Angular Distribution of Xe $5s \to \epsilon p$ Photoelectrons: Disagreement between Experiment and Theory

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The angular asymmetry parameter β for the Xe $5s \to \epsilon p$ photoelectrons has been studied with use of synchrotron radiation ($h\nu$ =28–65 eV). The present results show that the relativistic random-phase approximation theory does not satisfactorily describe the Xe 5s photoionization process close to the Cooper minimum and thus require a renewed theoretical approach. The 5s partial photoionization cross section was obtained over the same photon region and the results agree with experimental values found in the literature.

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Photoelectron studies of the outer s subshell in rare gases using synchrotron excitation give a sensitive test of the importance of a proper treatment of relativistic and correlation effects in atomic theory. In the nonrelativistic approximation, the angular asymmetry parameter β is required to take the value of 2 independent of photon energy since there is only one channel open for the photoelectric process.[1,2] However, when relativistic effects are included, at least two channels exist for the photoelectric process leading to a variation of the value of β, especially close to a Cooper minimum.[3] The importance of a relativistic treatment and the incorporation of many-body effects in theoretical calculations of β are shown in Fig. 1 which gives theoretical[4-6] and experimental[7,8] results for the angular asymmetry parameter β for the 5s subshell of xenon as found in the literature. From a comparison with the very scarce amount of experimental data, it seems as if the relativistic random-phase approximation (RRPA) calculations[5] including interchannel correlations between the 4d-, 5s-, and 5p-subshell channels would give a fairly good agreement between theory and experiment. However, the very few experimental points available do not really allow a critical test of the theory, at least not concerning the strength of the minimum. It was therefore deemed valuable to make a more comprehensive experimental study of the behavior of the angular asymmetry parameter β as a function of photon energy for the 5s subshell ($h\nu$ =28–65 eV) of Xe. Also included in the measurement was a determination of the partial photoionization cross section for the 5s subshell over the same photon region. It will be shown that the present experiment reverses earlier appraisal and indicates shortcomings of theory in this sensitive test case.

The angle-resolved photoelectron spectra were taken with an electron spectrometer designed and built at the Oak Ridge National Laboratory.[9] The photons were obtained from the storage ring Tantalus I, at Stoughton, Wisconsin, and monochromatized by a toroidal grating monochromator.[10] In the experiment, $\frac{2}{3}$ of the 5s data were taken with a 10-V preacceleration and the rest with a 20-V preacceleration.

The differential cross section for a randomly oriented molecule can be expressed in terms of the angular asymmetry parameter β. The value of this parameter can, within the dipole approximation, be obtained experimentally by the following relationship[10,11]:

$$\beta = 4(R-1)/[3P(R+1)-(R-1)].$$

Here R is $I(0°)/I(90°)$, where $I(0°)$ and $I(90°)$ are the intensities of photoelectrons moving in the di-

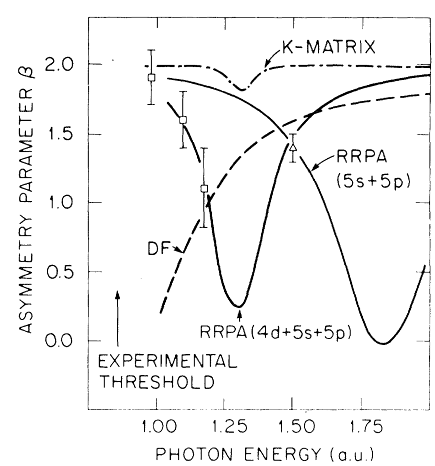

FIG. 1. Photoelectron angular asymmetry parameter β for the 5s subshell of xenon. Theory: dashed line, Dirac-Fock calculation, Ref. 4; solid line, relativistic random-phase calculations, RRPA, Ref. 5; dot-dashed line, K-matrix calculation, Ref. 6. Experiment: triangle, Ref. 7; squares, Ref. 8.

rection parallel and perpendicular, respectively, to the polarization vector. The polarization, P, was determined from measurements on the He 1s orbital where β is assumed to be 2.0. The photoelectron intensity was also measured as a function of the angle θ between the polarization vector and the direction of the photoelectron and the appropriate $\cos^2\theta$ dependence was obtained. In the photon energy range covered by this experiment, the polarization was (84–89)%.

Since our electron spectrometer is equipped with two electron analyzers at right angles to each other,[9] it is possible to record simultaneously the photoelectron intensities needed for the calculation of β, which means that the outcome of a β measurement is insensitive to changes in the beam current or pressure variations in the source cell. Being able to utilize this feature is of course very much dependent on the long-term stability of the relative sensitivity of the analyzers. Calibration measurements were therefore performed during the progress of the experiment, giving good confidence in the procedure. As a further precaution we also made some measurements of the β value using only one analyzer, rotating it to the 0° and 90° positions, respectively. The results of these measurements are consistent with the two-analyzer data.

A complicating factor in the analysis of the data is the mixing of the *NOO* Auger lines with the 5s photoelectron line. The excitation of the Auger lines in this photon energy region is due to second-order radiation emerging from the monochromator. However, since photoelectron lines move with a change of the monochromator setting whereas Auger transitions are unchanged in energy, it was possible to correct for the influence of the Auger transitions by carefully comparing electron spectra adjacent in photon energy. In the cases where we were faced with interference with the comparatively intense second-order 4d photoelectron lines, we found it necessary to use a radiation filter (TiMgTi) which, at the expense of overall intensity, for all practical purposes removed the second-order radiation.

Our experimental results for the energy behavior of the photoelectron angular asymmetry parameter β for the 5s subshell of xenon are shown in Fig. 2. Also included in the figure is the result from the many-body relativistic random-phase-approximation calculation[5,12] which includes interchannel correlations between the 5s, 5p, and 4d channels, and the K-matrix calculation of Huang and Starace.[6] In order to compensate, at least partially, for the differences in theoretical and experimental binding energies used for the 5s subshell, we have chosen to plot the β_{5s} value as a function of photoelectron energy, thereby referring all data to the same energy threshold (see Fig. 2). The experimental results give a value of β between 1.8 and 1.9 for the high photon energies which is in fair agreement with both calculations. When approaching the Cooper minimum from the high-energy side, the β_{5s} value starts to decrease and goes to a shallow minimum of 1.4 to 1.5 in the region of the Cooper minimum. From the present data it is not possible to deduce whether the β value starts to increase for still lower photon energies closer to the threshold or not, but taking into account the experimental data of White *et al.*[8] also shown in Fig. 2, there seems to be a trend towards higher β values closer to threshold. As seen in Fig. 2, the present results agree within error limits with the earlier measurements of White *et al.*[8] and Southworth *et al.*[13] whereas the single point of Dehmer and Dill[7] falls outside our data.

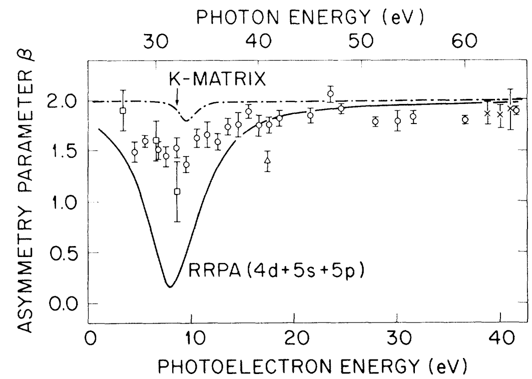

FIG. 2. Comparison of theoretical and experimental results for the 5s angular asymmetry parameter β. The theoretical curves have been shifted by -4.1 eV in order to reflect the same 5s threshold energy as the experiment. Theory; dot-dashed line, K-matrix results, Ref. 6; solid line, RRPA results, Ref. 12. Experiment: circles, this work; triangle, Ref. 7; squares, Ref. 8; crosses, Ref. 13.

Although the two theoretical calculations give a variation of the β_{5s} value with a minimum in the same energy region, the width and the strength of each β curve are quite different. As mentioned above, the very few experimental data[7,8] previously available seemed to strongly favor the RRPA calculations[5,12] but the present data clearly show that the theoretical treatment is far from an agreement with experiment. According to Huang and Starace[6] the probable reason for the comparatively shallow curve of the K-matrix calculation is the use of nonrelativistic Hartree-Fock wave functions in describing the Xe core and to a lesser extent the neglect of ground-state correlations treated in the RRPA calculations. However, from a comparison with the present results it is evident that the RRPA calculation overestimates the strength of the nonrelativistically forbidden $^3P_1$ channel which is responsible for the decrease in the β value. In this context it is interesting to return to Fig. 1 where one can see from the two RRPA calculations that correlation effects are very important not only for the prediction of the energy position of the minimum in the β_{5s} curve but also for the absolute value. Although the $4d$ threshold ($h\nu = 2.5$ a.u.) lies comparatively high above the $5s$ threshold, the addition of the $4d$ interchannel correlation gives a large change in the theoretical predictions. It would therefore be interesting to see to what extent the inclusion of the $4p$ and $4s$ interchannel interactions would improve the theoretical results. In addition to these correlations, the interactions with two-electron configurations could be important for the weak $5s \to \epsilon p$ channel. Our preliminary experimental results indicate that correlation satellites,[14] including the one containing the $5s^5 5p^4(^3P)5d(^2S)$ configuration, are more intense than the $5s$ photoelectron line through the Cooper minimum.

As a further test of the theory we present our results on the partial photoionization cross section for the $5s$ subshell of xenon. The relative partial photoionization cross sections were obtained from measured intensities according to a procedure previously described.[10,11] The absolute values were calculated from literature values for Xe $5p$,[15] using measured branching ratios. The present values together with experimental values found in the literature[15-17] are shown in Fig. 3. The solid line represents RRPA calculations[12] energy shifted as described in the caption of Fig. 2. There is a fairly good agreement between different experimental data. A comparison with the RRPA calculations[12] shows that the theory predicts quite reasonable values in the region of the Cooper minimum, whereas it overestimates the $5s$ partial photoionization cross section for higher photoelectron (photon) energies. This is even more evident for slightly higher photon energies[11,15] than covered in the present experiment and may be due to an exaggeration of the effect of the $4d$ delayed maximum by the theory, pulling σ_{5s} up too high in that region. It is interesting to note that the nonrelativistic random-phase-approximation-with-exchange calculations of Amusia and Cherepkov[18] give results similar to the relativistic calculations in this case.

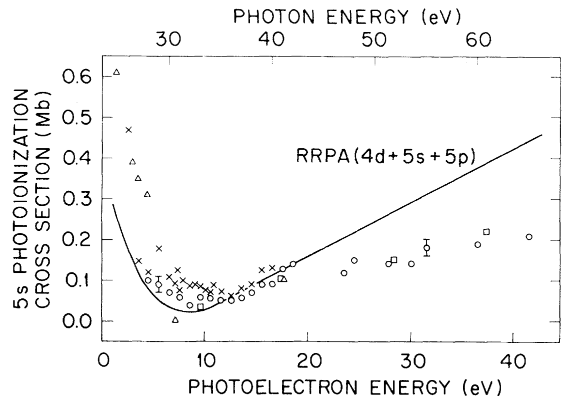

FIG. 3. Comparison between RRPA theory, Ref. 12, and experimental results for the 5s partial photoionization cross section of xenon vs photoelectron energy. The theoretical curve, solid line, is energy shifted as in Fig. 2. Experiment: circles, this work; squares, Ref. 15; triangles, Ref. 16; crosses, Ref. 17. Typical errors are indicated in two places.

To conclude, the present data show that contrary to previous inferences, the behavior of the angular asymmetry parameter β for the $5s$ subshell of xenon is not satisfactorily described by the present theory. The reason for this is not fully understood and as a matter of fact somewhat surprising since for example the theoretical predictions of the RRPA method have been shown to be in good overall agreement for both the $5p$ (Ref. 9) and the $4d$ (Ref. 19) subshells of xenon. As suggested above, it would be interesting to extend the RRPA calculations to include interactions with the $4p$ and $4s$ channels and the configurations reached by two-electron transitions.

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