PHYSICAL REVIEW B VOLUME 13, NUMBER 12 15 JUNE 1976

X-ray photoemission from mercury in vapor and condensed phases

James S. Jen and T. Darrah Thomas

Department of Chemistry and Radiation Center, Oregon State University, Corvallis, Oregon 97331

(Received 15 December 1975)

The $4f$ ionization potentials for mercury in the vapor phase have been measured relative to the vacuum level; those for mercury condensed on gold, silver, and copper have been measured relative to the Fermi level. Correction for the work function of the solids, determined in a separate experiment, gives the ionization potentials of the condensed mercury relative to the vacuum. The vapor-phase ionization potentials are greater than those for condensed phases by 3.3 eV for $f_{7/2}$ electrons and 3.0 eV for $f_{5/2}$ electrons; these differences are nearly independent of the substrate. This shift is attributed to extra-atomic relaxation energies. Two models, a localized electron (exciton) model and an equivalent-cores thermochemical model, predict relaxation energies for these and other systems with reasonable accuracy. The splitting between the $f_{7/2}$ and $f_{5/2}$ levels is 4.01 eV in the gas phase and 3.7 eV in the solid phase. The change in splitting on condensation may be due to energy-loss phenomena peculiar to the surface.

I. INTRODUCTION

In the simplest model of ionization potentials it is assumed that only one electron changes its wave function during ionization; the wave function for all of the other electrons remains frozen. It is well known, however, that the other, spectator, electrons will rearrange after ionization, thus lowering the energy of the final state. The ionization potential, which is the difference between the energies of the initial and final states, will, therefore, be lower than that predicted by the frozen-orbital approximation (Koopmans's theorem). The decrease in energy is known as the relaxation energy.[1]

For free atoms, the relaxation energy arises only from rearrangement of electrons on that atom. For atoms in condensed phases or in molecules, however, there will be an additional relaxation because of polarization of electrons on nearby atoms. This relaxation energy is known as the extra-atomic relaxation energy.[1] Experimental values of this quantity range from about 0–12 eV.[2,3]

When an atom (or molecule) is condensed from the gas phase to the solid or liquid phase, its core-ionization potentials may shift either because of a change in the chemical state of the species (oxidation, reduction, dissociation) or because of extra-atomic relaxation due to the presence of nearby atoms. To understand the shifts of core ionization potentials on condensation, it is important to have knowledge of the magnitudes of extra-atomic relaxation energies.

Metals provide almost ideal systems for studying extra-atomic relaxation energies. There is no change in oxidation state on condensation, and, hence, only a small change in core ionization potentials due to chemical effects is expected. Metals are conductors and, therefore, present none of the charging problems or reference-level problems found in insulators. Among the metals, mercury is particularly suitable since it is easily studied in both vapor and condensed phases.

A simple model has been developed by Ley, Kowalczyk, McFeely, Pollak, and Shirley[2] for predicting the extra-atomic relaxation energies for metals. According to this model electrons flow from the conduction band of the metal to the site of core ionization in order to neutralize exactly the positive change generated in the photoionization. The total energy is lowered by the interaction energy between the core hole and the added electron, which resides in a normally unoccupied atomic orbital of the core ionized atom. It is assumed that no energy is required to move the electrons in the conduction band. The extra-atomic relaxation energy depends, in this model, only on properties of the core-ionized atom and not on properties of the substrate. It is of interest, in testing this model, to measure the extra-atomic relaxation energy for the same atom on several different substrates. We present below results of our measurements of the extra-atomic relaxation energy for mercury condensed on copper, silver, and gold. These data provide an opportunity to test the ability of the model developed by Ley *et al.* to predict the value of the relaxation energy and its dependence on substrate.

In addition to comparing our results with the predictions of the model proposed by Ley *et al.* we have shown that the equivalent-cores approximation[4] together with a Born-Haber cycle can be used to predict the shift of core-ionization potential on condensation. A comparison between these predictions and experimental results for a wide range of metals is given.

Core-ionization potentials of gas-phase species are normally reported relative to the vacuum level; those for conductors are given relative to the Fermi level. In order to adjust these to a common basis it is necessary to add the work function to the values relative to the Fermi level. It is, however, well known that the substrate work function depends on the presence of adsorbed material. We have, therefore, measured the work functions for the various samples we have used under the vacuum conditions of the photoemission experiments.

II. EXPERIMENTAL PROCEDURE AND RESULTS

All of the measurements of core-ionization potentials were made in our cylindrical-mirror photoelectron spectrometer.[5] In every case the exciting radiation was aluminum $K\alpha$ x rays. Three different configurations were used, one for the vapor phase and two for the solid phase.

A. Vapor-phase measurements

Mercury vapor was obtained by putting a drop of pure mercury on the head of the x-ray tube, which is also the bottom of the gas sample chamber (see Fig. 5 of Ref. 5). The heat (about 10 W) caused by electron bombardment of the head during x-ray production was sufficient to produce an adequate amount of mercury vapor in the gas cell. Each measurement, however, required about 24 h, even for the strong $4f$ lines. A typical gas-phase spectrum is shown on the left-hand side of Fig. 1.

In each run neon gas was introduced to mix with the mercury vapor for calibration; the kinetic energies of various electrons ejected from neon during irradiation with aluminum x rays are well known.[6,7] Peak positions were determined by least-squares fitting of Gaussian functions to the peaks. The average of five separate measurements of the $4f$ ionization potentials in mercury vapor are given in Table I, referenced to the vacuum level. The agreement with the values reported by Siegbahn[8] is excellent.

B. Condensed-phase measurements

Samples of condensed-phase mercury were prepared by evaporating, in vacuum, pure metal (copper, silver, or gold) onto an aluminum-foil substrate. After a rather thick metal film had been deposited, mercury was evaporated, in vacuum, onto the metal coating. The whole sample was then heated slightly to evaporate the physisorbed mercury and leave only chemisorbed and amalgamated mercury.

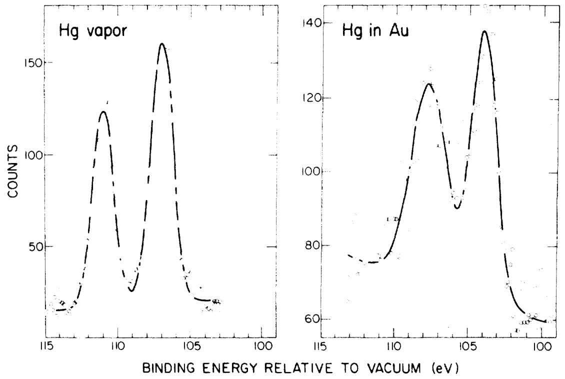

FIG. 1. X-ray photoelectron spectra of mercury vapor and mercury condensed onto gold.

The foils so prepared were used in one of two ways. In one method the foil served as window to the x-ray tube, with the aluminum (facing toward the electron gun) as anode [Fig. 4(a) of Ref. 5]. X rays passed through the aluminum foil and the metal deposit before exciting the mercury. In the other method the foil was rolled into a cylinder and placed above the regular anode of the x-ray tube [Fig. 4(b) or Ref. 5]. In this configuration the x rays strike the surface of interest before passing through the substrate. For some samples no aluminum substrate was used. The mercury was evaporated in vacuum directly onto a cleaned gold foil. The spectra were then taken using the second method described above.

A typical condensed-phase spectrum is shown on the right-hand side of Fig. 1. There is a noticeable shift between the gas phase and the condensed phase and also a distinct change in the shape of the spectrum.

Core-ionization potentials of these samples were measured using the gold $4f$ lines for calibration. Where gold was not part of the substrate, the gold spectra were run immediately after or

TABLE I. Hg $4f$ electron binding energies in gas phase and on various substrates (eV).

	$4f_{7/2}$	$4f_{5/2}$	Reference
Gas phase	111.10(6)	107.09(5)	Vacuum
Gold	103.05(7)	99.36(5)	Fermi level
Silver	103.63(8)	99.90(7)	Fermi level
Copper	103.27(7)	99.63(5)	Fermi level
Gold	107.8(1)	104.1(1)	Vacuum [a]
Silver	107.9(1)	104.2(1)	Vacuum [a]
Copper	107.8(1)	104.1(1)	Vacuum [a]

[a] Work functions given in Table II have been used to convert the values relative to the Fermi level to values relative to the vacuum level.

before the mercury spectra. Since the binding energies in gold, relative to the Fermi level, are known (83.45 eV for the $4f_{7/2}$ line[9]), this method of calibration gives the mercury ionization potentials relative to the Fermi level. The results of our measurements for the mercury condensed on copper, silver, and gold, relative to the Fermi level are given in Table I.

During the course of each run, oxygen 1*s* and carbon 1*s* signals were monitored. No strong signals were found indicating that the surfaces remained relatively clean.

C. Work-function measurements

A number of techniques are available for measuring work functions. We have used the space-charge-limited-diode method because of the simplicity of the apparatus and technique. An excellent discussion of this method has been given by Knapp.[10]

Samples used in the work-function measurements were prepared in the same way as those for the photoelectron spectroscopy. The measurements were made in the vacuum system of the spectrometer (about 10^{-6} Torr). Prior to each measurement, the sample surface was bombarded by electrons (~1 keV) emitted from the cathode of the diode. All measurements were taken relative to a clean gold surface, for which the work function is well known. The work functions we have determined are given in Table II, together with the value for gold we have used as a reference. Because of the difficulty of measuring extremely low currents (10^{-10}–10^{-13} A), these results are accurate to only about 0.1 eV. However, our results are close to those reported by others. For instance, the 0.5-eV difference between pure gold and gold contaminated with mercury is in good agreement with that report by Huber[11] and by Riviere.[12]

D. Shift between gas phase and condensed phase

Ionization potentials for mercury on copper, silver, and gold are given in Table I relative to the vacuum level. These have been obtained by adding the measured work functions given in Table II to the ionization potentials relative to the Fermi level given in Table I. Within the limits of our measurement of the work function, the value of the ionization potential relative to the vacuum level is independent of the substrate.

TABLE II. Work functions for mercury-covered surfaces and for gold (eV).

Material	Work function	Reference
Au	5.22(5)	a
Hg-Au	4.7(1)	b
Hg-Ag	4.3(1)	b
Hg-Cu	4.5(1)	b

[a] Reference 11.
[b] This work.

TABLE III. Shift in binding energy between gas phase and condensed phase (eV).

	$4f_{7/2}$	$4f_{5/2}$
Hg-Au	3.3	3.0
Hg-Ag	3.2	2.9
Hg-Cu	3.3	3.0

The differences between the gas-phase ionization potentials and those in the condensed phase, all measured relative to the vacuum level are presented in Table III. We attribute these differences almost entirely to extra-atomic relaxation energy, for reasons that are discussed below. We note that these relaxation energies are independent of substrate, and are different for the two kinds of 4*f* electrons. Further discussion of these results is presented below.

E. Splitting

For the gas-phase measurements, the photoelectron spectrum shows two lines separated by 4.01 ± 0.06 eV. This separation, which is in good agreement with the value of 4.0 reported by Siegbahn,[8] arises from spin-orbit splitting. The ratio of peak areas, 1.37 ± 0.02, is in reasonable agreement with the statistical ratio 8/6 = 1.33.

In the solid phase we measure the separation to be 3.7 ± 0.1 eV, independent of substrate. After we submitted this paper it came to our attention that similar experiments have been done recently by Siegbahn and co-workers[13] who have investigated both gaseous and condensed mercury. Their results show no difference between the gas-phase and condensed-phase splittings.

In view of the discrepancy between our results and theirs, it is important to look at the experimental basis for our numbers and the differences between our experiments and theirs. We note first that splittings we have obtained are reproducible. In five measurements on mercury in gold, eight in silver, and four in copper we obtain values of 3.69 ± 0.10, 3.73 ± 0.06, and 3.64 ± 0.05 eV, respectively. (The uncertainties are the standard deviations of the mean.)

The low signal-to-background ratio in our measurements compared to theirs presumably arises because in ours the mercury is a minor component concentrated near the surface of the substrate. The observed spectrum could conceivably be distorted by impurities (especially those that segregate near the surface), by energy-loss phenomena peculiar to the surface, or by crystal fields associated with the bonding of the mercury to the substrate.

We consider first the possibility of impurities. In early experiments we detected a peak due to silicon impurity on the surface of the aluminum substrate. This was, however, clearly distinguishable from the peaks due to mercury. This part of the experiment was repeated using samples that were prepared by evaporating mercury directly onto a pure-gold-foil substrate, hence eliminating the possible silicon impurity from aluminum. The results were the same as those of mercury onto gold on an aluminum substrate. Furthermore, we were able to show from the spectrum of the clean gold substrate that the background in the region of the mercury peaks was featureless.

In general, we would expect impurities to be present in varying amounts in different samples, giving rise to a wide range of splittings and to intensity ratios that differ markedly from the statistical ratio. This is not the case. The spread of values for the splitting is the same in the solid phase as in the gas phase. The area ratios are 1.16 ± 0.07, 1.26 ± 0.06, and 1.24 ± 0.04 for mercury on gold, silver, and copper, respectively; all are reasonably close to the statistical value.

To further investigate the possibility that there is an impurity peak distorting the shape of the spectrum we have tried additional fitting procedures. First, we have fit a typical spectrum with two peaks constrained to be separated by 4.0 eV, the spin-orbit splitting in mercury vapor, and a third peak, unconstrained. This procedure gave an $f_{7/2}$ peak with a width of 1.4 eV, substantially narrower than in the gas phase, and an $f_{7/2}/f_{5/2}$ peak-area ratio of 0.86, quite far from the statistical ratio of 1.33. Second, we have fit the same data with two peaks constrained to be separated by 4.0 eV and to the statistical area ratio of 1.33; a third peak was unconstrained. In this case, χ^2 was worse than in the other fits and the unconstrained third peak was about 25 times as broad as the other peaks and was of negligible amplitude.

Finally, we have prepared a sample with a coating of mercury so thick that initially the spectrum due to the gold substrate was unobservable. We followed the mercury and gold spectra while the mercury evaporated and the gold was revealed. The splitting for the mercury remained at about 3.7 eV throughout the series of measurements, which cover a wide range of ratios of mercury to substrate. The gold splitting was determined to be 3.65 eV, in good agreement with values reported by others.[7]

In Sec. III we consider and reject the possibility that the solid-phase splitting is significantly affected by crystal fields. We are left, therefore, with the possibility that the energy-loss phenomena for atoms near the surface are different from those in the bulk and sufficiently important to produce a significant distortion of the observed spectra. If this is the case, it is presumably the energy-loss features of the $f_{7/2}$ peak that distort the position of the $f_{5/2}$ peak; the position of the $f_{7/2}$ should be unaffected. To explore this possibility we have fit our data to Gaussian peaks with exponential tails, with both peaks constrained to have the same shape and the correct area ratios. For the spectrum studied, the splitting changed from 3.8 eV with symmetric peaks to 3.9 eV with asymmetric peaks. The change is in the right direction though not large enough to completely explain our results.

III. DISCUSSION

The essential features of our results are that the energy to remove a core electron from condensed mercury to the vacuum is independent of whether the substrate is copper, silver, or gold and is less than the core binding energy in the gas phase by 3.3 eV for $4f_{7/2}$ electron and 3.0 eV for $4f_{5/2}$ electrons. The work function, however, depends on the substrate and, accordingly, the binding energies relative to the Fermi level are dependent on the substrate.

The change in core ionization potential between the free atoms in the gas phase and those in the condensed phase arises from two major effects. First, there is a change in the initial-state charge distribution due to rearrangement of valence electrons when mercury forms bonds to the surrounding atoms. Second, there is the final-state relaxation energy described above due to the rearrangement of extra-atomic electrons to neutralize the charge on the mercury atom. These two sources of shifts in the core-ionization potentials are discussed in more detail below.

Similar measurements have been made by Citrin and Hamann[14] who determined the core-ionization potentials of various noble gases implanted in the same substrates that we have used: copper, silver, and gold. For ionization potentials relative to the Fermi level they find results qualitatively similar to ours: The ionization potentials increase in the order gold, copper, silver. Quantitatively, however, the effects they have observed are different in that they find a large step between gold and silver and a small step between silver and copper. Our results are the reverse of this.

By adding work-function corrections, Citrin and Hamann have obtained ionization potentials relative to the vacuum level and, from these together with gas-phase ionization potentials, the extra-atomic relaxation energies. They conclude that this relaxation energy increases from copper to gold to silver. Their result is in disagreement with our conclusion that the relaxation energy is independent of the substrate.

Citrin and Hamann have used a value of 4.0 eV for the work function of pure silver—about 0.3 eV lower than the value sometimes reported. Using the larger value reduces the spread in relaxation energies to the point that values for different substrates are approximately within experimental error of one another. Furthermore, it has been noted by Yates and Erickson[15] that adsorption of xenon on a tungsten surface changes the work function by about 1 eV; it is also known that adsorption of mercury on gold lowers the work function by 0.5 eV. Although these situations are not directly comparable to that of Citrin and Hamann, in which the impurity atoms are imbedded in the metal rather than present as a surface impurity, it seems reasonable to suppose that the appropriate work function is not necessarily that of the pure metal.

A. Initial-state effects

When atoms of the same element combine to give a molecule or solid we may anticipate that there will be changes in the core-ionization potentials because of rearrangement of the valence electrons. We can estimate the magnitude of these shifts by comparing orbital energies for single atoms with those for the corresponding homonuclear diatomic molecules.[16,17] Such a comparison is given in Table IV, where we give the difference between these two quantities for the elements lithium through fluorine, for which Hartree-Fock calculations are available. The predicted shifts range from −0.70 eV for lithium to 1.64 eV for oxygen. The largest shifts are associated either with the smallest atoms or with the most tightly bonded molecules. If the bonding is strong, the valence electrons undergo major redistribution upon bond formation; if the atoms are small, the effects of this distribution are relatively large.

TABLE IV. Change in 1*s* orbital energy when two atoms condense into a molecule.

	$E_{\mathrm{at}} - E_{\mathrm{mol}}$
Li	−0.70 eV
Be	−0.16
B	+0.22
C	+0.90
N	+1.39
O	+1.64
F	+1.08

For the metal systems considered here, the bonding is relatively weak and the atoms are relatively large. The dissociation energy of Hg_2 is 0.06 eV compared to 1 eV for Li_2.[18] The heats of vaporization are 13.6 kcal/mole for mercury and 32.2 kcal/mole for lithium.[19] An appropriate measure of the atomic size is the expectation value $\langle 1/r\rangle e^2$ for the valence electrons; for mercury 6*s* electrons this quantity is 10 eV, for lithium 2*s*, 9.4 eV.[20] We may, therefore, expect that the shift in core-ionization potentials from this source will probably be substantially less than 1 eV.

When atoms of different elements combine to give a molecule or solid, there are likely to be changes in core-ionization potentials because of the transfer of electrons from the more electropositive to the more electronegative species. We can estimate the magnitude of this shift by using the point-charge model.[21] We assume that the electron transfer is from the mercury to the nearest neighbors (or vice versa). Then the shift in core-ionization potential ΔE can be written

$$\Delta E = q(k - e^2/R),$$

where q is the charge transferred, k is the change in core ionization potential per valence electron removed to infinity, and R is the distance between the mercury atom and the nearest host atoms. If we assume metal atomic radii, then e^2/R is about 5 eV for all of the systems considered here. For mercury 6*s* electrons k is about 10 eV. The quantity ΔE is than about $5q$ eV; it will be smaller if electrons are transferred from the host to the mercury 6*p* orbitals.

The magnitude of q depends on the relative electronegativities of mercury and the host. Various sources[22-24] of electronegativity values indicate that mercury has an electronegativity greater than, equal to, and less than that of copper; greater than and equal to that of silver; and less than and equal to that of gold. Perhaps the best estimate of the relative electronegativities can be obtained from the heat of formation of the appropriate amalgams. In general, heats of formation of amalgams are at most a few kcal/mole,[25] suggesting that the electronegativity difference between the constituents is quite small. On this basis, we conclude that q will be quite small and that ΔE will be correspondingly small.

It is not possible, on the basis of the foregoing arguments, to exclude the possibility that the observed 3-eV shift between the gas phase and the condensed phase is due to initial-state effects. It seems likely, however, that these effects will be significantly less than that observed.

B. Final-state effects: localized-electron model

Ley *et al.*[2] have proposed a model for calculating extra-atomic relaxation energies in which it is assumed that one electron flows from the conduction band to an orbital on the core-ionized atom, exactly neutralizing the charge produced in the ionization. This electron is localized on one of the previously vacant orbitals of the core-ionized atom. The relaxation energy is the energy of interaction between the added electron and the core hole.

The appropriate wave functions to use are, as has been pointed out by Ley *et al.* not those of the original atom but those of the atom with one higher atomic number. For the system under consideration here, the equivalent-core atom for mercury is thallium. Using values from Mann[26] for the appropriate Coulomb and exchange integrals in thallium, we calculate the extra-atomic relaxation energy in mercury to be 4.2 eV, in approximate agreement with our experimental value.

According to this model the extra-atomic relaxation energy in metals depends only on the properties of the atom ionized and not on the substrate. Our results are in agreement with this prediction. It would be interesting to measure extra-atomic relaxation energies in alloys consisting of metals that have rather different extra-atomic relaxation energies in the pure material.

It has been noted by Ley *et al.* that the electron is not in fact localized on the ionized atom but is spread out over nearby atoms of the host. For thallium the average radius of the $6p$ orbital is 2.1 Å,[20] while the distance to the nearest neighbors is 2.8 Å. The actual orbital occupied by the extra electron is, therefore, largely located on the surrounding atoms.

C. Final-state effects: thermochemical model

The equivalent-cores thermochemical model[4] can be used to predict the extra-atomic relaxation energies of core electrons from known heats of reaction and work functions. Let us consider the following reactions, with their corresponding enthalpy changes.

$$\mathrm{Hg}(c) = \mathrm{Hg}(v)\,, \quad \Delta H_1 = \Delta H_{\mathrm{vap}}(\mathrm{Hg})\,.$$

The notation v refers to mercury in the vapor phase and c to mercury in the condensed phase, assumed to be pure mercury for this illustration.

$$\mathrm{Hg}(v) = \mathrm{Hg}^{*+}(v) + e^-\,, \quad \Delta H_2 = I(4f, \mathrm{Hg}, v)\,.$$

The symbol Hg^{*+} represents the mercury atom missing a core electron. The ionization potential I is that of a $4f$ electron from mercury in the vapor phase.

$$\mathrm{Hg}^{*+}(v) = \mathrm{Tl}^+(v)\,, \quad \Delta H_3$$

ΔH_3 is the core exchange energy. The core-ionized mercury is replaced with a thallium ion, which has the same core charge and the same valence structure as the mercury ion.

$$\mathrm{Tl}^+(v) + e^- = \mathrm{Tl}(v)\,, \quad \Delta H_4 = -I(6p, \mathrm{Tl}, v)\,,$$

$$\mathrm{Tl}(v) = \mathrm{Tl}(c)\,, \quad \Delta H_5 = -\Delta H_{\mathrm{subl}}(\mathrm{Tl})\,,$$

$$\mathrm{Tl}(c) = \mathrm{Tl}(\mathrm{Hg})\,, \quad \Delta H_6 = 0\,.$$

Pure thallium becomes a trace impurity in a mercury substrate. For very dilute solutions of thallium in mercury, $\Delta H_6 = -0.03$ eV,[27] or very nearly 0.

$$\mathrm{Tl}(\mathrm{Hg}) = \mathrm{Tl}^+(\mathrm{Hg}) + e^-\,, \quad \Delta H_7 = \phi(\mathrm{Hg})\,.$$

For this reaction we need the work function, ϕ, of the material containing the thallium impurity. We will assume this to be the work function of the pure material.

$$\mathrm{Tl}^+(\mathrm{Hg}) = \mathrm{Hg}^{*+}(c)\,, \quad \Delta H_8 = -\Delta H_3$$

ΔH_8 is the core exchange energy. The assumption of the equivalent cores model is that the energy changes in the two core-exchange steps are equal and opposite.

$$\mathrm{Hg}^{*+}(c) + e^- = \mathrm{Hg}(c)\,, \quad \Delta H_9 = -I(4f, \mathrm{Hg}, c)\,.$$

The nine reactions complete a Born-Haber cycle; the sum of the enthalpy changes must be 0. Summing and rearranging, we have

$$I(4f, \mathrm{Hg}, v) = I(4f, \mathrm{Hg}, c) - \phi(\mathrm{Hg}) - \Delta H_{\mathrm{vap}}(\mathrm{Hg}) + \Delta H_{\mathrm{subl}}(\mathrm{Tl}) + IP(6p, \mathrm{Tl}, v)\,.$$

The extra-atomic relaxation is, according to this model, equal to $-\Delta H_{\mathrm{vap}}(\mathrm{Hg}) + \Delta H_{\mathrm{subl}}(\mathrm{Tl}) + I(6p, \mathrm{Tl}, v) - \phi(\mathrm{Hg})$, which is 2.9 eV.[28] The prediction is in excellent agreement with the weighted average of 3.1 from our measurements. A similar calculation for bismuth gives 3.4 eV in comparison with an experimental value of 3.6 eV.[2]

For mercury condensed on different substrates, various terms in these expressions must be modified. In particular, these will be the heats of vaporization (1), sublimation (5), mixing (6), and the work function of the substrate (7). There will be cancellation between ΔH_1 and ΔH_5, which appear with opposite sign, but which presumably

TABLE V. Comparison of experimental and predicted relaxation energies (eV).

Element	Core level	R_{ex} (Expt.) [a]	R_{ex} (Thermo.) [b]	R_{ex} (Exciton) [a]
Na	$2s, 2p$	5.3	5.8	5.0
Mg	$2s, 2p$	2.5	3.6	4.9
Al	$2s, 2p$	5.1	4.5	6.0
K	$2s, 2p$	5.5	5.0	3.9
Ca	$2s, 2p$	8.4	7.4	10.7
Sc	$2s, 2p$	5.5	7.2	12.0
V	$2s, 2p$	9	8.2	13.2
Cr	$2s, 2p$	6.6	2.5	15.2
Mn	$2s, 2p$	10.5	7.9	13.3
Fe	$2s, 2p$	9.4	9.1	17.3
Ni	$2s, 2p$	12.5	13.4	18.4
Cu	$3d$	2.9	2.7	4.8
Zn	$3d$	3.4	3.4	4.8
Cd	$4d$	3.0	2.9	4.2
Pb	$4f_{7/2}$	3.5	3.6	5.2
Hg	$4f_{5/2}$	3.3 [b]	2.9	4.2
	$4f_{7/2}$	3.0 [b]		

[a] From Ref. 2.

[b] This work.

shift in the same direction. The work functions we have measured for the different substrates are within a few tenths of an eV of that of mercury. We would expect, therefore, only minor changes in our calculated value if we had used correct values for the various thermodynamic quantities.

We have used this model to calculate extra-atomic relaxation energies for a number of other metals for which experimental values are available.[29,30] The results are summarized in Table V and in Fig. 2 together with predictions given by Ley *et al.*[2] using the model discussed above. (In making the thermochemical calculations for transition metals it is necessary to take into account the fact that the outer electron configuration of one metal may differ from that of the singly charged ion of the next. For instance the valence configuration for Fe^{*+} is $3d^6 4s^2$; the corresponding configuration in the equivalent-core species Co^+ is at 5 eV above the ground state, which is $3d^8$.)

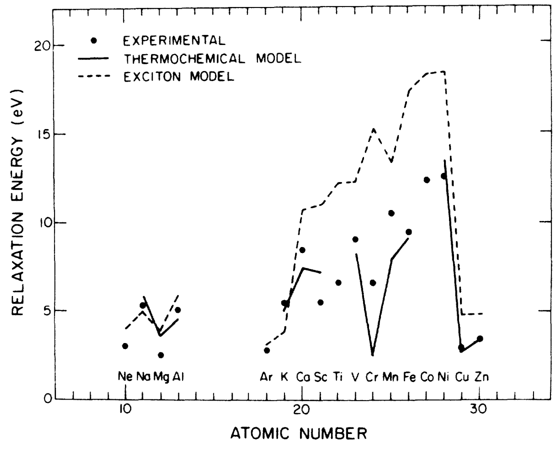

FIG. 2. Experimental extra-atomic relaxation energies compared with values calculated by exciton and thermochemical models.

We see from the results presented in Table V and Fig. 2 that in most cases there is reasonably good agreement between the experimental data and the predictions of the thermochemical model. In particular the model successfully accounts for the large relaxation energies observed for transition metals. Part of the discrepancies that are seen may be due to our assumption that ΔH_6, the heat of mixing of the impurity with the host, is always zero.

D. Change in splitting

In the gas phase there is a difference of 4.01 eV, due to spin-orbit interaction, between the two peaks in the mercury spectrum. In the solid phase this splitting is 3.7 eV, and to within less than 0.1 eV, is independent of the substrate. In addition, there is a change in line shape on condensation, as can be seen from Fig. 1. The $f_{5/2}$ peak is relatively lower and broader in the condensed phase than in the gas phase.

We consider the possibility that this change in splitting might be due to a crystal-field or ligand-field effect. As a first approach we assume that the mercury ion is fully embedded in the host as a member of a cubic-close-packed lattice.

The electron that neutralizes the charge on the ion is taken to be distributed over the 12 nearest neighbors and produces the crystal field. Since the crystal has cubic symmetry, we need consider only the P_4 and P_6 parts of the potential.[31] The order of magnitude of the interaction will be $\langle r^4\rangle/R^5$ for P_4 and $\langle r^6\rangle/R^7$ for P_6, where r refers to the radius of the f electron and R to the nearest-neighbor distance. For mercury embedded in gold these quantities are about 10^{-3} and 10^{-5} eV, respectively. A more rigorous calculation using conventional methods[31,32] indicates that such a crystal field would split the $\frac{7}{2}$ and $\frac{5}{2}$ peaks by about 3×10^{-5} eV. These perturbations are much too small to account for the observed changes.

We next consider the possibility that the mercury ion is adsorbed on the surface and that the neutralizing charge is directly below it. In this case we must consider P_2 terms. The perturbation will be of order $\langle r^2\rangle/R^3$, which is about 0.04 eV, still too small. The P_1 term could cause mixing between the f orbitals and nearby d orbitals. The matrix elements for this interaction are less than $\langle r\rangle/R^2$, which is about 0.4 eV. Since these are second-order perturbations and the nearest d levels are 90 eV away from the f levels we can expect negligible contributions from this mixing.

The estimated changes in splitting given above must be modified by shielding or antishielding due to polarization of the outer electrons. For f electrons in the rare earths, the outer electrons are, for the most part, shielding.[33,34] If the situation is the same for mercury, then the actual crystal-field splittings will be even smaller than we have estimated. Even if the outer electrons are antishielding, the value of the antishielding parameter appears to be small.[34]

It would appear, then, that the potential due to charges external to the ion is too small to cause the observed change in splitting between the gas phase and the condensed phase.

IV. SUMMARY

We have shown that the $4f$ ionization potentials for mercury in the gas phase are 3.0 eV ($4f_{5/2}$) and 3.3 eV ($4f_{7/2}$) greater than the corresponding ionization potentials for mercury condensed onto copper, silver, and gold. This difference, which we attribute to extra-atomic relaxation, is independent of the substrate to within about 0.1 eV.

Two models, one thermochemical and one based on localizing a neutralizing electron at the site of the ionized atom account quantitatively for the observed relaxation energies. We show also that the thermochemical model gives reasonable predictions for extra-atomic relaxation energies in other metals; the same result has previously been demonstrated for the localized-electron model.

The splitting between the $f_{7/2}$ and $f_{5/2}$ levels changes from 4.0 eV in the gas phase to 3.7 eV in the condensed phase. We have been unable to account for this shift by any reasonable crystal field. It may be due to distortion of the peaks by energy-loss phenomena peculiar to the surface.

ACKNOWLEDGMENTS

This work was supported in part by the U. S. Energy Research and Development Administration. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We are indebted to P. Citrin for helpful comments on an early version of this paper, to B. Mills who supplied us with a copy of the curve-fitting program GAMET that was used for some of the least-squares fits, and to S. R. Smith who adapted the program to our computer.

---

[1] A general review of relaxation effects has been given by R. L. Martin and D. A. Shirley, in *Electron Spectroscopy: Theory, Techniques, and Applications*, edited by A. D. Baker and C. R. Brundle (Academic, New York, to be published).

[2] L. Ley, S. P. Kowalczyk, F. R. McFeely, R. A. Pollak, and D. A. Shirley, Phys. Rev. B 8, 2392 (1973).

[3] S. P. Kowalczyk, L. Ley, R. L. Martin, F. R. McFeely, and D. A. Shirley, Discuss. Faraday Soc. (to be published).

[4] W. L. Jolly, in *Electron Spectroscopy*, edited by D. A. Shirley (North-Holland, Amsterdam, 1972), p. 629.

[5] P. H. Citrin, R. W. Shaw, Jr., and T. D. Thomas, in *Electron Spectroscopy*, edited by D. A. Shirley (North-Holland, Amsterdam, 1972), p. 105.

[6] T. D. Thomas and R. W. Shaw, Jr., J. Electron. Spectrosc. 5, 1081 (1974).

[7] G. Johansson, J. Hedman, A. Berndtsson, M. Klasson, and R. Nilsson, J. Electron. Spectrosc. 2, 295 (1973).

[8] K. Siegbahn, J. Electron. Spectrosc. 5, 33 (1974).

[9] C. K. Jorgensen, Theor. Chim. Acta 24, 241 (1972). It is to be noted, however, that values reported for this quantity vary by as much as 1 eV. The correct value may be different from the one we have used; in this case the energies we have reported should be adjusted accordingly.

[10] A. G. Knapp, Surf. Sci. 34, 290 (1973).

[11] E. E. Huber, Jr., Appl. Phys. Lett. 8, 169 (1966).

[12] J. C. Riviere, in *Solid State Surface Science*, edited by M. Green (Dekker, New York, 1969), Vol. 1, Chap. 4.

[13] K. Siegbahn, Uppsala University Institute of Physics report UUIP-909, 1975 (unpublished). S. Svensson, N. Mårtensson, E. Basilier, P. Å. Malmquist, U. Gelius, and K. Siegbahn, J. Electron. Spectrosc. (to be published).

[14] P. H. Citrin and D. R. Hamann, Phys. Rev. B 10, 4948 (1974).

[15] J. T. Yates, Jr., and N. E. Erickson, Surf. Sci. 44, 489 (1974).

[16] E. Clementi and C. Roetti, At. Data Nucl. Data Tables 14, 177 (1974).

[17] P. E. Cade and A. C. Wahl. At. Data Nucl. Data Tables 13, 339 (1974).

[18] G. Herzberg, *Spectra of Diatomic Molecules* (Van Nostrand, Princeton, 1950), pp. 537 and 546.

[19] R. T. Sanderson, *Chemical Periodicity* (Reinhold, New York, 1960), p. 86.

[20] J. B. Mann, Los Alamos Scientific Laboratory report LA 3691, 1968 (unpublished).

[21] D. W. Davis, D. A. Shirley, and T. D. Thomas, J. Am. Chem. Soc. 94, 6565 (1972).

[22] M. C. Day and J. Selbin, *Theoretical Inorganic Chemistry* (Reinhold, New York, 1962), p. 114.

[23] Reference 19, p. 32.

[24] C. S. G. Phillips and R. J. P. Williams, *Inorganic Chemistry* (Oxford University, New York, 1965), Vol. I, p. 114.

[25] *International Critical Tables* (McGraw-Hill, New York, 1929), Vol. V, p. 189.

[26] J. B. Mann, Los Alamos Scientific Laboratory report LA-3690, 1967 (unpublished).

[27] G. N. Lewis, M. Randall, K. S. Pitzer, and L. Brewer, *Thermodynamics*, 2nd ed. (McGraw-Hill, New York, 1961), p. 388.

[28] For these calculations, heats of vaporization, first ionizational potentials and work functions were taken from D. A. Johnson, *Some Thermodynamic Aspects of Inorganic Chemistry* (Cambridge University, Cambridge, 1968); R. E. Dickerson, *Molecular Thermodynamics* (Benjamin, New York, 1969); and Ref. 12.

[29] Y. S. Khodeyev, H. Siegbahn, K. Hamrin, and K. Siegbahn, Chem. Phys. Lett. 19, 16 (1973).

[30] The experimental values are taken from the compilation given in Ref. 2.

[31] A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Clarendon, Oxford, 1970), Chap. 16.

[32] K. R. Lea, M. J. M. Leask, and W. P. Wolf, J. Phys. Chem. Solids 23, 1381 (1962).

[33] R. E. Watson and A. J. Freeman, Phys. Rev. 133, A1571 (1964).

[34] R. M. Sternheimer, M. Blume, and R. F. Peierls, Phys. Rev. 173, 376 (1968).