

Enhanced Vibrations at Surfaces with Back-Bonds Nearly Parallel to the Surface[†]

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It has been discovered that several very different surfaces exhibit a common property: unusually large vibration amplitudes of the outermost atoms, well beyond the enhancement normally expected at typical clean surfaces. These special surfaces are ice $\text{H}_2\text{O}(0001)$, $\alpha\text{-Al}_2\text{O}_3(0001)$, $\alpha\text{-Ga}(010)$, and $\text{Si}(111)-(2\times 1)$. The root-mean-square vibration amplitudes in these surfaces are at least double the bulk values. The common cause that may explain these vibration amplitudes is that the surface atoms (or molecules in the case of ice) only have back-bonds that are nearly parallel to the surface. In this geometry, vibrations, especially perpendicular to the surface, involve primarily bond bending rather than bond stretching/compression: since bond bending is relatively soft, the corresponding vibration modes can have larger amplitudes. It is suggested that theory examine and confirm this cause of enhanced surface vibration amplitudes and explore its implications for other phenomena such as adsorption and catalysis.

Introduction

Atoms at surfaces can have larger vibration amplitudes than in the three-dimensional bulk solid,^{1,2} and surface premelting can therefore occur at lower temperatures than in the bulk.^{3,4} While there are few experimental determinations of surface vibration amplitudes, they generally suggest an enhancement by some 40–50% relative to bulk vibration amplitudes, in qualitative agreement with theory.

One simple way to understand this phenomenon is that surface atoms have greater freedom to move perpendicular to the surface, since there are fewer bonds that confine them in the perpendicular direction: those are primarily the “back-bonds” that hold the surface atoms attached to atoms in the deeper layers. Going one step further, if one eliminates those back-bonds that are primarily oriented perpendicular to the surface and retains only bonds that are more parallel to the surface, the surface atoms will be mainly held in the surface plane by other atoms in or near that same surface plane. This implies that vibrations *perpendicular* to the surface involve primarily softer bond bending rather than stiffer bond stretching/compression.

An alternative but equivalent point of view invokes Rayleigh surface waves, which have lower frequencies than corresponding bulk phonon waves and enhance the amplitudes of atomic vibrations at surfaces compared to the bulk. Removing bonds perpendicular to the surface would further lower the frequencies of Rayleigh waves and further enhance the vibration amplitudes.

Another class of structures with enhanced vibrations is exemplified by adsorbed molecules such as carbon monoxide (CO); as is well known,^{5,6} these molecules usually stand perpendicular to the surface, leaving the oxygen bonded only to the carbon and thus relatively free to swing *parallel* to the surface with very large amplitudes.

Several examples of the former case have been uncovered in recent years during surface structural studies, in which root-

mean-square (rms) vibration amplitudes as large as double or even triple the bulk values have been observed. These analyses, the results of which are discussed in the next four sections, mainly used low-energy electron diffraction (LEED)^{7,8} to interpret experimentally measured diffraction intensities in terms of atomic positions and vibration amplitudes. The sensitivity of this technique is sufficient to clearly detect enhanced vibrations. However, with the available experimental data sets of limited size, it is not possible to draw conclusions regarding any anisotropy of the surface vibration amplitudes; furthermore, the technique as usually practiced is more sensitive to vibrations perpendicular to the surface than to parallel vibrations. It is also impossible to rule out some amount of static disorder in such structures, since such disorder affects diffraction in a way similar to dynamic vibrations.

The four surfaces in question are the following:

- ice $\text{H}_2\text{O}(0001)$:⁹ in this unreconstructed molecular surface, the outermost molecular layer vibrates with such large amplitudes that it is almost “invisible” to LEED, even at 90 K: the Debye–Waller factor makes its back-reflections relatively weak; it is found that their rms vibration amplitudes are at least double and possibly triple the bulk value;
- $\alpha\text{-Al}_2\text{O}_3(0001)$:¹⁰ this unreconstructed surface of an ionic compound, which is terminated in an Al layer, has outermost Al atoms that vibrate with rms amplitudes about double those in the bulk, at room temperature;
- $\alpha\text{-Ga}(010)$:¹¹ this “anisotropic metal” can be viewed as being composed of covalent Ga_2 dimers or “molecules” that are cut in half at the unreconstructed surface, leaving loosely bound “monomers”: these vibrate with about double the rms amplitude of the bulk, at room temperature;
- $\text{Si}(111)-(2\times 1)$:¹² the familiar “modified Pandey” reconstruction of the $\text{Si}(111)$ surface also exhibits rms vibration amplitudes of its outermost atoms that are about double the bulk value, at room temperature.

Ice $\text{H}_2\text{O}(0001)$. Figure 1 illustrates the surface structure found for ice $\text{H}_2\text{O}(0001)-(1\times 1)$.⁹ This ice film, grown on a $\text{Pt}(111)$ substrate, exhibits the common hexagonal phase Ih and exposes

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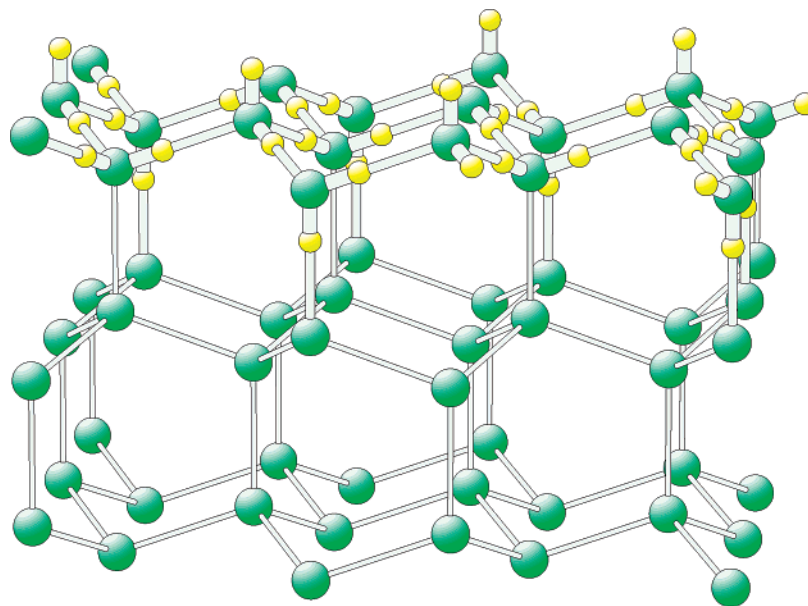


Figure 1. Surface structure of $\text{H}_2\text{O}(0001)$.⁹ The oxygen atoms are drawn green, with hydrogen atoms in yellow; hydrogen is shown only in the outermost two molecular layers.

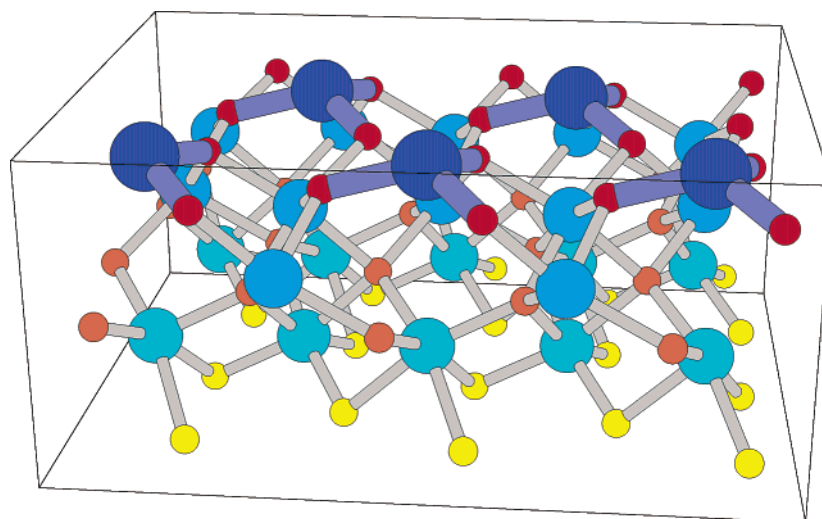


Figure 2. Surface structure of $\alpha\text{-Al}_2\text{O}_3(0001)$.¹⁰ The aluminum atoms are drawn in various shades of blue that mark their depth below the surface, darkest being near the surface. The oxygen atoms are shown in red/orange/yellow, with increasing depth.

its (0001) surface without reconstruction. The oxygen atoms form a lattice that is similar to that of wurtzite, composed of a stack of molecular “bilayers”, with threefold rotation axis perpendicular to the surface. This lattice is composed of tetrahedrally arranged molecules linked by hydrogen bonds. In the surface termination shown in Figure 1, the outermost molecules are hydrogen-bonded to the next layer of molecules by bonds that are inclined by only $109.5 - 90 = 19.5^\circ$ from the surface plane (this assumes ideal tetrahedral angles; this inclination angle could not be determined with LEED). As a result, vibrations perpendicular to the surface involve mostly bond bending and are thus likely to be soft.

The structural study of this surface was performed on an ultrathin ice film using dynamical low-energy electron diffraction (LEED) at 90 K. The LEED analysis was relatively insensitive to the outermost molecular layer drawn in Figure 1, and at face value would favor a model that omits that outermost monolayer, leaving only a “half-bilayer”. However, total-energy calculations and molecular dynamics (MD) simulations indicate that this layer must be present for energy stabilization and that

this outermost layer has large vibration amplitudes.⁹ Both LEED and MD simulations find that the outermost water molecules have enhanced vibrational amplitudes making them almost undetectable by LEED even at 90 K. The MD simulations of the half-bilayer terminated surface (which omits the outermost monolayer of Figure 1) yield results inconsistent with the LEED findings, thus excluding this model.

The rms vibration amplitude of H_2O molecules in bulk ice is approximately 0.10 \AA at 90 K. The MD simulations indicate vibration amplitudes that decrease into the surface toward the bulk value, starting at about 0.25 \AA in the outermost molecular layer. A more refined LEED analysis suggests optimum rms vibration amplitudes of $0.25\text{--}0.33 \text{ \AA}$, with large error bars. It therefore seems that, even at the low temperature of 90 K, the outermost water molecules have rms vibration amplitudes that could be 3 times larger than in bulk ice.

$\alpha\text{-Al}_2\text{O}_3(0001)$. Figure 2 shows the surface structure of sapphire $\alpha\text{-Al}_2\text{O}_3(0001)-(1 \times 1)$.¹⁰ The outermost atoms (aluminum) are drawn in dark blue, with thick bonds to the second layer (oxygen). As can be seen, because of large relaxations

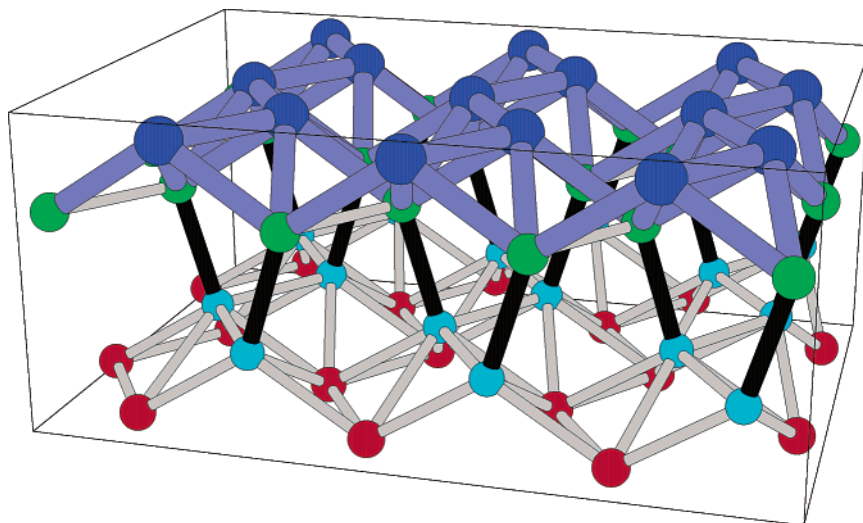


Figure 3. Surface structure of α -Ga(010).¹¹ The bulk structure has a large unit cell containing pairs of “dimerized” Ga atoms, here shown linked by black bonds that are roughly perpendicular to the (010) surface (at top). The outermost Ga atoms (dark blue) have lost their dimer companions, remaining bonded to other, more distant atoms through strongly tilted bonds (drawn thick and blue).

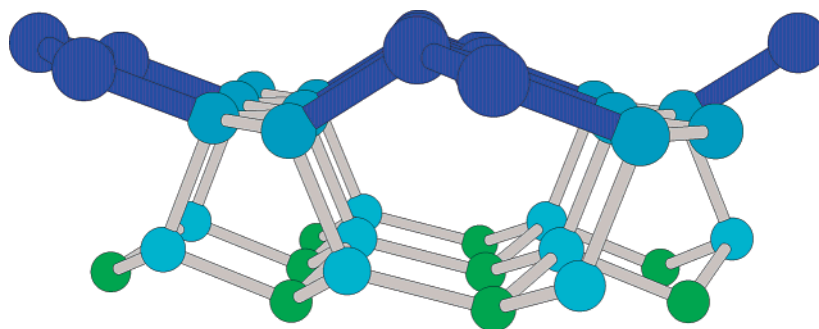


Figure 4. Surface structure of Si(111)-(2 \times 1),¹⁰ exhibiting the modified Pandey model. The large, dark-blue atoms form slightly tilted zigzag rows that are linked to the next layer through bonds that are nearly parallel to the surface.

which reduce the first interlayer spacing, these bonds are nearly parallel to the surface: they are inclined by only 15° from the surface plane.

Because of a debate about the possible influence of surface preparation on the surface structure, sapphire surfaces were prepared for this investigation in three different ways, and the experimental LEED data were analyzed using an exhaustive search of possible models. For all sample-processing conditions, the clearly favored structure has a single Al layer termination and a large first interlayer contraction of approximately 85% with respect to the bulk spacing, as illustrated in Figure 2.

In addition, it appears that the topmost Al layer has unusually large vibrational amplitudes at room temperature. Such vibrations may in fact account for the substantial difference between the interlayer contractions determined by zero-temperature calculations and finite-temperature experiments.

The rms bulk vibrational amplitudes in α -Al₂O₃ are about 0.12 Å at room temperature. For the surface aluminum atoms, the vibrational amplitude perpendicular to the surface is determined by LEED to be about 0.24 Å, double the bulk value.

α -Ga(010). Figure 3 represents the atomic surface structure of α -Ga(010)-(1 \times 1).¹¹ The black bonds, nearly perpendicular to the surface, identify “dimers” in the bulk structure: pairs of atoms that are strongly bonded together, at the expense of other, weaker bonds. (In the bulk, metallicity is only present in the so-called buckled planes, where the ends of the dimers overlap, leading to a strong anisotropy in the Fermi surface and the

transport properties. In a certain sense, we may view the α -Ga structure as a layered crystal where quasi-two-dimensional and metallic buckled layers are separated by covalent molecular bonds, linking the dimers.)

This structure was determined using LEED at room temperature, which is not far below the bulk melting temperature of 303 K. The result indicates that the surface is not reconstructed and that dimers are cut at the surface, forming a two-dimensional metallic structure with only minimal lateral displacements of the atoms. The topmost interlayer distance is 1.53 Å, corresponding to a spacing expansion of 2% from the bulk. As illustrated in Figure 3, these nondimerized surface atoms remain connected through relatively weaker bonds to deeper atoms: the back-bonds are inclined by about 34° from the surface plane. The relative weakness of these remaining bonds may also contribute to the softness of the vibration modes.

The rms vibration amplitudes in bulk Ga are about 0.13 Å at room temperature (the bulk Debye temperature being about 350 K). The LEED analysis finds a best-fit value of double that amplitude, about 0.26 Å, for the outermost atoms. Similar results have been obtained by X-ray diffraction: surface rms vibration amplitudes are found which are 1.5–2 times larger than in bulk Ga.¹³

Si(111)-(2 \times 1). Figure 4 shows the Si(111)-(2 \times 1) surface structure. Using LEED, this structure was recently reanalyzed and refined, showing that the “modified Pandey model” remains valid, but involves strongly enhanced vibration amplitudes of

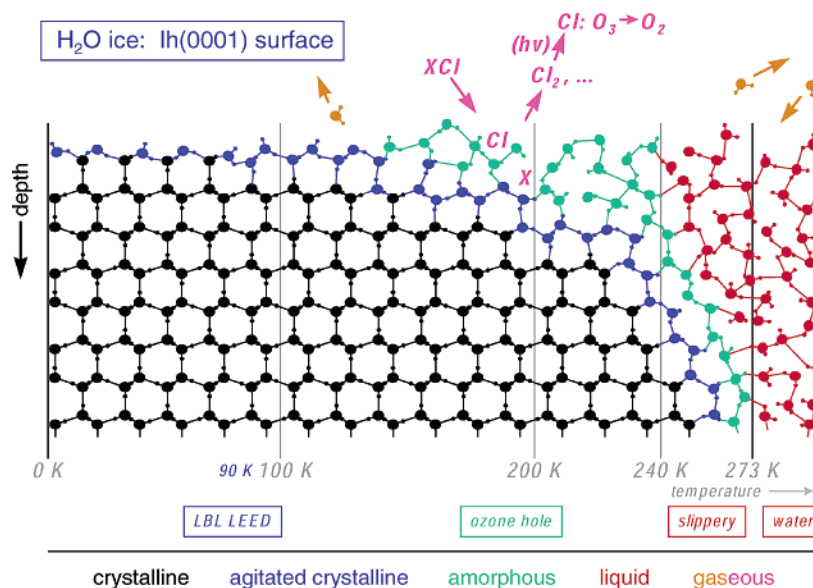


Figure 5. Schematic representation of the surface structure of water ice as a function of temperature, from absolute zero to beyond the melting point. The surface is oriented toward the top of the figure, with the gas phase above it. Colors code the degree of ordering and physical state of H₂O molecules, as indicated along the bottom margin.

the outermost atoms.¹² This model involves a tilted zigzag row of π -bonded surface atoms, shown as large, dark-blue spheres in Figure 4. The bonds between these surface atoms and the atoms in the next layer are inclined by 21 and 32°, respectively, from the surface plane.

Since the earlier determination of the modified Pandey model,¹⁴ a series of new or modified models had been proposed for this much-studied surface structure, including a reverse-tilted π -bonded chain model,¹⁵ a three-bond scission model,¹⁶ and a π -bonded chain model with enhanced vibrations.¹²

The recent study¹² distinctly favors the earlier modified π -bonded chain model, but with strongly enhanced vibrations. It obtains convincingly better agreement between theory and experiment by allowing enhanced vibrations of the outermost two atoms: the rms vibration amplitude optimizes to about 0.25 Å, more than double the bulk value of about 0.11 Å.

Discussion and Conclusions

A class of surface structures has been identified in which unusually large vibration amplitudes were detected with LEED. While the surfaces are quite disparate in physical character (ranging from insulating water ice, via ionic aluminum oxide and semiconducting silicon, to “anisotropically metallic” gallium), they share one distinct geometrical property: the outermost atoms are connected to deeper atoms exclusively through back-bonds that are oriented nearly parallel to the surface. For each of these four surfaces, rms vibration amplitudes have been detected that are at least double and, in ice, possibly triple the bulk value.

One may speculate on the relationship between these enhanced surface vibration amplitudes and surface premelting^{3,4} as well as other phenomena. In ice, surface premelting occurs,^{9,17} and it is very likely that the large vibration amplitudes seen at 90 K in the outermost molecular layer can be viewed as precursors to an amorphous surface layer, which with increasing temperature then becomes “liquidlike”. This is schematically illustrated in Figure 5, in which “agitated crystalline” describes the enhanced vibrations discussed in this paper, color-coded in blue. “LBL LEED” marks the 90 K structural study described

here. “Ozone hole” refers to the role of ice near 200 K in catalyzing the ozone hole over Antarctica:¹⁷ this involves the dissociation of chlorinated molecules to produce Cl atoms that in turn break up ozone molecules into dioxygen (the exact mechanism is unknown, but presumably involves the amorphous surface layer of ice).

“Slippery” refers to a temperature range within which ice has particularly low friction, possibly because of the presence of a surface premelted layer acting as a banana peel,^{17,18} shown in red. There is anecdotal evidence which suggests that skating and skiing are in fact much harder below this temperature range, and this is supported by recent surface science results showing increasing friction with decreasing temperature in the range 130–170 K.¹⁹ This increased friction in fact may have been the main cause of the failure of Capt. Robert Falcon Scott’s tragic 1911–12 South Pole expedition: “The unusually cold conditions [about 233 to 243 K] had crippling effects not only in terms of frostbite, but also in the friction of the frigid snow that gripped at their skis and sledge runners”,²⁰ “like ... desert sand, not the least glide in the world”.²¹

In Ga, a recent X-ray diffraction study¹³ shows that the surface starts to premelt at 293 K, some 10 K below the bulk melting point. However, the picture regarding the cause of this surface premelting is complicated by the fact that the bulk itself already shows vibrational anomalies at about the same temperature. An interesting observation of this X-ray study is that the surface rms vibration amplitudes do not change up to the bulk melting point: since such amplitudes only make sense for the nonmolten part of the surface, this could be interpreted as constant vibration amplitudes at the receding solid–melt interface.

For clean Al₂O₃(0001) and Si(111)–(2×1), there is no evidence to my knowledge for any surface melting. The only clean surface of Si that appears to premelt (or at least disorder close to the bulk melting point) is Si(113),²² which is densely stepped.

It would be interesting to pursue the study of enhanced vibration amplitudes at surfaces with theory. It would be useful to examine the detailed cause and mechanism of this phenomenon, as well as the range of materials in which it may occur. Also, it would be of value to examine its relevance to other

physical and chemical processes at such surfaces, such as adsorption kinetics and catalysis.

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