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X-ray absorption in the region of the *K* edge measured on potassium vapor in a heat-pipe cell is analyzed. Excitation channels leading to single $1s$ vacancy as well as double $1s4s$ and $1s3p$ vacancies are identified by decomposition of spectral features and by comparison with excitation energies from a Dirac-Fock calculation. The analysis is relevant also for the interpretation of some features in the Ar $1s3p$ excitation.

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In comparison to excitation by charged projectiles, x-ray absorption provides a clean way for studying excited states of an atom. The features of x-ray absorption spectra can be correlated directly with excited states accessible from the ground state by selection rules, with single-electron excitations nicely separated from collective excitations by one or two orders of magnitude. The prevailing type of collective excitations, the multielectron excitations (MPE), can be resolved as tiny sharp features on the smooth energy dependence of the single-electron excitations. The clarity of the picture, however, is limited only to absorption spectra of elements in the monatomic state [1–8]. In spectra of molecular or dense samples, structural effects in the absorption prevail [9–15]. Absorption spectra of noble gases have provided a lot of detailed information on MPE. The theoretical studies of the subject may give an impression that all is understood in principle—yet the theoretical reconstruction of the measured data is relatively poor and patchy. It seems that the MPE spectra are governed by the idiosyncrasies of individual elements—each being a particular case of orbital coupling and configuration interaction, with few rules of wider application [4,16–19]. Thus, the need for further collection of data, particularly outside the noble-gas family is evident.

The recently measured absorption spectrum of atomic potassium in the *K*-edge region [20] provides new data on single $1s$ as well as multiple $1s4s$ and $1s3p$ excitations. Additional insight is obtained from comparison with spectra of related elements. Both alkaline-metal homologues, HOMOLOGUES, sharing with potassium the feature of a single s electron outside a closed shell, have been studied. For rubidium, a comprehensive spectrum of *K*-shell MPE is known [7,8], but the comparison is somehow limited due to the larger natural width of Rb; details observed in potassium are blurred in rubidium. On the other side, in sodium with smaller natural width, only a narrow region of the *K* edge including the valence coexcitations $1s3s$ has been studied [21]. The well-separated reaction channels in Na correlate directly to spectral features in potassium. However, the sensitivity of the Na experiment has not been sufficient to discern weak features of the $1s2p$ excitations.

The comparison with the edge features in the neighboring argon is particularly informative since Amusia, Baltenkov, and Zhuravleva [22], in a response to the experiment by Berry *et al.* [23], made a theoretical survey of the $1s$ excitation channels in both elements. A direct comparison between theory and experiment is thus possible.

The comparison of $1s3p$ excitations in argon and potassium is also fruitful. Although the configurations of analogous excited states are different, it could be expected that the loosely bound $4s$ electron in potassium should not affect the MPE spectrum much beyond the additional splitting due to its spin. The data, however, show a different picture: the $3p$ MPE group is strongly affected, so much that in modeling the two spectra, some light is shed on the controversy in explanations of the argon $1s3p$ excitations. Some additional insight is provided by the tentative spectrum of the K^+ ion, extracted for the purpose.

EXPERIMENT

The experiment with potassium vapor in a heat-pipe absorption cell, performed at the *E4* beamline of the Hasylab, DESY, has been described elsewhere [20]. Absorption spectrum with resolution of ~ 1 eV is measured in the energy region 3590–3670 eV encompassing the *K* edge, $1s4s$ and $1s3p$ excitation. Spectral features are recorded reproducibly up to 60 eV above the edge (Fig. 1). Further out, the noise of the heat-pipe operation prevails over weak $1s3s$ excitations.

The absorption spectrum of the K^+ ion is measured on a *K*-Ca silicate glass. The smooth structural signal due to oxygen neighbors is removed by a numerical procedure described earlier for Rb^+ ion and $4p$ elements [14,15]. Although a complete MPE spectrum cannot be extracted, the $1s3p$ feature is recovered with sufficient accuracy for comparison.

A remeasurement of Ar *K*-edge absorption was performed at the same experimental station [19].

ANALYSIS

In the analysis of the vapor data, a model of a measured spectral feature is constructed from the known energy dependence of the basic absorption channels—resonances and

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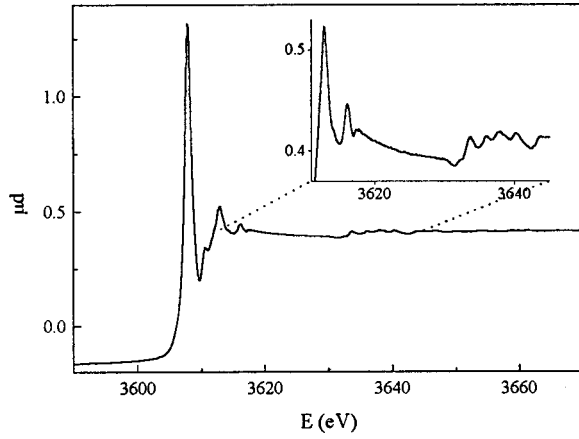


FIG. 1. The absorption thickness μd of the potassium vapor in the cell with magnification of small features in the inset.

edges [4,16]. Starting with the strongest channels, the parameters of the model (amplitudes, energies and widths) are determined by a least-squares fit. The components due to weaker transitions are consecutively added until the measured data is comprehensively exhausted and the residual of the fit is statistical noise. The model building blocks determined in this way should be considered physically significant.

NEAR EDGE STRUCTURE ($[1s]np$ AND $[1s4s]nln'l'$)

The apparent dissimilarity of near-K-edge spectra of three alkaline metals Na, K, and Rb (Fig. 2) arises from the large difference in the natural widths (0.30, 0.74, and 2.99 eV, respectively [24]): the basic components of the edge, however, are the same in all three spectra. A comparison between Na [21] and K shows that for every separate spectral feature in Na an analogous excitation channel can be identified in the model of the potassium edge. In the Rb spectrum, most of the details are washed out by the large natural width. Filipponi [25] has demonstrated, though, that a large part of this width can be removed with a numerical procedure if spectra are measured with sufficiently high signal-to-noise ratio. After this operation, K and Rb spectra look surprisingly similar.

In the model of the edge region (Fig. 2), the shape of the measured pre-edge peak in potassium is fully described by two resonance profiles at 3607.9 and 3608.8 eV, attributed to triplet and singlet $[1s]4p$ states, the former being 8.5 times stronger. Close to the main $[1s]$ absorption edge, the second transition $[1s]5p$ in the Rydberg series can be discerned along with the valence-electron coexcitations $[1s4s]5s4p$ and $[1s4s]5s5p$ with corresponding shake-up edges $[1s4s]4p$ and $[1s4s]5s$ beyond the edge; the values of respective model parameters are collected in Table I. A common value of 1.16 eV is adopted for linewidth of all components. The significant discrepancy of 0.9 eV between the calculated energy of the $[1s]$ threshold and the position of the absorption edge in the model can be explained following Teodorescu *et al.* [26]: an absorption edge is shifted to lower energies by the accumulation of unresolved resonant

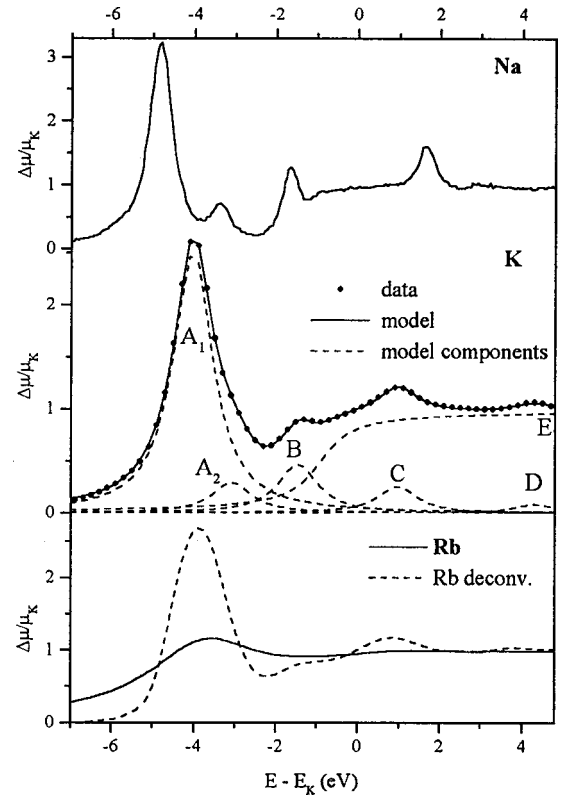


FIG. 2. The normalized near-K-edge contributions to photoabsorption in successive alkaline elements sodium, potassium, and rubidium. The spectra are aligned at the $1s$ ionization threshold (E_K) determined from the positions of preedge and postedge resonances and respective Dirac-Fock values. For potassium the model is also shown, the main components (listed in Table I) are indicated by bars: A_1/A_2 , $[1s]4p$ triplet/singlet; B , $[1s]5p$; C , $[1s4s]5s4p$; D , $[1s4s]5s5p$; E , apparent edge (see text). Together with the spectrum of atomic rubidium the deconvoluted spectrum [28] is shown.

TABLE I. Features in the near-K-edge spectrum of potassium. ΔE_{expt} and I_{expt} are least-squares values of model parameters: the energy relative to the $1s$ threshold (3611.9 eV, see Fig. 2) and the integrated cross section relative to that of the triplet $[1s]4p$. ΔE_{DF} is the Dirac-Fock energy [27] relative to $[1s]$ (3613.9 eV). All uncertainties are below 2 units of the last decimal place.

	ΔE_{expt} (eV)	I_{expt} (%)	ΔE_{DF} (eV)
$[1s]4p$ triplet	-4.0	100	-3.8
$[1s]4p$ singlet	-3.1	12	-2.8
$[1s]5p$	-1.4	19	-1.4
$[1s]6p$			-0.7
Edge	-0.9		
$[1s]$			0
$[1s4s]5s4p$	1.0	10	0.9
$[1s4s]4p$	2.7		2.7
$[1s4s]5s5p$	4.3	3	4.5
$[1s4s]5s$	5.4		5.9

transitions to high Rydberg states $[1s]np$. Its apparent position is the energy of the lowermost unresolved line in the Rydberg series.

In the Dirac-Fock calculation [27] the multiplet of the $[1s]4p$ configuration in K is split into two pairs of closely spaced levels. The levels are mixed in $(1s4s)4p$ LS coupling scheme, but 99.9% pure in $(4s4p)1s$ scheme. The lower group is a triplet $[(4s4p)^3P 1s]^2P_{1/2,3/2}$, while the higher is a singlet $[(4s4p)^1P 1s]^2P_{1/2,3/2}$. (The corresponding resonances in Na have been attributed [21] to the $[(1s3s)^3S]3p$ and $[(1s3s)^1S]3p$ transitions, with 1.5-eV splitting and 6.7 component ratio.) The calculated energy of the singlet is sensitive to configuration interaction: mixing with $[1s4s]3d4p$ and $[1s]5p$ configurations lowers the singlet-triplet splitting from 2.0 to 1.0 eV in complete agreement with the measurement and with other calculated cases of sp coupling in the same shell [28]. On the other side, the coupling of the outer electrons in different shells is negligible and the splitting almost vanishes as in the case of the resonances $[1s]5p$ and $[1s4s]5s4p$.

The comparison with argon provides a quantitative test of the theory. The pre-edge resonance is much more prominent in potassium than in argon. The ratio of 2.4 is obtained from experiment when the resonance strengths are measured in units of respective $1s$ photoionization cross section. Amusia, Baltenkov, and Zhuravleva [22] attribute the difference to the screening of the nuclear charge: the presence of the outer electron in $4s$ results in higher excitation probability. They report the ratio of 2.4 in the frozen-core approximation and 1.5 in the relaxed-core approximation. The excitation of $1s$ electron to $5p$, however, has almost the same strength and energy relative to $[1s]$ transition in both elements: ratio 1.0 is found in experiment. (Amusia calculates 1.42 in the frozen-core and 1.20 in the relaxed-core approximation.) The ratio of intensities of the resonant lines $[1s]5p$ and $[1s]4p$ is found to be 0.17 in K, 0.40 in Ar; Amusia, Baltenkov, and Zhuravleva report 0.20 and 0.34, respectively, in the frozen-core approximation, 0.29 and 0.37 in the relaxed-core approximation.

1s3p GROUP

Further structure in potassium absorption is observed above 3630 eV: a four-prong feature extends from 21 to 30 eV above the $1s$ ionization threshold (Fig. 3). The interval roughly coincides with the energies of resonance excitations of the $1s3p$ group, estimated by the Dirac-Fock model [27]. On the low-energy side, the structure begins with a small dip. Another dip at the high-energy end confirms the resonant character of the entire feature: the dip coincides with the estimated energy of the first significant $[1s3p]4p$ edge at 31 eV. Further on, the absorption spectrum exhibits several smaller sharp features, but they could not be reproducibly determined due to the coarse noise of the heat-pipe operation.

A comprehensive least-squares model of the feature shown in Fig. 3 comprises a Fano profile F , six resonances G_1-G_6 and an absorption edge H . A common value of 1.5 eV is obtained for the linewidth of the components. The in-

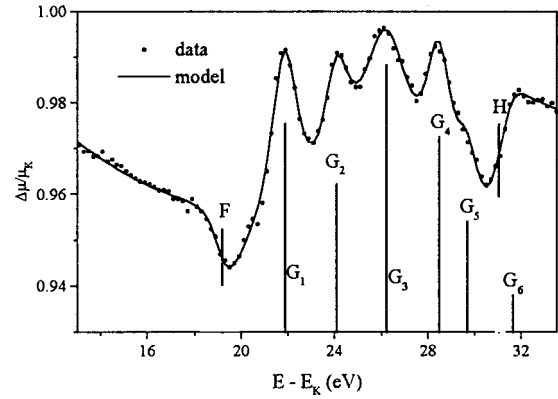


FIG. 3. Potassium $1s3p$ region. Positions of the model components are indicated by bars: F , Fano resonance; G_1-G_6 , Lorentz resonances; H , edge. The smooth trend of the photoabsorption cross section in the region is approximated by a linear function. The height of the G bars is used to indicate the amplitudes of the resonances in the scale. All widths are 1.5 eV.

crease from the value of the K-edge model is a result of the fine multiplet splitting. The considerable spread of the multiplets is the main point of interest since the corresponding structures in both related elements Ar and Rb seem much simpler, dominated by a narrow resonance and a subsequent edge as in single-electron excitations. (After natural width deconvolution of the $1s4p$ resonance in Rb, however, Filipponi shows that a similar many-prong feature may be hidden within [29]).

The Ar $1s3p$ feature has been a subject of considerable discussion. It is still an open question whether the resonance should be attributed mainly to the $[1s3p]4p^2$ double excitation [16], or to a single-electron dipole transition $1s \rightarrow 3p$ from the $[3p^2]3d^2$ component of the configuration-interaction ground state into $[1s3p]3d^2$ state [17,18]. The two processes cannot be distinguished on the basis of spectroscopic data since the energy intervals spanned by the final-state multiplets $[1s3p]4p^2$ and $[1s3p]3d^2$ largely coincide. The calculated transition probabilities for the two channels differ significantly between the authors but in principle both explanations are credible. The admixture of Ar $[3p^2]3d^2$ is about 4% of the ground state and it is only a single-electron $1s \rightarrow 3p$ transition to reach the $[1s3p]3d^2$ state. So the transition probability can be of the same order as that of the two-electron transition from the main component of the ground state to the $[1s3p]4p^2$ state.

The dilemma is elucidated by the potassium data. Potassium and argon differ in valence occupation but the inner $3p-3d$ interaction introduces an almost identical amount of the $[3p^2]3d^2$ configuration into both ground states (4.4% in Ar, 4.2% in K and K^+). Additional information is provided by the tentative $1s3p$ structure that has been extracted from the x-ray absorption fine structure (XAFS) signal of K^+ ion in glass. K^+ ion is a perfect intermediate case: it is isoelectronic with Ar, but the energies of core excitations are closer to those in K atom. Although the spectrum is crude, the transition from a dominant resonance to a many-prong feature can be clearly recognized in Fig. 4 where the $1s3p$ structure in Ar, K^+ ion, and K is shown aligned at the low-

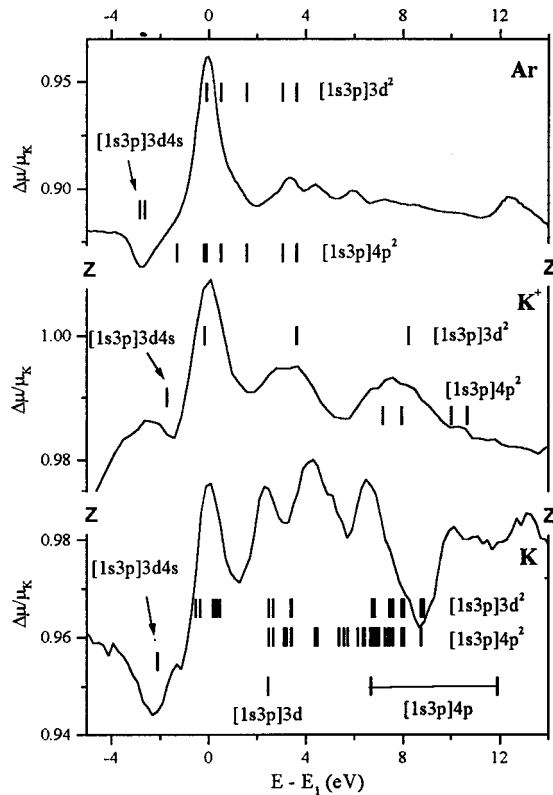


FIG. 4. The $1s3p$ group in the spectra of argon, potassium ion, and atomic potassium. Note the different amplitude scales: the scales are normalized to the respective K-edge steps. The bars indicate Dirac-Fock multiplet levels: only triplet $[(3p)3d]^3P \times [1s]4s$ levels of $[1s3p]4s3d$ are shown. The spectra are aligned at the first $1s3p$ peak; the scale of Dirac-Fock levels is slightly shifted for best match (-0.6 eV for Ar, -1.1 eV for K; the small shift for the ion includes the unknown chemical shift).

ermost peak. Together with each spectrum, the levels calculated in the mixing of $[1s3p]4p^2$, $[1s3p]3d^2$, and $[1s3p]4s3d$ configurations are plotted. A level is attributed to a configuration if its contribution exceeds 10%. In this way some levels are attributed to more than one configuration. The density of the levels may give some indication of spectral intensity, although without an estimate of transition probabilities, the picture may be misleading.

The average energy of $[1s3p]4p^2$ and $[1s3p]3d^2$ levels

TABLE II. Hartree-Fock calculation [30] of the configuration-average energies relative to the $1s$ ionization threshold for the co-excitation of the $3p$ electron. The observed relative energy of the lowermost resonance in the $1s3p$ feature is given in the last column.

	$[1s3p]4p^2$ (eV)	$[1s3p]3d^2$ (eV)	E_{expt} (eV)
Ar	19.2	20.0	19.3
K^+	24.3	16.9	
K	27.1	23.4	21.9
Ca	35.6	23.6	

in Ar, K^+ , and K is listed in Table II with extension to Ca to demonstrate the trends. The relative energy of the $[1s3p]4p^2$ level increases steadily from Ar to K and further to Ca with the increasing effective charge seen by electrons in $3p$ subshell, while the $4p$ level lies a few eV below the continuum in all cases. The collapse of the $3d$ wave function at the onset of the transition-element series results in a slower and irregular increase of the $[1s3p]3d^2$ energy with atomic number. Thus, the Hartree-Fock (HF) configuration-average energies [30] for both states are separated by almost 4 eV in K and less than 1 eV in Ar.

The same trend can be recognized in the Dirac-Fock calculation although large multiplet spread (5 eV in Ar and 10 eV in K and K^+) and the considerably strong mixing tend to obscure it. The calculated $[1s3p]3d^2$ multiplet is split into three groups of levels. Since the coarse distribution of the levels in the multiplet depends mainly on the strong $3p$ - $3d$ coupling [28] and only weakly on the occupation of the valence orbitals, it is qualitatively the same in Ar, K^+ , and K. In Ar, the $[1s3p]4p^2$ multiplet coincides with $[1s3p]3d^2$, while in the ion the multiplets are almost disjoint. In K atom the $4s$ - $4p^2$ interaction resulting from the partial screening by the $4s$ electron pulls the $[1s3p]4p^2$ to lower energies in a similar way as the $4s$ - $4p$ interaction in $[1s]4p$ level. So both multiplets overlap at the upper side of the structure.

Actually, the onset of the $1s3p$ features in the three spectra follows the calculated energies of the $[1s3p]3d^2$ multiplet. In the K spectrum, there are no $[1s3p]4p^2$ levels at the low-energy end of the feature. Thus, at least the lower part of the feature can be attributed to the $[3p^2]3d^2 \rightarrow [1s3p]3d^2$ channel exclusively. The potassium levels are spread over a wider energy range, and the total cross section for the bound-bound transition is twice that of Ar. This is close to, but less than the ratio of the $1s$ - $4p$ line intensities. So the $1s3p$ feature in Ar could be predominantly $[1s3p]3d^2$ as well, and the sharp and high resonance is just the result of a concentration of transition probability to a narrow group of multiplets.

Another spectral feature in the $1s3p$ group can be definitely identified from its shape. The small dip at the onset of the group is almost identical in both Ar and K, a trace can be found even in K^+ . In early discussions of Ar spectra it has been explained away with a tentative small peak at its lower side. Cooper [17] introduced the idea of a Fano resonance comprising the dip and the prominent peak, without making entirely clear what continuum process should be involved. Least-squares analysis of the spectral region shows unambiguously that there is a small Fano resonance separate from the prominent peak. For the nature of the continuum process, a hint can be found in [28]: the configuration mixing of the level with prevailing $[1s3p]4s3d$ character is likely to involve, beside $3d$, also higher d levels including those in continuum. In this way, the matrix element into the mixture of discrete and continuum levels exhibits a Fano profile. The triplet level of the $[1s3p]4s3d$ multiplet is indeed found close to the model Fano energy.

CONCLUSION

The small group of elements for which the spectrum of collective photoexcitations is determined directly and with

sufficient precision for a comprehensive modeling is expanded with potassium. The immediate vicinity of the K edge together with the valence $1s4s$ coexcitation follows qualitatively the features of the same region in the homologous Na. The quantitative analysis, however, shows that the coupling of the prominent $[1s]np$ excited state is basically different: the strongly coupling orbitals are $1s$ and $3s$ in Na, $4s$ and $4p$ in K. In the comparison with theoretical results for single-excitation transition probabilities of the K-Ar pair the relaxed-core approximation, surprisingly, provides no improvement over the frozen-core calculation.

The difference between K and Ar in the $1s3p$ coexcitation feature is even more dramatic. In both configuration-interaction admixture of the $[3p^2]3d^2$ configuration to the ground state strongly affects the excitation scheme, allowing a single-electron transition to the $[1s3p]3d^2$ state. Its energy shifts strongly with Z owing to the incipient collapse of the $3d$ orbital, while the concurrent $[1s3p]4p^2$ state remains largely unaffected. The coincidence of both multiplets in Ar

produces a sharp single resonance, while in K the wide spread of the mixed multiplet results in a four-prong feature. An intermediate case can be recognized in the corresponding feature in K^+ ion.

The study shows that even in the absence of a comprehensive theoretical reconstruction, the quantitative modeling of experimental data can provide decisive arguments in the explanation of spectral features. In this way, the process leading to the Fano resonance observed in the $1s3p$ excitation of both Ar and K is identified.

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