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Near-K-edge photoabsorption measurements in xenon

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Measurements of the absolute photoabsorption cross section near the K edge of Xe are presented. A region of increased slope extending from threshold to 600 eV above it is detected. Similar regions were found in Ar and Kr but of much smaller range. Theoretical cross sections using the hydrogenic approximation yield poor agreement with the data. Recent relativistic calculations including full relaxation and overlap correction are in excellent agreement with our measurements. The data yields an estimate of 11% for the contribution of multielectronic excitations to the cross section, somewhat lower than, but in reasonable agreement with, theory.

The structure of the near-edge photoabsorption spectrum of atoms depends very sensitively on the various single- and multielectronic processes involved, their relative importance and energy and Z dependence.[1,2] Measured spectra of this region are, therefore, subjects of choice for testing theoretical models for atomic structure and excitation processes. Measurements on isolated atoms, i.e., monoatomic gases, are mandatory for such studies since in solids, liquids, and multiatomic molecules x-ray-absorption near-edge structure (XANES), and extended x-ray-absorption fine structure (EXAFS) obscure the weak single-atom features of the spectrum not only near the edge but even hundreds of eV above it.[2(b)] In addition, absolute, rather than relative, cross sections are required for these studies. Such data are, however, quite scarce. The pioneering measurements of Materlik, Sonntag, and co-workers on the L edges of atomic vapors of rare earth[3] and other[4(a)] metals extend over a very limited energy range, and are on a relative, rather than absolute, scale. Of the noble gases, the natural candidates for such measurements, only the K edges of Ar (Refs. 5 and 6) and Kr (Refs. 7 and 8) have been studied in detail, although limited range, relative-scale measurements were published for the K edges of Ne (Ref. 9) and Xe (Ref. 10) as well. The detailed near-K-edge spectrum of Ar, measured by Deslattes *et al.*,[5] was repeatedly used to test various theoretical cross sections.[2,11,12] In particular, it enabled Tulkki and Åberg[11] to demonstrate the all important role of exchange-induced relaxation effects and the small, though non-negligible, contribution of post collisional interaction (PCI). They were also successful in reproducing the increased slope of the cross section observed in the measurements close to the edge. No similar calculations were published for Kr, although near-edge spectra as detailed as that of Ar is available.[7] By contrast, the K-edge region of Xe was studied in detail theoretically by Tulkki,[13] predicting relaxation and relativistic effects to be the decisive factors and PCI effects to be negligible. No suitable measured spectrum was, however, hitherto available to test these predictions.

We present here detailed absolute-scale measurements of the photoattenuation cross section of Xe near its K edge. Theoretical cross sections calculated using the screened hydrogenic approximation[14] with different screening constants are shown to be in poor agreement with the measured data. By contrast, Tulkki's[13] relativistic, full-relaxation calculations agree well with the measurements in the near-edge region indicating the importance of the mentioned effects.

The measurements were carried out at the RÖMO II bending magnet EXAFS station at HASYLAB, DESY, Hamburg, during a dedicated run at an energy of 3.7 GeV and a maximal current of 100 mA. An order sorting two-reflection 311 silicon monochromator controlled by a special feedback system[4(b)] was used. The flux at the sample was 10^7 photons/s. The effective full width at half maximum (FWHM) energy resolution calculated from the divergence of the beam was $\Delta E/E \approx 5\times10^{-4}$. Ar filled ionization chamber detectors were employed and tight-beam geometry observed throughout. For absolute cross-section calibration, no-sample scans were also measured. The Xe gas, of purity 99.995%, was contained in a 120-mm-long cell, having thin beryllium windows, at a pressure of 753 mm Hg at 20 °C. For the lack of a high-accuracy edge energy determination for the Xe K edge, on par with those of Breinig *et al.*[15] for the L edges, the edge energy was calibrated using the common procedure[4,6(a),15] of resolving the measured edge into discrete and continuum transitions of Lorentzian and arctangent shapes, respectively. The peak position of the first Lorentzian, representing the $1s \rightarrow 6p$ transition, was found to lie very close to the inflection point of the measured curve, and was assigned the energy $E_0 = 35561.4$ eV listed by Bearden and Burr.[16(a)] The K-level energy E_K was then taken as the position refined by the fit for the arctangent term, 2 eV higher. $E_K = 34563.4$ eV so obtained is very close to the value of 34563.1 eV derived from electron spectroscopy for chemical analysis (ESCA) measurements.[16(c)] The Xe K-level energy can also be derived by combining the accurate $L_{2,3}$ level energies measured by Breinig *et al.*[15] with $K\alpha_1$ and $K\alpha_2$ *emission* line energies. Using the Mosely interpolated values listed by Bearden[16(e)] we ob-

tain 34565 eV, while the best experimental values, measured recently by Deslattes, Kessler, and co-workers,[16(f)] yield 34565.4 eV. Both energies are within 2 eV of E_K given above. The $6p \rightarrow$ continuum interval obtained is also in good agreement with the optically derived[16(d)] interval of 2.4 eV.

The as-measured attenuation cross section is shown in Fig. 1, along with theoretical cross sections calculated using screened hydrogenic wave functions including quadrupole and octupole terms. Although this approximation is expected to be good for light atoms only, and not too close to the edge, it provides a convenient way of comparing theory with experiment as shown in previous studies.[5,7(b),7(c)] The curves correspond to four sets of screening constants σ_{nl} listed in Table I, the first two of which were calculated by Slater[17] and Clementi, Raimondi, and Reinhardt.[18] The other sets were calculated using[19]

$$\sigma_{nl} = Z - \bar{r}_{nl}^{H}/\bar{r}_{nl} , \quad (1)$$

where Z is the atomic charge, $\bar{r}_{nl}$ is the mean radius of the atomic nl orbital, and $\bar{r}_{nl}^{H} = [3n^2 - l(l+1)]/2$ is its mean hydrogenic radius. We calculated the mean radii using both nonrelativistic Hartree-Fock[20] (HF) and relativistic Dirac-Fock[21] (DF) methods. Note the large negative value of σ_{1s}^{DF} resulting from the considerable relativistic contraction of the $1s$ shell. This epitomizes the breakdown of the hydrogenic approximation for the $1s$ shell of Xe and results in the gross overestimation of the cross section seen in Fig. 1. By contrast, in Kr [Ref. 7(c)] where relativistic effects are small, σ_{1s}^{DF}, though negative, is very small and the calculated cross section yields excellent agreement with the measured spectrum. As nl increases, a progressively smaller reduction in σ_{nl}^{DF}, relative to the corresponding HF ones, is observed in Table I. This also results from relativistic shell contraction, though of decreasingly smaller magnitude due to the increase in screening and the orbital radius. The calculated DF cross section below the edge yields, however, the best agreement with the measurements.

TABLE I. Screening constants σ_{nl} and K-edge jump ratios δ_K for Xe. For a discussion see text.

nl	Ref. 17[a]	Ref. 18[b]	HF	DF
$1s$	0.30	1.079	0.697	−2.288
$2s$	4.15	14.197	4.361	1.379
$2p$	4.15	4.165	5.495	4.030
$3s$	11.25	18.424	11.640	9.680
$3p$	11.25	18.332	13.603	12.704
$3d$	21.15	14.053	16.545	16.500
$4s$	27.75	27.827	21.797	20.536
$4p$	27.75	29.043	24.400	23.907
$4d$	39.15	32.107	29.875	30.035
$5s$	45.75	39.782	35.070	34.311
$5p$	45.75	41.576	38.388	38.224
δ_K	6.94	9.24	7.19	7.17
δ_K (hydrogenic)[c]		7.15		
δ_K (McMaster *et al.*)[d]		6.08		
δ_K (McMaster *et al.*)[e]		5.48		
δ_K (Veigele)[f]		5.81		
δ_K (expt.)[g]		5.78		

[a]Slater.
[b]Clementi *et al.*
[c]No screening [Ref. 14(b)].
[d]Photoabsorption only (Ref. 22).
[e]Total attenuation (Ref. 22).
[f]Reference 23.
[g]Present results.

An important feature of the data is shown in Fig. 2 in which we plot the measured cross section divided by the hydrogenic HF one. Figure 2 clearly demonstrates the increased slope in the near-edge region. Similar effects were observed for Ar and Kr as well. In Ar it is limited to ~13 eV above threshold, while for Kr it extends to 100 eV above threshold. Here the range is much larger: ~600 eV. In fact, the slope flattens out to the hydrogenic one only a few keV above the threshold, the intermediate re-

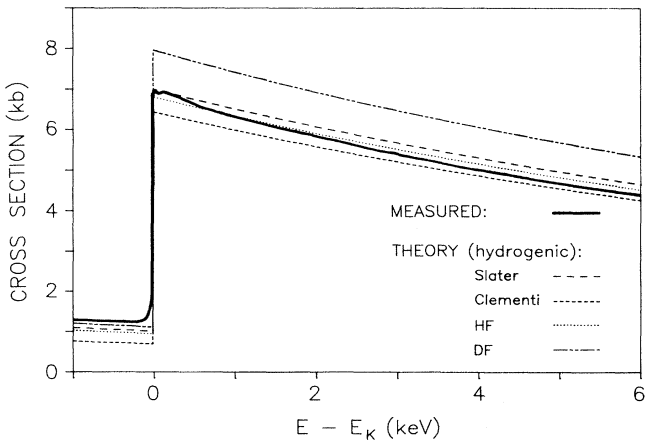

FIG. 1. Measured absolute attenuation cross section for Xe (heavy curve). The zero of the energy scale is at the K-edge energy $E_K = 34563.4$ eV. The theoretical curves employ the hydrogenic approximation with the screening constants given in Table I.

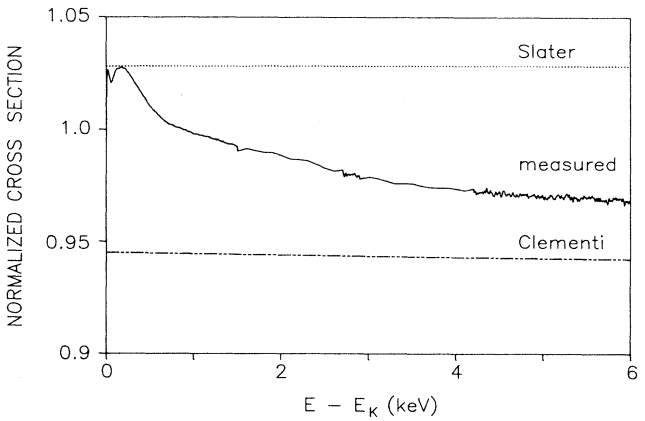

FIG. 2. The measured and theoretical cross sections divided by the hydrogenic HF theoretical one. Note the increased slope up to ~600 eV. Then the slope decreases, but flattens out only at ~4 keV.

gion having a smaller slope than the near-edge region but larger than the hydrogenic slope. An increase following a dip is observed in Figs. 1 and 2 at ~ 60 eV. This feature is most probably due to the opening of the simultaneous $1s+4d$ two-electron single-photon excitation channel, as indicated by its good alignment with the corresponding relativistic Dirac-Fock calculated energy. This and other possible two-electron features will be discussed elsewhere.

Table I lists the jump ratio δ_K from several sources, along with the value calculated from the measured spectrum. Although such a determination is, to some extent, imprecise due to the simultaneous two-electron contributions and the increased slope near the edge, most quoted values clearly overestimate the measured ones by 20%–60%. The exceptions are the semiempirical values of McMaster *et al.*,[22] one of which is calculated using photoabsorption only and the other includes scattering as well. Surprisingly, the simple approximation of Veigele,[23] $\delta_K = 3.5 + 125/Z$, yields the best agreement with the measured value.

In Fig. 3 we compare the measured spectrum with the relativistic calculations of Tulkki[13] for the $1s$ shell. The background due to higher shell absorption in the measured spectrum was fitted below the edge by the Victoreen[24] expression, $AE^{-3} - BE^{-4} + C$, and subtracted. Also shown in Fig. 3 is the measured data deconvoluted[25] using a Gaussian function which represents the smearing by the finite resolution of the spectrometer. As can be seen the smeared and deconvoluted cross sections are identical everywhere except in the close vicinity of the edge. When comparing the curves in Fig. 3, it is important to note that the theoretical results were calculated for single-electron photoabsorption only, while the measured curve includes contributions from two-electron excitations as well. Unlike in Ar and Kr, sharp two-electron features are not observed due to smearing by the large lifetime width of the K level,[26] 11.4 eV, and the comparable energy resolution. As the lowest-lying such transitions start already 10 eV above E_K, the slowly varying two-electron contribution starts practically at the edge and no clear single-electron region exists in the cross section. In view of this, and the estimated[27] 15%–20% contribution of two-electron shake-off excitations in the region of Fig. 3, it is clear that all but the relaxed DF calculations overestimate the measured cross section. The decrease found by Tulkki in the calculated cross section due to relativistic effects is clearly supported by the data. Although it is difficult to derive a precise estimate for this reduction from the data, the predicted 12% seems to be of the right magnitude. The importance of relaxation is further demonstrated by the good agreement between the deconvoluted data and the relaxed DF calculations in the vicinity of 10 eV, the most remote region from the single-electron bound-bound transitions but still below the two-electron excitation threshold. The relaxed DF curve has here the right magnitude and slope. Neglecting the overlap corrections in the DF calculation obviously yields in this region not only a cross section too low by a factor of 2, but also a positive decreasing slope, rather than the negative increasing one observed in the deconvoluted data. Finally note that at 100 eV, the difference between the calculated relaxed DF curve and the measured one is 11%. Although a few percent smaller, this is comfortably close to the estimated[27] 15%–20% two-electron contribution. We conclude, therefore, that our measurements strongly support Tulkkis[13] relaxed DF calculations for the near-edge region and his conclusions concerning the importance of relaxation and relativistic effects for Xe. Measurements on radon, where relativistic effects are expected to be three times as large and where multipolar contributions higher than the electric dipole are expected to be measurable, are called for to improve our understanding of the processes involved in photoabsorption near the edge.

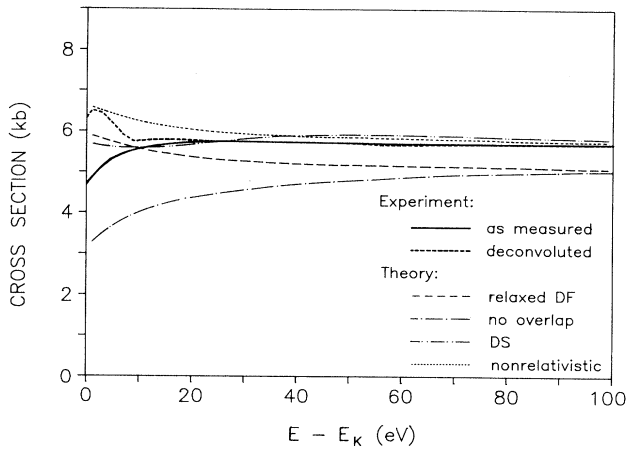

FIG. 3. Near-edge measured (heavy line) and theoretical relativistic cross sections of Tulkki (Ref. 13) for the $1s$ shell. Contributions from higher shells were subtracted from the measured data. Note that the energy range is much smaller than in the preceding figures.

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