

Surface-Induced Dipole Moments of Adsorbed Atoms*

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Atoms adsorbed on a metal surface acquire an induced dipole moment. An argument is presented which leads to a new mechanism responsible for these induced dipole moments.

It is generally observed that when molecules of a gas are adsorbed on a metal surface the work function of that surface is changed. The magnitude and direction of change depends on the molecular species and types of metal surfaces.¹ In particular noble-gas atoms adsorbed on metal surfaces decrease the work function. The interpretation is that the adsorbed atom acquires a dipole moment.² The positive end of the dipole faces away from the metal. The usual assumption in the literature² is that a surface field due to the surface dipole layer (caused by electron overflow into the vacuum) is responsible for the polarization of the molecule. It is pointed out in this Letter that there is an alternative mechanism which may be responsible for some or all of the polarization of the adsorbed molecule. It is a dynamic interaction of the same type as the Van der Waals interaction.

The Van der Waals interaction of a nonpolar molecule with a metal surface was first calculated by Lennard-Jones.³ He assumed the instantaneous dipole of the atom charge distribution interacting with its image in the metal. The interaction energy that he finds is

$$\epsilon = -\frac{e^2 \langle r^2 \rangle}{12R_0^3} = -\frac{\hbar\omega\alpha}{8R_0^3}, \quad (1)$$

where R_0 is the distance from the atom to the metal surface, e the electron charge, $\hbar\omega$ an average excitation energy, and α the polarizability of the atom. Subsequent calculations by Bardeen,⁴ and Margenau and Pollard,⁵ which treated the behavior of the metal more physically, gave results which are similar to those of Lennard-Jones except multiplied by a factor, depending on the parameters of the metal, which is typically of the order of $\frac{1}{2}$. This factor occurs because the metal electrons do not respond to the fluctuating external potential instantaneously and do not shield completely the potential from the inside of the metal.

When one considers the work function change of metals by noble-gas adsorption, one may sus-

pect that the induced dipole of the noble-gas atom occurs because an orbital electron would like to be nearer its image charge. In effect the potential that the electrons see is skewed toward the metal by the image charge.

For simplicity closed-shell atoms will be considered interacting with the instantaneous image charge, that is, the Lennard-Jones model. The instantaneous potential due to the image charges that the electrons see is

$$V = \frac{-e^2}{8R_0^3} \sum_i (z_i^2 + \frac{1}{2}\rho_i^2) - \frac{3e^2}{16R_0^4} \sum_i (z_i^3 + \frac{1}{2}z_i\rho_i^2), \quad (2)$$

where $\rho_i^2 = x_i^2 + y_i^2$ and z_i is the distance of the electron from the nucleus toward the surface along the normal to the surface. Retardation effects are neglected as is reasonable for short distances.⁶

The first term in Eq. (2) is just the Lennard-Jones term for the Van der Waals interaction with the surface. The second term is odd in the coordinate z_i . In first order perturbation theory there is no contribution from this term to the energy; it does, however, give an antisymmetric component to the wave function. Using this wave function the expectation value of the position of the electron $\langle \sum_i z_i \rangle$ does not vanish but is displaced toward the surface. A further implicit assumption in the use of the potential of Eq. (2) is that each electron only sees its own image. The contribution from the other electrons will add essentially randomly and when averaged should give a very small contribution.

A simple variational technique⁷ is used to find the induced dipole moment. One takes a variational function

$$\varphi = (1+v)\psi_0, \quad (3)$$

where ψ_0 is the ground-state wave function of the unperturbed atom and v is a function of the electron coordinates and some variational parame-

ters. In particular

$$v = \sum_i \lambda_i z_i \quad (4)$$

is chosen. Note that the Van der Waals and the polarizing interaction are linearly independent. The energy change due to the second part of the potential of Eq. (2) is

$$\Delta E = \{ (V_2)_{00} + (2vV_2)_{00} + (\hbar^2/2m) \sum_i [(\nabla_i v)^2]_{00} \} \times \{ 1 + 2(v)_{00} \}^{-1/2}, \quad (5)$$

where $(V_2)_{00} = \langle \psi_0 | V_2 | \psi_0 \rangle$, etc. The energy change ΔE is now varied with respect to the parameters λ_i .

Finally, the interaction energy is

$$\Delta E = -\frac{9e^4 m}{128 \hbar^2 R_0^8} \sum_i \{ (z_i^4)_{00} + \frac{1}{2} (z_i^2 \rho_i^2)_{00} \} \quad (6)$$

and a dipole moment is

$$P = \langle \varphi | \sum_i e z_i | \varphi \rangle = \frac{3e^2 m}{4 \hbar^2 R_0^4} \sum_i (z_i^2)_{00} [(z_i^4)_{00} + \frac{1}{2} (z_i^2 \rho_i^2)_{00}]. \quad (7)$$

A case for which Eq. (7) may be solved exactly is the hydrogen atom. In this case one gets

$$p = 4.5ea_0^5/R_0^4, \quad (8)$$

where $a_0 = \hbar^2/e^2m$, the Bohr radius. This is exactly the same result which one gets using perturbation theory taking the ionization energy of hydrogen as the average energy in the energy denominator. Since the polarizability of a hydrogen atom is $\alpha = 4.5a_0^3$ one may express Eq. (8) as

$$P = 0.47ea_0^{1/2}\alpha^{3/2}/R_0^4. \quad (9)$$

The oscillator model of an atom may also be simply solved and yields a dipole moment⁸

$$P = 0.37ea_0^{1/2}\alpha^{3/2}/R_0^4. \quad (10)$$

The structure of Eq. (8) indicates that the induced dipole moment should be approximately proportional to $a_0^{1/2}\alpha^{3/2}/R_0^4$.

If one then uses Eq. (9) to calculate the induced dipole moment of Xe, where $\alpha = 4 \text{ \AA}^3$ and $R_0 = 2.09 \text{ \AA}$, the covalent radius, one finds $P = 0.7 \text{ D}$ for the

induced dipole moment. An experimental value of 0.95 D has been quoted by Palmberg⁹ for Xe and Pd(100).

Estimates, therefore, indicate that the image-charge polarization mechanism for inducing dipole moments at metal surfaces may be sufficient to account for the experimentally observed surface dipoles. It should be pointed out that this mechanism will be present no matter what other contributions there may be to the induced dipole moment, much like the Van der Waals forces, and will be the dominant mechanism at large distances from the surface.

Finally, it may be pointed out that similar interactions exist between free atoms. An interesting result of this analysis is that the induced dipole on one of a pair of atoms falls off as $1/R^4$ even though the energy contribution varies as $1/R^3$. The two interacting atoms together do not have a net dipole moment but rather a quadrupole moment. The electron clouds of the atoms are in effect repelled from each other.¹⁰

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¹⁰A. D. Crowell, to be published. When the work described here was substantially complete the author received a preprint by Professor Crowell dealing with the induced dipole moments of interacting atoms.