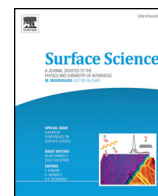




Contents lists available at ScienceDirect

Surface Science

journal homepage: www.elsevier.com/locate/susc

New physics and chemistry in high electrostatic fields

M.L. Karahka*, H.J. Kreuzer

Department of Physics and Atmospheric Science, Dalhousie University, Halifax, N.S. B3H 3J5, Canada

ARTICLE INFO

Available online xxx

Keywords:

High electric fields
Field-induced chemistry
Density functional calculations
Polymers
Condensed matter

ABSTRACT

Fields of the order of volts per meter exist along micron-sized tips. They are of the magnitude of fields inside atoms and molecules and can affect their electronic structure. This leads to a continuous periodic table resulting in new field-induced chemistry. We will present a tutorial treatment of this new physics and chemistry explaining such surprising phenomena like covalent bonding of helium to metal surfaces, metallization of semiconductors and insulators, and more.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Electric field effects on matter can be classified, rather arbitrarily, into two categories: in low fields, i.e. below roughly 10^{-1} V/Å, atoms and molecules only get polarized and their energy changes by $\mathbf{p} \cdot \mathbf{E}$. Likewise an ion at position \mathbf{r} of charge q gains an additional potential energy $q\mathbf{E}(\mathbf{r}) \cdot \mathbf{r}$. Fields larger than 10^{-1} V/Å are of the order of electrostatic fields inside atoms. They will affect the level structure of atoms and thus alter their chemical characteristics making and breaking new bonds in molecules. One of the first manifestations of the new physics and chemistry in high electrostatic fields came with the invention of the field ion microscope by Müller [1] and of the atom probe microscope [2,3]. The field ion microscope consists of a field emitter tip with the apex sharpened to a radius of the order of less than $1 \mu\text{m}$. Applying a voltage of several kV to a counter electrode some 10 cm away will create a field in the vicinity of the tip $E_0 = V_0/(k_f r_0)$ where V_0 is the applied voltage and r_0 is the radius of curvature; the field factor k_f accounts for the modification due to the shank of the tip. Analytical field distributions can be obtained when the tip and detector surface are approximated by either paraboloids or hyperboloids. When an imaging gas such as helium or neon is added to the vacuum chamber the gas atoms are polarized and accelerated to the tip in the inhomogeneous field where they are ionized over the surface atoms and accelerated to an imaging screen where an atomically resolved image of the surface structure of the tip is produced. At the best imaging field for helium, about 4 V/Å, helium is actually adsorbed at low temperature on the surface of the tip with a binding energy of about 0.4 eV, up by a factor of 100 from the binding energy in the absence of a field [4,5]. This dramatic change from a pure Van der Waals interaction at zero field to weakly covalent bonding is the result of raising the 1 s level of helium relative to the Fermi level of the metal by an amount $eE_0 d$ where d is the binding distance from the metal so that weak hybridization can occur.

Our aim in this paper is to review the fascinating new physics and chemistry in high electrostatic fields and to present intuitive pictures and explanations based on quantum mechanics. All calculations are done with density functional theory [6]. In the next section we will discuss the behavior of molecules in high electrostatic fields, i.e. diatomic molecules, polymers, and water whiskers, as examples. Then we look at field distributions on metal surfaces and show the importance of field enhancement above protrusions for ion imaging and field-induced surface reactions [7]. Lastly, we will explain the new discovery in semiconductors and insulators, namely that they turn metallic with their bandgap closing in high electrostatic fields [9,10].

2. Molecules in high electrostatic fields

Before we turn to molecules a few remarks about field ionization of atoms in high fields. In Fig. 1 we show the self-consistent electrostatic potential around an atom obtained from density functional calculations. Noteworthy is the fact that the Stark shift in the 4 s level is only about 20 meV in the highest field. Instantaneous ionization will occur when the applied field depresses the activation barrier below the ionization energy which for Zn happens around 3 V/Å. For lesser fields ionization takes a finite time due to tunneling.

2.1. Diatomic molecules in a field

We start with a diatomic, N_2 , and show in Fig. 2 the HOMO density distributions in zero field with the well-understood concentration of the bonding orbital between the two atoms.

Applying a strong field we see that electrons are transferred in the opposite direction to the field to create a field-induced dipole. In addition, one finds that the electron distribution now resembles very closely that of CO in the absence of a field, i.e. the field has transmuted the upper N atom (in the field direction) to act chemically like a C atom and the other N to become O-like! Indeed, the binding energy of N_2 of

* Corresponding author.
E-mail address: mkarahka@dal.ca (M.L. Karahka).

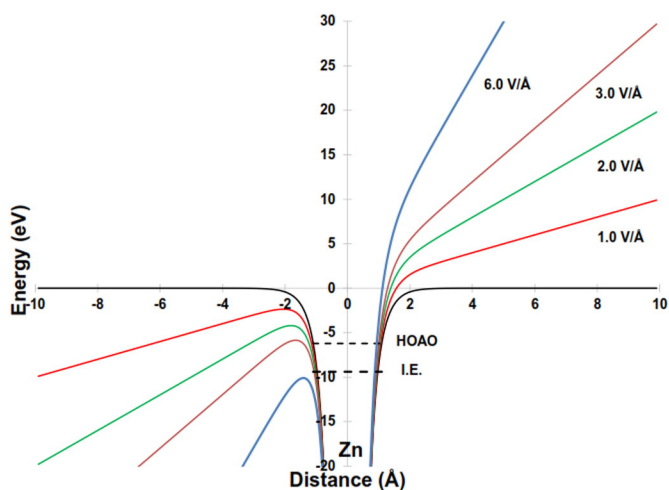


Fig. 1. Potential seen by the electrons in a Zn atom at various electrostatic fields. Dashed lines indicate the 4s level or highest occupied atomic orbital (HOAO) and 1st ionization energy (I.E.). The Stark shift will raise the HOAO by 20 meV at 6.0 V/Å.

9.7 eV in zero field is increased to 11.00 eV in a field of 6.2 V/Å, i.e. the same as that of CO in zero field. In addition, the vibrational frequency of N₂ is reduced from 7.3×10^{13} Hz in zero field to 6.6×10^{13} Hz in a field of 6.2 V/Å, very close to that of CO in zero field, 6.7×10^{13} Hz. Field dissociation happens at higher fields yet. To quantify this point further we show in Fig. 3 an electronic level scheme for N₂ in zero field and in a field of 6.2 V/Å and of CO in zero field demonstrating that the level scheme for N₂ in a field is indeed similar to that of CO in zero field.

Thus field-induced chemistry creates a continuous periodic table in the sense that the field alters the chemical characteristics of one element relative to a second one in a continuous fashion [7]. The rest of this paper will present a series of results to substantiate this claim.

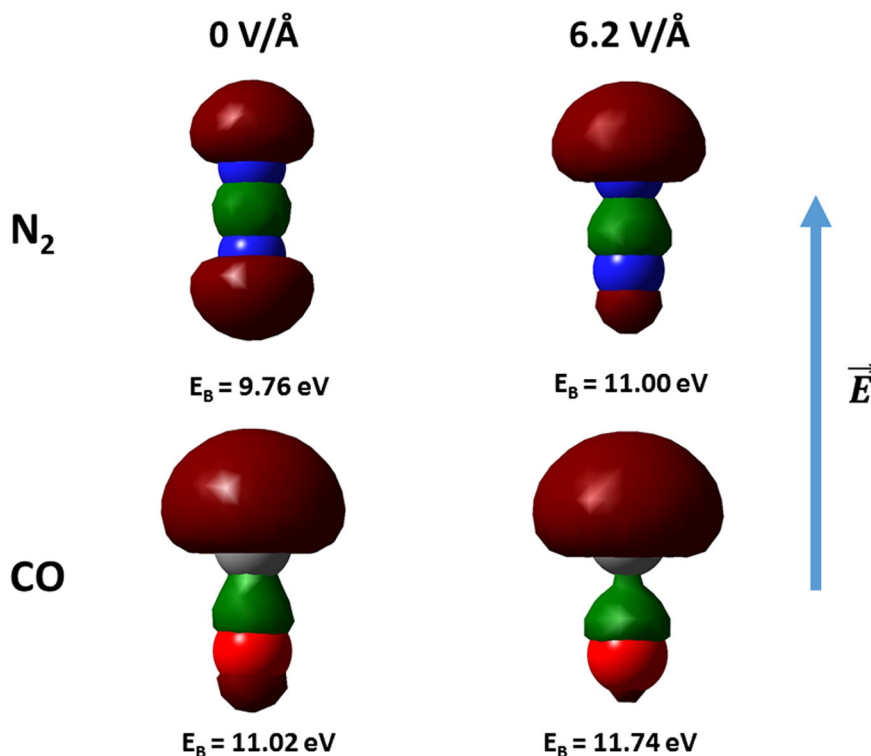


Fig. 2. Electronic bonding (green) and anti-bonding (burgundy) orbitals for N₂ (N blue) and CO (C gray, O red) in zero field and in 6.2 V/Å. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

As our next topic we look at field ionization and dissociation of a molecule, taking ZnO as an example, and plot in the right panel of Fig. 4 its potential energy as a function of the bond length obtained by subtracting the electronic energy of Zn and O from that of ZnO. As a small field is applied there remains a potential minimum at a bond length close to that in zero field but lowered in energy due to electron transfer from Zn to O creating an additional field-induced polarization. However, at larger distances the potential energy decreases linearly as $-neFz$ where n is an integer. This is the potential seen by the Zn^{*n*+} ion. The potential barrier is gradually lowered with increasing field until it finally disappears at the dissociation field strength. To complete the picture we also show in the left panel of Fig. 4 the potential seen by the electrons (equivalent to the Coulomb potential for the H atom) together with the HOMO level. With no field applied there is still a potential barrier between O and Zn allowing for enhancement on the O-side and a lowering on the Zn-side due to the internal charge transfer in the bond formation. As the field increases the HOMO level rises until, at the field strength where the potential barrier for the atoms disappears, it will actually be above the tunneling barrier so that it moves away from the molecule leaving behind an ion ready to field dissociate. If at lower fields the tunneling barrier is still nonzero the probability of ionization will be lower than 1, given by the tunneling probability which is quite low at a field of 1 V/Å where the barrier is quite wide, and considerably higher at 4 V/Å with a narrow and low barrier. Next we discuss field dissociation. In the absence of a field ZnO can be ionized by impact ionization for instance resulting in a stable ZnO⁺ ion. On the other hand, in the highest fields ionization occurs but the potential energy curve no longer has a minimum with the result that a Zn⁺ ion is accelerated away by the field with the O atom remaining fixed. We have plotted in Fig. 4 the Mulliken charge [8] on the Zn for a field of 4 V/Å: it is +1 all the way to a bond separation of 6 Å and then rises gradually to +2. Because the distance is now so great for an electron to tunnel to the O, it is unlikely that post-ionization will lead to a doubly charged Zn ion. These are of course model calculations, however, one could fix the oxygen to a metal surface and imposing a field to line the

Download English Version:

<https://daneshyari.com/en/article/5421529>

Download Persian Version:

<https://daneshyari.com/article/5421529>

[Daneshyari.com](https://daneshyari.com)