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Multielectron transitions above the krypton K edge

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The structures above the Kr K edge are reported and for the first time interpreted as due to multielectron transitions involving K, M, and N electrons. The cross section of the $1s\,3d$ multielectron transition is analyzed and an onset more rapid than the one expected according to the "shake" model is observed. This behavior is quite well described by a model proposed by Stöhr, Jaeger, and Rehr [Phys. Rev. Lett. **51**, 821 (1983)] based on the exchange interaction.

I. INTRODUCTION

Multielectron transitions in the x-ray region have been investigated in the past principally by studying satellite peaks in x-ray emission,[1–3] x-ray photoemission,[4,5] and charged-ions spectra.[6]

To explain the production of multiple-vacancy or multiple-excitation states which give rise to satellite peaks in x-ray photoemission and x-ray emission spectroscopy of inner shells, the validity of the "shake" model based on the sudden approximation[7] is usually recognized. In this approximation the change in the Hamiltonian is so rapid that the system can be left, through a monopole transition, in an excitation (shake-up) or second-ionization (shake-off) state.

The sudden approximation is not valid if the excitation energy is small compared to the energy necessary for the second excitation or ionization. In this adiabatic limit, usually reached in x-ray absorption spectroscopy (XAS), the system can relax into the new ground state and the relaxation energy is given to the outgoing photoelectron, therefore the transition probability of a second electron should be negligible. Nevertheless, strong multielectron effects in absorption spectra of gases[8–10] and vapors[11] have been observed, and in solids there is some evidence for one-photon—two-electron and one-photon—three-electron transitions.[12–19] This implies that multielectron transitions in the adiabatic limit also take place and a model for multiple-vacancy production in this limit must be chosen.

Recently, two models describing the transition region between the adiabatic and sudden regime have been proposed. The first, developed by Stöhr, Jaeger, and Rehr,[20] is based on the exchange interaction between the two electrons involved in the process. According to this model, the energy dependence of the cross section for a multielectron transition is given by

$$\mu=\mu_s\{1-(\Delta E/E_{\rm ex})^2\}^2 , \tag{1}$$

where μ_s is the saturation value reached in the sudden limit, ΔE is the energy necessary for the second excitation or ionization and $E_{\rm ex}$ is the excitation energy of the second electron above the main edge threshold ($E_{\rm ex}=E_k+\Delta E$, where E_k is the kinetic energy of the second electron).

The second model, proposed by Thomas,[21] is based on a time-dependent potential and gives for the cross section

$$\mu=\mu_s \exp(-mr^2\Delta E^2/2\hbar^2 E_{\rm ex}) , \tag{2}$$

where m and r are the electron rest mass and mean radius of the second electron shell, respectively.

Only a few comparisons between these models and experimental data have been performed till now by monitoring in XPS experiments the satellite peak intensity as a function of excitation energy.[20–22] Stöhr, Jaeger, and Rehr found a qualitative agreement between their model and photoemission data for N_2 on Ni(110). Thomas showed that the time-dependent model can also take into account the rapid rise of the shake-up and shake-off cross section, but the comparison was not performed carefully at the onset where the models differ critically because at the onset it is difficult to distinguish the satellite peaks from the background.

In this paper we present the first study of the energy dependence of a multielectron-transition cross section measured in an x-ray absorption spectrum by investigating the K absorption edge of Kr gas at room temperature. In this case multielectron effects can be well studied, particularly at the onset, and a decisive comparison between the two models can be made. We also identify the main multielectron-transition contributions above the edge.

The study of multielectron transitions in XAS is also important since it helps to clarify their role in absorption spectra.[23,24] In molecules and solids, absorption spectra are usually interpreted within the one-electron framework as scattering of the photoelectron by neighboring atoms. Recent results reported by Benfatto *et al.*[25] show that multielectron excitations must be taken into account to explain completely the observed x-ray absorption near-edge structure (XANES) on the Mn K edge of MnO_4 in

solution. Studies on solid rare gases by Malzfeldt and coworkers[26,27] show that the usual subtraction of the continuous atomic background (a polynomial fit) causes multielectron effects to introduce anomalous frequencies in the extended absorption fine structure (EXAFS) which give rise to anomalous peaks in the Fourier transform.

These and other results on solid-state systems[28] clearly indicate that multielectron effects must be carefully considered and removed in order to obtain correct structural information from XANES and EXAFS. The study of these effects in simple systems like gases gives important information on the energy position and energy dependence of the cross section. This information can lead to the identification of similar features in very structured solid-state spectra.

II. EXPERIMENTAL PROCEDURE

The Kr-gas absorption spectrum was recorded using synchrotron radiation produced in a six-pole wiggler at the Adone wiggler facility,[29] with 1.5-GeV electrons at a circulating current of 40—60 mA. The radiation was monochromatized with a Si(220) channel cut crystal and the calculated energy resolution (combined intrinsic crystal resolution and vertical angular divergence of the beam) was about 3 eV. Utilizing this value and the measured full width at half maximum (FWHM) of the peak A (see Sec. III A) we obtained 2.9 eV for the energy width of the Kr K level; this value is in good agreement with the ones obtained by theoretical calculations.[30] The x-ray beam was detected by two ionization chambers filled with Xe gas.

In the energy range investigated, neither the optical elements of the beam line nor possible impurities in the gas can simulate the observed spectral features. Also contribution of higher harmonics in the x-ray beam is negligible since the critical energy of the synchrotron-radiation spectrum is about 2.4 keV. Furthermore we also verified the absence of spurious features due to the monochromator (glitches) in the spectrum.

III. RESULTS AND DISCUSSION

The experimental spectrum after pre-edge-subtraction is shown in Fig. 1. The energy range has been divided into two regions. The first one, "suprathreshold," starts about 10 eV above the K edge and shows a peak, a change of slope, and other structures. The second region starts about 100 eV above the edge and shows two shoulders followed by a change of slope.

A. Suprathreshold region

To identify the suprathreshold-region structures shown in Fig. 2, we have compared our spectrum with the Ar and Ne spectra recorded by Deslattes *et al.*[10] and Esteva *et al.*,[9] respectively. The Kr, Ar, and Ne suprathreshold regions are shown in Fig. 3. Considering that for each spectrum the energy resolution and core lifetime are different, similarities among these spectra can be observed.

Deslattes *et al.* have identified features in the Ar spectrum as due to multielectron transitions involving $1s$ and

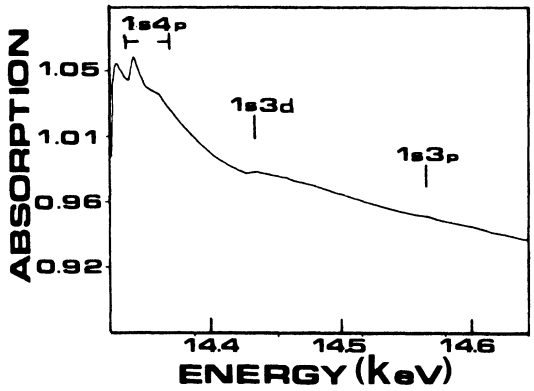

FIG. 1. Absorption spectrum above the Kr K edge after pre-edge-subtraction. The region of the $1s4p$ multielectron transition and the onsets of $1s3d$ and $1s3p$ double ionization are shown.

$3p$ electrons. They also observed that the $Z+1$ approximation retains a certain utility in determining the energy position of multielectron transitions. Recent work by Tulkki and Åberg[31] confirms this multielectron interpretation by showing that the *one*-electron photoionization cross section including relaxation cannot explain the Ar suprathreshold structures.

Structures 1 and 2 of the Ne spectrum have been identified by Esteva *et al.*, using $1s$ XPS Ne data, as multielectron transitions involving $1s$ and $2p$ electrons.

Similarities among the spectra and the atomic structures of Ne, Ar, and Kr (closed-shell systems) would also suggest that the Kr structures can be ascribed to multielectron transitions involving in this case $1s$ and $4p$ elec-

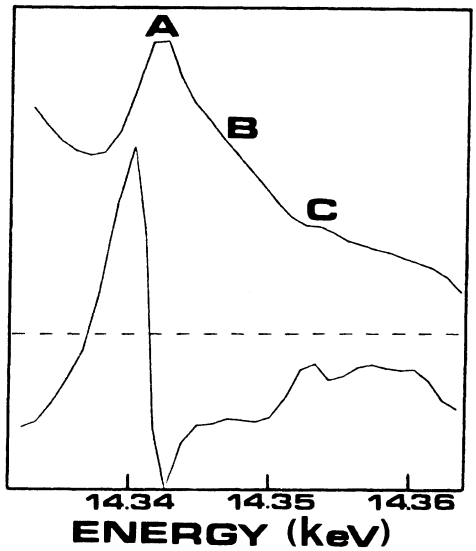

FIG. 2. Suprathreshold structures above the Kr K edge (top curve) and their first derivative (bottom curve). The A, B, and C features are due to transitions of $1s$ and $4p$ electrons to double excitation, excitation plus ionization, and double-ionization states, respectively.

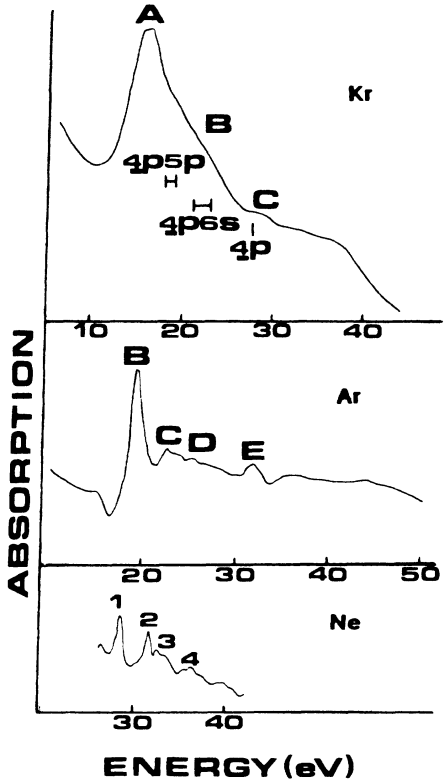

FIG. 3. Comparison of Kr suprathreshold structures with Ar (Ref. 10) and Ne (Ref. 9). The energy scales refer to the onset of the one-electron continuum. Some excited states of the rubidium optical spectrum relative to the Rbi $4p^6$ limit (which is put in coincidence with the Kr $1s$ threshold) are shown below the Kr spectra.

trons. We have identified each particular transition assuming the validity of the $Z+1$ approximation using Rb-atom[32] optical data.

Our assignments, together with the ones for Ar and Ne, are reported in Table I. The onset of the Kr $1s$ electron continuum has been located 4.7 eV above the edge (maximum in the first derivative). This value has been obtained by assuming a Lorenzian profile of 4 eV FWHM (combined experimental resolution and $1s$ level width) for the $1s \rightarrow 5p$ discrete transition and evaluating, in the $Z+1$ approximation, the energy separation between this transition and the continuum which is 2.7 eV.

We have assigned the first peak A to the transition to the discrete double excitation state $\underline{1s\,4p\,5p^2}$ (hole states underlined). Its cross section, compared to the K edge, is about 1.3%. The corresponding Ar peak (transition to $\underline{1s\,3p4p^2}$ state) is narrower due to different experimental resolution and lifetime, and the similar Ne structure (transition to $\underline{1s\,2p\,3p^2}$ state) is split by the exchange interaction, which is lower in Ar and Kr whose core hole is deeper.[9] This assignment is also confirmed by the $Z+1$ approximation (Table I).

A close relationship was found between the $\underline{4p\,5p}$, $\underline{4p\,6s}$ Rb configurations and feature B, and between the $\underline{4p}$ ionization state of Rb and feature C of the Kr spectrum. Therefore, the slope change B is associated with transitions to the $\underline{1s\,4p\,5p}$ and $\underline{1s\,4p\,6s}$ single-ionization shake-up states, and peak C with transition to the $\underline{1s\,4p}$ double-ionization shake-off state. It can be observed in Table I that our assignments are consistent with identifications of similar Ar structures.

Following this interpretation of Kr and Ar features we can now also explain structures 3 and 4 in the Ne spectrum which were not interpreted by Esteva *et al.* Structure 3 is due to transition to the $\underline{1s\,2p\,3p}$ state and structure 4 to transition to the $\underline{1s\,2p}$ state. The $Z+1$ approximation confirms that the latter structure is at the right energy position for double ionization.

B. $K+M$ region: energy dependence of cross section

Let us now consider the structures far from the edge. Two shoulders are observed at about 113 and 235 eV, respectively, above the main edge, in close agreement with the ionization energies of the M electrons evaluated in the $Z+1$ approximation, 112 and 114 eV for d electrons and 240 and 250 eV for p electrons. Consequently the two shoulders have been associated with the onsets of double transition processes involving $1s\,3d$ and $1s\,3p$ electrons.[33]

To analyze the cross-section behavior for multielectron

TABLE I. Assignments of spectral features for rare-gas suprathreshold energy region and electronic configurations. The experimental energy position of the Kr features and the estimated energy position of the Kr configuration, obtained from Rb optical data in the $Z+1$ approximation, are also shown. The estimated energy ranges take into account multiplet splitting. The indeterminacy in experimental energies is an upper limit for the error due to the monochromator resolution.

Kr feature	Kr config.	Energy above $1s$ (eV)	Rb config.	Energy above[a] $4p^6$ (eV)	Ar feature	Ar[b] config.	Ne feature	Ne[c] config.
A	$\underline{1s\,4p\,5p^2}$	16 (±2)		15.4–16.4	B	$\underline{1s\,3p4p^2}$	1	$\underline{1s\,2p\,3p^2}$
							2	
B	$\underline{1s\,4p\,5p}$	18–23 (±2)	$\underline{4p\,5p}$	18–19	C	$\underline{1s\,3p4p}$	3	$\underline{1s\,2p\,3p}$[d]
	$\underline{1s\,4p\,6s}$		$\underline{4p\,6s}$	21–23	D	$\underline{1s\,3p\,5p}$		
						$\underline{1s\,3p\,5s}$		
C	$\underline{1s\,4p}$	27–30 (±2)	$\underline{4p}$	27.5	E	$\underline{1s\,3p}$	4	$\underline{1s\,2p}$[d]

[a] Reference 32.
[b] Reference 10.
[c] Reference 9.
[d] Our attributions.

transitions in the region between the adiabatic and sudden regime, contributions from double-excitation processes must be neglected because in XAS they contribute only peaks at fixed energies. As noted above, the double-excitation contribution to $1s4p$ multielectron transitions due to transition to the $\underline{1s4p}5p^2$ state is strong. Therefore, even though the overlap between the initial and final discrete states for M electrons is smaller than for N electrons we can suppose that the $\underline{1s3p}5p^2$ contribution to the $1s3p$ multielectron transition is not negligible. On the other hand, according to selection rules for monopole transitions, the same final state cannot be reached by $1s$ and $3d$ electrons. Therefore, the contribution of double-excitation processes to the cross section of the $1s3d$ multielectron transition is smaller than for the $1s3p$ transition and the energy dependence of the $1s3d$ transition is the most suitable for studying the cross-section behavior in the adiabatic limit.

The cross section of such a transition shows a rapid onset. This rapid rise, which has also been observed in the absorption spectrum of Xe,[34] cannot be explained by the shake theory which predicts a negligible cross section in the adiabatic limit and a slow rise up to the sudden limit.

To see if the two proposed models can explain such interesting behavior, we have compared the experimental cross section with Eqs. (1) and (2).

A *direct* comparison can be done only after carefully subtracting the one-electron cross-section contribution. This contribution cannot be obtained with enough accuracy either directly from the experimental spectrum or theoretically. Nevertheless, since the variation of the one-electron cross section is smooth, the first derivative of the absorption cross section should hardly be influenced by the one-electron cross-section energy dependence. In particular this is true at the onset, in the region of rapid rise, where, as previously observed, the two models differ significantly. The first derivative comparison is shown in Fig. 4. It is evident that, independently of the μ_s and r values used,[35,36] the observed experimental shape and the one predicted by the time-dependent model are completely different from one another.

On the other hand, the exchange-interaction model fits the data quite well, particularly at the onset. However, the experimental onset in the last part of the shoulder is still more rapid than predicted by the model. This could partly be due to contributions coming from transitions to discrete states. These contributions may also explain the difference between the experimental value of μ_s and the theoretical one calculated in the sudden limit.

Our results show that the rapid onset cannot be taken into account by models (both shake and time dependent) which do not consider explicitly the interaction between electrons, and that the exchange interaction plays a crucial role in the adiabatic limit.

Nevertheless other kinds of interaction could contribute to the cross section at the onset. Indeed, we believe that electron correlation and configuration interaction, which are usually considered in *outer*-shell photoemission[4,37,38] as well as for inner shells in the sudden limit[39–41] (multiconfiguration shake theory), play a more important role than previously believed in determining the cross section

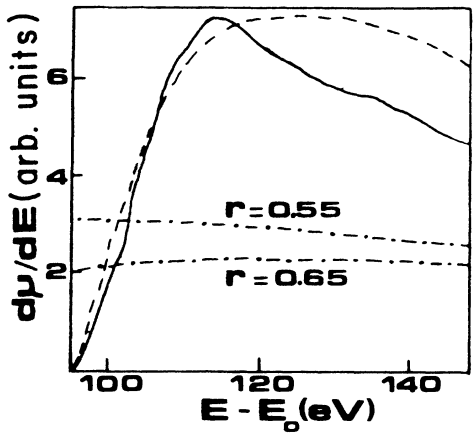

FIG. 4. Comparison of the first derivative of the experimental $1s3d$ cross section (solid line) with that of the time-dependent (dash-dot line) and exchange-interaction (dashed line) models. The value of $\mu_s=4.5$ was used in Eq. (1) to obtain best agreement with experimental data (whereas shake theory gives 3.6 for shake-up plus shake-off cross section[35]). The same value of μ_s was used in Eq. (2). The values of $r=0.65$ Å and $r=0.55$ Å are the $4s$-shell mean radius and a lower limit for the $3d$-shell radius,[36] respectively.

in the adiabatic limit. This hypothesis seems to be supported by the results of Salem and co-workers[12–16,19] and Kumar, Scott, and Salem[18] on $K+L$, $L+L$, and $K+K$ double-ionization processes in several solid-state systems. These measurements show a cross-section onset more rapid than the one we have observed for $K+M$ Kr electrons, and $K+L$ Ar electrons. Electron correlation is particularly evident for $K+K$ and $L+L$ double ionizations.[14,16,18,19] In these cases the saturation value of the cross section is even higher than the one predicted by the sudden approximation.

IV. CONCLUSIONS

In this work we have shown that the structure above the Kr K edge can be explained as due to multielectron transitions. Our results, together with the results on Ar and Ne, show that multielectron processes have considerable importance in interpreting absorption spectra of rare gases. The analysis of the $1s3d$ multielectron transition shows that the onset of the cross section is more rapid than expected according to shake- and time-dependent models. A model based on the exchange interaction partly explains the cross-section behavior at the onset. We suggest that electron correlation should be taken into account to explain fully the observed experimental behavior.

It is necessary to get more data on multielectron-transition cross sections in various systems and develop more accurate models in order to remove possible "noise" in structural-inversion procedure and understand completely the mechanism for multiple-vacancy production in the adiabatic limit.

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