

COMMENTS

Comment on Surface Crystal-Field Effects in the Photoemission of Xe†

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Recently Waclawski and Herbst reported, in the photoemission spectrum of Xe, the splitting of the $P_{3/2}$ level of Xe adsorbed on the (100) surface of tungsten. The observed splitting was interpreted as being the consequence of the surface crystal field. Several inconsistencies in their model are pointed out and it is shown that the splitting may be accounted for, predominantly, by the induced image field of the final-state ion. An experimental test is suggested which would help remove the ambiguity.

Recently Waclawski and Herbst¹ have reported on ultraviolet photoelectron spectroscopy (UPS) measurement of Xe adsorbed on the (100) surface of tungsten. They observed two well-separated peaks from the Xe $5p$ levels which are split via the spin-orbit interaction into $P_{3/2}$ and $P_{1/2}$ states. Furthermore the $P_{3/2}$ state is further split, by the interaction with the surface, into two states about 0.3 eV apart. The separation between the center for the $P_{3/2}$ states and the $P_{1/2}$ state is the same as in the gas phase, although their position with respect to the vacuum has been shifted.

A calculation was presented by Waclawski and Herbst in which they speculate that the splitting of the $P_{3/2}$ state may be due to the crystal field of the surface tungsten atoms. The calculation assumes that each surface ion (and the bcc ion below the surface layer) is partially denuded of electrons having a net positive charge of $Z|e|$. The Xe atom occupies a fourfold site at the center of the square mesh formed by the ions of the (100) surface. Assuming this crystal field, they used first-order perturbation theory similarly to Rao and Weber² in the calculation. In order to get the observed splitting of the $P_{3/2}$ state they had to assume a positive charge of $Z \approx 0.5$ on each of the surface ions and on the second-layer atom.

There are a number of problems with this model. First of all they assumed a large charge residing on the metal surface ions with the neutralizing electron charge presumably located at least on the outside of the center of the adsorbed ion. This charge distribution would produce an electrostatic surface potential of about 50 eV in contradiction to the calculation of Lang and Kohn³

who found the electrostatic contribution to the work function to be about 7 eV for $r_s = 2$ and less for larger r_s . Also if one assumes this surface field one finds that the induced dipole moment of the adsorbed Xe atom would be too large. One obtains a dipole moment of 2.9 D as compared to the measured value for Xe on the (100) surface of tungsten of about 1 D.⁴ There are other mechanisms to account for the induced dipole moment.⁵⁻⁷ There will be a contribution by the crystal field to the splitting of the $P_{3/2}$ state but it should be much smaller than postulated by Waclawski and Herbst.

There are several other contributions to the splitting of the $P_{3/2}$ level which were not considered by Waclawski and Herbst. In photoemission the final state of the system is a positive ion adsorbed on the surface. The negative image charge in the surface will then create a field at the position of the ion.⁷ The field of the image charge is opposite to that of the assumed positive surface charge and would tend to cancel it, necessitating a still larger surface charge to obtain the experimentally observed splitting. The second contribution is due to the van der Waals interaction of the hole state, created in the photoemission, with the substrate. The third contribution is due to the perpendicular field gradient of the electrons spilling out past the surface. There will be some effects due to exchange interaction; however, since they are difficult to estimate, they will not be considered further. Correlation effects are included in the van der Waals interaction. Estimates of the magnitudes of the various contributions to the splitting of the $P_{3/2}$ state will be given next.

In photoemission an electron is removed from the $5p$ shell of a Xe atom. As a result of spin-orbit coupling one gets two states in the gas phase, $P_{3/2}$ and $P_{1/2}$. The $P_{3/2}$ is fourfold degenerate and the $P_{1/2}$ is doubly degenerate. The interaction with the surface further splits the $P_{3/2}$ state into two levels each doubly degenerate. One level consists of states labeled by the quantum numbers $m_J = \frac{3}{2}, -\frac{3}{2}$ and it will be referred as I; the other level consists of states labeled by the quantum numbers $m_J = \frac{1}{2}, -\frac{1}{2}$ and will be referred to as II. The z axis is taken perpendicular to the surface. The charge distribution of I looks like a doughnut parallel to the surface, and that of II looks like a dressed-up cigar perpendicular to the surface. The charge distribution for $P_{1/2}$ is spherically symmetric.

The splitting of I and II due to the image potential is found to be

$$\Delta_1 = \frac{2}{5} e^2 \langle r^2 \rangle / (2d)^3, \quad (1)$$

where d is the distance from the adatom to the image plane. Physically the splitting occurs because the positive hole in the cigar-shaped state II comes nearer the image charge of the ion whereas, on the average, the doughnut-shaped state I is further away from the image charge. State II therefore is lower in energy than state I. If the splitting were due to a positive crystal field in the surface the relative positions of states I and II would be reversed.

The position of the image plane to be used in Eq. (1) is somewhat ambiguous, although a number of papers concerning the problem have appeared.^{8,9} With the Xe atom resting in a slight depression, as postulated by Waclawski and Herbst, a reasonable estimate of the Xe-atom-image-plane distance might be $d = 1.7 \text{ \AA}$. With this value of the atom to image-plane distance and with $\langle r^2 \rangle = 1.8 \text{ \AA}^2$ (Ref. 1) the splitting of states I and II due to the image field is $\Delta_1 = 0.26 \text{ eV}$.

A second contribution to the splitting of the $P_{3/2}$ state is the van der Waals interaction with the substrate of the hole state created by the photoemission. Taking the simplest model for the interaction due to Lennard-Jones, one finds for the splitting

$$\Delta_2 = \frac{2}{15} e^2 \langle r^2 \rangle / (2d)^3, \quad (2)$$

a value $\frac{1}{3}$ that of the splitting due to the image charge. However the above contribution is overestimated since no account was taken for the finite response of the substrate electron system to the fluctuating field of the $5p$ hole. The effect of

the nonideal response of the substrate surface is to reduce interaction by about a factor of 2,¹⁰ giving a value of about $\Delta_2 = 0.04 \text{ eV}$.

The third contribution to be estimated is due to the gradient in the electric field which arises from the electron charge distribution "spilling out" past the substrate ions.¹¹⁻¹³ A simple expression for the surface potential, due to Smith, is used to estimate the splitting due to this effect. The result is

$$\Delta_3 = (4\pi/15) n e^2 \langle r^2 \rangle \exp[-\beta d], \quad (3)$$

where $n = 0.38 \text{ electrons/\AA}^3$ and $\beta = 1.30 \text{ a.u.}$, the parameter found by Smith describing the electron-charge-distribution decay outside of the surface. The magnitude of the splitting then is $\Delta_3 = 0.12 \text{ eV}$. This is an upper limit since using a surface charge distribution due to Appelbaum and Hamann¹³ which is closer to the self-consistent calculation of Lang and Kohn¹² gives a value of $\Delta_3 = 0.06 \text{ eV}$. The direction of the splitting, however, is opposite to the above two mentioned mechanisms and in the same direction as the crystal-field splitting of Waclawski and Herbst.

The result of the three contributions discussed here is a splitting of the $P_{3/2}$ levels of $\Delta \approx 0.19 \text{ eV}$ to 0.25 eV . This is somewhat short of the experimentally observed $\Delta \approx 0.3 \text{ eV}$. The difference may be made up by exchange effects and crystal-field effects due to the "waffling" of the electron charge distribution. It may be pointed out that no interaction potential in first-order perturbation theory will move the states $P_{3/2}$ and $P_{1/2}$ relative to each other as is indeed observed experimentally.

As a result of this analysis it is predicted that the ordering of the levels is opposite to that given by Waclawski and Herbst; namely, level II is lower in energy than level I. One needs to remember, however, that the electron which leaves a final-state hole in level II will have the higher energy.

The angular electron-emission distribution for the two levels can be used to decide their relative positions in energy and therefore to give further information as to the mechanism responsible for the splitting.

Note added.—After this paper was submitted for publication, there appeared a Letter to the Editor by J. A. D. Matthew and M. G. Devey, J. Phys. C **9**, L413 (1976) which considers the splitting of the $P_{3/2}$ levels due to the interaction of the hole with its instantaneous image in the surface. Their result differs from Eq. (1) by a numerical

factor since Eq. (1) was obtained using the field of the image of the ion. Matthew and Devey do not consider the other possibilities for interaction nor do they consider the ordering of the split states with respect to the splitting by the crystal field.

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⁷It should be noted that, because of the Franck-Condon principle, one is still probing the physisorbed configuration.

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¹³J. A. Appelbaum and D. R. Hamann, *Phys. Rev. B* **6**, 1122 (1972).

ERRATUM

MOTION OF CLUSTERS ON SURFACES. Uzi Landman, Elliott W. Montroll, and Michael F. Shlesinger [*Phys. Rev. Lett.* **38**, 285 (1977)].

The following corrections, which do not affect the conclusions of the paper, should be made:

Equations (2), (5), and (6) should read

$$\left. \begin{matrix} a \\ \alpha \end{matrix} \right\} = \nu_a \exp\{-[E_a \mp g(V)]/kT\}, \quad (2)$$

$$\nu_a \exp(-E_a/kT) = t^{-1} \langle I_2(t) \rangle f(V, T) [1 + R_{12}(T)], \quad (5)$$

$$f(V, T) = \frac{1}{2} \operatorname{csch}[g(V)/kT]. \quad (6)$$