Double photoexcitation $[2(s,p)4(p,d)]$ in the Xe-isoelectronic series Cs^+ , Ba^{2+} , La^{3+}

A. Kodre, I. Arcon, M. Hribar, M. Štuhec, F. Villain, P. Parent

► To cite this version:

A. Kodre, I. Arcon, M. Hribar, M. Štuhec, F. Villain, et al.. Double photoexcitation $[2(s,p)4(p,d)]$ in the Xe-isoelectronic series Cs^+ , Ba^{2+} , La^{3+} . Journal de Physique IV Proceedings, 1994, 04 (C9), pp.C9-397-C9-400. 10.1051/jp4:1994966 . jpa-00253529

HAL Id: jpa-00253529

<https://hal.science/jpa-00253529>

Submitted on 1 Jan 1994

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Double photoexcitation $[2(s,p)4(p,d)]$ in the Xe-isoelectronic series Cs^+ , Ba^{2+} , La^{3+}

A. Kodre, I. Arčon, M. Hribar, M. Štuhec, F. Villain* and P. Parent*

Jožef Stefan Institute, Jamova 39, 61111 Ljubljana, and Department of Physics, University of Ljubljana, Slovenia

** LURE, Université Paris-Sud, 91404 Orsay, France.*

Abstract: Using the standard ansatz, the single, strongly dissipated harmonic component of EXAFS in aqueous medium is eliminated from L-shell absorption spectra of Xe-like ions Cs^+ , Ba^{2+} , La^{3+} . The remaining structures in the spectra are interpreted as double photoexcitations into $[2(s,p)4(p,d)]$ vacancy states: they are analogous to the corresponding structures in absorption spectra of xenon, their energies agree fully with MCDF energies. Their relative probabilities are found to increase along the isoelectronic series, proportionally to the intensity of the "white line" $2p \rightarrow 5d$. For the first time, an "adiabatic" change of double excitation features is studied.

1. INTRODUCTION

Accompanying the photoexcitation of the core electrons, excitations of electrons in the two outermost shells have been observed in x-ray absorption spectra. Most of the reliable data is derived from experiments on noble gases [1]. In condensed phase and molecular gases, XANES and EXAFS pervade the corresponding energy region, leaving little hope to uncover the small underlying multielectron photoabsorption structures [2,3]. However, in liquid phase, and generally in disordered media, EXAFS is limited to a single, strongly dissipated harmonic component. Using the standard EXAFS ansatz, this component can be eliminated from the spectra numerically, and the multiple-absorption effects conveniently recovered.

We have employed this procedure on L-shell absorption spectra of Xe-like ions Cs^+ , Ba^{2+} and La^{3+} in aqueous solutions. In conjunction with a recent experiment on xenon [4], the results show, for the first time, the effect of contraction of an isoelectronic system due to increasing nuclear charge, on transition probabilities for multiple photoexcitations.

2. EXPERIMENT

The absorption spectra of the ions in the aqueous solutions were measured at the EXAFS 3 beamline at LURE, Orsay, with an Si(311) double-crystal monochromator, and a liquid absorption cell allowing reproducible measurements on liquid layers of thickness as low as 0,15 mm. Absorption of 0,3 M solutions of CsCl, BaCl₂ and La(NO₃)₃ in the energy region of the L-edges of the ions was scanned in 0,25 eV steps, at the energy resolution of the monochromator of 0,4 eV. Absorption in the water medium was measured on equivalent anionic solutions.

The Xe L-subshell spectra, used for comparison, were measured in a gas absorption cell at the EXAFS II beamline at HASYLAB, DESY, Hamburg, with resolution of 1 eV.

Figure 1. La³⁺ absorption spectrum above the L₃-edge. (...) - experiment; (—) - EXAFS ansatz.

The procedure of removing the EXAFS component is shown in the clearest case of the L₃ subshell spectrum of La³⁺ ion (Fig. 1). Above the subshell edge a simple damped sine wave of EXAFS is seen, with some unrelated short-range structure. Although the outermost-shell excitations [2p5(s,p)] remain hidden in the near-edge structure, the excitations to the second outermost shell can be extracted, after subtraction of the EXAFS ansatz. The remaining spectral structure is analogous to the spectrum of [2p4d] excitations in Xe. The leading resonance appears close to the MCDF energy of the La³⁺ [2p4d]5d² state and the subsequent edge at the corresponding shake-up limit. The same pattern is recognized in the absorption spectra of Cs⁺ and Ba²⁺, although less clearly resolved because of stronger attenuation by water and Cl ions at correspondingly lower energy ranges. The isolated double-excitation structures for the three L subshells in all three ions and the Xe atom are shown in Fig. 2, together with corresponding MCDF energy ranges of excited-state multiplets.

Figure 2. Resonant double-photoexcitation structures for the three L-subshell absorption spectra of Xe, Cs⁺, Ba²⁺ and La³⁺ with the corresponding MCDF energy ranges of the excited-state multiplets. EXAFS ansatz is subtracted from the measured data in the case of the three ions, and a second-order polynomial in the case of Xe. Relative energy scale with origin at respective L-edges is used. Cross-sections are normalized to respective L-subshell ionization cross-sections.

3. RESULTS AND DISCUSSION

From the comparison of the spectra in Fig. 2. some conclusions on the process of double photoexcitation can be drawn. The gradual change in the shape of the leading resonance along the isoelectronic series points to its composite structure and should give clue for the identification of its components. Interestingly, the relative strength of the multielectron excitations almost doubles for each consecutive member of the series, reaching extraordinary 4% for $[2p4d]5d^2$ at La^{3+} . An increase of similar extent is found in the intensity of the "white line" $2p \rightarrow 4d$ at the 2p-subshell edges (Table I). Another instance of this increase makes the resonant excitations to the $[2p4p]$ vacancy state, not observed in the state-of-art gas-absorption experiment on Xe, clearly resolved in the La^{3+} spectrum. The apparent mismatch in the relative positions of these excitations in the L_2 and L_3 regions confirms the identification: the strongest transitions with the proper 1P multipolarity in both multiplets lead to $[2p_{1/2}4p_{1/2}]$ and $[2p_{3/2}4p_{3/2}]$ states, respectively. The broad structure h observed in Xe, is confirmed as a "shape" resonance by its absence from the spectra of ions [5].

We have shown in this report that multiple photoexcitations can be studied in absorption spectra of ionic solutions. With the use of the new media, the range of atomic systems amenable to the experiment is expanded considerably. The study of closely related systems should provide better insight into the details of the process. As an example, the development of an absorption structure in a series of equivalent atomic systems with a small change of a constitutive parameter, can be followed.

Acknowledgment: This work was supported by Ministry of Science and Technology of Slovenia.

Table 1. Intensities of the leading double-electron resonance $[2p4d]$ relative to the L_3 -edge jump. The value for the corresponding resonance in Xe is taken as unit. The relative intensity of the "white line" $2p \rightarrow 5d$ at the 2p-subshell edge is given for comparison.

Element	Relative intensities vs. Xe	
	Leading resonance	"White line"
Cs^+	1.6	2.1
Ba^{2+}	3.1	3.4
La^{3+}	4.4	4.0

4. REFERENCES

- [1] Schaphorst S. J., Kodre A., Ruscheinski J., and Crasemann B., Aberg T., and Tulkki J., Chen M. H., Azuma Y., Brown, G. S., Phys. Rev. A **47** (1993) 1953-1966 and ref. therein
- [2] Frahm R., Drube W., Arçon I., Glavič-Cindro D., Hribar M., and Kodre A., 2nd European Conference on Progress in X-ray Synchrotron Radiation Research, Rome 2.-6. October 1989, edit.: Balerna A., Bernieri E. and Mobilio S., Conf. Proceedings V25, Bologna, (1990), p.129-132
- [3] Kodre A., et al., Phys. Rev. A **45** (1992) 4682-4687
- [4] Kodre A., Arçon I., Štuhec M., Glavič-Cindro D., Drube W., HASYLAB Jahresbericht 1993, p.181-184
- [5] Becker U., et al., Phys. Rev. A **39**, (1989) 3902-3911.