc.	
Designation[a]	Obs.	Obs.	Calc.	Obs.[b]	Len.	Vel.	Obs.[c]	Len.	Vel.	Obs.[c]	Len.	Vel.
$3s3p^{6\,2}S$ [d]	100	100	100	100	100	100	100	100	100	100	100	100
$3s^23p^4(^1D)3d\,^2S$	19(2)	15(2)	13.5	15(2)	15.9	15.0	17[e]	17.3	16.1	17(1)	17.6	15.7
$4d\,^2S$	6(3)	7(3)	6.9	8(3)	8.5	8.0	10(2)	9.5	8.7	10(2)	9.7	8.3
$5d\,^2S$			3.8		4.8	4.5	4(2)	5.4	4.9		5.5	4.6
$6d\,^2S$			2.3		2.9	2.8		3.4	3.0		3.4	2.8

[a] See Smid and Hansen, Ref. 8.

[b] Spears, Fischbeck, and Carlson, Ref. 13.

[c] Adam *et al.*, Ref. 14. Measurements at 43 eV are included in this reference but neither the $4d$ nor the $5d$ satellite was observed at this energy and the $3d$ and $4s$ peaks were not resolved.

[d] This peak is used as reference.

[e] A possible deconvolution of the unresolved $3d$ and $4s$ peaks.

sidered also.

As can be seen from Fig. 2, the calculations also predict for Kr and Xe only a small increase of satellite intensities relative to the main line with decreasing photon energy. For Xe, the experimental results are at first sight in clear disagreement with this prediction. A measurement[15] at 87.7 eV shows systematically lower relative intensities than found at 1487 eV,[16] while measurements at 40.8 eV,[17] and very recently at 33 eV,[18] seem to show considerably higher satellite intensities than found at 1487 eV. However, we believe that the latter results are due to the $5p^{-1}$ satellites being stronger than the $5s^{-1}$ satellites at low energy and overlapping these.[19] The present results, although not expected to be very accurate at low energy, lend support to such an interpretation.

In conclusion, the calculations presented in this Letter lead to the prediction that the influence of the photon energy on the ns^{-1} satellite intensities in photoelectron spectra of the rare gases is fairly small in lowest order of approximation. This prediction is in good agreement with recent measurements in Ar. Inclusion of the effect improves the agreement between our *ab initio* calculations and experiment and the good quantitative agreement corroborates our previous conjecture[1,8] that the disagreement between photoelectron and $(e, 2e)$ satellite spectra is due to difficulties in the interpretation of the latter.

---

[1] J. E. Hansen, Commun. At. Mol. Phys. **12**, 197 (1982).

[2] H. Derenbach and V. Schmidt, J. Phys. B **16**, L337 (1983).

[3] A. Fahlman, T. A. Carlson, and M. O. Krause, Phys. Rev. Lett. **50**, 1114 (1983).

[4] W. R. Johnson and K. T. Cheng, Phys. Rev. A **20**, 978 (1979).

[5] G. Wendin and A. F. Starace, Phys. Rev. A **28**, 3143 (1983).

[6] F. A. Parpia and W. R. Johnson, J. Phys. B **17**, 531 (1984).

[7] I. E. McCarthy and E. Weigold, Phys. Rep. C **27**, 275 (1976).

[8] H. Smid and J. E. Hansen, J. Phys. B **16**, 3339 (1983).

[9] H. P. Kelly, in *Atomic Physics 8,* edited by I. Lindgren, A. Rosén, and S. Svanberg (Plenum, New York, 1983).

[10] E. E. Salpeter and M. H. Zaidi, Phys. Rev. **125**, 248 (1962); V. L. Jacobs and P. G. Burke, J. Phys. B **5**, L67 (1972); T. N. Chang, J. Phys. B **13**, L551 (1980); K. A. Berrington, P. G. Burke, W. C. Fon, and K. T. Taylor, J. Phys. B **15**, L603 (1982).

[11] T. Ishihara, J. Mizuno, and T. Watanabe, Phys. Rev. A **22**, 1552 (1980).

[12] L. V. Chernysheva, N. A. Cherepkov, and V. Radojevič, Comput. Phys. Commun. **18**, 87 (1979).

[13] D. P. Spears, H. J. Fischbeck, and T. A. Carlson, Phys. Rev. A **9**, 1603 (1974).

[14] M. Y. Adam, F. Wuilleumier, S. Krummacher, V. Schmidt, and W. Mehlhorn, J. Phys. B **11**, L413 (1978).

[15] M. Y. Adam, F. Wuilleumier, N. Sandner, V. Schmidt, and G. Wendin, J. Phys. (Paris) **39**, 129 (1978).

[16] U. Gelius, J. Electron Spectrosc. **5**, 985 (1974).

[17] S. Süzer and N. S. Hush, J. Phys. B **10**, L705 (1977).

[18] A. Fahlman, M. O. Krause, and T. A. Carlson, J. Phys. B **17**, L217 (1984).

[19] J. E. Hansen and W. Persson, to be published.