

The effect of crystallography on the Hg 5*d* branching ratios

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The Hg 5*d*_{5/2} and 5*d*_{3/2} cross sections and branching ratios were measured in the photon energy range between 26 and 105 eV for Hg overlayers on Ag (100) and Cu (100). The branching ratios deviate from the nonrelativistic statistical value of 1.5, reaching values of 8.0. Data are presented that establish a direct relationship between the branching ratio and the long-range crystallographic structure of the Hg overlayers. This relationship is a consequence of the formation of a band structure from the shallow mercury 5*d* eigenstates.

INTRODUCTION

The branching ratio of atomic core levels has been found to be quite effective in distinguishing between atomic and solid state effects in materials.¹ Since calculations²⁻⁶ of the branching ratio based upon the atomic potentials are accurate, solid state effects¹ can be distinguished from atomic phenomena.⁷⁻¹⁰ Furthermore, and in contrast to absolute cross section measurements, branching ratio data can be obtained with a high degree of precision. Comparison of the branching ratios with the partial cross sections can provide insight into the screening processes that accompany the photoemission process.

For Hg overlayers on Ag (100), several earlier results¹¹⁻¹⁷ have established the system as particularly interesting, in part because ordered and disordered overlayers of comparable thickness can be studied. Hg overlayers on Ag (100) adopt an fcc phase which is not the natural phase of bulk Hg. These overlayers exhibit an electronic band structure consistent with this fcc phase. Both the band structure and the cross sections of the Hg 5*d* levels have recently^{16,17} been shown to depend upon the long-range crystallographic order and the homogeneous "in plane" strain energy.¹⁷ In the present investigation we are able to report that the branching ratio possesses a striking dependence on the long-range order and lattice constant. We have studied Hg overlayers on both Ag (100) and Cu (100) and characterized the 5*d* branching ratios and partial cross sections in order to probe the hybridization of the shallow Hg 5*d* core levels to form bands.

Hg overlayers on Ag (100) are particularly well suited for investigating the effects of long-range crystallographic order upon electronic structure and the branching ratio of the Hg 5*d* states in particular. Several studies of Hg, both experimental^{1,7,8} and theoretical²⁻⁴ of atomic Hg as well as Hg compounds¹ have been previously conducted by other investigators and provide a reference for the comparison.

EXPERIMENTAL

Previous reports¹¹⁻¹⁷ have established that Hg overlayers on Ag (100) and Cu (100) form ordered overlayers.

Since the goal of our investigation is the relationship between overlayer long-range crystallographic order and branching ratio, we have studied several coverages of mercury on Ag (100) and Cu (100). In each case, we measured the integral photoemission intensities from the Hg 5*d*_{5/2} and 5*d*_{3/2} levels, which possess binding energies of 8 and 10 eV below the Fermi edge, respectively. For each coverage of Hg on Ag (100) we observed a new electronic state^{11,13,14} for ordered overlayers on Ag (100) that is absent for disordered overlayers. For Hg on Cu (100) we investigated the *c*(2×2) and high coverage *c*(4×4) [0.62 Hg atoms per Cu (100) surface atom] overlayers. No such new 5*d* electronic state is observed with either ordered overlayers on Cu (100). A coverage of 0.6 monolayer is the smallest thickness that exhibits the new electronic state for mercury adsorbed on Ag (100). The new 5*d* state possesses a binding energy of about 7.2 eV and is included in the 5*d*_{5/2} oscillator strength unless otherwise noted.

The EDC's were obtained using polarized light with the vector potential parallel with the surface unless noted otherwise. The photoelectrons were collected normal to the surface as described elsewhere.¹⁴ The light source for the photoemission studies was the 800 MeV synchrotron of the Synchrotron Radiation Center at Stoughton, Wisconsin, dispersed by either a glancing incidence monochromator or a 3 m toroidal grating monochromator.

Long-range order (or lack thereof) was ascertained using low energy electron diffraction. We have noted that adsorption of mercury on Ag (100) at 90 to 120 K leads to the formation of ordered Hg films while adsorption at 30 K results in disordered films. We observe that the adsorption of 1 monolayer and 2 monolayers of Hg continue the Ag (100) fcc structure (bulk Hg is rhombohedral), and 5 monolayers exhibit a cubic *p*(1×4) ordering.¹⁴ For Cu (100), mercury adsorption at room temperature is possible and with the adsorption of one monolayer of mercury on Cu (100), the overlayer adopts the *c*(2×2) overlayer structure^{13,18} as determined by low energy electron diffraction. With continued deposition at 200 K on Cu (100) to about 18 L Hg exposure (uncorrected for ionization gauge position and cross section) a *c*(4×4) overlayer is formed with an in-plane Hg-Hg

lattice constant of 3.22 Å as confirmed by atom beam scattering (ABS).¹⁸ All overlayers were free of contamination to the limit of our Auger electron spectroscopy system (1 at %) and deposited and analyzed as previously described.^{11,13}

The branching ratios were determined from photoemission spectra taken at each specific photon energy. The branching ratios were obtained from the energy distribution curves by subtraction of the background photoemission signal (using a polynomial background) and integrating the areas under the 5*d*_{3/2} or 5*d*_{5/2} features. The compiled branching ratios are then plotted as a function of incident photon energy.

The partial cross sections were obtained from the integral intensities for each 5*d*_{3/2} or 5*d*_{5/2} feature normalized for incident photon flux for the data taken of the Hg overlayers on Ag (100). For the overlayers on Cu (100), the partial cross sections are estimated from the peak intensities with the monochromator operating at seriously degraded resolution and are normalized for photon flux.

RESULTS

The data presented here covers the range of Hg overlayer thicknesses for which a new Hg state at approximately 7.2 eV binding energy is observed with mercury adsorption on Ag (100). These Hg overlayer thicknesses correspond to the coverages one, two and five monolayers of adsorbed Hg on Ag (100).

The one monolayer Hg overlayer continues the face-centered-cubic structure of the Ag (100) substrate and is observed to have the new electronic state previously reported,¹¹⁻¹⁷ as shown in Fig. 1. The fitting obtained from these spectra is very good as can be seen from Fig. 1. We have calculated the branching ratio from the photoemission data by including and excluding the new electronic state at 7.2 eV binding energy from the Hg 5*d*_{5/2} oscillator strength in the data analysis. The branching ratios, in the photon energy range of 50 to 70 eV, obtained by including the new electronic state in the 5*d*_{5/2} oscillator strength (+) and excluding the new state (□) are presented in Fig. 2. The gas phase results⁷ (—) are also included for comparison. Including the new photoemission feature in the branching ratio increases the ratio appreciably (approximately 50%) compared with the Hg 5*d* branching ratio estimated from the data without including the new electronic state in the Hg 5*d*_{5/2} oscillator strength. The maximum in the branching ratio, when the new state is included, is at a photon energy of 61 eV and is approximately double the statistical value, and the gas phase results at this photon energy. The branching ratio is much closer to the results obtained for gaseous Hg when the new electronics state oscillator strength is not included as part of the 5*d*_{5/2} oscillator strength.

By increasing the Hg overlayer thickness to two monolayers, we observed further changes in the branching ratio. The two monolayer and five monolayer overlayers exhibit both well-ordered and disordered overlayers. The new electronic state was present in the photoemission spectra of the well-ordered overlayers and absent for the disordered overlayers. Figure 3 illustrates the branching ratio for well-or-

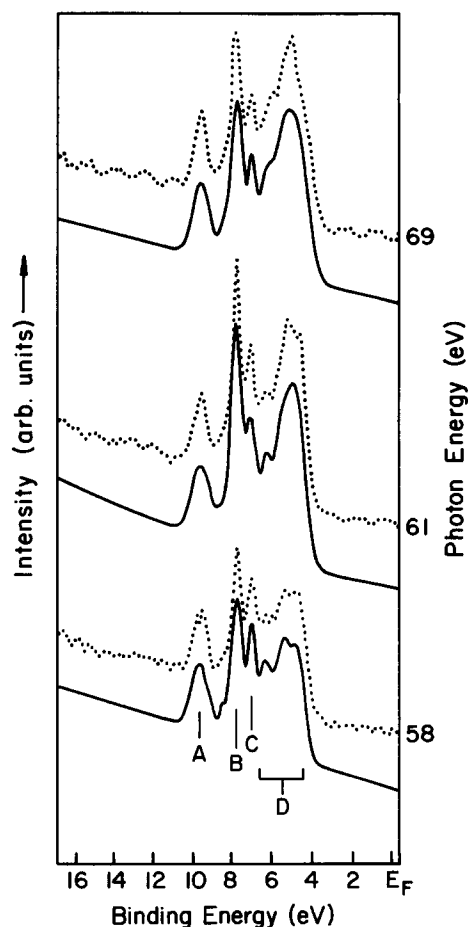


FIG. 1. The photoemission spectra for one monolayer of Hg on Ag (100) for various photon energies. Also shown are the fits to the spectra (···), offsetted from the experimental data, used to calculate the branching ratios. Features corresponding to the Hg 5*d*_{3/2} state (A), the Hg 5*d*_{5/2} state (B), the additional 5*d* state at about 7.2 eV (C), and the silver *d* bands (D) are indicated.

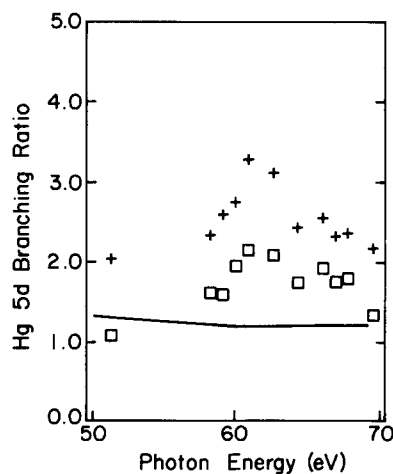


FIG. 2. The branching ratios for the Hg 5*d* states as a function of photon energy for one monolayer of Hg adsorbed on Ag (100) at 90 K. (+) shows the results for the 5*d*_{5/2} to 5*d*_{3/2} intensity ratio with the third 5*d* feature intensity included with 5*d*_{5/2} intensity, while (□) shows the ratio without the intensity of the new electronic state (the third 5*d* feature) included in the branching ratio. The solid line indicates the gas phase results (Ref. 7).

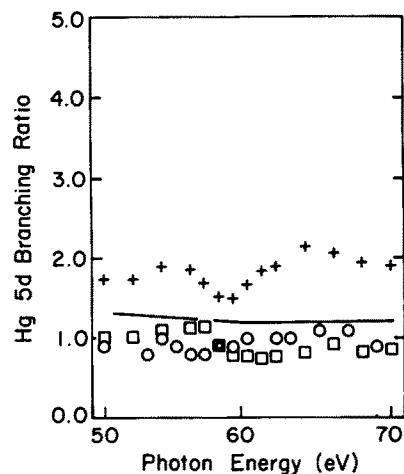


FIG. 3. The branching ratio for the Hg 5d states as a function of photon energy for two monolayers of Hg adsorbed on Ag (100). (+) represents the 5d ratio for an ordered overlayer adsorbed at 90 K and with the third 5d Hg feature included in the ratio, while the (□) symbols indicate the ratio for this overlayer without incorporation of the third feature intensity. (○) indicates the $5d_{5/2}$ to $5d_{3/2}$ ratio for a disordered two monolayer overlayer of Hg on Ag (100) at 30 K.

dered two monolayer overlayers (crosses) and disordered two monolayer overlayers (open circles) obtained by depositing Hg onto an Ag (100) sample held at 90 and 30 K, respectively, in the photon energy range from 50 to 70 eV. Note that the disordered two monolayer overlayers closely resembles the gas phase Hg results.⁷ The well-ordered Hg overlayers exhibit a significantly higher branching ratio by comparison, some 10% to 40% higher than the gas phase results.

A five monolayer Hg overlayer can also be deposited as a well ordered or disordered overlayer. The well-ordered Hg overlayer exhibits a LEED pattern consistent with a crystal-

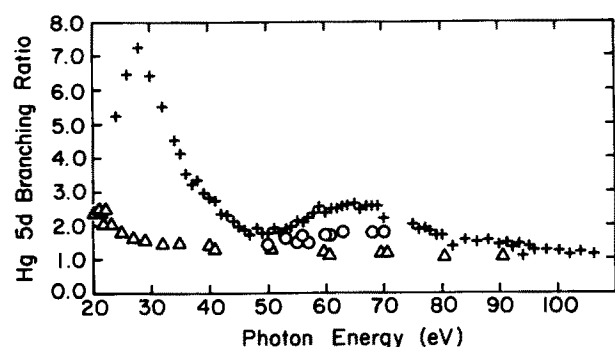


FIG. 4. The branching ratios of the Hg 5d states for a five monolayer thick overlayer of Hg on Ag (100) as a function of photon energy. (+) shows the ratio for an ordered overlayer and the third feature intensity included in the ratio. (△) shows the ratio for gaseous monoatomic Hg (Ref. 7). (○) shows the results for a disordered overlayer.

lographic $p(1 \times 4)$ cubic orientation. The branching ratios obtained for the well ordered and disordered five monolayer Hg overlayers are illustrated in Fig. 4. We observed a dramatic difference between the well-ordered overlayer (+) and a disordered Hg overlayer of equal thickness (○) as shown in Fig. 4. The well-ordered Hg overlayer exhibits two maxima in the branching ratio, a sharp (FWHM = 4 eV) maximum of 7.2 at a photon energy of 28 eV and a broad maximum of 2.6 at about 68 eV photon energy. The gas phase results⁷ exhibit corresponding branching ratios of about 1.7 and about 1.4 at photon energies of 28 and 68 eV, respectively. The disordered Hg overlayer exhibits a branching ratio similar to that of gas phase Hg, differing by not more than 15% from the statistical value except at photon energies less than 25 eV. This result, of a comparatively high branching ratio at photon energies below 25 eV has been previously reported for HgS.¹

The photoemission spectra (energy distribution curves) for five monolayers of the well-ordered $p(1 \times 4)$ Hg overlayers on Ag (100) at 90 K are shown in Fig. 5, for various photon energies. For the same coverage, shown in Fig. 6, the photoemission spectra for the disordered Hg overlayers ad-

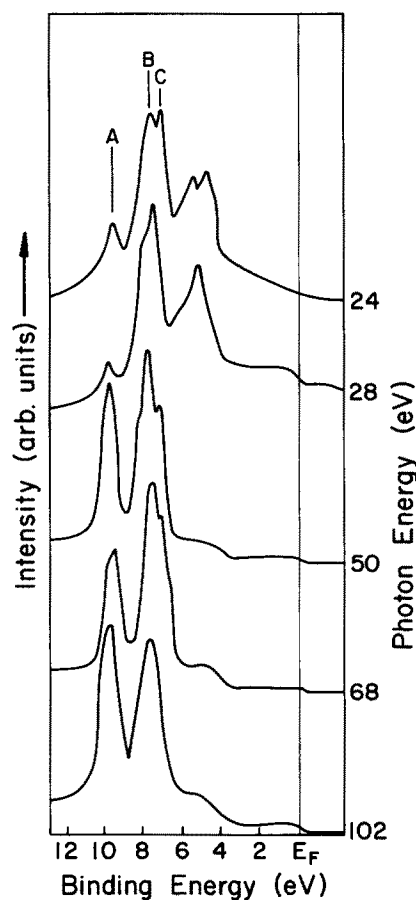


FIG. 5. The photoemission spectra for five monolayers of Hg on Ag (100) for various photon energies. The spectra from an ordered overlayer adsorbed at 90 K, with the overlayer order confirmed from the observation of the $p(1 \times 4)$ LEED pattern. The three Hg 5d bands are indicated by A, B, and C. The $5d_{3/2}$ (A) and $5d_{5/2}$ (B) character bands exhibit no dispersion.

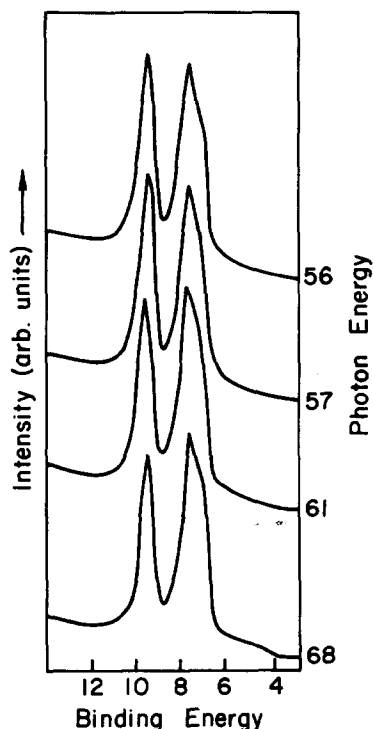


FIG. 6. The photoemission spectra for five monolayers of Hg adsorbed on Ag (100) at 30 K. The coverage is identical to the coverage in Fig. 4. The overlayer exhibits no evidence of long-range order.

sorbed on Ag (100) at 30 K may be noted for an absence of the third Hg 5*d* photoemission feature observed for the ordered Hg overlayers. A comparison of Fig. 5 and Fig. 6 reveals the photoemission spectra are distinctly different for

well-ordered and disordered five monolayer Hg overlayers (the spectra are normalized to the 5*d*_{5/2} peak). The spectra support the results presented in Fig. 4. The branching ratio cannot be appreciably affected by the Ag (100) substrate since the Hg overlayer is quite thick and the photoemission intensity contribution from the Ag substrate is quite small (Figs. 5 and 6). We have also measured the Ag (100) cross sections across this photon energy region and have not observed any resonant enhancement of the silver 4*d* photoemission intensity that would account for either narrow maximum at 28 eV nor the broad maximum at 68 eV photon energy in the Hg 5*d* branching ratio (as seen in Fig. 7).

We have directly examined the Hg 5*d* branching ratios for well-ordered and disordered two and five monolayer overlayers of Hg on Ag (100), and apart from the large deviations from the statistical branching ratio of 1.5 observed at photon energies at 28 and 58 eV, the branching ratio for the ordered overlayers is observed to take a value near 2.3. This result is consistent with the changes in the integral intensities. For most photon energies, a comparison of the total integral intensities of the Hg 5*d*-like states observed with two and five monolayer thick films of Hg suggests a substantial difference in 5*d*_{3/2} and 5*d*_{5/2} intensities for ordered and disordered Hg overlayers. The integral intensities for both the 5*d*_{3/2}- and 5*d*_{5/2}-like states (neglecting any intensity contribution from the new third 5*d*-like state) are generally about 25% smaller for the ordered two and five monolayer films than for the disordered films, correcting for monochromator transmission and photon flux.

The occupied density of states for mercury monolayers on Cu (100) are not complicated by any additional 5*d*-like electronic state. The branching ratio for both the *c*(2×2) and *c*(4×4) Hg overlayers closely resembles the branching ratios of the gaseous Hg atom, even for very ordered *c*(4×4)

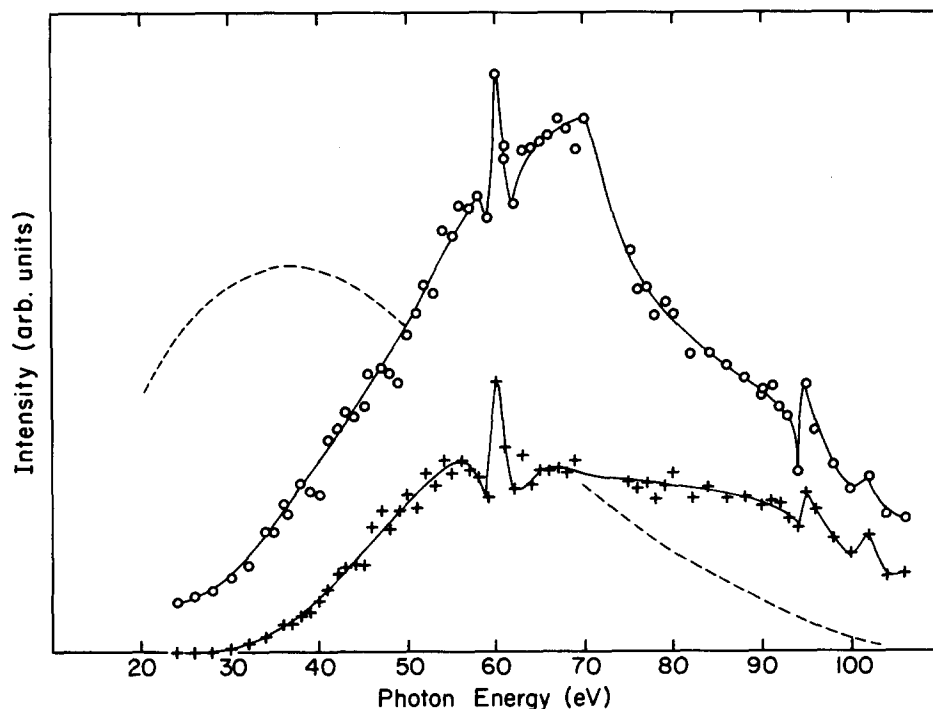


FIG. 7. The partial photoemission cross sections of the Hg 5*d*_{5/2} states (O) and the 5*d*_{3/2} state (+) as a function of photon energy for five monolayers of Hg on Ag (100) at 90 K. The integral intensities are corrected for the monochromator transmission and synchrotron flux as described elsewhere (Refs. 12 and 16). The dashed line indicates the qualitative partial cross sections observed for the 5*d* state of gaseous Hg (Refs. 7 and 28).

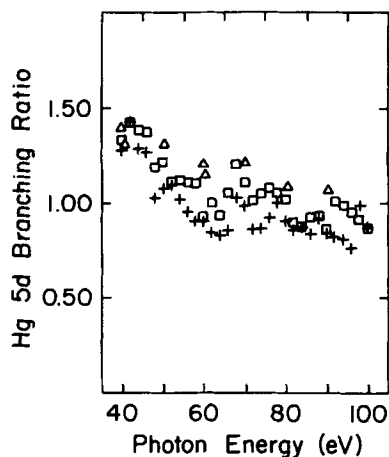


FIG. 8. The mercury 5*d* branching ratios for an ordered $c(2 \times 2)$ overlayer on Cu (100). The branching ratio with a light incidence angle of 32° (mostly *s*-polarized light) is shown as (\square) while the branching ratio determined with a light incidence angle of 60° with respect to the surface normal (mostly *p*-polarized light) is shown as (+). In both cases the photoelectrons were collected normal to the surface. For comparison the gas phase data is shown as (\triangle) from Ref. 7. Note the similarity between the three sets of data.

monolayer films with a 3.22 \AA lattice constant (as determined by LEED and ABS) as seen in Figs. 8 and 9. The branching ratios for Hg overlayers on Cu (100) are not affected, seriously, by the orientation of the vector potential of the incident light as indicated by the results plotted in Fig. 8.

The partial cross sections of the Hg 5*d* features do differ for a square lattice of Hg atoms with a lattice constant 3.62 \AA as opposed to 3.22 \AA as seen in Fig. 10. The overlayers with

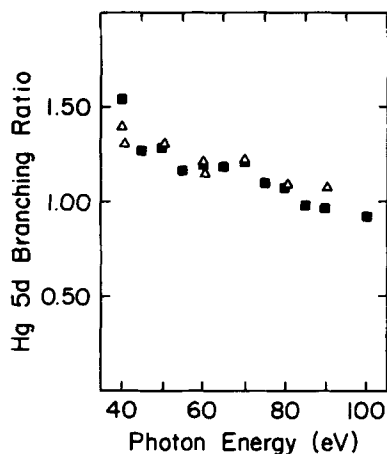


FIG. 9. The mercury 5*d* branching ratio for a disordered 2 atomic diameter thick film of mercury adsorbed on Cu (100). The data (\square) was taken with a light incidence angle of 32° so that the vector potential of the incident light is largely in the plane of the surface [as is the case with the data taken from the Hg overlayers on Ag (100)]. The gas phase data from Ref. 7 is also shown (\triangle).

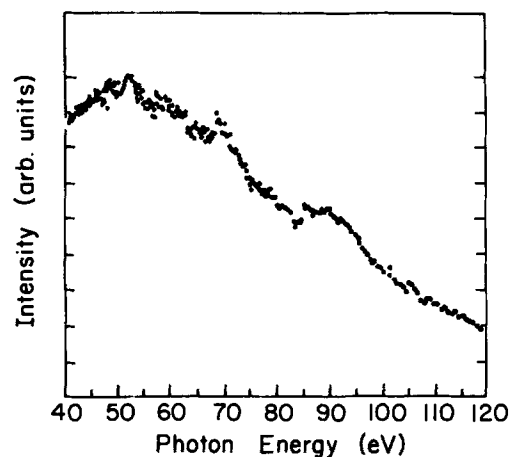
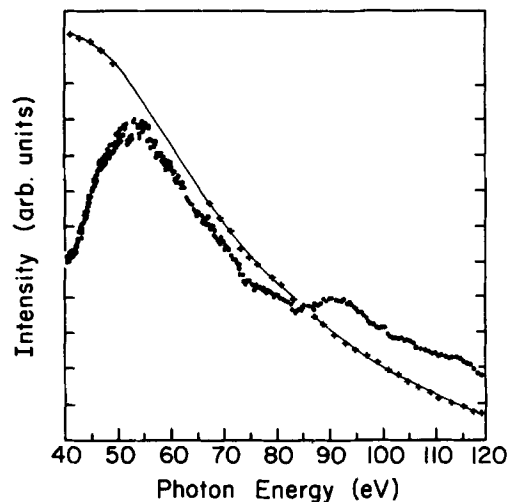


FIG. 10. The relative partial cross sections for the Hg 5*d*_{5/2} feature for mercury overlayers on Cu (100). The partial cross sections are shown for the $c(2 \times 2)$ overlayer (top) and the $c(4 \times 4)$ overlayer (bottom). The Hg–Hg lattice constants are 3.62 and 3.22 \AA , respectively, as determined by ABS. The gas phase partial cross section is shown at top (---+---+) from Refs. 29 and 30.

the smaller lattice constants for Hg nearest neighbors have a much broader giant resonance. Furthermore, the smaller the lattice constant, the greater the photon energy of the giant resonance maximum as seen in Figs. 7 and 10. For all of the Hg overlayers, the giant resonance maximum is at a photon energy greater than that observed for gaseous Hg (approximately 35 eV photon energy).

DISCUSSION

The results obtained are noteworthy in several respects. When the new Hg photoemission feature [observed with Hg overlayers on Ag (100)] is included in the oscillator strength of the Hg 5*d*_{5/2} state, then the branching ratios observed for thin-ordered Hg overlayers on Ag (100) reach much higher values than those previously reported for other Hg systems,^{1,7,8} including gas phase and Hg compound results. The previous reports indicate that for Hg compounds, the maximum ratio is about 2.3 at a photon energy of 23 eV ,¹

though results with dimethylmercury¹⁹ have found that the branching ratio reaches a value as high as 3 below 30 eV. The ratio is consistently higher than the theoretical predictions of the free atom.²⁻⁴ It should be noted that the theoretical predictions assumed that the branching ratio is atomic in origin, and did not take long-range crystallographic order into account.

Taking long-range crystallographic order into account in estimating the branching ratio is clearly necessary, as Figs. 3 and 4 demonstrate. The branching ratio of the disordered Hg overlayers on Ag (100) resembles the gas phase branching ratio, while the deviation in the branching ratio is clearly apparent when the thin Hg overlayer is ordered. The local crystallographic order (nearest and next nearest neighbor) of Hg atoms is unlikely to differ for the amorphous Hg overlayer (adsorbed at 30 K) and the ordered Hg overlayer (adsorbed at 90 K).¹⁵ The difference between the two overlayers must lie in the presence or absence of long-range crystallographic order. As noted by Mott and others,²⁰ the radial distribution functions indicate that crystalline and amorphous systems possess nearly identical nearest and next nearest neighbor spacings. Further, as reported in detail elsewhere,^{16,17} both the 5*d*_{5/2} and the 5*d*_{3/2} Hg states possess cross sections that depend on the long-range crystallographic order. To our knowledge, this is the first report of the branching ratio exhibiting a dependence on the long-range crystallographic order.

Photoemission diffraction can alter the partial photoemission cross sections^{21,22} and as a consequence can alter the branching ratios. These diffraction related changes to the partial cross sections can occur only at specific photon energies, and result in changes only over small (about 2 eV) photon energy regions as discussed elsewhere.^{20,21} For the branching ratios to be characteristic of diffraction, the ratio should dramatically increase or decrease as photoelectrons with the kinetic energy of the 5*d*_{5/2} satisfy the diffraction condition. This should be followed by a decrease or increase (a change in the opposite direction) in the branching ratio at approximately 2 eV greater photon energy as photoelectrons with the same kinetic energy (but not from the 5*d*_{3/2} state) satisfy the diffraction condition. It is also worth noting that the large deviations of the branching ratios from the statistical value of 1.5 observed at 28 and 58 eV not only cover too broad a photon energy range to be explained by photoelectron diffraction, but do not correspond to features in the partial cross sections characteristic of photoelectron diffraction (Fig. 7).

To obtain the large deviations in the branching ratio, it is insufficient simply to have long-range order and a square lattice of Hg atoms. The photoemission results from Hg overlayers on Cu (100) show that a square ordered lattice of Hg atoms can also have a 5*d* branching ratio similar to that of the gas phase (Fig. 8). Expanding the in-plane Hg–Hg lattice constant from 2.87 to 3.22 or 3.62 Å is sufficient to alter both the 5*d* band structure^{13,18} and change the branching ratio. Since the Hg overlayers on Ag (100) and Cu (100) share a common square lattice net,^{13,18} the results for Hg on Cu (100) also do not support any explanation invoking diffraction. The dependence upon lattice constant, as well as

long-range crystallographic order, suggests (as discussed below) the 5*d* levels hybridize (given sufficient overlap of the atomic orbital wave functions¹³) to form a band altering the branching ratio.

Partial cross sections for the 5*d*_{5/2} (including the third 5*d* state) and 5*d*_{3/2} have been plotted in Fig. 7 for a five monolayers ordered Hg overlayer on Ag (100). The resonances in these partial cross sections have been discussed elsewhere.¹² All the unusual features in the Hg 5*d* partial cross sections, seen in Fig. 7, also cannot be explained by photoelectron diffraction, since both the sharp (1 to 2 eV full width at half-maximum) partial cross section resonance features at 59 eV and the broad feature (35 to 45 eV full width at half-maximum) at about 65 eV are altered by the crystallographic order.¹⁶ The necessary conditions for photoelectron diffraction^{21,22} are not satisfied for all of the partial cross section features. We have carried out dynamical diffraction calculations and are unable to reproduce a substantial number of the photoemission resonances.

The shift in the broad feature in the relative partial cross sections from a photon energy of 65 eV for a lattice constant of 2.89 Å (Fig. 7) to 55 eV for a lattice constant of 3.22 to 3.62 Å (Fig. 10) does tend to suggest that adatom hybridization does play a dominant role in determining the cross sections and distribution of oscillator strength. The increased half width of this broad feature has been taken to be another indication of hybridization of the Hg 5*d* levels between adjacent Hg atoms.¹⁷ It is clear that for Hg on Cu (100), where there is no additional 5*d*-like photoemission feature, the lattice constant decrease that occurs upon the phase transition of the Hg overlayer [from *c*(2×2) to *c*(4×4)] is accompanied a change in the Hg 5*d* partial cross section [Fig. 10]. Thus even though there is no substantial change in the branching ratio, changes in the screening processes still affect the photoemission process.

Large deviations of the branching ratio have been previously reported for gas phase systems,²³ but these reports also point out that the large deviations from the statistical average arise from resonances. In the present instance, neither Ag²⁴ nor Hg^{7,12,25} exhibit any resonances in the relevant photon energy ranges. The presence of the new electronic state demonstrably and significantly affects the branching ratio. When the influence of the new electronic state is removed either by our data analysis [the results for one monolayer on Ag (100)] or by growing disordered overlayers [results for two monolayers and five monolayers on Ag (100)], or by increasing the lattice constant [the results for Hg on Cu (100)] the branching ratio more closely approaches that observed for gaseous Hg.

An understanding of the origin of the new third 5*d* Hg state appears to be essential to developing any understanding of the observed large deviations of the branching ratios for the ordered Hg overlayers from those branching ratios observed with gaseous Hg and disordered overlayers. While the new 5*d* state is not a simple surface state, as has been demonstrated conclusively elsewhere,¹⁴ this does show considerable conservation of two dimensionality of state as expected for a state arising from the adatom–adatom hybridization within a very thin (one monolayer) Hg

overlayer.^{11,14} We note that this new $5d$ state is not a surface state because the intensity of the state is related to the amount of adsorbed mercury and the state does not conserve two dimensionality of state for thicker (approximately five monolayer) films.¹⁴ There is little doubt that this feature is a consequence of the electronic structure of the Hg overlayer.¹⁴ Furthermore, this third feature is not a result of the electronic structure of the Ag (100) substrate since the feature does not attenuate in intensity with increasing overlayer thickness.^{11,14} It is observed for Hg overlayers on other metal substrates¹³ and cannot be reconciled with the electronic structure of the Ag (100) substrate.¹⁴ The decrease of the partial $5d_{3/2}$ and $5d_{5/2}$ photoemission cross sections (neglecting the new state) in the transition from disordered to ordered Hg overlayers suggests that the new $5d$ state is made of approximately one electron from the $5d_{3/2}$ state and two electrons from the $5d_{5/2}$ state. The apparent contributions of the $5d_{5/2}$ and $5d_{3/2}$ states to the new Hg $5d$ state oscillator strength is consistent with the general deviation of the branching ratios, observed for the ordered five and two monolayer Hg overlayers, of 2.3 as compared to the more statistical value of 1.5 approximated by the disordered overlayers and gaseous Hg. The shift in the oscillator strength, apparent from a comparison of the photoemission spectra similar to those shown in Figs. 5 and 6, as well as from the branching ratio results suggests that the third mercury $5d$ state is a band formed from the hybridization of atomic $5d_{3/2}$ and $5d_{5/2}$ states of adjacent Hg atoms. This is consistent with the experimentally determined band structures of mercury overlayers on Ag (100).

This new $5d$ -like state formed by the hybridization of the $5d_{3/2}$ and $5d_{5/2}$ atomic states is a "bonding" state and a simple molecular orbital approach to the resulting band structure dictates that the unoccupied states above the metal Fermi energy must be now closer to the Fermi energy. This expectation arises from the fact that the new $5d$ -like band has a binding energy considerably smaller than the $5d_{3/2}$ and $5d_{5/2}$ spin-orbit split doublet. The new $5d$ band has already been demonstrated to have considerable $d_{xz,yz}$ character.¹⁴ There are contributions of this character wave function to the initial state eigenspinors that make up both the $5d_{5/2}$ and $5d_{3/2}$ states so that forming the new $5d$ band from both the $5d_{3/2}$ and $5d_{5/2}$ spin-orbit split doublet cannot be excluded on the basis of symmetry arguments.

When the lattice constant is insufficiently small to permit the hybridization of the atomic Hg $5d$ states as is the case for Hg overlayers on Cu (100), then there is no observed Hg $5d$ band structure.¹³ Furthermore, as seen in Fig. 8 the $5d$ branching ratios are characteristic of the atomic branching ratios and are insensitive to the incident vector potential orientation (also characteristic of the atomic like core level states).

A shift in electron distribution from the $5d_{3/2}$ to $5d_{5/2}$ states may be a consequence of our chosen method of including the "new" $5d$ feature with the $5d_{5/2}$ state, as is indicated above. While the apparent shift in electron distribution is suggestive of a change in spin-orbit interaction, we do not feel that this is the basis for the branching ratios observed with ordered Hg overlayers on Ag (100). Changes in the

spin-orbit interaction can result in substantial changes in the $5d$ branching ratio.²⁶ The changes in the branching ratios that we have observed are consistent²⁶ only with very substantial changes in the adatom-adatom hybridization and changes in the chemical state of Hg. Unfortunately, changes in the $5d_{5/2}$ to $5d_{3/2}$ spin-orbit binding energy splitting expected with a change in the spin-orbit interaction²⁶ are not observed.^{10,11,13} Furthermore, there is no reason to expect a large change in the electron occupancy of $5d$ states 7 to 10 eV below the Fermi energy, particularly when this change must be greater than is observed for a compound such as HgS,¹⁰ nor is it clear why the spin-orbit interactions (a largely intra-atomic interaction) should be affected by long-range crystallographic order (indicating an extra-atomic many electron interaction). Dimethylmercury has also been found to have a third $5d$ photoemission feature very much akin to the one reported in this study.¹⁹ Since Hg(CH₃)₂ has also been found to exhibit a branching ratio that differs substantially from atomic mercury and this difference has been attributed differences in the outgoing f wave potential between Hg and Hg(CH₃)₂,¹⁹ as in good agreement with this work.

A study of Pb overlayers on Ni (100) notes a change in the Pb $5d_{5/2}$: $5d_{3/2}$ branching ratio with overlayer thickness.²⁷ No structural analysis was reported; we are therefore unable to conclude from whether the branching ratios from these overlayers depends on crystallography, but again it seems probable that the potential for the outgoing photoelectron is affecting the branching ratio.

CONCLUSION

The branching ratio is commonly regarded as atomic in origin and this is generally believed to be true for the Hg $5d$ states as well;²⁸ solid-state effects in HgS¹ alter the branching ratio by about 30% over a 5 eV photon energy range. For the Hg overlayers on Ag (100), the branching ratio changes dramatically with changes in the overlayer long-range crystallographic order. For these Hg thin films, the branching ratio is, therefore, not predominantly atomic nor predominantly nearest neighbor in origin. The implication is that one or both of the Hg $5d_{5/2}$ and $5d_{3/2}$ states contribute to form an itinerant band. This conclusion is further supported by earlier reports¹⁴ that the new electronic state disperses with electron momentum parallel to the surface. The partial cross section results presented here also suggest that there is strong relationship (possibly due to adatom hybridization) between lattice constant and the Hg $5d$ electronic structure, in particular with the distribution of $5d$ oscillator strengths. The present results establish that the branching ratio of Hg states, commonly viewed as atomic in origin,²⁸ is affected by the overlayer long-range crystallographic order. Furthermore, it is abundantly clear from the Hg $5d$ branching ratios that the "third" Hg $5d$ state, observed with the ordered Hg overlayer thin films, is not a simple "atomic-like" state. The origin of this state, while apparently a result of $5d_{3/2}$ and $5d_{5/2}$ electronic contributions, remains elusive.

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