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Photoelectron Measurements of the Mercury 4f, 5p, and 5d Subshells

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ABSTRACT

Photoelectron spectra of atomic mercury have been taken using photon energies between 50 and 270 eV. The relative cross sections, subshell branching ratios and angular distribution asymmetry parameters of the 4f, 5p, and 5d subshells are reported. In addition, the 4f asymmetry parameter was measured up to 600 eV. These quantities show dramatic effects accompanying Cooper minima in the 5d and 5p subshells and a large centrifugal barrier in the $4f \rightarrow \epsilon g$ channel. Comparisons are made with relativistic random-phase approximation (RRPA) and Dirac-Slater (DS) calculations. Intershell correlations appear responsible for features in the measured 4f asymmetry parameter at the 4d threshold and in the calculated 5d branching ratio at the 5p threshold.

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I. INTRODUCTION

Mercury is the heaviest stable element with closed electronic shells and an appreciable vapor pressure at low temperatures. Relativistic effects in photoionization are thus readily studied in mercury. An absorption spectrum has been reported over a wide energy range,¹ but photoemission studies have been limited to photon energies below 50 eV,² and the discrete energies 132.3 eV³ and 1486.6 eV.⁴ In this paper we report the first photoemission studies of atomic mercury through the photon energy range 50-270 eV, with some additional data, based on second-order light, up to $h\nu = 600$ eV. The 4f, 5p, and 5d subshells were studied.

Several theoretical approaches, which treat exchange, correlation, and relativistic effects in varying degrees of approximation, have been developed and applied to mercury. The 4f partial cross section and photoelectron angular distribution have been calculated by both Shyu and Manson⁵ and by Keller and Combet Farnoux⁶ using both the Hartree-Slater (HS) and Hartree-Fock (HF) models. Keller and Combet Farnoux have also calculated the 5d and 5p partial cross sections. These studies highlight the influence of intrachannel interactions that are included in HF but not in HS. Walker and Waber⁷ have done Dirac-Slater (DS) calculations on the 5d subshell. With this relativistic theory they are able to predict the branching ratio and the spin-orbit resolved angular distributions. Manson⁸ has performed DS calculations on both the 5d and 4f subshells. Recently Radojević and Johnson⁹ have used the relativistic random-phase approximation (RRPA) to model the photoionization

of mercury over the energy range covered by our experiment. Their method includes both relativistic effects and electron correlations (intershell as well as intrashell). They have coupled all 17 relativistic outgoing channels originating from the 4f, 5p and 5d subshells and have calculated cross sections, branching ratios, and photoelectron angular distributions for each subshell.

Keller and Combet Farnoux have pointed out that the choice of threshold energies in ab initio calculations affects not only the positions of features but also the shapes of the curves. In their HS and HF calculations, they used HS ionization thresholds in order to be self-consistent. On the other hand, Radojević and Johnson employed experimental binding energies in an attempt to account for some of the many-body effects not included in RRPA calculations. Manson has used DS values. These various choices differ greatly. In the 4f subshell, the DS binding energy lies 30 eV from the HS value, and neither is within 10 eV of experiment. The effects of changing thresholds on the shapes of the curves have not been fully explored.

The experiment is described in Sec. II. Results are presented and discussed in Sec. III, and conclusions are listed in Sec. IV.

II. EXPERIMENTAL

The experiment was performed at the Stanford Synchrotron Radiation Laboratory on a grazing incidence "grasshopper" monochromator with a 1200 λ/mm holographically ruled grating. The ultra-high vacuum monochromator was vacuum isolated from our sample chamber by a 1500 $\text{\AA}$ thick window. We used an aluminum window for energies below the aluminum $L_{2,3}$ edge at 72 eV and we used a vitreous carbon window for energies above 75 eV. For the spectra taken with second-order light above 280 eV we again used the aluminum window.

The magnitude of the second-order light was determined by comparing the first-order and second-order intensities of the neon 2p photoline. It was only appreciable ($> 2\%$) below 150 eV with the carbon window. A correction for the second-order light is necessary in the relative cross-section measurements, where the total light intensity, as monitored by a sodium salicylate scintillator and phototube, is used to normalize the data at different photon energies. Because accurate measurements of the energy dependence of the sodium salicylate efficiency are not available, it was assumed to be constant.¹⁰

Photoelectron spectra were measured with the double-angle time-of-flight (DATOF) system in which the pulsed time structure of the synchrotron radiation is used to measure the flight times of electrons ejected at two angles. This method has been described in detail elsewhere.^{11,12}

The angular distribution of photoelectrons emitted by linearly polarized light in the nonrelativistic dipole approximation has the form

$$\frac{d\sigma(\epsilon, \theta)}{d\Omega} = \frac{\sigma(\epsilon)}{4\pi} [1 + \beta(\epsilon)P_2(\cos \theta)] \quad (1)$$

where θ is the angle between the polarization vector of the light and the momentum vector of the photoelectrons. By measuring the electron spectra at two angles, it is possible to determine both the cross section, $\sigma(\epsilon)$, and the angular distribution asymmetry parameter, $\beta(\epsilon)$, as functions of electron energy, ϵ . In this work, one analyzer was placed at $\theta = 54.7^\circ$, the "magic" angle where $P_2(\cos \theta) = 0$, and another at $\theta = 0^\circ$. Cross section measurements require knowing the relative transmission of the 54.7° analyzer as a function of kinetic energy and retarding voltage. The asymmetry parameter measurements, however, only require knowing the relative transmission of the two analyzers. Calibration of the spectrometer is accomplished by measuring count rates for the neon 2s and 2p lines, for which $\sigma(\epsilon)$ and $\beta(\epsilon)$ are known.¹³ We have corrected for an estimated linear polarization of 98%. However, because of the calibration procedures,¹¹ our derived $\beta(\epsilon)$ values are quite insensitive to the actual value of the polarization.

Representing the angular distribution by Eq. 1 assumes the validity of the dipole approximation, and it is important to know for what values of the photon energy, atomic number, and quantum numbers n and ℓ this is true. The measurement of cross sections at 54.7° (the "magic" angle) are also dependent upon Eq. 1. Kim et al.¹⁴ found that for the inner shells of heavier elements multipole effects are important even at threshold. For outer subshells they found that the non-dipole effects are small for photoelectron energies below 1 KeV. Recent work by Wang et al.¹⁵

has shown that while the quadrupole matrix element may be small, its contribution to low-energy angular distributions can be appreciable when the dipole intensity is at a minimum (e.g. a Cooper minimum). This would be particularly pronounced in s shell ionization where only $s \rightarrow \epsilon p$ matrix elements occur. For subshells with $\ell > 0$, the $\ell \rightarrow \epsilon(\ell-1)$ dipole channel should still dominate over non-dipole channels in regions where the $\ell \rightarrow \epsilon(\ell+1)$ dipole matrix element is small. We therefore expect the dipole approximation, and therefore Eq. 1, to be valid for all of the subshells addressed in this study.

The oven used to produce the mercury vapor was described earlier.¹² A vapor pressure of ~0.3 torr (100 °C) was attained behind a 1.6 mm diameter nozzle. The temperature was monitored by a thermocouple, but the vapor-pressure corrections needed for cross-section measurements were determined by frequently repeating spectra.

Systematic errors introduced into the asymmetry parameter are probably less than 5% of the quantity $\beta+1$. For branching ratios the probable magnitude of the errors will depend upon the difference between the kinetic energies of the two peaks. If the energy separation is large, the errors may be ~5%; if small, the systematic error will be less. Additional random scatter in the absolute cross-section measurements, on the order of 10%, is due to uncertainty in the sample pressure correction. This scatter appears as correlated fluctuations in the cross sections of the different subshells and is not present in the branching ratios.

A representative spectrum is shown in Fig. 1. The observed

photoelectron lines are listed in Table I along with their binding energies. In addition to the lines in Table I, a set of $N_{6,7}^0, 4, 5^0, 4, 5$ Auger lines with constant kinetic energies between 59 and 72 eV were observed.¹⁶

A retarding cage inside each analyzer allows us to slow the electrons for the final 17 cm of the 28 cm path length. The analyzer resolution, which results primarily from the finite interaction volume, was ~3% of the kinetic energy after retarding. Retarding potentials up to 115 volts were used to resolve the 4f and 5d spin-orbit doublets. Generally, the analyzer and monochromator resolutions were adjusted to provide a total resolution (FWHM) of <2 eV for the 4f doublet and, for some spectra, <1 eV for the 5d doublet. We deconvoluted some of these doublets by a least-squares fitting method that used Gaussian functions with low-energy exponential tails. The weak $5p_{1/2}$ and $5p_{3/2}$ peaks have large natural linewidths (6.2 and 5.6 eV respectively).³ The 5p peaks were fitted by Lorentzians with fixed widths and, where possible, fixed doublet spacings.

The error bars for the fitted data represent standard deviations from the computer fits. For raw data the error bars represent counting statistics only.

III. RESULTS AND DISCUSSION

The format of this section will be to describe in each subsection a derived parameter (e.g. cross section) for all three subshells, with a discussion given in text for each subshell. A summary paragraph appears at the end of each subsection.

A. Cross Sections

To put our cross-section data on an absolute scale it is necessary to have an experimental measurement of the total cross section at one energy. Using the absorption data of Cairns et al.,¹⁹ with the adjustment of Dehmer and Berkowitz,²⁰ we have normalized our data so that the 5d partial cross section is 8 Mb at 70 eV. We note that the adjustment in Ref. 20 is only approximate, but should be good to within 30%. We have plotted all of the theoretical curves, which were given in terms of kinetic energy, from the experimental thresholds, thus eliminating energy shifts due to the different choices of thresholds in the calculations.

In Fig. 2 are plotted our 5d cross-section measurements, together with earlier absorption measurements and the RRPA and DS curves. Two RRPA curves are represented in Fig. 2. The calculation that produced the curve below 65 eV² included interchannel coupling with the 6s channels, while the higher energy calculation⁹ included coupling with the 4f and 5p channels. This difference is probably responsible for the discontinuity between the two curves at 65 eV. Both data and theories show the 100-fold decrease from 50 eV to the Cooper minimum, which can be seen

near 190 eV in the data. The minimum is not apparent in the theoretical curves. Above 190 eV, the DS curve lies significantly below the data. Above 70 eV, the RRPA curve has about the same shape as the DS curve but its magnitude is larger by a factor of 2. Neither of the calculations include core relaxation or double ionization. A Dirac-Fock calculation that includes core relaxation has been performed²¹ below 55 eV and it gives better agreement than either the DS or RRPA calculations.

Although the 6s photoelectron peak (B.E. = 10.4 eV) is unresolved from the 5d peak in almost all of our spectra, we expect its effect to be insignificant, because the cross section for the 6s shell is much smaller than that for the 5d shell above 70 eV photon energy.

The 4f cross section is plotted in Fig. 3. The large centrifugal barrier acting on the ϵ_g continuum electrons causes a "delayed onset" of the 4f cross section, clearly exhibited in the data. In fact, the decrease in the $4f \rightarrow \epsilon_d$ partial cross section can be seen below 150 eV before the ϵ_g contribution to the 4f cross section becomes dominant. Both the RRPA and the DS curves show larger fractional increases than the data between 150 and 270 eV, but the RRPA curve agrees better with the data both in this respect and in the position of the minimum. The RRPA 4f:5d branching ratio (not shown) is in good agreement with our measurements below 170 eV, and it deviates by a factor of 2 near 270 eV. The agreement of this ratio with the DS theory is significantly worse.

The $5p_{3/2}$ and $5p_{1/2}$ cross sections are plotted in Fig. 4. In both subshells the experimental cross section drops more quickly than the

RRPA curve. The changes in curvature in $\sigma(5p_{3/2})$ near 180 eV and in $\sigma(5p_{1/2})$ near 190 eV are assigned to Cooper minima in these subshells.

In summary, the experimental cross sections generally show the expected energy variations, with minima being readily observed in every case. The 4f "delayed onset" character due to the angular momentum barrier for the g-wave is clearly present. The RRPA cross sections are a factor of 2 too large; however, the RRPA calculated 4f:5p:5d branching ratios generally agree to within 10%, with the notable exceptions being those involving $\sigma(4f)$ above 200 eV and $\sigma(5p)$ below 160 eV.

B. Spin-Orbit Branching Ratios

Deviations of spin-orbit branching ratios from their statistical $(l+1)/l$ value arise from the "kinetic-energy" effect,²² caused by the different kinetic energies of photoelectrons from the two spin-orbit members at a given photon energy. Additional deviations are due to differences in the initial and final radial wavefunctions of the two states. Ron, Kim, and Pratt²³ have recently surveyed some of the non kinetic-energy effects that cause deviations in subshell branching ratios. They found that, for higher Z elements, deviations are amplified by the presence (and by the energy separation) of Cooper minima in dominant channels. They also concluded that these effects should be larger for np subshells than for nd or nf subshells.

The DS⁸ and RRPA^{2,9} calculations of the $5d_{5/2}:5d_{3/2}$ branching ratio are shown in Fig. 5, along with experimental points from this work and from experiments with line sources. The 5d cross section (Fig. 2)

has a large shape resonance peaking near 40 eV and a Cooper minimum near 190 eV. The experimental branching ratio starts well above the statistical value near threshold² and then drops monotonically to a minimum value of ~ 1.1 near 90 eV. The DS theory predicts this trend qualitatively, while the RRPA result shows an additional feature at 85 eV that may be due to intershell correlations with the 5p subshell. The RRPA curves at high and low energies do not join smoothly, presumably due to the different sets of coupled subshells used in the two calculations, as mentioned earlier in connection with the 5d cross section. This point needs further study.

The 4f subshell cross section has no Cooper minimum because the 4f radial wavefunction has no nodes, but there is a shape resonance due to the ϵ_g centrifugal barrier, and a cross-section minimum near 150 eV. Our 4f branching ratio data are shown in Fig. 6 with a curve predicted by both the RRPA and DS theories. The curve shows a maximum in the branching ratio between 150 and 200 eV. Our measurements confirm the existence of a maximum rising above 1.5 but the detailed shape is unclear from the data because of non-statistical scatter arising from uncertainties in background corrections. The slower increase in the cross section above 160 eV shown in Fig. 3 should appear as a smaller branching ratio, due to the kinetic-energy effect. This is apparent near 200 eV in Fig. 6.

The large spin-orbit splitting in the 5p subshell (18.6 eV) leads to large deviations in the branching ratio from its statistical value of 2.0. Calculation of the $5p \rightarrow \epsilon s$ and $5p \rightarrow \epsilon d$ cross sections by Keller and

Combet Farnoux show that the ϵs channel is dominant for the first 200 eV above threshold and that the ϵd channel goes through a Cooper minimum. The RRPA calculation⁹ of the branching ratio shown in Fig. 7 shows an increase from ~ 1.1 at 110 eV to ~ 2.8 at 220 eV. Our data show the ratio starting near 0.85, 25 eV above the $5p_{1/2}$ threshold, and increasing to ~ 2.2 at $h\nu = 200$ eV. The gap in our data arises from the Auger group moving through the 5p lines. A much more careful study would be required to fill in the gap. The larger slope in our cross section data (Fig. 4) is probably responsible for the lower branching ratio.

In summary, deviations from statistical ratios, and variations with energy, were observed for all three subshells. Both RRPA and DS theory predicted the experimental ratios quite well. Evidence was found for a large kinetic-energy effect in the 5p shell and for a small shape resonance effect in the 4f shell. The RRPA theory alone predicted details in the 5d curve that may arise from interchannel coupling. More work is clearly needed on these branching ratios.

C. Asymmetry Parameters

The energy variation of the calculated angular distribution asymmetry parameter, $\beta(\epsilon)$, often complements the variations in the cross section and branching ratio. In the case of Cooper minima, the predicted effects on the $\beta(\epsilon)$ parameter are typically more pronounced than the effects on the other parameters. Few data are available to test these predictions. For example, we report below the first $\beta(\epsilon)$ measurements on any 4f and 5d subshells over a substantial energy range.

The 5d-shell $\beta(\epsilon)$ parameter shows large oscillations. These are due to a Coulomb phase-shift change just above threshold,¹⁵ then a shape resonance, and then a Cooper minimum. Using the central-field approximation, the $\beta(\epsilon)$ parameter is given in LS coupling by the Cooper-Zare formula²⁴

$$\beta(\epsilon) = \frac{\ell(\ell-1)R_{\ell-1}^2 + (\ell+1)(\ell+2)R_{\ell+1}^2 - 6\ell(\ell+1)R_{\ell-1}R_{\ell+1}\cos(\Delta_{\ell+1,\ell-1})}{(2\ell+1)[\ell R_{\ell-1}^2 + (\ell+1)R_{\ell+1}^2]} \quad (2)$$

where $R_{\ell+1}$ and $R_{\ell-1}$ are radial dipole matrix elements and $\Delta_{\ell+1,\ell-1}$ is their phase difference. At a Cooper minimum, where $R_{\ell+1} = 0$ Eq. 2 simplifies to

$$\beta(R_{\ell+1} = 0) = \frac{\ell-1}{2\ell+1} . \quad (3)$$

Eqs. 2 and 3 were derived neglecting configuration interaction, fine-structure splitting, and the spin-orbit interaction between the outgoing electron and the ion. If we ignore these complications, we find that the Cooper minimum for the 5d shell should be located where $\beta(\epsilon)$ reaches 0.2, which is at 190 eV in Fig. 8. The data in Fig. 2 confirm this value, whereas the theoretical curves do not.

The DS and RRPA curves for $\beta(\epsilon)$ are generally in good agreement with our data, but they differ by 10-20 eV in the energy of steepest descent and in the value of $\beta(\epsilon)$ for energies above the Cooper minimum. It may be that the position of steepest descent, which is due to a cancellation in the R_f radial integral, is extremely sensitive to both the accuracy

of the integrating code and the nature of the theory. A similar sensitivity was observed in the position and depth of the minimum in $\beta(\epsilon)$ for the Xe 5s Cooper minimum.²⁷

The theoretical curves of $\beta(\epsilon)$ for the unresolved 4f subshell, together with our results, are displayed in Fig. 9. All of these theories show the same general feature, but none reproduce the data quantitatively. The most sophisticated of the theories (RRPA) has the energy of the maximum in $\beta(\epsilon)$ 10 eV too high and the $\beta(\epsilon)$ curve above 200 eV too large by 0.2 units.

The two 4f spin-orbit members have different $\beta(\epsilon)$ values at a given photon energy. Most of this difference results from a kinetic-energy effect. In Fig. 10 we have plotted $\beta(7/2) - \beta(5/2)$ against photon energy along with the RRPA calculated curve. The differences calculated from DS theory are almost identical. The data and the theory are in qualitative agreement.

Fig. 11 shows $\beta(\epsilon)$ for the 4f subshell from threshold up to a photon energy of 600 eV. All but three of the points above 280 eV were taken using second-order light and an Al window. The calibration of the relative efficiencies of the analyzers was done with second-order Ne 2s and 2p peaks. The uncertainty in the calibration for kinetic energies above 300 eV introduces an uncertainty in the slope of the points in Fig. 11 ($\sim 0.2 \beta$ units at $h\nu = 600$ eV) but it remains a smooth function. The sudden increase in $\beta(\epsilon)$ at 380 eV is probably the result of inter-channel coupling with the 4d ionization channels. Using first order perturbation theory, each 4f transition amplitude is the sum of a direct

and a correlation amplitude, the latter resulting from a virtual excitation of the 4d shell.²⁸ The correlation can therefore effect both the 4f cross section and the 4f $\beta(\epsilon)$.

The $4d_{5/2}$ and $4d_{3/2}$ thresholds are at 366.0 and 385.4 eV, respectively,³ where the monochromator bandpass was approximately 7 eV. RRPA calculations of the 4d channels²⁹ (without coupling to other continua) show the cross section to be slowly varying and a factor of 10 less than the 4f cross section at 400 eV. The calculated 4d spin-orbit branching ratio and the $\beta(\epsilon)$ parameter show large fluctuations near threshold which may be manifesting themselves in the 4f $\beta(\epsilon)$. We were unable to measure the 4d photoelectron peaks directly because of their small cross sections and large natural linewidths (4 eV).

Changes in $\beta(\epsilon)$ due to coupling with newly opened channels have been observed in $\beta_{5p}(\epsilon)$ at the 4d threshold in Xe.³⁰ However, in the Xe case the 4d cross section is much larger than the cross sections for the 5s and 5p channels.

Figs. 12(a) and (b) show the $5p_{1/2}$ and $5p_{3/2}$ asymmetry parameter measurements and the RRPA curves. Again, the gaps in these data are caused by the presence of Auger electrons. The two states show substantial differences beyond that due to the kinetic-energy effect. Our data show $\beta(5p_{1/2})$ dropping to zero, while $\beta(5p_{3/2})$ drops to a value of -0.3. The minimum in each parameter is due to the Cooper minimum in the ϵd channel. If we apply Eq. 3, we would expect the unresolved $\beta(\epsilon)$ to drop to zero. Because we have measured the resolved $\beta(\epsilon)$'s it may be more appropriate to know what value of $\beta(\epsilon)$ we would

expect at the minimum in the limit of jj coupling. Walker and Waber¹⁷ have shown that for s -subshell ionization ($j=1/2$), in which only two relativistic continuum channels are accessible, the expression for $\beta(\epsilon)$ takes on a simple form in jj coupling:

$$\beta(\epsilon, j=1/2) = \frac{2R_{3/2}^2 + 4|R_{3/2}R_{1/2}^*|}{R_{1/2}^2 + 2R_{3/2}^2} \quad (4)$$

For ionization from a $p_{1/2}$ subshell (again $j=1/2$), the expression for $\beta(\epsilon)$ is identical. For the $p_{1/2}$ subshell, $R_{1/2}$ and $R_{3/2}$ are radial matrix elements with the $\epsilon s_{1/2}$ and $\epsilon d_{3/2}$ continuum orbitals. When the $R_{3/2}$ matrix element equals zero we obtain $\beta(5p_{1/2}) = 0$, in agreement with experiment. It is not as easy to apply Walker and Waber's formalism to $\beta(5p_{3/2})$ because there are three continuum orbitals ($\epsilon s_{1/2}$, $\epsilon d_{3/2}$ and $\epsilon d_{5/2}$) and the $R_{3/2}$ and $R_{5/2}$ matrix elements (for the ϵd channels) need not go through zero at the same energy. If they did, we would again obtain $\beta = 0$. Of course, in the general many-electron case the radial matrix elements are complex and need not go identically to zero.

The RRPA calculation of $\beta(5p_{1/2})$ shows $\beta(\epsilon)$ falling only to 0.5. This is a result of mixing with the $4f$ subshell ionization channels, because an 11-channel calculation, which includes only the $5p$ and $5d$ subshells, shows $\beta(5p_{1/2})$ dropping to 0.0 at 280 eV.²⁹

In summary, the asymmetry parameter of the mercury $4f$, $5d$, and $5p$ shells behave approximately as predicted by the DS and RRPA models, but there are important differences between experiment and theory. The

predicted $\beta(\epsilon)$ values are too high in the high energy limit for the 4f and 5d subshells and at all energies for the 5p shell. Both theories predict the centrifugal-barrier induced maxima in the 4f shell to be too wide, with the consequent overestimation of the photon energies where $\beta(\epsilon)$ descends most steeply. In addition, a feature was observed in $\beta(4f)$ at 380 eV which we attribute to interaction with the 4d channel.

IV. CONCLUSIONS

Several noteworthy features have been exhibited in the photoionization of Hg above 50 eV.

The Cooper minimum in the 5d shell photoionization is observed in both the cross section and the asymmetry parameter. The 5d branching ratio was found to drop as low as 1.1 although we were unable to test the RRPA prediction that shows oscillating features due to interaction with the 5p shell.

In the 4f shell, the centrifugal barrier in the ϵ_g channel was observed as a shape resonance in the asymmetry parameter and as a delayed onset in the cross section. An additional oscillation in $\beta(\epsilon)$ has been attributed to interaction with the 4d shell.

The 5p shell, which has the largest spin-orbit splitting, was found to have a branching ratio of 0.85 at low kinetic energies. The two spin-orbit members were found to have different values of β at their respective Cooper minima.

The DS and RRPA theories correctly predict the shapes of all of the parameters although there are several quantitative differences. Among these, the delayed onset of the 4f cross section shows the worst agreement. There is good agreement with the branching ratios calculated by RRPA, but there is a factor of 2 difference between the calculated absolute cross sections and the present results. This difference may partially reflect the absence of relaxation in RRPA. Experimentally, there is a need for a reliable absolute absorption measurement as well as measurements of the $\text{Hg}^{++}/\text{Hg}^+$ ratio.

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Table I. Binding Energies in eV for Observed Mercury Subshells

<u>Subshell</u>	<u>B.E. (From Ref. 4)</u>
$5d_{5/2}$	14.9
$5d_{3/2}$	16.7
$5p_{3/2}$	71.6
$5p_{1/2}$	90.3
$4f_{7/2}$	107.1
$4f_{5/2}$	111.1

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FIGURE CAPTIONS

- Fig. 1 TOF photoelectron spectrum of Hg taken at $\theta=54.7^\circ$. There are 5.08 channels per nanosecond, and the accumulation time was 500 sec. The 4f peak at 131 eV is due to second-order light. The 5d peak reaches a maximum of 5200 counts/channel.
- Fig. 2 The 5d cross section. The solid curves represent the RRPA calculations, Refs. 2 and 9. There is a discontinuity between the two calculations near 65 eV. The dashed curve represents the DS calculation, Ref. 8. The dashed-dot curve is from absorption measurements (Refs. 19 and 20). The data was normalized to $\sigma(70 \text{ eV}) = 8 \text{ Mb}$. This sets the scale for all our cross-section data.
- Fig. 3 The 4f cross section. Solid curve- RRPA-length from Ref. 9; dashed curve- DS from Ref. 8.
- Fig. 4 The cross section of the $5p_{3/2}$ (upper) and $5p_{1/2}$ (lower) states. RRPA curves from Ref. 9.
- Fig. 5 The $5d_{5/2}:5d_{3/2}$ subshell branching ratio. The solid circles are from this work; open circles from Ref. 17; x's from Ref. 18; square from Ref. 4. The first two x's coincide with measurements from Ref. 20. The solid curves are from two RRPA calculations, Refs. 2 and 9; dashed curve DS theory, Ref. 8. The accuracy of the first two open-circled measurements are $\pm 20\%$ and the third $\pm 40\%$. No estimates of the uncertainty for the other line-source measurements were published.

- Fig. 6 The $4f_{7/2}:4f_{5/2}$ branching ratio. Solid curve from RRPA, Ref. 9. The DS theory, Ref. 8, also follows the solid curve.
- Fig. 7 The $5p_{3/2}:5p_{1/2}$ branching ratio. The solid curve RRPA-length and dashed curve RRPA-velocity are taken from Ref. 9.
- Fig. 8 The 5d angular distribution asymmetry parameter. The solid curve is RRPA, Refs. 2 and 9; dashed curve, DS from Ref. 8. Experimental measurements below 45 eV (Refs. 25 and 26) are in excellent agreement with the RRPA curve.
- Fig. 9 The 4f asymmetry parameter. The theoretical curves are: solid- RRPA, Ref. 9; dashed-dot HF, Ref. 6; dotted- HF, Ref. 5; dashed- DS theory, Ref. 8.
- Fig. 10 The difference between the $4f_{7/2}$ and $4f_{5/2}$ $\beta(\epsilon)$ parameters. The solid curve is the RRPA calculation from Ref. 9 which is almost identical to the DS curve from Ref. 8.
- Fig. 11 The 4f asymmetry parameter.
- Fig. 12 Asymmetry parameter, $\beta(\epsilon)$, for the $5p_{3/2}$ (upper) and $5p_{1/2}$ (lower). The RRPA curves are from Ref. 9.

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Figure 1

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Figure 2

Figure 3

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Figure 4

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Figure 5

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Figure 6

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Figure 7

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Figure 8

Figure 9

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Figure 10

Figure 11

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XBL 8210-3033

Figure 12

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