# Modeling Corrosion, Atom by Atom

*by Christopher D. Taylor*

In the late 20th century, computer programs emerged that could solve the fundamental quantum mechanical equations that control the interactions of atoms that give rise to bonding. These tools, first applied to molecules and bulk solid materials, then began to be applied to surfaces and, in the early 21st century, to electrochemical environments.[1] Commercial and open-source programs are now readily available and can be used on both desktop and high-performance computing platforms to solve for the electronic structure of a given configuration of atomic centers (nuclei) and, in so doing, provide the basis for determining a whole host of properties, including electronic and vibrational spectra, electrical moments such as the system dipole, and, most importantly, the energy and forces on the atoms.[2-4] Other derived properties include the extent to which each atom is charged and bond-orders, although to compute these latter properties one of a variety of methods for dividing up and quantifying the electron density associated with each atom must be selected.[5]

The physics behind these codes is complex, and, challengingly, has no rigorous analytical solution that can be obtained within a finite allotment of time. Thus, the computer programs themselves take advantage of approximations that allow for a feasible solution but, at the same time, constrain the accuracy of the result. Nonetheless, solutions can usually be reliably obtained for model systems representing materials, interfaces, or molecules that do not exceed thousands, and, more realistically, hundreds of atoms.[6] Given that system sizes of hundreds or thousands of atoms amount to no more than the smallest nanoparticle of a substance, the question arises: What can atomistic simulations teach us about corrosion?

The answer to this question lies in the ability for atomistic simulation to confirm or deny key hypotheses associated with potential corrosion mechanisms. By directly simulating the structure of a molecule, its spectroscopic signatures, or the energetics of the bond-making and bond-breaking processes it engages in, much information can be gained that is useful to the interpretation of experiment and the verification of proposed theories. For instance, if a certain mechanistic step has a considerably large activation barrier (as computed from quantum mechanics), we can assume that it will not proceed unless somehow catalyzed. Furthermore, if a given atomic configuration is found to be metastable through molecular simulation, then we can predict that, over time, it will decay to a lower energy state. Furthermore, using periodic boundary conditions, it is possible to mimic the effects of semi-infinite surfaces (thus effectively going beyond the hundreds or thousands of atoms limit), albeit ensuring that careful attention is paid to address spurious results that may arise from image-image interactions.

In this report we give several examples. In the first case we show how the computation of the properties of molecular systems can provide some insight as to their overall properties, and draw an example from the field of molecular design of corrosion inhibitors. In the second, we show how periodic boundary conditions can be applied to simulate the chemisorption of environmental species, such as chloride, hydroxide and ammonia, on to semi-infinite metallic surfaces. Then, we show how this technique can also be applied to simulate the structure and properties of the metal/oxide interface. Finally, we provide an illustration of how atomistic methods are being used to begin to simulate the challenging topic of modeling the non-equilibrium states associated with material dissolution.

## Designing Corrosion Inhibitors

Quantum chemical evaluation of corrosion inhibitors began with Vosta and Eliasek in 1971.[7] Since then, the ability to rapidly evaluate the molecular structure and electronic properties of relatively small inhibitor molecules (dozens of atoms) has led to a proliferation of similar studies, at varying levels of sophistication (Fig. 1). At one

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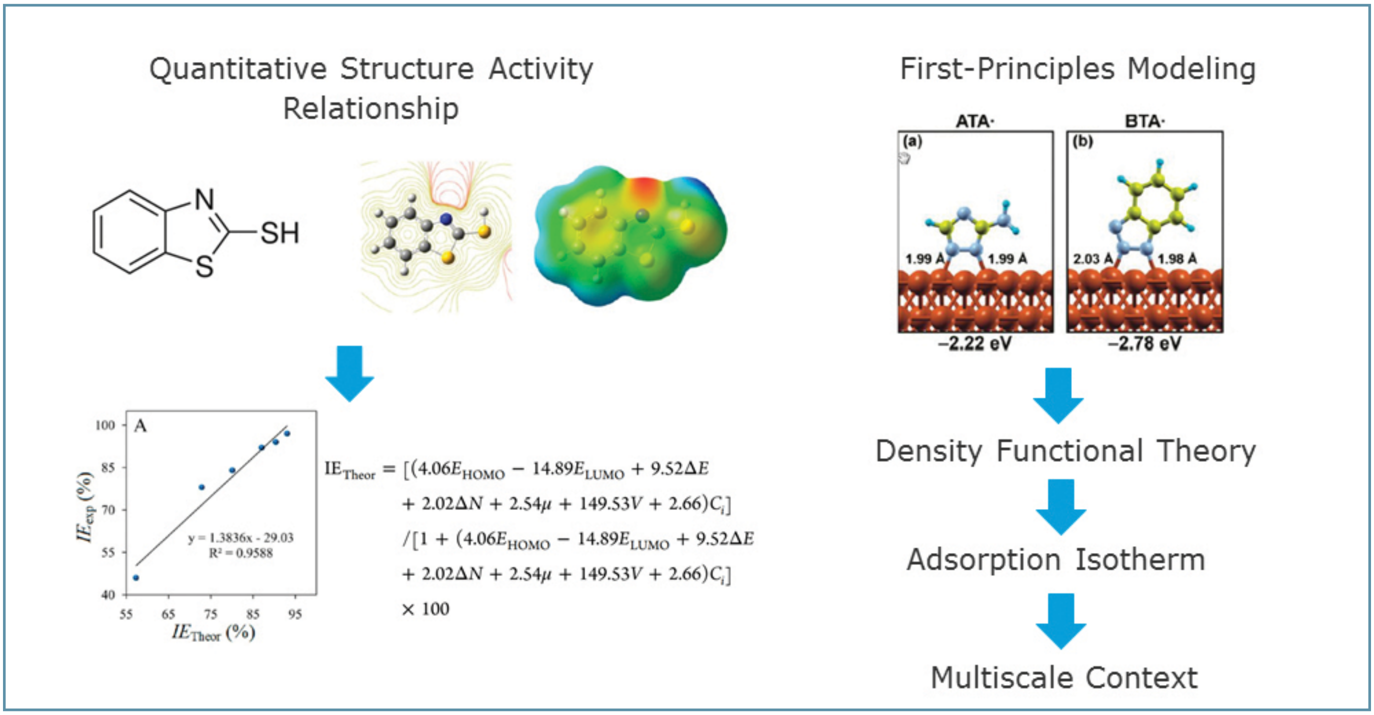

**Fig. 1**. *Two approaches that utilize quantum mechanics to model inhibitor performance. Reproduced with permission from* Ind. Eng. Chem. Res. ***52*** *14875-14889 (2013) (© American Chemical Society, 2013) and* J. Am. Chem. Soc. ***132*** *16657-16668 (2010) (© American Chemical Society, 2010).*

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extreme, data-driven approaches take the outputs of quantum chemical simulations (atomic charges, electronegativity, the energy gap between filled and unfilled molecular orbitals) as descriptors that are correlated against inhibitor efficiency with machine-learning approaches. This approach is called QSAR: quantitative structure active relationships.[8-15] At the other extreme, direct simulation of the inhibitor binding mode to a metal surface has been used to address the fundamental mechanisms of inhibition.[16-23]

The relationship of inhibitor efficiency to the quantum mechanical properties of the inhibitor molecule is quite complex. Inhibitor molecules typically have a three-part structure, consisting of an anchor chemical group (like an amine, thiol, or imidazoline group), a backbone (for example, a saturated or unsaturated carbon chain), and substituent groups that have been suggested to provide fine-tuning of the surface-inhibitor interaction and the inhibitor-inhibitor interactions that control the properties of the self-assembled monolayer that forms upon inhibitor adsorption.[24,25] The interaction of the inhibitor with the material itself will depend upon the composition, crystal structure, and uniformity of the outermost layers of the material, possibly sulfides, oxides or oxy-hydroxides, or, where the passive layers have been breached, a bare metal surface itself. Molecular simulation makes it possible to begin to deconstruct the various elements of this problem, and, as each element becomes tractable with time, they can then be reconciled to form an overall multiscale model.

The QSAR approach implicitly combines all of these complex micro-processes together and proposes that the inhibitor efficiency, like any physical observable, A, should be obtainable (at least in principle) by applying the appropriate quantum mechanical operator, $\mathcal{A}$, to the wavefunction Ψ via the inner-product[3]

$$\langle A\rangle = \int_{-\infty}^{+\infty} \Psi^{*} \mathcal{A} \Psi \, dx = \langle \Psi | \mathcal{A} | \Psi \rangle \qquad (1)$$

The challenge to the QSAR community is that the quantum mechanical operator for inhibitor efficiency is not well known, and must be dependent upon several factors, such as surface quality, pH, temperature, ion-speciation, etc. The premise behind the QSAR approach, then, is that given the mystery surrounding the proper mathematical form of the operator $\mathcal{A}$, it might instead be possible to approximate $\mathcal{A}$ in terms of the other, more readily computable, molecular properties. Hence the use of machine-learning approaches to parameterize the inhibitor efficiency in terms of a growing set of molecular descriptors that may or may not have any direct relevance to the inhibitor mechanism. The key dangers in this approach are over-fitting of the black-box numerical model due to the relative abundance of quantum chemical descriptors compared to the relatively small set of inhibitor efficiency data points, and the likely possibility that the quantum chemical descriptors alone may not be sufficiently informative for capturing the complexity of the molecule-surface interaction.

The mechanistic approach, on the other hand, is more time-consuming, and requires a significant investment of research labor and cpu-hours to deconstruct the inhibition mechanism across the environment, interfacial, and near-surface domains into its elements and then reassemble them into a comprehensive science-based model. Pieces of this model, attainable through current molecular simulation methods, include the calculation of partition coefficients of the inhibitor between oil (or polymer) and aqueous phases,[26] the effect of the inhibitor molecule on multiphase flow,[27] the simulation of inhibitor diffusivity and the calculation of pKa's,[28] the adsorption of the inhibitor molecule onto various possible surface phases and presentations (*i.e.*, exposed Miller indices),[19,20,22,29-36] and the efficiency with which the inhibitor molecules can form a coherent, self-assembled monolayer that adequately protects the surface from corrosion.[24,37,28] Given that these kinds of simulations are more configurationally complex, progress in this area is on-going; more time consuming than the QSAR methods, but with potentially higher pay-offs in terms of understanding and inhibitor design.

## Competitive Adsorption and Ammonium Chloride Corrosion

Ammonium chloride salts that form due to the combination of ammonia and hydrogen chloride vapors during industrial refining can lead to severe corrosion when they absorb water from the atmosphere, forming highly saturated salt solutions containing ammonia, ammonium cations, and chloride anions as well as water and its dissociation products $H^+$ and $OH^-$.[39-43] To address some mechanistic aspects of the corrosion system that forms due to the uptake of water by ammonium chloride salts (*i.e.*, a phenomenon known as deliquescence), we used density functional theory to calculate the free energy change associated with the adsorption of these ions from the aqueous phase to an iron surface (used to mimic the surface of the mild steel; it was assumed that, in the worst case, depassivation had already occurred).[44] For example, the adsorption of chloride leads to a free energy change associated with the reaction

$$Cl^-(aq) + * \rightarrow Cl(ads) + e^- \qquad (2)$$

where * indicates a vacant adsorption site on the metal surface (possibly occupied by water, or one of the other ions present, Fig 2).

On the other hand, it is possible that water can adsorb, with the loss of a proton to form a surface adsorbed hydroxide, via the reaction

$$H_2O(aq) \rightarrow OH(ads) + H^+ + e^- \qquad (3)$$

The free energy consists of the internal energies of the atoms and molecules, that are defined by their electronic and nuclear structure, the enthalpies and entropies associated with the vibrational modes (these are determined by quantum mechanics), configurational entropy (which is dependent upon the concentration in solution, and the acid-base equilibria), and the pH and electrochemical potential.[45]

By calculating the free energy of chemisorption from a combination of the calculated surface adsorption energies, tabulated data for pKa's and the chlorine/chloride electrochemical potential, it was possible to then rank the ions according to their tendency to adsorb on the metal surface. Consequently, it was discovered that there exist particular regions of pH and potential in which the chloride ion has sufficient thermodynamic driving force to interfere with the adsorption of oxygen, thus limiting the surface's ability to protect itself through repassivation. The pH-potential regimes identified correlate with the boundary conditions observed in the field for ammonium chloride corrosion.[41,42,46] In this way, atomistic simulation was used to provide an explanation for the role of ammonium chloride salts in accelerating corrosion of mild steel.

## Understanding Passivity by Modeling Metal/Metal-Oxide Interfaces

It has been remarked that the self-limiting formation of oxide films is a vital condition for the metals-based civilization that humanity presently enjoys.[47] While oxides and metals are both relatively well understood from a crystallographic point of view, the structure of the thin films of oxides that passivate metal surfaces is not as well defined, and may vary depending on the crystallographic orientation of the surface, the electrochemical or atmospheric growth conditions, and the presence of impurities and other anion/cations that may be present in the environment. Furthermore, the interface provides an unusual two-phase state, whereby the symmetries, bonding and charge-states of the metallic and oxide phases must achieve a compromise that optimizes the Gibbs' free energy within the given kinetic constraints. Atomistic simulations provide a means for sampling this potential energy surface as a function of the possible geometric arrangements of ions and neutral species that might exist at the metal/oxide interface.

The transition from chemisorbed layers to the first few layers of oxide on nickel was examined for close-packed and stepped surfaces using density functional theory.[48] The gradual evolution of the $Ni^{2+}$

charge state was monitored as a function of the extent of this initial oxidation. Differential activities were also observed for step sites compared to the terraces. The oxidation of nickel was observed to proceed first by a gradual filling of the first monolayer of the surface with oxygen, and then by a reconstructed layer that created a mixed Ni-O-Ni bilayer. A key mathematical physics challenge still needs to be resolved for accurately simulating such two-phase systems, due to the very different electron correlation properties of the oxide phase versus the metallic phase. Similar studies have been performed on Tc(0001) (see Fig. 3), Mg(0001) and Pt(111).[49-51]

Molecular dynamics simulations based upon the use of classical interatomic potentials have been performed for studying the passivation of metals including nickel, iron, aluminum, and zirconium.[52-54] The development of "reactive force fields" has allowed a new generation of molecular dynamics simulations to be performed that can take into account not only changes in local geometry of atoms, but also changes in their oxidation state, which typically lead to more drastic changes in the properties of the material.[55,56] These simulations have been used to examine the mechanisms of oxide growth (as mediated by point-defects), and the effects of temperature and surface orientation.

## Watching Virtual Metal Atoms Dissolve

The process of metal dissolution involves some mystery, due to the transition of a neutral metal atom bound to its neighbors through metallic bonding across the electrochemical double layer, and its emergence as a cationic species with its own solvation shell and shed of its excess valence electrons. The unresolved physical issues surrounding this phenomenon have in recent years been highlighted in a series of papers by Eliezer Gileadi.[57-59] Considering the quantum and atomistic nature of this process, it is well suited to investigation by quantum chemical simulations. However, there are a number of hidden complexities to the problem. An effort combining molecular dynamics and constrained geometry optimization was made to simulate the process by which Cu adatoms dissolve from a nanoparticle surface facet.[60,61] The change in potential energy of the dissolving ion, as a function of its progress across the electrochemical double layer was shown to be highly dependent on the extent to which the coordination sphere of water molecules was allowed to relax. This last point was found to be potentially the greatest limitation to contemporary simulations of the dissolution process.

A multiphysics approach was made by Pinto *et al*. who used the electron transfer theory of Marcus-Hush to model the deposition of a silver atom in its neutral/cation superposition state as it crossed the electrochemical double layer.[62-64] Using classical molecular dynamics the authors showed that the silver cation could in fact retain a large portion of its solvation sheath quite close to the electrode. Quantum mechanical evaluation of the density of states was used to estimate the coupling constant for electron transfer and the attachment energy of silver atoms from the terrace to the kink sites on the surface. Collectively, the results showed that silver ions have a rapid deposition (and, therefore, dissolution) rate due to the ability for the solvated ion to approach very close to the electrode surface, and the long-range overlap of the silver ion's s-orbital with the sp-band of the electrode. For multivalent ions, it was suggested that a series of one-electron steps would be required, as the multivalent ions possess strong secondary solvation sheaths that would prevent as close an approach to the electrode as permitted to the univalent silver. Although the focus of the paper was on deposition, the same logic applies to the process of dissolution.

## Summary Remarks

Atomistic models based upon the fundamental quantum mechanical interactions between ions and electrons are currently being used to assess the quality of proposed mechanisms in corrosion science, as well as providing quantitative insights into the thermodynamic and kinetic constraints associated with these mechanisms. Currently, the limitations of the methods restrict modeling to systems of "molecular" proportions, or, when using periodic boundary conditions, to relatively idealized (*i.e.*, high translational symmetry) two-dimensional systems

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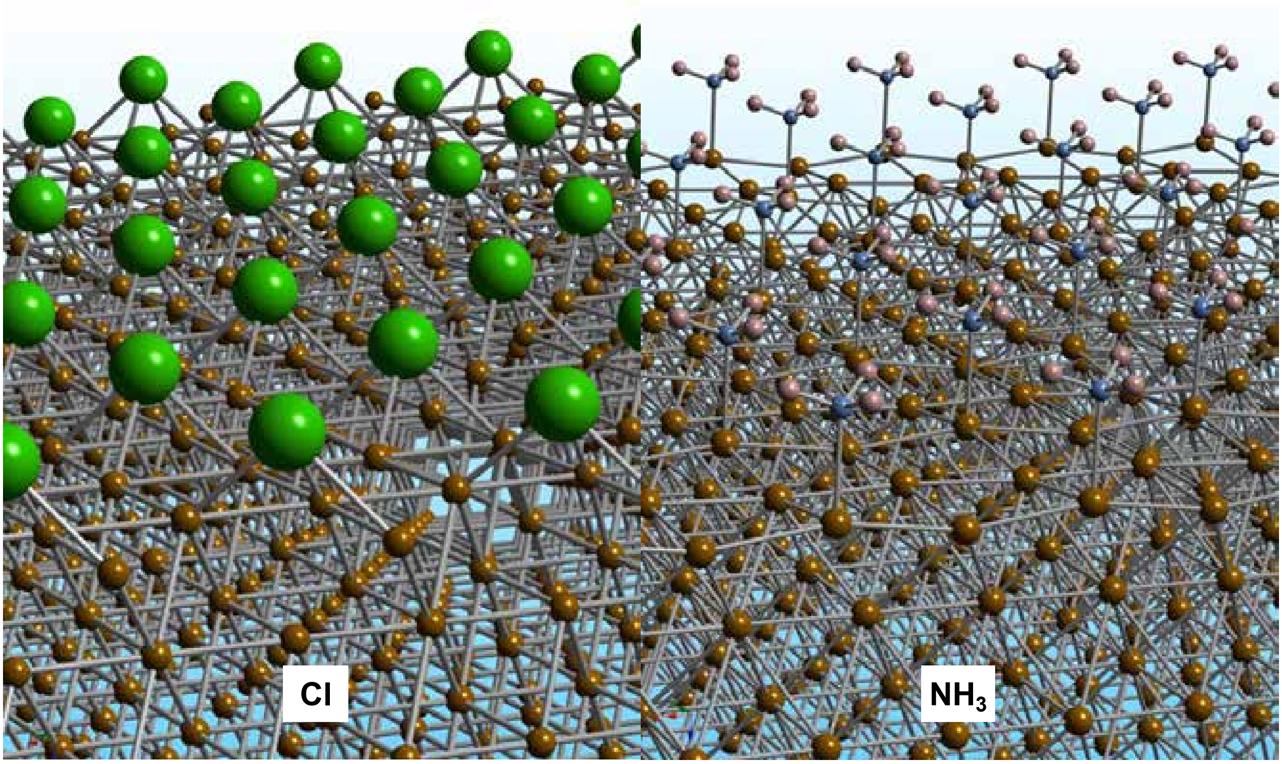

**Fig. 2.** *Ball and stick representation of the optimized geometries of (a) chloride and (b) ammonia on the Fe(110) surface.*

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such as low-index surfaces. Three-dimensional periodic models have been used to model the interaction of impurity elements, such as hydrogen, with point-defects.[65]

To conclude this overview, three categories of atomistic modeling for corrosion science are suggested:

- **Available now:** Calculation of molecular and surfaces properties for comparison with experiment, such as vibrational mode analysis and bond-lengths; prediction of thermodynamic properties of stable and metastable phases, such as two-dimensional surface phases; assessment of kinetic barriers to non-electrochemical reactions; limited treatment of the role of electrode potential and solvent in affecting reaction kinetics.

- **Challenging but possible to achieve with current methods:** Simulation of metal/metal-oxide/oxy-hydroxide interfaces through classical and charge-transfer interatomic potentials; properties of inhomogeneous alloy systems; treatment of dynamic complexity in solvent rearrangement by the metal/electrolyte interface; the role of point- and line-defects in corrosion mechanisms.

- **Longer standing challenges requiring algorithmic and computational advances:** Multiphysics and multiscale integration of quantum mechanics and classical molecular dynamics simulations with coarse-grained and continuum level models, including at the process engineering scale; accurate treatment of electron transfer and solvent rearrangement effects on the kinetics of electrochemical reactions; quantification of uncertainty from fundamental physics-based models and its propagation across multiscale hierarchies.

## About the Author

**Christopher D. Taylor** is a Senior Research Scientist at DNV GL's Materials Research and Innovation division located in Dublin, Ohio. Dr. Taylor also holds a position as Associate Research Professor in the Fontana Corrosion Center in the Materials Science and Engineering Department at The Ohio State University. Dr. Taylor's research focuses on linking fundamental atomistic and molecular simulations of the microprocesses responsible for corrosion within the context of multiscale/multiphysics models for the purposes of lifetime prediction, materials design, and risk assessment. Dr. Taylor received his BSc with Honors in Chemistry at the University of Western Australia, and his MS in Chemistry from the University of Memphis. He received his PhD in Engineering Physics from the University of Virginia under the direction of Robert Kelly (Materials Science & Engineering) and Matthew Neurock (Chemical Engineering). He may be reached at Christopher.Taylor@dnvgl.com.

## References

1. J. Hafner, Atomic-Scale Computational Materials Acience, *Acta Mater.*, **48**, 71 (2000).
2. E. Kaxiras, *Atomic and Electronic Structure of Solids*, Cambridge University Press, Cambridge, England (2003).
3. I. N. Levine, *Quantum Chemistry*, p. 505-510, Prentice Hall, Upper Saddle River, NJ, (2000).
4. J. Bernholc, Computational Materials Science: The Era of Applied Quantum Mechanics, *Phys. Today*, **Sept. 1999**, 30 (1999).

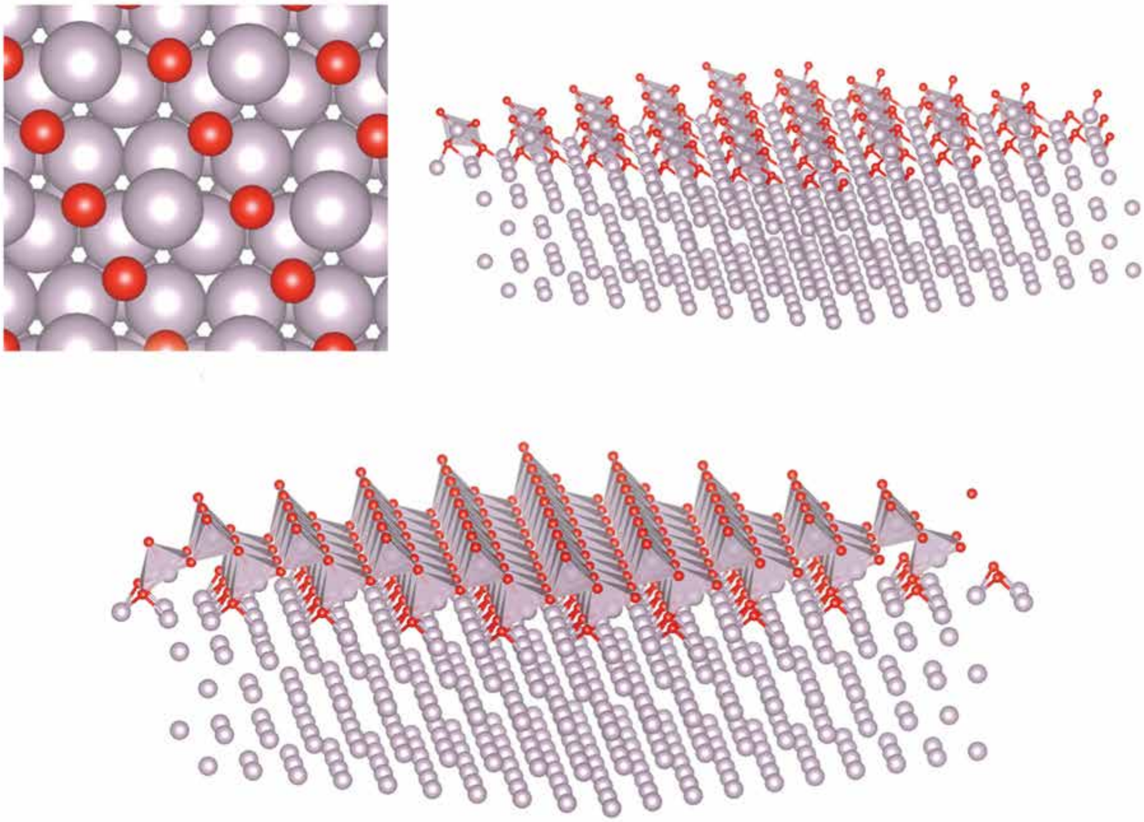

**Fig. 3.** *The oxidation of the close-packed surface of technetium, Tc(0001) at various stages:(a) 0.5 ML of* $TcO_2$*, (b) 1 ML of* $TcO_2$*, and (c) 2 ML of* $TcO_2$*. Reproduced with permission from* J. Phys. Chem. *C. 118 10017-10023 (2014) (© American Chemical Society, 2014).*

5. R. Bader, A*toms in Molecules: A Quantum Theory*, Oxford University Press, New York, NY (1990).
6. J. K. Norskov, F. Abild-Pederson, F. Studt, and T. Bligaard, Density Functional Theory in Surface Chemistry and Catalysis, *Proc. Natl. Acad. Sci.*, **108**, 937 (2010).
7. J. Vosta and J. Eliasek, Study on Corrosion Inhibition from Aspect of Quantum Chemistry, *Corros. Sci.*, 11, 223 (1971).
8. W. Durnie, R. De Marco, A. Jefferson, and B. Kinsella, Development of a Structure-Activity Relationship for Oil Field Corrosion Inhibitors, *J. Electrochem. Soc.*, **146**, 1751 (1999).
9. W. Durnie, R. De Marco, B. Kinsella, A. Jefferson, and B. Pejcic, Predicting the adsorption properties of carbon dioxide corrosion inhibitors using a structure-activity relationship, *J. Electrochem. Soc.*, **152**, B1 (2005).
10. E. E. Ebenso, T. Arslan, F. Kandemirli, N. Caner, and I. Love, Quantum Chemical Studies of Some Rhodanine Azosulpha Drugs as Corrosion Inhibitors for Mild Steel in Acidic Medium, *Int. J. Quantum Chem.*, **110**, 1103 (2009).
11. E. E. Ebenso, T. Arslan, F. Kandemirlı, I. Love, C. l. Öğretır, M. Saracoğlu, and S. A. Umoren, Theoretical Studies of Some Sulphonamides as Corrosion Inhibitors for Mild Steel in Acidic Medium, *Int. J. Quantum Chem.*, **110**, 2614 (2010).
12. E. E. Ebenso, M. M. Kabanda, L. C. Murulana, A. K. Singh, and S. K. Shukla, Electrochemical and Quantum Chemical Investigation of Some Azine and Thiazine Dyes as Potential Corrosion Inhibitors for Mild Steel in Hydrochloric Acid Solution, *Ind. Eng. Chem. Res.*, **51**, 12940 (2012).
13. M. Finsgar, A. Lesar, A. Kokalj, and I. Milosev, A Comparative Electrochemical and Quantum Chemical Calculation Study of BTAH and BTAOH as Copper Corrosion Inhibitors in Near Neutral Chloride Solution, *Electrochim. Acta*, **53**, 8287 (2008).
14. G. Gece, The Use of Quantum Chemical Methods in Corrosion Inhibitor Studies, *Corros. Sci.*, **50**, 2981 (2008).
15. L. C. Murulana, A. K. Singh, S. K. Shukla, M. M. Kabanda, and E. E. Ebenso, Experimental and Quantum Chemical Studies of Some Bis(trifluoromethyl-sulfonyl) Imide Imidazolium-Based Ionic Liquids as Corrosion Inhibitors for Mild Steel in Hydrochloric Acid Solution, *Ind. Eng. Chem. Res.*, **51**, 13282 (2012).
16. K. F. Khaled, Monte Carlo Simulations of Corrosion Inhibition of Mild Steel in 0.5 M Sulphuric Acid by some Green Corrosion Inhibitors, *J. Solid State Electrochem.*, **13**, 1743 (2009).
17. A. Kokalj, S. Peljhan, M. Finsgar, and I. Milosev, What Determines the Inhibition Effectiveness of ATA, BTAH, and BTAOH Corrosion Inhibitors on Copper?, *J. Am. Chem. Soc.*, **132**, 16657 (2010).
18. K. F. Khaled, Molecular Simulation, Quantum Chemical Calculations and Electrochemical Studies for Inhibition of Mild Steel by Triazoles, *Electrochim. Acta*, **53**, 3484 (2008).
19. C. Arrouvel, B. Diawara, D. Costa, and P. Marcus, DFT Periodic Study of the Adsorption of Glycine on the Anhydrous and Hydroxylated (0001) Surfaces of Alpha-Alumina, *J. Phys. Chem. C*, **111**, 18164 (2007).
20. S. Irrera, D. Costa, and P. Marcus, DFT Periodic Study of Adsorption of Glycine on the (0001) Surface of Zinc Terminated ZnO, *J. Mol. Struct. THEOCHEM*, **903**, 49 (2009).
21. S. Irrera, D. Costa, K. Ogle, and P. Marcus, Molecular Modeling by DFT of 1,2-diaminoethane Adsorbed on the Zr-terminated and O-terminated, Anhydrous and Hydroxylated ZnO(0001) Surface, *Superlatt. Microstruct.*, **49**, 19 (2009).
22. M. M. Islam, B. Diawara, P. Marcus, and D. Costa, Synergy between Iono-Covalent Bonds and van der Waals Interactions in SAMs Formation: A First-Principles Study of Adsorption of Carboxylic Acids on the Zn-ZnO(0001) Surface, *Catal. Today*, **177**, 39 (2011).
23. A. Motta and D. Costa, AIMD Evidence of Inner Sphere Adsorption of Glycine on a Stepped (101) Boehmite AlOOH Surface, *J. Phys. Chem. C*, **116**, 23418 (2012).
24. A. Edwards, C. Osborne, S. Webster, D. Klenerman, M. Joseph, P. Ostovar, and M. Doyle, Mechanistic Studies of the Corrosion Inhibitor Oleic Imidazoline, *Corros. Sci.*, **36**, 315 (1994).
25. S. Papavinasam, Mitigation - Internal Corrosion, in *Corrosion Control in the Oil and Gas Industry*, p. 374-399, Elsevier, London, England (2014).
26. A. V. Marenich, C. J. Cramers, and D. G. Truhlar, Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions, *J. Phys. Chem. B*., **113**, 6378 (2209).
27. X. Tang, S. Richter, and S. Nesic: An Improved Model for Water Wetting Prediction in Oil-Water Two-Phase Flow, Paper 2393 presented at Corrosion 2013, Orlando, FL, 2013.
28. S. Sastre, R. Casasnovas, F. Munoz, and J. Frau, Isodesmic Reaction for pKa Calculations of Common Organic Molecules, *Theor. Chem. Acc.*, **132**, 1310 (2013).
29. L. C. Cheng, A. B. Bocarsly, S. L. Bernasek, and T. A. Ramanarayanan, Coadsorption of Ethanethiol with Sulfur, Oxygen, and Water on the Fe(100) Surface, *LANGMUIR*, **12**, 392 (1996).
30. O. Borck, P. Hyldgaard, and E. Schroder, Adsorption of Methylamine on Alpha Al2O3(0001) and Alpha Cr2O3(0001): Density functional theory, *Phys. Rev. B*, **75**, 035403 (2007).
31. K. Y. Foo and B. H. Hameed, Insights into the Modeling of Adsorption Isotherm Systems, *Chem. Eng. J.*, **156**, 2 (2010).
32. Y. Y. Gao, N. Zhao, W. Wei, and Y. H. Sun, Ab Initio DFT Study of Urea Adsorption and Decomposition on the ZnO(1011) Surface, *Comp. Theor. Chem.*, **992**, 1 (2012).
33. Y. Jiang and J. B. Adams, First Principles Calculations of Benzotriazole Adsorption onto Clean Cu(111), *Surf. Sci.*, **529**, 428 (2003).
34. Y. Jiang, J. B. Adams, and D. H. Sun, Benzotriazole Adsorption on Cu2O(111) Surfaces: A First Principles Study, *J. Phys. Chem. B.*, **108**, 12851 (2004).
35. S. Peljhan and A. Kokalj, DFT Study of Gas Phase Adsorption of Benzotriazole on Cu(111) Cu(100), Cu(110) and Low Coordinated Defects Thereon, *Phys. Chem. Chem. Phys.*, **13**, 20408 (2011).
36. W. D. Tang, Y. Y. Gao, W. Wei, and Y. H. Sun, Adsorption of Urea onto a ZnO(1011) Surface, *Acta Physico-Chimica Sinica*, **26**, 1373 (2010).
37. D.-S. Kong, S.-L. Yuan, Y.-X. Sun, and Z.-Y. Yu, Self-assembled Monolayer of o-aminothiophenol on Fe(110) Surface: A Combined Study by Electrochemistry, in situ STM, and Molecular Simulations, *Surf. Sci.*, **573**, 272 (2004).
38. Z. Zhang, S. H. Chen, Y. H. Li, S. H. Li, and L. Wang, A Study of the Inhibition of Iron Corrosion by Imidazole and its Derivates Self-Assembled Films, *Corr. Sci.*, **51**, 291 (2009).
39. R. Cohen-Adad and J. W. Lorimer, Editors, *Alkali Metal and Ammonium Chlorides in Water and Heavy Water (Binary Systems)*, Vol. 47, Oxford, International Union of Pure and Applied Chemistry, Oxford, England (1991).
40. O. Forsen, J. Aromaa, and M. Tavi, Corrosion Resistance of Different Materials in Dilute Ammonium Chloride-Bearing Environments, *Corros. Sci.*, **35**, 297 (1993).
41. A. M. Sedenkov, Increase of Corrosion Resistance of Steel and Cast Iron in Ammonium Chloride Media by Surface Modification, *Prot. Met.*, **22**, 118 (1986).
42. V. A. Shimbarevich and K. L. Tseitlin, Influence of Ammonia Concentration and Temperature on Corrosion of Carbon Steel in Ammonium Chloride Solutions, *Prot. Met.*, **15**, 455 (1979).
43. V. A. Shimbarevich and K. L. Tseitlin, Influence of Ammonia on Corrosion of Stainless Steels and Titanium in Ammonium Chloride Solutions at 200oC, *Prot. Met.*, **17**, 144 (1981).
44. C. D. Taylor, Predictions of Surface Electrochemistry of Saturated and Alkaline NH4Cl Solutions Interacting with Fe(110) from Ab Initio Calculations, *Corrosion* (NACE), **68**, 591 (2012).

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45. P. W. Atkins, *Physical Chemistry*, 6th Ed., p. 485, 925-927, and 942, Oxford University Press. Oxford, England (1998).
46. M. A. Pletnev, S. G. Morozov, and V. P. Alekseev, Peculiar Effect of Chloride Ions on the Anodic Dissolution of Iron in Solutions of Various Acidity, *Prot. Met.*, **36**, 202 (2000).
47. D. D. Macdonald, On the Existence of our Metals-Based Civilization. I. Phase-Space Analysis, *J. Electrochem. Soc.*, **153**, B213 (2006).
48. O. Olatunji-Ojo and C. D. Taylor, Changes in Valence, Coordination and Reactivity that Occur upon Oxidation of Fresh Metal Surfaces, *Philos. Mag.*, **93**, 4286 (2013).
49. M. F. Francis and C. D. Taylor, First-Principles Insights into the Structure of the Incipient Magnesium Oxide and Its Instability to Decomposition: Oxygen Chemisorption to Mg(0001) and Thermodynamic Stability, *Phys. Rev. B*, **87**, 75450 (2013).
50. E. F. Holby, J. Greeley, and D. Morgan, Thermodynamics and Hysteresis of Oxide Formation and Removal on Platinum (111) Surfaces, *J. Phys. Chem. C*, **116**, 9942 (2012).
51. C. D. Taylor, Oxidation of Technetium Metal as Simulated by First Principles, *J. Phys. Chem. C*, **118**, 10017 (2014).
52. S. K. R. S. Sankaranarayanan and S. Ramanathan, Low Temperature Oxidation and Ultrathin Oxide Growth on Zirconium in the Presence of Atomic Oxygen: A Modeling Study, *J. Phys. Chem. C.*, **112**, 17877 (2008).
53. T. J. Campbell, G. Aral, S. Ogata, R. K. Kalia, A. Nakano, and P. Vashishta, Oxidation of Aluminum Nanoclusters, *Phys. Rev. B*, **71**, 205413 (2005).
54. R. Subbaraman, S. A. Deshmukh, and S. K. R. S. Sankaranarayanan, Atomistic Insights into Early Stage Oxidation and Nanoscale Oxide Growth on Fe(100), Fe(111) and Fe(110) Surfaces, *J. Phys. Chem. C*, **117**, 5195 (2013).
55. A. C. T. van Duin, S. Dasgupta, F. Lorant, and W. A. Goddard III, ReaxFF: A Reactive Force Field for Hydrocarbons, *J. Phys. Chem. A*, **105**, 9396 (2001).
56. F. Streitz and J. Mintmire, Electrostatic Potentials for Metal-Oxide Surfaces and Interfaces, *Phys. Rev. B*, **50**, 11996 (2004).
57. E. Gileadi, Can an Electrode Reaction Occur without Electron Transfer Across the Metal/Solution Interface?, *Chem. Phys. Lett.*, **393**, 421 (2004).
58. E. Gileadi, Charge and Mass Transfer across the Metal/Solution Interface, *Isr. J. Chem.*, **48**, 121 (2008).
59. E. Gileadi, Problems in Interfacial Electrochemistry that have been Swept Under the Carpet, *J. Solid State Electrochem.*, **15**, 1359 (2011).
60. C. Taylor, M. Neurock, and J. Scully, First-Principles Investigation of the Fundamental Corrosion Properties of a Model Cu38 Nanoparticle and the (111), (113) Surfaces, *J. Electrochem. Soc.*, **155**, C407 (2008).
61. C. D. Taylor, The Transition from Metal-Metal Bonding to Metal-Solvent Interactions during a Dissolution Event as Assessed from Electronic Structure, *Chem. Phys. Lett.*, **469**, 99 (2009).
62. N. S. Hush, Electron Transfer in Retrospect and Project. 1: Adiabatic Electrode Processes, *J. Electroanal. Chem.*, **460**, 5 (2009).
63. R. A. Marcus: *J. Chem. Phys.*, **24**, 966 (1956).
64. L. M. C. Pinto, E. Spohr, P. M. Quaino, E. Santos, and W. Schmickler, Why Silver Deposition is so Fast: Solving the Enigma of Metal Deposition , *Angew. Chem. Int. Ed.*, **52**, 7883 (2013).
65. G. Lu and E. Kaxiras, Hydrogen Embrittlement of Aluminum: The Crucial Role of Vacancies, *Phys. Rev. Lett.*, **94**, 155501 (2005).