Photoion yield spectra of singly and doubly charged lanthanides in the region of the 5p excitation: The elements La, Ce, Pr, Nd, Sm, and Eu

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Using synchrotron radiation, an atomic beam technique, and a time-of-flight spectrometer the photoion yield spectra of the singly and doubly charged lanthanides La, Ce, Pr, Nd, Sm, and Eu in the region of the 5p excitation between 20 and 40 eV were measured. The experimental results are discussed within the concept of autoionizing atomic states and the production of doubly charged photoions by stepwise processes. For Pr, as an example, the partial cross sections of the subshells $6s_{1/2}$, $4f_{5/2}$, $5p_{3/2}$, and $5p_{1/2}$ were calculated with the method of the time-dependent local-density approximation, and the results are compared with the Pr^+ and Pr^{2+} signals.

I. INTRODUCTION

The first measurements of the lanthanide absorption spectra in the range of the 5p excitation between 20 and 40 eV were reported by Tracy,[1] who investigated the elements Sm, Eu, Dy, Ho, Er, Tm, and Yb. The spectra are dominated by broad asymmetric resonances which lie above the $5p^5\,^2P_{3/2}$ thresholds. For the heavier elements Dy, Ho, Er, Tm, and Yb strong discrete lines are observed for transitions to $^2P_{3/2}$ based levels. In the special case of Yb with the closed 4f subshell, Tracy[1] could assign these discrete lines essentially to four series $5p \rightarrow nd$ converging to the spin-orbit limits $5p^5\,^2P_{3/2}$ and $^2P_{1/2}$ at 31.35 and 37.52 eV.

After the photoexcitation or photoionization of the 5p electrons, the rearrangement of the core takes place by the emission of one or two electrons and/or by the emission of photons. These processes can be studied by the technique of photoelectron or photoion spectroscopy or by the detection of the fluorescence. We have used a time-of-flight spectrometer to obtain the relative cross sections for single and double photoionization of the lanthanides in the region of the 5p excitation. Similar experiments for the more easily vaporizable elements Sm, Eu, Tm, and Yb were performed by Holland and Codling[2] and Holland *et al.*[3]

II. EXPERIMENTS

The synchrotron radiation of the 800-MeV electron storage ring BESSY in Berlin was used for the photoexcitation of the atoms. The radiation was dispersed by a 1 m Seya monochromator equipped with a 1200 lines/mm grating. The photon flux was monitored by a sodium-salicylate coated photomultiplier. The monochromator output was focussed on an atomic beam which was produced by the thermal evaporation of the metals in an effusion oven heated by electron impact. The temperatures which were necessary for the production of a particle density of about 10^{11} cm^{-3} in the interaction region were in the range of about 900 K for Eu, 1000 K for Sm, 1600 K for Nd, 1800 K for Pr, and 2000 K for La and Ce. The photoions were extracted from the interaction region by short pulses (120 V amplitude, 1 μs width, 25 kHz repetition rate) which served as the start signals for a time-of-flight spectrometer. After identification of the mass and charge spectra in a multichannel analyzer, appropriate time windows were used for the simultaneous detection of the singly and doubly charged photoions as a function of the photon energy.

III. RESULTS

The results of the photoion yield spectra for the singly and doubly charged lanthanides La, Ce, Pr, Nd, Sm, and Eu in the region of the 5p excitation are shown in Fig. 1. In a later paper we shall present the results for Gd, Tb, Dy, Ho, Er, Tm, and Yb. For each element the scale is arbitrary and independent of the others. Several systematic trends can be observed.

(1) The discrete resonances, which may be mainly attributed to $5p \rightarrow nd$ transitions, are dominant for the singly charged ion signals X^+. These resonances occur preferably in the region below the $5p\,^2P_{3/2}$ limits. Therefore, these parts of the X^+ signals should be described mainly as resulting from the autoionization of atomic levels based on $5p^5\,^2P_{3/2}$. For the heavier elements there is an increasing tendency that these discrete lines of the X^+ signals are reproduced by the corresponding X^{2+} signals (though with small amplitudes, as can be seen for Sm^{2+} and Eu^{2+}). The average of the discrete lines in all X^+ spectra reveals roughly a broad two-peak structure.

(2) The X^{2+} signals have a pronounced shape-resonance-like asymmetric peak at the "high energy" part of the spectrum above the $5p\,^2P_{3/2}$ limits, which dominates the spectra in the region of the 5p ionization.

The doubly charged ions can be created by direct double ionization where the photon energy is shared by both electrons resulting in a broad background of the corresponding photoelectron spectra. The cross section of this process, however, is usually much smaller than those of

stepwise processes like the photoionization of the $5p$ electron followed by the Auger decay of the $5p$ hole. Discrete resonances in the X^{2+} signals should be explained by the excitation of atomic levels $X\,5p^5nl$ which decay in a two-step process to doubly charged ions. Tracy[1] proposed for the $5p^5(^2P_{1/2})$ based levels the spin-flip mechanism for the first step via $X\,5p^5(^2P_{1/2})nl \rightarrow X^+\,5p^5(^2P_{3/2})+e^-$, which is followed by the Auger decay to X^{2+}. Especially for the light elements of the lanthanides, however, there should be a large influence of $6s \times 5d$ mixing in the presence of the $5p$ hole as was convincingly demonstrated by Connerade *et al.*[4,5] for the two-step autoionization in Ba.

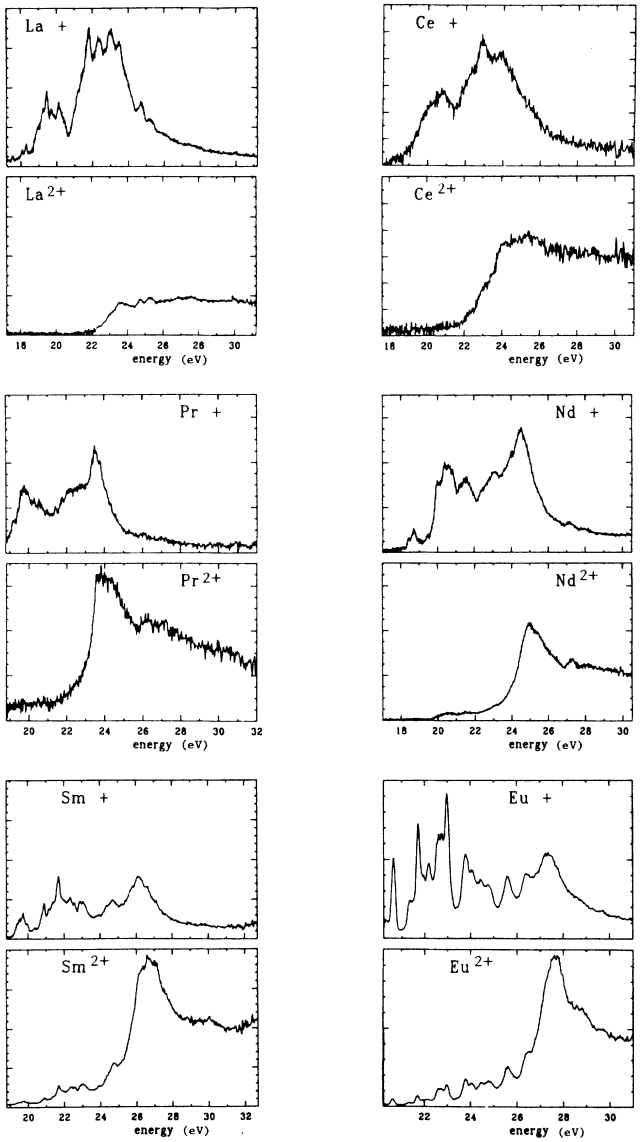

FIG. 1. Photoion yield spectra of the singly and doubly charged lanthanides La, Ce, Pr, Nd, Sm, and Eu in the region of the $5p$ excitation. The scales of the different elements are arbitrary and independent of each other.

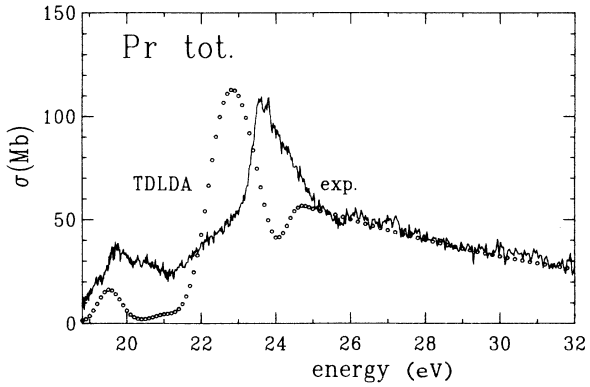

FIG. 2. The sum of the Pr^+ and Pr^{2+} signals and the total photoionization cross section of Pr in the region between 19 and 32 eV calculated with the method of the time-dependent local-density approximation (TDLDA).

For a better understanding of the spectra, we have calculated the partial photoionization cross sections of the different subshells $5p$, $4f$, $5d$, and $6s$ using a relativistic version[6] of the time-dependent local-density approximation (TDLDA). The TDLDA is closely related to the random-phase approximation with exchange (RPAE),[7]

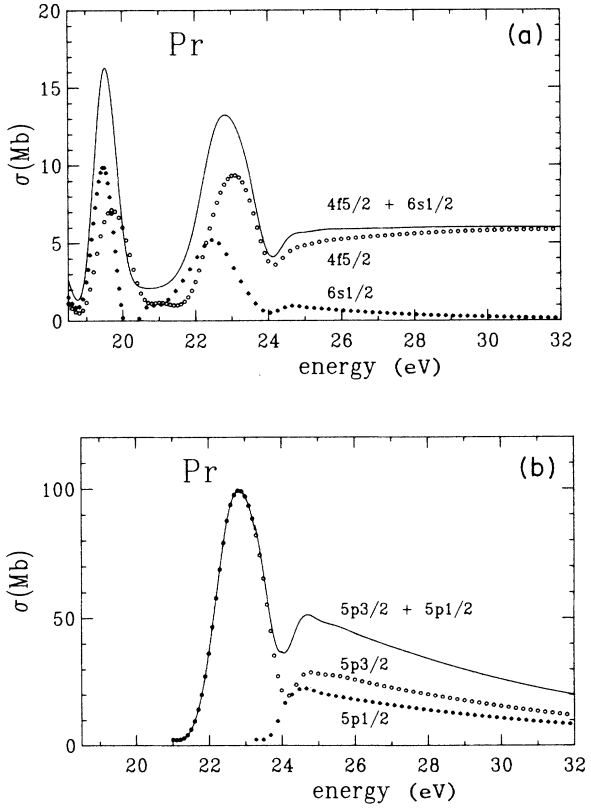

FIG. 3. The partial photoionization cross sections of the subshells Pr $6s_{1/2}$, $4f_{5/2}$, $5p_{3/2}$, and $5p_{1/2}$ in the region between 19 and 32 eV calculated with the method of the time-dependent local-density approximation (TDLDA).

but instead of Hartree-Fock orbitals, LDA orbitals are used. In this method the external potential v_{ext} of the photon field induces a displacement in the electronic charge distribution, which gives rise to an induced potential. From this induced potential the frequency dependent polarizability $\alpha(\omega)$ and the cross section for photoabsorption $\sigma(\omega)=4\pi(\omega/c)\mathrm{Im}\alpha(\omega)$ can be calculated.

Figure 2 gives, as an example, the total cross section of Pr in the region between 19 and 32 eV as the sum of the partial cross sections of the subshells $6s_{1/2}$, $4f_{5/2}$, $5p_{3/2}$, and $5p_{1/2}$ starting from the ground state configuration $4f^3 6s^2$. Relativistic orbital energies[8] and the Gunnarsson-Lundqvist formula[9] for the exchange-correlation function were used for these calculations. The comparison with the experimental curve, which is the sum of the Pr^+ and Pr^{2+} signals shows good agreement in the broad features although there is a shift of about 1 eV for the peaks at 23 and 25 eV. As the calculations did not take into account any multiplet splitting, one cannot compare the different widths and amplitudes.

For the separate interpretation of the Pr^+ and Pr^{2+} signals, the partial cross sections of the subshell $6s_{1/2}$, $4f_{5/2}$, $5p_{3/2}$, and $5p_{1/2}$ are shown in Fig. 3. The sum of $6s_{1/2}$ and $4f_{5/2}$ should be discussed in connection with the Pr^+ signal, whereas the ionization of the $5p_{3/2}$ and $5p_{1/2}$ electrons with the subsequent Auger decay should lead to Pr^{2+}. The comparison of $\sigma(4f_{5/2})+\sigma(6s_{1/2})$ with the Pr^+ signal yields a qualitative agreement with the two-peak structure of the experimental results. Good agreement is obtained by the comparison of $\sigma(5p_{3/2})$ and $\sigma(5p_{1/2})$ with the Pr^{2+} signal where the structures of the experimental curve are quite well reproduced.

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[1]D. H. Tracy, Proc. R. Soc. London, Ser. A **357**, 485 (1977).
[2]D. M. P. Holland and K. Codling, J. Phys. B **14**, L359 (1981).
[3]D. M. P. Holland, K. Codling, and R. N. Chamberlain, J. Phys. B **14**, 839 (1981).
[4]J. P. Connerade, S. J. Rose, and M. A. P. Martin, J. Phys. B **12**, 253 (1979).
[5]J. P. Connerade and M. A. P. Martin, J. Phys. B **13**, L373 (1980).
[6]D. A. Liberman and A. Zangwill, Comput. Phys. Commun. **32**, 75 (1984).
[7]A. Zangwill and P. Soven, Phys. Rev. A **21**, 1561 (1980).
[8]K.-N. Huang, M. Aoyagi, M. H. Chen, B. Crasemann, and H. Matz, At. Data Nucl. Data Tables **18**, 243 (1976).
[9]O. Gunnarsson and B. I. Lindqvist, Phys. Rev. B **13**, 4274 (1976).