

## Increased Image Brightness Caused by Field Adsorption in Field-Ion Microscopy\*

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We explain the observations that field-adsorbed rare-gas atoms increase the ionization rate near the tip in the field-ion microscope. This increase results from exchange effects associated with antisymmetrization of the electronic states appearing in the time-dependent perturbation theory for the ionization process. Other effects, such as resonance associated with the adsorbate potential well, are unimportant. We obtain order-of-magnitude agreement with experiment, although the predicted field dependence of the enhancement does not agree with Rendulic's observations.

### INTRODUCTION

In 1969, Müller<sup>1</sup> observed that in the presence of intense electric fields, rare-gas atoms are adsorbed above metallic atoms of field-ion-microscope (FIM) tips. Tsong and Müller<sup>2</sup> identified the adsorption mechanism as the attractive interaction between the effective dipole moment induced in protruding surface atoms in the presence of the applied electric field, and the dipole moment induced in the adsorbate. One may view this as a bonding of the adsorbate due to the increase in (negative) polarization energy associated with the increased electric field strength in the region lying just above protruding surface atoms.

Following this, Schmidt, Reisner, and Krautz<sup>3</sup> demonstrated photographically that an important effect of the adsorption was a brightening of the images for the surface atoms on which a Ne atom was adsorbed. Rendulic<sup>4</sup> has recorded the image intensity for individual surface atoms in time as adsorption and desorption take place, has observed the enhancement in ionization rate on various crystal planes, and has established<sup>5</sup> the relative enhancement in ionization rate for Ne as opposed to He as the adsorbed species. Recently, Janssen and Jones<sup>6</sup> have also observed the intensity variation in time as adsorption and desorption take place.

In the present paper we shall be concerned primarily with the enhancement process, so that details of the surface structure are reduced in importance. Accordingly, we shall deal with an idealized metal consisting of a noninteracting electron gas in a uniform positive background. Our primary aim is to demonstrate the importance of exchange effects in giving rise to the observed enhancement. For this purpose, we employ Hartree-Fock wave functions for the atoms, undistorted by the electric field or by atomic interactions. While work on the effects of field distortions in the atomic orbitals is in progress, the results of the present analysis lead us to believe that the basic cause for the enhancement can be understood

in terms of simple exchange effects. As will be seen the over-all magnitudes of the adsorbed Ne and He enhancement factors and the dependence of the ionization rates as a function of He-atom distance above the surface are in reasonable agreement with experiment; however, the ratio of calculated Ne to He enhancement factors shows a field dependence which exhibits a marked difference from that observed by Rendulic,<sup>5</sup> the discrepancy being most severe for low field strengths.

A previous theoretical investigation of changes in ionization rates owing to the presence of adsorbates was carried out by Alferieff and Duke.<sup>7</sup> In a one-dimensional approximation, they calculated the change in ionization rate associated with the introduction of a square potential well, representing the adsorbate, between the surface and the ionizable atom. While their calculations led to altered ionization rates when the ionizable atom was held far from the surface, there was no over-all increase in ionization rate owing to the added potential. The changes which did occur resulted from transmission resonances within the adsorbate potential. In the present calculation, we treat the adsorbate and the atom to be ionized in a more realistic fashion—we assume these atoms to have standard atomic structure in a three-dimensional calculation. Accordingly, the effects of the adsorbate potential well are implicitly taken into account, as well as effects associated with its electronic structure. The principal results of this research are the following.

(i) There are no bound states for He or Ne negative ions; also, resonances in the electron scattering cross sections are nonexistent for the energies involved in the present problem. (The lowest important resonance in electron-Ne scattering lies at approximately 50-eV kinetic energy—an energy much higher than those available in the present problem.) Accordingly, resonance effects cannot play a role in the enhancement of field ionization. To include alterations in tunneling rates owing to the presence of the (negative) adsorbate potential, in the absence of resonance, one would

have to admix excited He configurations with the ground state, while maintaining orthogonality with the adsorbate orbitals. We assume this admixture to be very small in He-noble-gas interactions, owing to the large excitation energies of the contributing excited states.

(ii) Virtual intermediate states, such as one in which the adsorbate is ionized and the He atom is neutral, are unimportant by virtue of the large energy separation between the initial and intermediate configurations, and small matrix elements between these configurations, particularly at low field values.

(iii) Exchange effects owing to the overlap with the adsorbate orbitals constitute the major effect in the enhancement. Because of these effects, in the present calculation, Ne acts as a good conducting path for ionization whereas adsorbed He increases the ionization rate to a lesser degree.

Accordingly, the statement by Müller<sup>8</sup> that tunneling by close-range orbital overlap is important in producing the image is substantiated by the present results. However, Müller's statement<sup>9</sup> that tunneling is enhanced requires theoretical specification, and the proposed increase in the tunneling rate owing to the reduction of the potential barrier by the adsorbate<sup>10</sup> is not important according to conclusion (i) above.

#### THEORETICAL CONSIDERATIONS

We view the initial state in the ionization process as one in which orbitals of the type occurring in the isolated He atom which is to be ionized and the adsorbate *A*, which may be either He or Ne, and the orbital corresponding to the *N* electrons of the metal appear in a Slater determinant<sup>11</sup>  $\psi_i$ . The final states  $\psi_{\mathbf{k}}$  are represented by similar determinants, containing one less orbital for the He ion, all of the adsorbate orbitals and *N*+1 metallic orbitals, of which  $\mathbf{k}$  specifies the wave vector for the additional metallic orbital. In any conventional description for the orbitals,  $\psi_{\mathbf{k}}$  and  $\psi_i$  would not be strictly orthogonal, since the *k*th metallic orbital and the ionizable He orbital would overlap. Accordingly, in doing time-dependent perturbation theory, one must retain terms which represent the lack of orthogonality and do not ordinarily appear in expressions for the transition rate between an initial state and degenerate states belonging to a continuum. In an alternative description, we could cast the final states, which are degenerate with  $\psi_i$ , into a Schmidt orthogonalized form, say

$$|i\rangle \text{ represents } \psi_i, \quad (1)$$

$$|\mathbf{k}\rangle \text{ represents } \psi_{\mathbf{k}} - \langle \psi_i | \psi_{\mathbf{k}} \rangle \psi_i,$$

such that one now has a complete set of orthogonal

states so far as those which are degenerate with  $\psi_i$  are concerned. In terms of these states, the conventional expression for ionization rate *w* is

$$w = (2\pi/\hbar)\rho(E_i) |\langle i | \mathcal{H}' | \mathbf{k} \rangle|^2, \quad (2)$$

where  $\rho(E_i)$  is the density of final states about  $|\mathbf{k}\rangle$ , with  $|\mathbf{k}\rangle$  representing a typical final state. In order for a final state  $\psi_{\mathbf{k}}$  to be defined as degenerate with  $\psi_i$ , the He atom to be ionized must be separated by a distance further than the critical distance  $Z_c$  from the metallic surface<sup>12</sup> (see Fig. 1).

With the states defined in Eq. (1), *w* can be written

$$w = (2\pi/\hbar)\rho(E_i) |\langle \psi_i | \mathcal{H}' | \psi_{\mathbf{k}} \rangle - \langle \psi_i | \psi_{\mathbf{k}} \rangle \langle \psi_i | \mathcal{H}' | \psi_i \rangle|^2. \quad (3)$$

Here  $\mathcal{H}'$  is defined through the relation

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}', \quad (4)$$

where  $\mathcal{H}$  is the total Hamiltonian for the system, and  $\mathcal{H}_0$  is a Hamiltonian which is diagonalized by  $\psi_i$ . In view of this definition of  $\mathcal{H}_0$ ,  $\langle i | \mathcal{H}_0 | \mathbf{k} \rangle$  is zero in Eq. (2),  $\mathcal{H}'$  may be replaced by  $\mathcal{H}$  in Eq. (3), and it is seen that the transition rate in that form simply relies upon one using realistic initial and final states, and calculating the matrix ele-

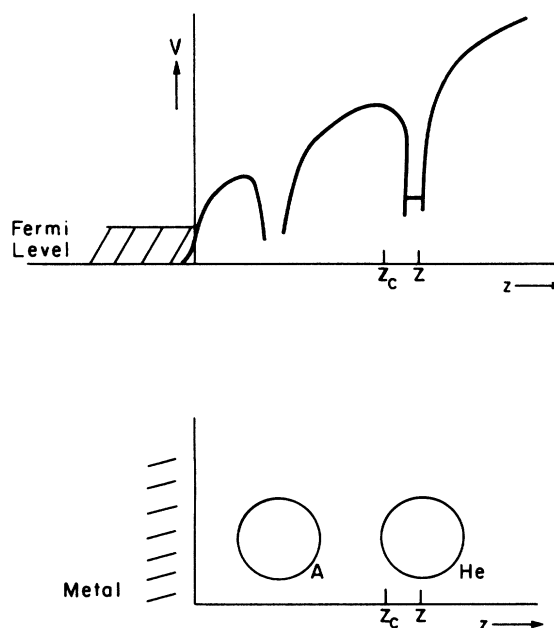


FIG. 1. Atomic positions and potential for a He valence electron in the presence of the He nucleus, adsorbed atom *A*, metal surface, and uniform electric field. In this figure, the He atom is separated from the surface by a distance greater than  $Z_c$ , the distance at which the initial electronic energy equals the Fermi energy for the metal.

ments with the total Hamiltonian. Finally, we may write the total Hamiltonian as

$$\mathcal{H} = \mathcal{H}'' + E_i, \quad (5)$$

with

$$E_i = \langle i | \mathcal{H} | i \rangle. \quad (6)$$

The constant term cannot contribute to Eq. (3), while by definition, the diagonal matrix element of  $\mathcal{H}''$  in Eq. (3) vanishes. Hence,

$$w = (2\pi/\hbar)\rho(E_i) |\langle \psi_i | \mathcal{H}'' | \psi_{\bar{\mathbf{k}}} \rangle|^2 \quad (7)$$

is obtained, so that with  $\mathcal{H}''$  as defined above, we need not concern ourselves about the lack of orthogonality between  $\psi_i$  and  $\psi_{\bar{\mathbf{k}}}$ .

The states  $\psi_i$  and  $\psi_{\bar{\mathbf{k}}}$  are single-configuration wave functions which have the form (aside from normalization factors)

$$\psi_i = \det | u_1 \cdots u_N u_{A_1} \cdots u_{A_n} u_{H\mathbf{e}_1} u_{H\mathbf{e}_2} | \quad (8)$$

and

$$\psi_{\bar{\mathbf{k}}} = \det | u_1 \cdots u_N u_{\bar{\mathbf{k}}} u_{A_1} \cdots u_{A_n} u_{H\mathbf{e}_1} |, \quad (9)$$

assuming that the He orbital  $u_{H\mathbf{e}_2}$  is to be ionized.<sup>13</sup> In these expressions,  $u_{A_1} \cdots u_{A_n}$  represent the  $n$  orbitals of the adsorbed rare-gas atom,  $u_1 \cdots u_N$  represent the degenerate-Fermi-gas orbitals (which will henceforth be neglected) and  $u_{\bar{\mathbf{k}}}$  represents the metallic orbital to which the ionization takes place, lying just above the Fermi energy.

We conceive of the atomic orbitals as those appropriate to isolated atoms in the presence of the uniform electric field, in the absence of the metal, since it is the metal itself which gives rise to the ionization. In fact, if we think of the field by itself as contributing to the ionization rate, we are confusing the effects of elastic deformation with ionization. But this is precisely the result of

using orbitals undistorted by the uniform field. We take as our Hamiltonian the expression

$$\mathcal{H} = \mathcal{H}_A + \mathcal{H}_{e-1i} + \mathcal{H}_{e-m} + eF \sum_i z_i \Big|_{z_i > 0}, \quad (10)$$

where  $\mathcal{H}_A$  is the sum of atomic Hamiltonians for the He and adsorbed atoms,  $\mathcal{H}_{e-1i}$  is the interaction between the electrons and the ion image,  $\mathcal{H}_{e-m}$  is the interaction between the individual electrons and the metal surface (including the electron-electron-image interaction), and the last term represents the effects of the uniform field in the region above the metallic surface  $z > 0$ . Since the terms other than  $\mathcal{H}_A$  are sums of single-electron interactions, we view the perturbation  $\mathcal{H}''$  as a collection of single-electron Hamiltonians [ $h''(i)$  for the  $i$ th orbital] each centered on its own nucleus positioned at  $\bar{\mathbf{R}}_i$  above the surface as follows:

$$\begin{aligned} h''(i) = & h_{e-1i}(\bar{\mathbf{R}}_i, \vec{\mathbf{r}}) + h_{e-m}(z_i) + eFz_i \Big|_{z_i > 0} \\ & - \left( [h_{e-1i}(\bar{\mathbf{R}}_i, \vec{\mathbf{r}}) + h_{e-m}(z_i) + eFz_i]_{\vec{\mathbf{r}}_i = \bar{\mathbf{R}}_i} \right. \\ & + \frac{d}{dz_i} [h_{e-1i}(\bar{\mathbf{R}}_i, \vec{\mathbf{r}}) + h_{e-m}(z_i) \\ & \left. + eFz_i]_{\vec{\mathbf{r}}_i = \bar{\mathbf{R}}_i}(z_i - Z_i) \right). \end{aligned} \quad (11)$$

The constant terms evaluated at  $\vec{\mathbf{r}}_i = \bar{\mathbf{R}}_i$  arise by virtue of subtraction of the expectation value in Eq. (6) from  $\mathcal{H}$  to form  $\mathcal{H}''$ , and the terms linear in  $(z_i - Z_i)$  are subtracted by virtue of the fact that these are uniform-field-type terms, which are already included in the Hamiltonian diagonalized by the field distorted orbitals and are therefore again compensated by constant terms in  $E_i$ . With the single-electron operators given by Eq. (11), it is straightforward to obtain the matrix element appearing in Eq. (7) in the form

$$\langle \psi_i | \mathcal{H}'' | \psi_{\bar{\mathbf{k}}} \rangle = \frac{\langle u_{H\mathbf{e}} | h'' | u_{\bar{\mathbf{k}}} \rangle - \sum_i [\langle u_{H\mathbf{e}} | u_{A_i} \rangle \langle u_{A_i} | h'' | u_{\bar{\mathbf{k}}} \rangle + \langle u_{H\mathbf{e}} | h'' | u_{A_i} \rangle \langle u_{A_i} | u_{\bar{\mathbf{k}}} \rangle]}{[1 - \sum_i |\langle u_{H\mathbf{e}} | u_{A_i} \rangle|^2]^{1/2} [1 - \sum_i |\langle u_{\bar{\mathbf{k}}} | u_{A_i} \rangle|^2]^{1/2}} \quad (12)$$

to lowest order in the overlap integrals, the sum being taken over adsorbate atom orbitals having the same spin. This matrix element could be viewed alternately as a matrix element on the single-electron operator  $h''$  between the initial and final orbitals in the transition, each orthogonalized to the other orbitals having the same spin in the adsorbed atom with which they overlap, i. e.,

$$\begin{aligned} \phi_{H\mathbf{e}} = & \left( u_{H\mathbf{e}} - \sum_i \langle u_{A_i} | u_{H\mathbf{e}} \rangle u_{A_i} \right) \\ & \times \left( 1 - \sum_i |\langle u_{A_i} | u_{H\mathbf{e}} \rangle|^2 \right)^{-1/2} \end{aligned} \quad (13)$$

and

$$\begin{aligned} \phi_{\bar{\mathbf{k}}} = & \left( u_{\bar{\mathbf{k}}} - \sum_i \langle u_{A_i} | u_{\bar{\mathbf{k}}} \rangle u_{A_i} \right) \\ & \times \left( 1 - \sum_i |\langle u_{A_i} | u_{\bar{\mathbf{k}}} \rangle|^2 \right)^{-1/2}. \end{aligned} \quad (14)$$

Schematic drawings of  $\phi_{H\mathbf{e}}$ , with and without a He atom adsorbed on the surface, are shown in Fig. 2.

Because  $h''$  is largest in the overlap region between the adsorbed atom and the metal, the terms involving  $\langle u_{H\mathbf{e}} | h'' | u_{A_i} \rangle$  in Eq. (12) are small compared with the others, so that (noting that the de-

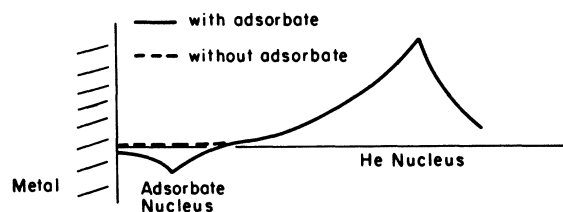


FIG. 2. Helium orbital  $\phi_{\text{He}}$  with [Eq. (13)] and without adsorbate.

nominator is nearly unity) we obtain, finally,

$$\langle \psi_i | \mathcal{H}'' | u_{\mathbf{k}} \rangle \simeq \langle u_{\text{He}} | h'' | u_{\mathbf{k}} \rangle - \sum_i \langle u_{\text{He}} | u_{A_i} \rangle \langle u_{A_i} | h'' | u_{\mathbf{k}} \rangle. \quad (15)$$

Thus, one could view the He electron as partly existing as the orbitals of the adsorbed atom, thereby giving rise to an altered ionization rate.

$$\eta = \int_{Z_c}^{\infty} dZ_{\text{He}} \int_0^{R_0} R_{\text{He}} dR_{\text{He}} e^{-\phi/kT} \left| \langle u_{\text{He}} | h'' | u_{\mathbf{k}} \rangle - \sum_i \langle u_{\text{He}} | u_{A_i} \rangle \langle u_{A_i} | h'' | u_{\mathbf{k}} \rangle \right|^2 \times \left( \int_{Z_c}^{\infty} dZ_{\text{He}} \int_0^{R_0} r_{\text{He}} dR_{\text{He}} \left| \langle u_{\text{He}} | h'' | u_{\mathbf{k}} \rangle \right|^2 \right)^{-1}. \quad (17)$$

#### DISCUSSION AND RESULTS

In the present paper, we approximate the matrix elements in Eq. (17) by those calculated using atomic wave functions undisorted by the uniform electric field in order to illustrate the influence of the exchange enhancement in the ionization process. (The effects of electric field distortions<sup>14</sup> will be considered in a later paper.) The distance between the metallic surface ( $z=0$ ) and the adsorbed atom is taken to be the atomic diameter of the adsorbate, 1.54 Å for Ne and 1.44 Å for He. The results of calculation are quite insensitive to the exact location of the adsorbate, however. The form for  $h_{\text{e-m}}$  has been given by Boudreaux and Cutler,<sup>15</sup> while the final state  $u_{\mathbf{k}}$  is a plane wave which exponentially decays outside the metal surface in the presence of the field, according to the WKB approximation. The Hartree-Fock wave functions given by Herman and Skillman are assumed for He and Ne.<sup>16</sup>

The calculated enhancement factors for He and Ne as the adsorbed species are shown in Fig. 3, as functions of electric field strength. The rise in  $\eta_{\text{He}}$  with increasing field strength at low fields is associated with the fact that as  $Z_c$  decreases, the angle occupied by the adsorbed atom, which

The ratio of ionization rates associated with a given metallic site, with and without the adsorbed atom  $A$ , may now be specified through an enhancement factor  $\eta$  given by the expression

$$\eta = \frac{\int d\vec{R}_{\text{He}} w(\vec{R}_{\text{He}}, \vec{R}_A) \exp[-\phi(|\vec{R}_{\text{He}} - \vec{R}_A|)/kT]}{\int d\vec{R}_{\text{He}} w_0(\vec{R}_{\text{He}})}, \quad (16)$$

where  $w$  and  $w_0$  indicate ionization rates in the presence of the adsorbed atom and without the adsorbed atom, respectively, and  $\phi$  represents the intermolecular potential energy of He in the presence of the adsorbate. The integration is over transverse distances  $R_{\text{He}}$  out as far as the radius  $R_0$  of the surface atom (beyond that, the ionization would contribute to the image of a neighboring atom) and over all elevations of the He atom above the surface. As mentioned above, there is no contribution for distances less than  $Z_c$ , however. Accordingly,  $\eta$  is given by

forms a conducting path for the He electron, increases as viewed from the He nucleus. (This tendency is compensated by the longer tail of the

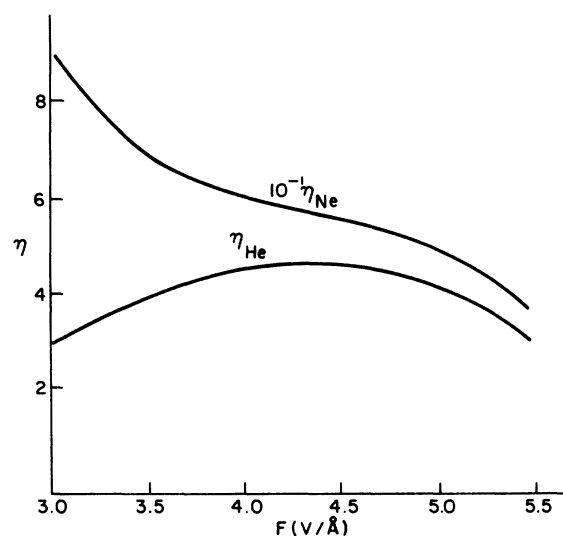


FIG. 3. Variation of the calculated enhancement factor with electric field strength.

$2p$  orbital in the case of Ne.) The relatively wide angle through which ionization takes place without an adsorbed atom does not show as great a sensitivity to  $Z_c$ . The decline in  $\eta$  at higher field strengths arises from the increased importance of the repulsion between He and the adsorbed atom as  $Z_c$  is decreased. Finally, we should mention that we have calculated high values for  $\eta$  with Ar as the adsorbate, ranging between  $10^3$  and  $10^4$  with the approximations made in the present treatment. (These values would probably be substantially reduced if field distortions in the atomic orbitals<sup>14</sup> were taken into account.)

The ratio of calculated enhancement factors for Ne and He as the adsorbed species,  $\eta_{\text{Ne}}/\eta_{\text{He}}$ , is shown in Fig. 4 together with values measured by Rendulic,<sup>5</sup> as a function of field strength. While the theoretical values of this ratio are somewhat larger than observed, both are of the order of 10. More serious is the fact that the electric field dependence of this ratio does not show qualitative agreement with the observed ratios as a function of field strength. The discrepancy at lower field strengths might be lessened through the inclusion of electric field distortions,<sup>14</sup> however. The observed decrease in this ratio at higher fields ( $\geq 3.7$  V/Å) is presumably caused by He supply limitations,<sup>5</sup> so that the comparison with present theory is meaningful only for the lower field strengths.

The general magnitude of the ionization rates appears to be reasonable in the present treatment, being  $\sim 10^8$  sec<sup>-1</sup> at  $Z_c$  for field strengths of 4.5 V/Å, without adsorbate. The ionization rates also

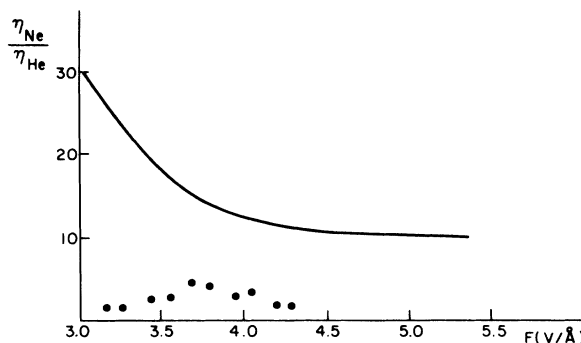


FIG. 4. Ratios of enhancement factors for adsorbed Ne and He. Data points are taken from Rendulic (Ref. 5).

show a variation with distance between the He atom and the tip surface in agreement with that observed by Müller and Tsong.<sup>17</sup> The energy distribution half widths of the helium ions are calculated to be 0.24 Å without an adsorbate, 0.19 Å with Ne adsorbed, and 0.14 Å with He adsorbed.

In conclusion, we believe that we have developed a theory capable of explaining the increase in image brightness in the FIM arising from the physical adsorption of inert atoms on the metallic surface, through the simple inclusion of exchange effects.

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<sup>13</sup>The ionization rate calculated with these states should be doubled to account for the possibility of orbital  $u_{\text{He}}$ , being ionized. In addition, in Eq. (9),  $u_{\text{He}}$  should be interpreted as a He ion orbital, as opposed to a He atom orbital.

<sup>14</sup>The principal effects of field distortion are experienced in the distant parts of overlapping atomic and metallic wave functions. Referring to the individual factors appearing in Eq. (17), (a) the matrix elements  $\langle u_k | \hat{h} | u_{A_i} \rangle$  will not be substantially affected due to the proximity of the adsorbate to the metal, (b) the overlap integrals  $\langle u_{\text{He}} | u_{A_i} \rangle$  might not be drastically altered, since the field causes  $u_{A_i}$  to decrease while  $u_{\text{He}}$  increases in the region of overlap; however, (c) the matrix elements  $\langle u_{\text{He}} | u_{A_i} \rangle$  will be decreased more if the adsorbate is a large atom than if it is small, since the region of overlap lies farther from the adsorbate nucleus for larger adsorbates. Finally, (d)  $\langle u_{\text{He}} | \hat{h} | u_k \rangle$  will increase by virtue of the larger distance ( $z_c$ ) separating the He atom and the metal. Accordingly, we expect these influences primarily to reduce the enhancement factors (particularly at lower field strengths where  $z_c$  is largest), especially for the heavier adsorbates.

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