PHYSICAL REVIEW A VOLUME 24, NUMBER 5 NOVEMBER 1981

Photoionization of positive ions. III. Mercury

K. D. Chao and Steven T. Manson*
Department of Physics and Astronomy, Georgia State University, Atlanta, Georgia 30303
(Received 26 May 1981)

Calculations of the photoionization of the $4f$ and $5d$ subshells in the mercury isonuclear sequence have been performed within the framework of a Hartree-Slater central-field model. The results, obtained from the neutral to Hg^{33+}, show that removal of outer-shell electrons have virtually no effect on inner-shell cross sections even for subshells with delayed maxima and/or Cooper minima. The general systematics of the variation of $4f$ and $5d$ cross sections in the Hg isonuclear sequence is discussed.

I. INTRODUCTION

Photoionization of positive atomic ions is of importance in connection with plasma physics (especially CTR work), space, upper atmosphere, and astrophysics. Laboratory measurements are difficult and, to date, photoionization cross sections have been reported[1,2] only for Li^+ and Na^+. None have been measured for higher stages of ionization; thus the need for theoretical work.

In previous work,[3,4] we have investigated the isonuclear sequences of O($Z=8$) and Fe($Z=26$) (hereafter referred to as I and II, respectively).[5] These were done as examples of low-Z and intermediate-Z elements. In this paper, we consider Hg ($Z=80$) as representative of a high-Z species. In particular, we have investigated the $4f$ and $5d$ subshells, which have significant structures, well above threshold, in the neutral atom.

The basic aim of this work is twofold. First is to investigate the response of the photoionization cross-section inner shells to removal of outer electrons. In previous work (I and II) it was found that $\sigma_{nl}(h\nu)$, the cross section for a given nl subshell as a function of photon energy $h\nu$ remained constant, to within $\sim 3\%$, when electrons with a principal quantum number greater than n were removed. In this work, this finding is tested for subshells with structures extending more than 100 eV into the continuum in the neutral atom. In addition, we are concerned with the behavior of $\sigma_{nl}(h\nu)$ when electrons of the *same* principal quantum number are removed from the ion, with particular emphasis upon delayed maxima[6-11] and Cooper minima.[6-11]

II. METHOD AND ACCURACY OF CALCULATIONS

The cross sections described in this paper were calculated using Hartree-Slater (HS) wave functions[12] for initial discrete states and final continuum wave functions obtained using the HS potential appropriate to the initial state. This methodology has given reasonable results for neutral atoms.[7,11] The details are given in I and elsewhere.[6,8,10,11]

Insofar as assessing the accuracy of the calculations, the *only* experimental cross sections are for singly ionized Li and Na,[1,2] as mentioned above. We note that while calculations, using the same methods employed in this paper, give good agreement with these experimental results,[1,2] this agreement may not be indicative of the case of highly charged heavy ions. We can, however, get some idea of the validity of our results based upon the extensive experience with neutral atoms, where it has been found that away from threshold where Cooper minima and delayed maxima[6,11] are in evidence, the calculated results agree with experiment to within about 20%. In addition, as discussed in II, it is evident that as electrons are removed from an atom or ion, the nuclear potential seen by the ith electron, $-Ze^2/r_i$, remains intact, while the noncentral interelectron potential, $\sum_j e^2/r_{ij}$, decreases since fewer electrons, j, remain to interact with. Thus, the central potential increases relative to the noncentral with increasing stages of ionization, i.e., along an isonuclear sequence. Hence, it is expected that the central-field calculation used herein, will become more and more accurate with increasing stages of ionization. This is also borne

out by comparison with sophisticated multiconfigurational Hartree-Fock (MCHF) calculations.[13]

In this regard, we note that any multiplet structure is implicitly omitted in a central-field approximation. This, however, is only important in the threshold regions for open-shell atoms and ions where multiplet splitting in the final ionic state leads to several thresholds in place of a single one. In addition, this calculation is entirely nonrelativistic, which could be questionable for so heavy an element as mercury. It turns out, however, that the integrated subshell cross sections for Hg $4f$ and $5d$ are not significantly affected by relativistic interactions for the neutral atom.[14] We have no reason to suspect that the same does not hold true for the ions of mercury as well.

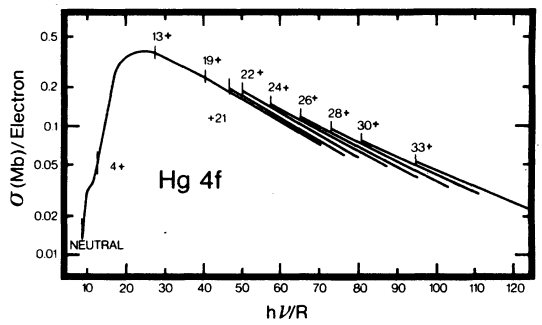

FIG. 1. Photoionization cross sections *per electron* for the $4f$ subshell in the Hg isonuclear sequence as a function of $h\nu$ in units of rydbergs (13.6 eV). Note that the curve for each stage of ionization represents a separate calculation.

III. RESULTS AND DISCUSSION

The ground-state outer-shell structure of the Hg($Z=80$) atom is $4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2$. Photoionization cross-section calculations have been performed for $4f$ and $5d$ subshells in the ground states of *all* members of the mercury isonuclear sequence Hg^{n+} from $n=0$ to $n=11$ ($5d$) and to $n=33$ ($4f$), i.e., all stages of ionization in which these subshells are occupied in the ground state. All cross sections are plotted per electron in order to abnegate the effects of changes in occupation number along the isonuclear sequence. To obtain the total subshell cross sections, our results must be multiplied by the occupation number.

A. $4f$ subshell

A selection of our results for the photoionization of $4f$ electrons in the Hg isonuclear sequence is given in Fig. 1, plotted versus photon energy $h\nu$. The outstanding feature of these results is that the $4f$ cross sections for Hg^0 through Hg^{20+}, *each arising from a separate calculation,* all lie essentially on the same curve (to within a few percent). The only effect of the removal of the outer-shell electrons is to shift the $4f$ threshold to higher energy.

The fundamental cause of this phenomenon is discussed in I and II. Briefly, the charge densities for atomic electrons are concentrated about $\langle r \rangle$. For $n=5$ and $n=6$ in Hg, these values are approximately $1a_0$ and $3.3a_0$, respectively[15] (a_0 is the Bohr radius), while for $n=4$ it is about $0.45a_0$.[15] Thus, to a good approximation, the charge densities of the $n=5$ and 6 electrons lie wholly outside the $n=4$ shell generally, and outside of the $4f$ subshell, in particular. Their removal, then, only changes the potential inside by a constant amount, thereby changing the ionization potential of the inner shells. But since spherical charge distributions change the potential in inner regions where they do not extend by a constant amount, i.e., they exert no forces, their removal can have no other effect.

Upon breaking into the $4f$ subshell the cross section, of course, changes as seen for Hg^{21+} and higher stages of ionization in Fig. 1. The change is small and amounts to about a 15% increase for each subsequent stage of ionization, the curves remaining roughly parallel. The increase is due to the decrease in screening owing to removal of electron with the same principal quantum number.

It is also of interest to note that the hydrogenic approximation (with both inner and outer screening) does poorly at all stages of ionization. In Fig. 2 the comparison is shown for the neutral atom to Hg^{20+}, all of which lie along the same curve, in each case. As expected, the hydrogenic is far too large at the lowest energy, by about two orders of magnitude, and has an entirely incorrect spectral shape. At the higher energies, the hydrogenic drops below our results and is seen to be diverging with increasing energy. For still higher stages of ionization, the situation is shown in Fig. 3, where the divergence of the present results and the hydrogenic results are seen. The behavior of the hydrogenic results can be easily understood. The hydrogenic formulation employs an effective charge, Z_E, and the cross section scales with this Z_E. The Z_E is determined by energy considerations which are sensitive to the intermediate region of r. Thus, for

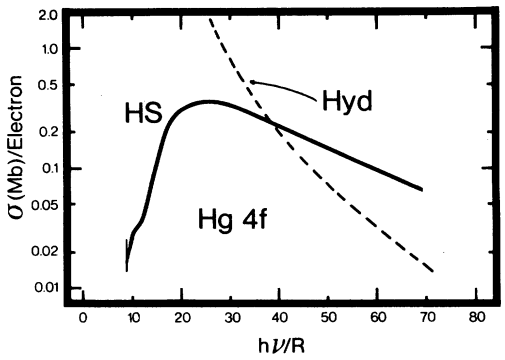

FIG. 2. Comparison of the photoionization cross sections *per electron* for the $4f$ subshell of Hg^0 through Hg^{20+} in the Hartree-Slater (HS, solid line) and hydrogenic (HYD, dashed line) approximations.

low energies, where the dipole matrix elements are determined principally at large r, near the outer edge of the atom or ion, the hydrogenic Z_E is much too large resulting in an unrealistically large cross section; at higher energies, where the small-r region near the nucleus is most important, the converse is true and the hydrogenic cross section is much too small. Thus, at no stage of ionization will the hydrogenic results be accurate over a broad photon energy range.

B. 5*d* subshell

Selected results for the $5d$ subshell of Hg and its ions are presented in Fig. 4. Again we find that when only $n=6$ electrons are removed, $\sigma_{5d}(h\nu)$ remains essentially constant, only through Hg^{2+} in

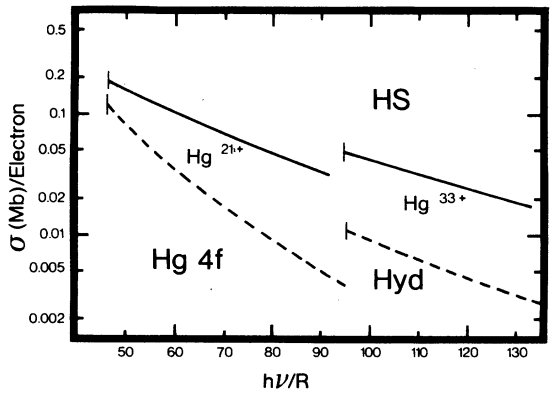

FIG. 3. Comparison of the photoionization cross sections *per electron* for the $4f$ subshells of Hg^{21+} and Hg^{33+} in the Hartree-Slater (HS, solid line) and hydrogenic (HYD, dashed line) approximations.

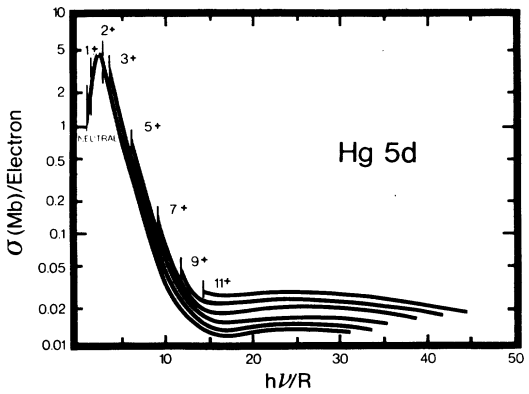

FIG. 4. Photoionization cross sections *per electron* for the $5d$ subshell in the Hg isonuclear sequence as a function of $h\nu$ in units of rydbergs (13.6 eV). Note that the curve for each stage of ionization represents a separate calculation.

this case. For higher stages of ionization starting with Hg^{3+}, where electrons from the $5d$ subshell are removed, the cross sections *per electron in the subshell* increase somewhat with stages of ionization, by about 12% per stage, and remain roughly parallel.

The $5d$ cross section differs from the $4f$ in that there is a minimum caused by a zero in the $5d \rightarrow f$ channel, a Cooper minimum.[6-11] This minimum, of course, remains at the same $h\nu$ for the neutral atom and Hg^{1+} and Hg^{2+}. For higher stages of ionization, where the $5d$ is broken into, it moves in toward lower $h\nu$, but only very slightly. The minimum, which is located at $h\nu/R=13.85$ for the neutral atom is at $h\nu/R=13.03$ for Hg^{10+}, and the inward movement is roughly linear with increased stage of ionization. For Hg^{11+}, threshold overtakes the minimum which now lies in the discrete. Note that the zero in the $d \rightarrow f$ matrix element does not necessarily correspond to the minimum in the cross section owing to the energy dependence of the $d \rightarrow p$ cross section. Thus, as seen in Fig. 4, the slight minima in the $5d$ cross sections appear at somewhat different energies than quoted above and *do not* correspond to the zeros in the $d \rightarrow f$ channels.

The comparison with hydrogenic results, shown in Fig. 5, is similar to that of the $4f$ subshell. In this case, the comparison is even worse owing to the lack of a Cooper minimum in the hydrogenic approximation. It is evident from Fig. 5 that for the $5d$, as was the case for $4f$, the hydrogenic results are of no use as an indicator of either spectral shape or cross-section magnitude.

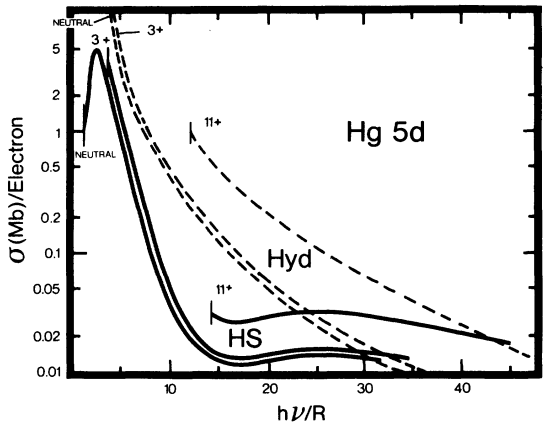

FIG. 5. Comparison of the photoionization cross sections *per electron* for the 5*d* subshells of various members of the Hg isonuclear sequence in the Hartree-Slater (HS, solid line) and hydrogenic (HYD, dashed line) approximations.

IV. FINAL REMARKS

It is clear from the results presented that the phenomenology found for low- and intermediate-Z cases in I and II persists for high Z as well; $\sigma_{nl}(h\nu)$ remains unaffected in an isonuclear sequence as long as the electrons removed are of greater principal quantum number than n. The spectral features of delayed maxima and Cooper minima do not have any effect upon the phenomenon. In addition, even when electrons from the given shell are removed, the spectral shape remains very similar with the cross section per electron increasing almost linearly with increasing stages of ionization. Further, we have found that even for highly charged ions, the hydrogenic predictions are very poor indicators of both spectral shape and magnitude.

Although this paper has only considered the two subshells of Hg with the most structure in the continuum, it is quite clear that the conclusions hold for all subshells. We therefore expect these general ideas, based on this work and I and II, to be true of all isonuclear sequences throughout the periodic system.

ACKNOWLEDGMENT

This work was supported by the U.S. Army Research Office.

*This paper is based upon a thesis submitted to the Department of Physics, Georgia State University, in partial fulfillment of the requirements for the M.S. degree.

[1]T. B. Lucatorto and T. J. McIlrath, Phys. Rev. Lett. 37, 428 (1976).

[2]T. J. McIlrath and T. B. Lucatorto, Phys. Rev. Lett. 38, 1390 (1977).

[3]D. W. Missavage and S. T. Manson, Phys. Rev. A 15, 1001 (1977).

[4]R. F. Reilman and S. T. Manson, Phys. Rev. A 18, 2124 (1978).

[5]K. D. Chao, J. L. Dehmer, U. Fano, M. Inokuti, S. T. Manson, A. Msezane, R. F. Reilman, and C. E. Theodosiou, in *Beam-Foil Spectroscopy*, edited by I. A. Sellin and D. J. Pegg (Plenum, New York, 1976), Vol. 2, pp. 637–641.

[6]S. T. Manson, Adv. Electron. Electron Phys. 41, 73 (1976).

[7]S. T. Manson, Adv. Electron. Electron Phys. 44, (1977).

[8]J. W. Cooper, Phys. Rev. 128, 681 (1962).

[9]J. W. Cooper, Phys. Rev. Lett. 13, 762 (1964).

[10]S. T. Manson and D. Dill, in *Electron Spectroscopy: Theory Techniques and Applications*, edited by C. R. Brundle and A. D. Baker (Academic, New York, 1978), Vol. 2, pp. 158–196.

[11]S. T. Manson and J. W. Cooper, Phys. Rev. 165, 126 (1968).

[12]F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Englewood Cliffs, New Jersey, 1963).

[13]A. Msezane, R. F. Reilman, S. T. Manson, J. R. Swanson, and L. Armstrong, Phys. Rev. A 15, 668 (1977).

[14]B. R. Tambe, W. Ong, and S. T. Manson, Phys. Rev. A 23, 799 (1981).

[15]J. B. Mann, Los Alamos Scientific Report No. LA-3691 (unpublished).