7 HIGHLIGHT OF THE MONTH

Paint by Numbers: Oxide surface Chemistry using First-Principles MD

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Abstract

We discuss the motivation for using first-principles molecular dynamics to study surface chemistry, and highlight the strengths of the method. Water adsorption on the TiO_2 (110) surface is investigated, and the results show that the molecule dissociates on the defect-free surface. Analysis of the vibrations of the adsorbed species reveals a surprisingly complex spectrum for one of the surface hydroxyl groups. This is used to show how first-principles simulations can help in the interpretation of experimental results.

7.1 Introduction

It's a safe bet that you know someone who is studying Titanium Dioxide, or that you are doing so yourself. A good reason why is that everyone uses TiO_2 in surprisingly large quantities: If recently you have painted your house, took a holiday in the sun, carried home shopping in plastic bags, brushed your teeth or sucked a polo-mint, you used a product containing the stuff, and failing all these then the paper upon which Ψ_k newsletter is printed probably contains TiO_2. This wide-ranging utility stems from the the powder being an ideal white pigment (almost all manufactured things white contain it), and therefore an equally good opacifier (coloured plastic, for example, needs to have an opaque base for the coloured pigment). Titanium is the ninth most abundant element in the Earth's crust, and its ores, including ilmenite ($FeTiO_3$) and naturally-occuring rutile are processed worldwide to yield over \$6Bn-worth of TiO_2 each year.

Aside from good commercial reasons to study TiO_2, it is a very tough problem for condensed-matter theory. The production and uses of TiO_2 all rely in some way on its surface properties. It is commonly acknowledged that our understanding of oxide surfaces is quite rudimentary when compared with that of metals or semiconductors [1]. Transition-metal oxides have the complication of an empty (in the case of TiO_2) or partially-occupied d-band, which for example gives rise to variable oxidation states: titanium's stable oxides include TiO_2 (rutile structure) and Ti_2O_3 (Corundum) with family of Magnéli phases which occur between, and TiO_x (rocksalt or a distortion of it) where x ranges from $0.6 < x \leq 1.28$. Concomitant is a variety of electronic and magnetic properties. The interplay of electronic and physical structure remains largely unexplored, and even basic questions of surface structure and chemistry are open. This is well illustrated by the question of water adsorbtion on the surfaces. Water is always present in air and therefore reacts with TiO_2 powders during processing and storage. In addition, the observation [2] of photoelectrolysis of water by TiO_2 stimulated much effort to understand adsorption, and it must be remembered that water is a good experimental probe of the surface. However, (metaphorically) ask four experimentalists what happens to water at the (110) surface and you may hear:

"The surface is completely inert"

"It adsorbs only dissociatively"

"It adsorbs both dissociatively and molecularly"

"It adsorbs only molecularly"

As Henrich and Cox note (ref. [1], pp321), this sees to cover most possibilities! This is not to decry experiments on oxide surfaces, which are notoriously difficult; rather it reflects the problems inherent in the material and in interpretating the experimental results. The vexed question of water dissociation has been addressed by many groups and reviewed by Henrich and Cox in their excellent book, and we have given a brief, up-to-date review [3].

This whole situation sounds like a clarion-call for first-principles simulations, and indeed there have been many impressive works recently on oxides [4], including MgO surfaces [5], water on MgO using Hartree-Fock [6] and first-principles dynamics [7], Al_2O_3 surfaces [8], SnO2 stoichiometric and reduced surfaces [9] and TiO_2 surfaces [10, 11, 12, 13]. We are working on several aspects of TiO_2 surface structure and chemistry [14, 15], and here we will describe some surprising results from first-principles molecular dynamics calculations of water on the (110) surface [3].

7.2 Why use first-principles molecular dynamics?

Molecular dynamics (MD) has been around for a long time, and it is almost 40 years since the first report of an MD simulation of condensed matter [16]. If one is interested in thermal properties it is perhaps the most obvious way of using a computer to generate a phase-space trajectory for an assembly of interacting atoms, and amounts simply to the stepwise integration of Newton's

equations of motion from a completely specified starting point. The ergodic principle guarantees that time averages over these phase-space trajectories are equivalent to ensemble averages, and we have, therefore, every macroscopic observable that can be related to atomic motions through statistical mechanics [17]. These include time dependent quantities such as transport coefficients which explicitly involve the dynamical motion of the atoms and their correlation in time [18, 19]. Also, MD can also be used to investigate relaxation towards equilibrium, and as such is a way to explore the configuration-space of a system so as to find the global minimum. The techniques of MD and the many algorithmic innovations which have been made are described in the books by Mike Allen and Dominic Tildesley [20] and Jim Haile [21].

The problem has always been that the only tractable prescriptions for the atomic interactions were simple potential models, and for a long time MD taught us rather more about statistical-mechanics and thermodynamics than it did about real materials. To be fair, many very sophisticated and accurate potentials have been derived for every class of material and applied to great effect, but the ubiquitous stumbling block has been the treatment of systems in which chemical bonding changes. While the effects of changes in bonding may be taken into account in an average way so that e. g. phase transitions may be approximately treated, there is no way to replace the quantum mechanics when one is interested in molecular reactions at surfaces.

This was the situation until the mid-80's, when Car and Parrinello published their seminal work on a unified approach to electronic structure and MD [22]. This synthesis of ideas is by now very familiar and has been well-reviewed in the literature [23, 24]. The following decade saw a quite remarkable increase in the ambitions and achievements of first-principles calculations, fuelled by algorithmic developments and computer speedup, the latter providing a huge impetus through the advent of massively parralel machines. The abstracts of the recent Ψ_k Network Conference report Car-Parrinello MD calculations on metals, semiconductors and insulators, surface reactions, carbon polymorphs and even biological systems. Car-Parrinello style simulations, be they static or dynamic, are capable of describing the quantum mechanical behaviour of valence electrons — the chemical bond — through density-functional theory. The method is also efficient enough to be used for the many evaluations of energy and forces which are needed for MD. In short, the MD technique can be used to treat the making and breaking of chemical bonds.

It is generally true that most things can be calculated using static simulations, and that they are usually much more cost-effective — so why do dynamical simulations? There are two reasons which we have already mentioned: firstly, MD provides an unbiassed way to both sample phase space (to calculate statistical- mechanical quantities) or to explore configuration space (finding the best geometry), and secondly it yields time-dependent quantities. The first reason is not neccessarily a very good one in all cases, since Monte Carlo methods are in general far superior in the calculation of statistical-mechanical quantities in solids and liquids [1]. However, because of the small number of degrees of freedom and the low energy barriers encountered, the configura-

[1] There are no special technical reasons to favour MD or Monte Carlo when using potential models. However, *First-principles* MD is different: a crucial aspect of the technique is the extrapolation of the wavefunctions after each increment of the atomic positions. This is naturally achieved, and in fact in the original Car-Parrinello prescription both the atoms *and* the wavefunctions are evolved through equations of motion, via the trick of associating a fictitious mass with the wavefunction coefficients.

tion space of a small molecule on a surface is readily sampled by quite short MD simulations. In the present case, where we are interested in the adsorption and possible dissociation of water on TiO_2 (110), this means that we can find adsorption geometries in an automatic way, rather than by guessing the most favourable configuration(s) and relaxing them to mechanical equilibrium. Therefore, one type of simulation we report here involves simply starting with a water molecule above the surface and letting it go to see what happens. By using several starting positions and orientations of the molecule, we can investigate the possible adsorption mechanisms. The second reason to do MD is often not so strong either. Take the case of the vibrations of a crystal: these can readily be calculated by MD, but so can they by diagonalization of the dynamical matrix, and to boot the latter is in general cheaper to do and more accurate. However, static methods do not give information about anharmonic effects, or equivalently about the effect of the ionic configuration on vibrational frequencies. So the justification for the calculation of vibrational frequencies by MD is that anharmonic effects might be significant. In the other class of simulation we report here we have used MD to calculate the frequencies of vibration of the adsorbates, and as will be shown we find some very surprising results which would not be given by a lattice-dynamical method.

7.3 Surface chemistry experiments

Experimental studies of surface chemistry gain indirect information about the adsorbed species. This includes even the modern microscopies such as scanning-tunneling microscopy — witness the effort being made to understand STM images. This means that the results must be interpreted in terms of systems in which the signal for the particular experimental technique is known, or alternatively, in terms of a model of the system being studied. For example, temperature-programmed desorption (TPD) measurements show that adsorbed species are bound at certain energies, but does not give enough information to say what it is that is bound with those energies. As another example, high-resolution electron-energy loss spectroscopy (HREELS) reveals the vibrational spectrum of a surface with an adsorbed molecule, but features in the spectrum must be interpreted in terms of the known vibrational signals of the clean surface, those of molecules in the gas phase, and those taken from other adsorption experiments with the same molecule.

The water molecule has three normal modes of vibration, two high-frequency "stretch" modes in which the length of the stiff hydrogen bonds vary, and one "bending" mode in which the lengths of these bonds are basically constant and the angle between them is varying. The stretch modes are usually well separated from crystal phonon modes which makes them a clear signal in experiment. The presence or absence of the bending mode is often taken as sufficient evidence for molecular or dissociative adsorbtion of water on a surface, and in addition it is assumed that the two different types of hydroxyl group formed upon dissociation will produce two distinct, sharp, high-frequency signals.

Both TPD and HREELS have been used by Henderson *et al* [25] in a recent study of water adsorbtion on TiO_2 (110). Henderson argues that at 130 K, water dissociation occurs only at rather low coverages ($\sim$ 0.1 monolayer (ML)) and suggests that this occurs at defect sites. The vibrational spectra were used to support the view that the majority of first-layer adsorption was

molecular, in particular, a feature at 1625 cm^{-1} identified as the water bond-bending mode, and features around 3400 cm^{-1} which were assigned to the O-H stretch modes of the molecule. Dissociative adsorption was linked with an O-H stretch feature at 3690 cm^{-1} and it was noted that *two distinct O-H frequencies expected from the two types of hydroxyl formed by dissociated water could not be observed.*

Simulations can help to interpret experiments. To go further, this is one of the most important uses of simulation, since working in tandem the two approaches both benefit, and the end result is greater than they can achieve apart. As a corollary, it is certainly not possible to answer all questions by one technique alone. In this work we have attempted to make contact with the HREELS experiments on the water-TiO_2 system, and while we cannot offer a full interpretation of the experimental results we can certainly help to understand part of them.

7.4 Techniques

We have used a variant of the `cetep` code (Cambridge and Edinburgh Total Energy Package [26]), the parallel version of `castep` (CAmbridge Sequential Total Energy Package [23]), running on the 512-node CRAY T3D at the Edinburgh Parallel Computer Centre, to perform our calculations. The generalised-gradient approximation (GGA, [27]) is used in preference to the local density approximation (LDA) as it provides a more accurate description of molecular dissocation energies and of hydrogen bonding [28]. A plane wave cutoff energy of 750 eV was found to converge the total energy of the 6-ion TiO_2 unit cell to 0.07 eV. The calculated lattice parameters (experimental values [29] in parenthesis) are 4.69 (4.594) and 2.99 (2.959) Å for a and c respectively, while the internal coordinate u was 0.306 (0.305). The slight overestimation of the lattice parameters (2% for a) is typical for the GGA.

A 3D supercell was used to model the surface, with a 2×1 area exposed on each side of a slab separated by a vacuum region. The (110) surface has rows of oxygen ions along [001] which are called bridging oxygens: these sit above the flat surface which contains fivefold- and sixfold-coordinated titanium ions. In order to minimise the computational cost the Brillouin zone sampling was restricted to the Γ-point and the hydrogen mass was set to 3 a.m.u. This higher mass allows a longer time step to be used in the MD simulation without affecting configuration energies or equilibrium statistical averages such as vibrational mean-square displacements. The overall shape of the hydrogen vibrational spectra will also be unaffected, but the frequencies will be lower. This is taken into account when interpreting frequencies. The vibrational frequencies of a single water molecule have been computed within the harmonic approximation in order to validate this approach, and are shown in table 1. With a mass of 1 a.m.u excellent agreement with experiment is obtained. A mass of 3 a.m.u lowers the angle-bending frequency to 29 THz, still well clear of the TiO_2 lattice vibrations, and allows us to use a time-step of up to 2 fs in the MD. The bond length and bond angle of the water molecule were found to be 0.967 Å and 105°, again in excellent agreement with the experimental values of 0.957 Å and 104.5° [30].

Other aspects of the simulations are quite standard, and full technical details have been published elsewhere [3].

Mode	Expt.	M_h =1	M_h= 3
Sym. stretch	109.6	111	66.6
Asym. stretch	112.6	114	70.9
Bond bend	47.82	46.6	28.8

Table 1: Calculated DFT-GGA harmonic frequencies for the three vibrational modes of water. The values obtained for two hydrogen masses M_h are shown, along with the experimental values from reference [30].

7.5 Simulation results

7.5.1 Stage 1: adsorption

After relaxation and equilibration of the ions in the slab at 500 K, a water molecule was placed on each surface in the simulation box in a variety of initial configurations. This corresponds to a coverage of half a monolayer. Initial, random velocities corresponding to a temperature of 500 K were assigned for all the ions; the water molecules were *not* given an overall velocity directed towards the surface to hasten adsorption.

The behaviour observed in the dynamical simulations was as follows: in the early stages the molecule was drawn down to the surface rapidly, and its favourable orientation was in the (001) plane, with the oxygen atom pointing towards the the surface; when the oxygen atom is within about 2.7 Å of a bridging oxygen ion, there is strong interaction between a hydrogen and the bridging oxygen; this hydrogen atom is captured by the bridging oxygen, and the hydroxyl remnant of the water molecule adsorbs above the fivefold Ti site. It was noticable that while the hydroxyl remnant is rather free with respect to its orientation, the hydrogen ion bonded to the bridging oxygen prefers to point towards the "water" oxygen from whence it came. This pattern of dissociative adsorption was seen for several initial orientations of the water molecules, and is apparently insensitive to the hydrogen positions as long as the molecule is near to a fivefold Ti site. The dissociation described took about 0.4 ps, and during a further 0.8 ps simulation time there was no change in the average hydroxyl positions. Almost identical behaviour was observed in similar simulations of water adsorption on SnO_2 (110), which has the same rutile crystal structure as TiO_2.

We have performed similar calculations starting with water molecules over the 6-fold coordinated Ti site. Here, we chose orientations in which the hydrogen ions were closest to the bridging oxygens, but we could not find a position in which the molecule was attracted to the surface. This is in contrast to the 5-fold site simulations. MD simulations did not result in either physisorption or dissociation at the 6-fold site. Instead, the water molecule drifted away from the site and would presumably dissociate at the 5-fold site given sufficient simulation time.

After relaxation of the ions at the end of these simulations, the geometry confirms that the water molecule is dissociated. For convenience we will use the term "terminal hydroxyl" to describe the O-H fragments which originate from the water molecule, and "bridging hydroxyl" to indicate the O-H group formed by a bridging oxygen and a hydrogen ion. The terminal hydroxyl bond

length of 0.97 Å is little changed from that in the water molecule while in the bridging hydroxyls it is somewhat longer - 1.00 Å. The distance between the oxygen of the terminal hydroxyl and the hydrogen of the bridging hydroxyl is about 1.8 Å, and the H-O-H angle is about 120°. The energy of adsorption obtained from our Γ-point calculations is 1.35 eV per H_2O at half-ML coverage. Our calculated geometry is in good agreement with static, multiple k-point DFT-GGA calculations [12]. The static calculations yielded an adsorption energy of 1.08 eV at monolayer coverage, and also indicated that at lower coverages the adsorption energy should increase. Our dynamical calculations provide strong support for the dissociation geometry being the most favouable, since we did not observe physisorption in our simulations.

7.5.2 Stage 2: vibrational spectra for the adsorbates

We have used MD to calculate the vibrational power spectra of the hydrogen atoms from the temporal Fourier transform of their velocity autocorrelation function (vacf). We recall that, since we are using a hydrogen mass of 3 a.m.u., our calculated frequencies are lower than those that would be obtained with normal H_2O, and must be corrected for purposes of comparison. The harmonic analysis (table 1) indicates a correction factor of 1.61-1.67 for the water molecule stretch frequencies, which we will use here. The vacf's were calculated up to 1.05 ps, with time origins at every time-step, giving a resolution of ±0.5 THz. The vacf's were multiplied by a windowing function prior to transformation, in order to suppress termination ripples.

Before considering the hydroxylated surface, we report calculations on an isolated water molecule, which provide both a check on our methods and a necessary reference point. The computational details were the same as already described, except that a cubic simulation box of 7 Å was used. Starting from the relaxed geometry, the ions were given random velocities in the plane of the molecule. The power spectra calculated at low temperature yielded frequencies in exact agreement with those found by harmonic analysis (table 1), and no appreciable anharmonic shift was found at 500 K.

To calculate the vibrational frequencies characteristic of the adsorbed species we started from the relaxed ionic configuration of the hydroxylated surface. The power spectrum from a 120 K simulation is shown in figure 1. The contributions from terminal and bridging hydroxyls are shown separately. As well as the low-frequency vibrations of the slab, there are clearly several high-frequency modes, and an absence of any power around the 29 THz water bond-bending frequency. Notice that the sharp peak at 69 THz is associated with the terminal hydroxyl groups, and the broad, multipeak structure around 60 THz corresponds to bridging hydroxyl vibrations. The terminal hydroxyl mode frequency is very similar to those of the stretch modes in water. More surprising is the behaviour of the bridging hydroxyls: their slightly greater bond length suggests that their vibrations may be lower in frequency than the terminal hydroxyls, but quite obviously one cannot associate a single mode to their vibrations. Analysis of the ionic trajectories reveals that the broadening occurs because the hydrogen on the bridging hydroxyl interacts strongly with the terminal hydroxyl oxygen. The length of this hydrogen bond, and hence the strength of interaction, is largely determined by the low-frequency motions of the oxygen ions. Using the correction factor of 1.61-1.67, we estimate that the vibrational spectrum of the hydroxylated surface would exhibit a sharp peak between 111-115 THz (3800-3930 cm^{-1}),

and a broad feature spanning 89-100 THz (2970-3330 cm^{-1}).

7.6 Conclusions

Our results show that water does dissociate on the non-defective TiO_2 (110) surface. This is really a re-statement of the conclusion drawn from previous static calculations, but it does strengthen those conclusions since we have made a thorough search to find other adsorption geometries. We have not explicitly dealt with inter-molecular interactions in these calculations. Of course, the water molecule on the surface interacts with its periodic images, but the latter are at a fixed spacing and orientation with respect to the molecule. This means that the effects of hydrogen bonding between adjacent molecules cannot be investigated in our system. In previous studies [6] we have estimated the inter-molecular interactions as a function of separation, and for this situation the energies involved are small compared to the dissociation energy. Our finding dissociative adsorption in these circumstances is consistent with Henderson *et al* [25].

An important conclusion from our work is that the vibrational spectrum of dissociated H_2O on TiO_2 (110) does not contain two clear hydroxyl stretch mode frequencies. Rather, there is a sharp feature around the H_2O stretch frequencies associated with terminal hydroxyl modes, and a broad range of frequencies associated with the vibrations of bridging hydroxyls. The broadening of the bridging hydroxyl frequencies is due to hydrogen bonding between the dissociation fragments. This underlines the fact that the vibrational behaviour of a molecule cannot neccessarily be interpreted through simple arguments or inferred from other situations. This is of course generally true for any property, but the point here is to emphasise how simulation can aid interpretation.

We hope we have demonstrated that first-principles MD is a very powerful tool for surface chemistry investigations, and that for appropriate systems and problems, its particular strenghts make it the technique of choice for the theorist. Finally, why not take a look at some vidoes made from these simulations, which are on the web site:

`http://www.dl.ac.uk/TCS/Staff/Lindan_P_J_D/`

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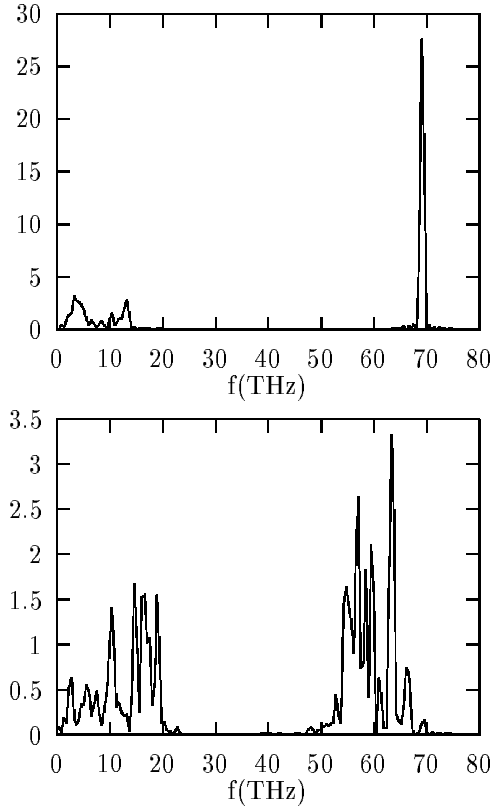

Figure 1: Power spectra for the hydrogen ions in the terminal hydroxyl (upper panel) and bridging hydroxyl (lower panel) groups after water dissociation. The simulation was at 120 K. Note that the frequencies are shifted because of the use of a large hydrogen mass. Note also the different y-scales used.