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X-ray absorption studies of two-electron–one-photon excitations in krypton

Moshe Deutsch
Physics Department, Bar-Ilan University, Ramat-Gan 52100, Israel

Michael Hart
Schuster Laboratory, University of Manchester, Manchester M13 9PL, United Kingdom

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X-ray photoabsorption measurements of simultaneous two-electron transition in krypton were carried out using synchrotron radiation. A full spectrum involving all $1s+nl$ electrons was detected. Nonrelativistic Hartree-Fock and, in particular, relativistic Dirac-Fock energy-level calculations are in good agreement with the data, as are those derived from the optical data of Rb in the $z+1$ approximation. The cross sections relative to that of the single $\underline{1s}$ ionization are found to decrease with shell number, from 2.2% for $\underline{1s4p}$ to 0.058% for $\underline{1s2s}$, i.e., slower than predicted theoretically. No indications are found for a preferred Coster-Kronig decay mode over the radiative one for the $\underline{1sns}$ levels.

Simultaneous multielectron processes in atoms present a challenge which goes beyond the current single-electron fixed-potential atomic models. They can provide important insight into electron correlations and excitation dynamics.[1] Hence the recent, rapidly increasing interest in such processes, which were studied by a variety of experimental methods such as heavy ion-atom collisions,[2] Auger,[1] electron capture,[3] x-ray emission,[4] and combined x-ray emission and absorption[5] spectroscopies.

The use of x-ray absorption spectroscopy which probes directly the electronic levels and interaction cross sections involved was hampered in part by the very low cross sections involved; 2 to 3 orders of magnitude below that of the single K electron excitation. Thus only very few absorption studies on noble gases,[5,6] transition metals,[7] and several mid-z elements[8] were published. With the advent of high-intensity synchrotron sources these restrictions were somewhat alleviated, resulting so far in two high-resolution studies in which the various bound-bound and bound-free simultaneous transitions of $1s+3p$ and $1s+3s$ electrons in Ar (Ref. 5) and $1s+4p$, $1s+4s$ and $1s+4p+4p$ electrons in Kr (Ref. 9) were clearly resolved and identified for the first time.

We report here a synchrotron radiation absorption study of two electron-one photon transitions involving $\underline{1snl}$ ($n=2,3,4$) electrons in Kr. The measured transition energies are in good agreement with nonrelativistic Hartree-Fock (HF)[10] and relativistic Dirac-Fock (DF)[11] calculations as well as levels derived using the $z+1$ approximation and optical data[12,13] of Rb. The measured relative edge discontinuities are found to decrease in correlation with energy and shell number from a value of $\sim 2\%$ for $\underline{1s4p}$ to $\sim 0.05\%$ for $\underline{1s2s}$.

The measurements were carried out at the Daresbury Laboratory Synchrotron Radiation Source, using a monolithic two reflection Si 220 monochromator and ionization chamber detectors. The effective resolution was $\lesssim 1$ eV. Total harmonic contamination was below 0.5% and varied smoothly in the regions of interest. The Kr gas was of 99.995+% purity, and the repeated scanning technique provided immunity from sudden primary radiation intensity changes. The energy scale was established using published data.[14] Further details were published elsewhere.[15]

The measured spectra are shown in Fig. 1 as plots of the difference between the data and a straight line fitted to it just below each edge. No sample scans for each region received the same treatment to ensure freedom from structures originating in spurious reflections in the monochromator, etc. The zero of the energy scale is at the onset of the one-electron cotinuum[14] $E(1s)=14327.17$ eV. The transition energies and edge discontinuities are listed in

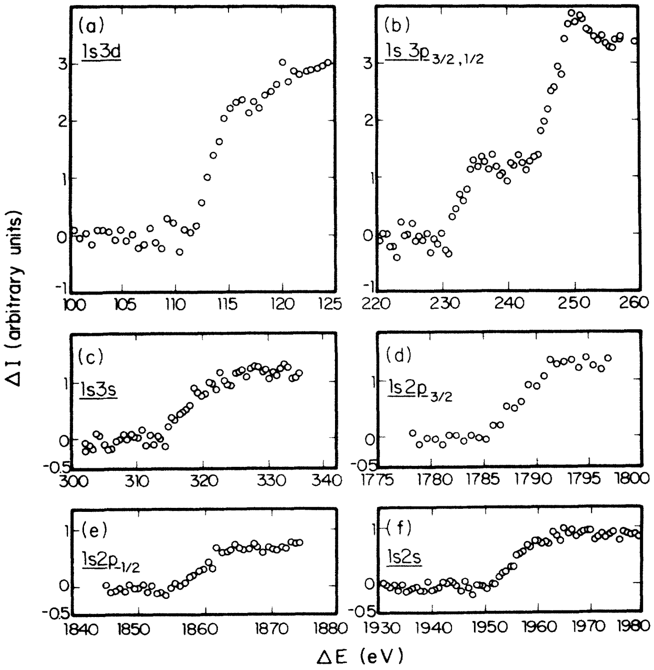

FIG. 1. Energy spectra of two-electron transitions in krypton. The excited electrons are indicated. The energy scale is relative to the onset of one-electron continuum $E(\underline{1s})=14327.17$ eV. Data are plotted as intensity differences. For details, see text.

TABLE I. Energies, lowest-lying configurations, and relative edge discontinuities of two electron transitions in krypton. ΔE, in electron volts, is relative to the Kr K edge $E(\underline{1s}) = 14\,327.17$ eV. DF, HF, and $z+1$ indicate Dirac-Fock and Hartree-Fock calculations, and levels derived from Rb optical data in the $z+1$ approximation, respectively.

Kr configuration	ΔE (eV) measurement	DF	HF	$z+1$[a]	$10^3\sigma/\sigma_K$ measurement	CN[b]
$\underline{1s4p}5s^2$	11 ± 2[c]	12.25	12.25		22 ± 2[c]	134.5
$\underline{1s4s}5s5p$	31.5 ± 0.8[c]	32.11	32.0		2.1 ± 0.3[c]	18.0
$\underline{1s3d}5s5p$	113.4 ± 0.8		113.2	113.4	2.0 ± 0.3	35.6
$\underline{1s3p}_{3/2}5s^2$	232.6 ± 0.8	239.2	235.4	239.8	1.1 ± 0.2	7.5
$\underline{1s3p}_{1/2}5s^2$	246.8 ± 1	248.2	244.4	248.7	1.5 ± 0.2	3.8
$\underline{1s3s}5s5p$	318.0 ± 1		308.3		1.0 ± 0.2	2.2
$\underline{1s3p}_{3/2}5s^2$	1788 ± 1.5	1797.6	1773.7		0.86 ± 0.15	1.8
$\underline{1s2p}_{1/2}5s^2$	1859 ± 1.5	1856.4	1832.5		0.49 ± 0.15	0.89
$\underline{1s2s}5s5p$	1956 ± 2		1970		0.58 ± 0.15	0.6

[a] Reference 13.

[b] Reference 16.

[c] Reference 9.

Table I along with those calculated using DF[11] and HF[10] methods and the optical data[12,13] of Rb in the $z+1$ approximation. The table also lists the theoretical shake-off cross sections of Carlson and Nestor.[16] The measured data listed for $\underline{1s4p}$ and $\underline{1s4s}$ excitations are taken from Ref. 9 and are more fully discussed there. As no edge structure was resolved in the transitions of Fig. 1 the DF and HF transition energies were taken as those of lowest-lying allowed transitions. For the same reason, an admittedly somewhat arbitrary but previously employed[7,8] procedure was adopted to calculate the cross section relative to that of the single $1s$ electron σ/σ_K, from the measured data, namely,

$$\sigma/\sigma_K = \ln(I/I')/\ln(I_K/I_K') \ ,$$

where I_K' and I' are the measured intensities just below the relevant edges, and I_K and I — just above it. The rapid saturation of the cross section, predicted by shake-up theory[17] and indicated by the data, provides a measure of justification for this procedure.

The theoretical energy levels, in particular the DF ones, are in excellent agreement with the measured values. The same holds for those derived from the scarce optical data, thus lending further support for the validity of the $z+1$ approximation. The DF derived splitting between $\underline{1s4p_{3/2}}$ and $\underline{1s4p_{1/2}}$ levels is only 0.8 eV and was not resolved. The barely visible structure above the edge in Fig. 1(a) may result from the ~1.6 eV j splitting of the $\underline{1s3d}$ states.

The theoretial cross sections of Carlson and Nestor[16] clearly much overestimate the measured ones, in particular for the outer electronic shells. Unlike previous studies[7,8] on solids the magnitude of σ/σ_K is clearly correlated with n and l, the principal and magnetic quantum numbers. Although the accuracy of our data is insufficient to support a definite conclusion on the monotonicity or otherwise of the decrease in the cross section with n and l, it is clear that the dependence is much weaker than predicted.[16] In contrast, it should be noted that the combined measured $\underline{1s2l}$ cross section $(1.93 \pm 0.26) \times 10^{-3}$ is satisfactorily close to that predicted by Åberg:[17] 3×10^{-3}. From Fig. 3 of Ref. 18 we deduce a ratio $R_{\text{theor}} = 1.48$ of the theoretical shake-up probability to the x-ray satellite intensity for the $\underline{1s2l}$ states. This is in close agreement with the same ratio as derived from our data and an extrapolation of Parratt's[18] measured satellite intensities: $R_{\text{exp}} = 1.43 \pm 0.15$. The deviation of this ratio from unity was attributed[5,18] mainly to the very strong fast Coster-Kronig (CK) transitions $\underline{1sns} \rightarrow \underline{1snp}$ which considerably reduces the number of $\underline{1sns}$ holes available for the slow radiative transitions generating the satellites. The same CK transitions were concluded to be responsible for the absence of $\underline{1s3s}$ related features in the *absorption* spectrum of Ar (Ref. 5). In Ne, the absence of the corresponding $\underline{1s2s}$ features[6] was attributed to the small number of the $2s$ electrons. None of these conclusions seems to be supported by our data for Kr. We detect sharp, well-defined features for all $\underline{1sns}$ transitions of roughly the same magnitude as the neighboring $\underline{1snp}$ transitions. These differences, if not an artifact, could indicate a z-dependent trend in the relative importance of intrashell electron correlations.

A resolution of this as well as numerous other important questions concerning the mostly unexplored field of multielectron transitions will have to await the availability of a systematic body of experimental data as well as the presently emerging unified theory of electron excitation including both single and multielectron effects.[19,20]

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