

Structural Isotope Effect in Water Bilayers Adsorbed on Ru(001)

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Using negligible-damage low energy electron diffraction we have found a structural isotope effect in water bilayers on Ru(001), in contrast to bulk ice where none exists. While the D₂O bilayer forms an extended commensurate $p(\sqrt{3} \times \sqrt{3})R30^\circ$ structure with known geometry, the H₂O bilayer is characterized by a striped domain structure 6.5 substrate lattice constants wide with essentially the same short range arrangements as for D₂O. This unexpected isotope effect is explained by a difference in H and D bond lengths (an Ubbelohde effect) and potentials, induced by the interaction with the substrate, and a consequent difference in the misfit to the substrate lattice.

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The behavior of water in condensed phases is dominated by its hydrogen bonds [1]. This is also the case for adsorbed phases of water on metal surfaces for which clustering from low coverages on and the tendency to form a stable “bilayer” (see below) have been found in many systems [2]. Since generally the strengths of hydrogen bonds are strongly influenced by the hydrogen isotope present, because of the influence of the mass on tunneling rates, zero point energies, and motional properties, many isotope effects are found in energetics and kinetics and even for geometrical parameters of hydrogen-bonded systems; the latter is known as the Ubbelohde effect [3]. Interestingly, this effect virtually vanishes for crystalline water ice under normal conditions: The lattice constants of hexagonal ice composed of H₂O or D₂O differ only by four parts in 10⁴ at atmospheric pressure which has been explained by the canceling of counteracting influences [4]. For adsorbed water, a kinetic isotope effect was reported in 1987 by Schmitz *et al.* [5] who found a dramatic change in thermal desorption spectroscopy (TDS) of the saturated bilayer on Ru(001) (which is particularly well defined) between H₂O and D₂O: For H₂O two roughly equal peaks separated by 40 K are found, while for D₂O the second peak is essentially suppressed. This was explained by different branching into desorption from the first state and conversion to a second one for the two isotopes. We have investigated in detail the structures of the bilayers of H₂O and D₂O on Ru(001) by qualitative and quantitative LEED and found a very interesting isotopic effect in the structure of these layers. Although the short range coordination of the layers is essentially identical, the long range order turns out to be considerably different, with D₂O forming an extended commensurate $p(\sqrt{3} \times \sqrt{3})R30^\circ$ layer, while the corresponding H₂O layer possesses a striped domain structure. This shows that the D₂O layer can adjust fully to the Ru substrate structure, while the H₂O layer possesses a residual strain which is relieved by periodic domain boundaries. Our methods allow us to exclude any radiation damage effects. These results are the first case of a structural isotopic effect found for crystalline water under any condition, and the first example of such an effect for any surface

layer; they also demonstrate a new type of registry influence on the geometry of a molecular network on a rigid template. This effect was certainly unexpected—no data or prediction for it existed previously. Nevertheless, we can understand it if we couple the existing general views of the influence of isotopic replacement on hydrogen bond lengths [3,4] with our knowledge of the detailed bilayer geometry and its physical reasons gained by our recent LEED *IV* analysis for the D₂O case [6].

The “bilayer” mentioned above is found as the stable adsorbate layer, set off clearly in TDS from multilayer formation, in many systems [2]. According to the model of Madey, Doering, and Williams [7] which was developed on the basis of the rules of Bernal, Fowler, and Pauling for hydrogen bonds [8], it is equivalent to two high density layers from the low pressure modifications of ice (I_h and I_c [1]): It consists of puckered hexagonal rings of water molecules, each sharing hydrogen bonds with its three nearest neighbors, of which those in the lower layer are bonded to the metal surface via a lone electron pair on the oxygen, while the upper half of the molecules are connected to them only via hydrogen bonds and have one H atom each pointing perpendicularly to the surface [7]. In the crystalline ices mentioned, the vertical distance between the oxygen atoms in the two layers is 0.96 Å. In our recent determination of this layer structure by LEED *IV* analysis [6] we have found that this distance on Ru(001) is only about 0.10 Å; the clearly differing Ru-O atom distances for the upper and lower molecules show, however, that the bonding configuration is still as in the original model. Physical reasons for this compression (dipole–mirror-dipole interaction for the upper, bond angle widening for the lower molecule induced by the donor bond to the metal) have been proposed [6].

For this work we used an UHV system with background pressure below 5×10^{-11} mbar. The Ru(001) surface, prepared by standard methods, was saturated with H₂O or D₂O (isotopic purity in both cases better than 99.9%) via a doser constructed to ensure homogeneous coverage, at a sample temperature of 150 K. This procedure eliminates multilayers and produces well-ordered, reproducible

bilayers. These showed the mentioned kinetic isotope effect in TDS [5]: two TDS peaks of roughly equal integrals (around 170 and 212 K at 1.0 K/s) for H_2O , but a single peak (at 179 K, with a tail containing 11% of the total coverage) for D_2O . Furthermore, hydrogen TDS showed that about 12% of the initial coverage dissociates during molecular TDS for H_2O , while *no* dissociation occurs for D_2O . For a discussion of these and other kinetic effects and for further details see Ref. [9].

Because of the very high irradiation sensitivity of adsorbed water—in normal LEED apparatus a water-induced superstructure fades within a few seconds—a necessary prerequisite of this work was the development and use of a video LEED apparatus which allows data to be taken with minimum electron doses. It consists of a backview three-grid LEED optics whose fluorescent screen is observed by a Peltier cooled slow scan charge-coupled device (CCD) camera with high spatial and dynamic resolution. At a given electron energy, the entire LEED image is stored simultaneously; all evaluation of the data (spot intensities and profiles, background definition and subtraction, and extraction of IV curves) is done off line. Together with low beam currents (<300 nA) and provisions to deflect the beam off the sample during data transfer and energy adjustment, electron doses could be lowered to about 0.1 electron per molecule for a single image, the most important mode here. By shifting the beam over the surface periodically, an entire IV scan was possible with three to nine electrons per water molecule (at 50 eV, $12 e^-/\text{mol}$ lead to an intensity decrease of about 30%; see also Refs. [6] and [9]). Thus any degradation of images by electron irradiation was avoided, as was also verified by comparing data taken under varied beam conditions. This was particularly important since it could not be excluded *a priori* that the observed differences of LEED patterns might not stem from a different radiation sensitivity of adsorbed H_2O and D_2O —strong isotope effects are well known in electronically induced dissociation and desorption phenomena of adsorbates on metals [10].

LEED patterns obtained under these provisions showed a clear qualitative difference for saturated bilayers of D_2O and H_2O , respectively. While H_2O was characterized by a streaky pattern with satellites (called the N_1 structure from now on), as reported before and attributed to a domain structure [7] (see Fig. 1), the D_2O layer exhibited a sharp $p(\sqrt{3} \times \sqrt{3})R30^\circ$ pattern. The latter case lends itself nicely to IV analysis, and therefore it was used to deduce its atomic geometry, as mentioned above [6]. Most importantly in our context, the IV curves for the H_2O pattern (integrating over the satellite spots for the integral order beams, and over the split beams around the $\sqrt{3}$ positions, see Fig. 1, for the superstructure beams) were virtually identical to those of the well-defined D_2O spots (see Fig. 2). This shows clearly that the local molecular configuration is essentially identical in both cases and only the long range order is different—commensurate over distances of the order of the terrace

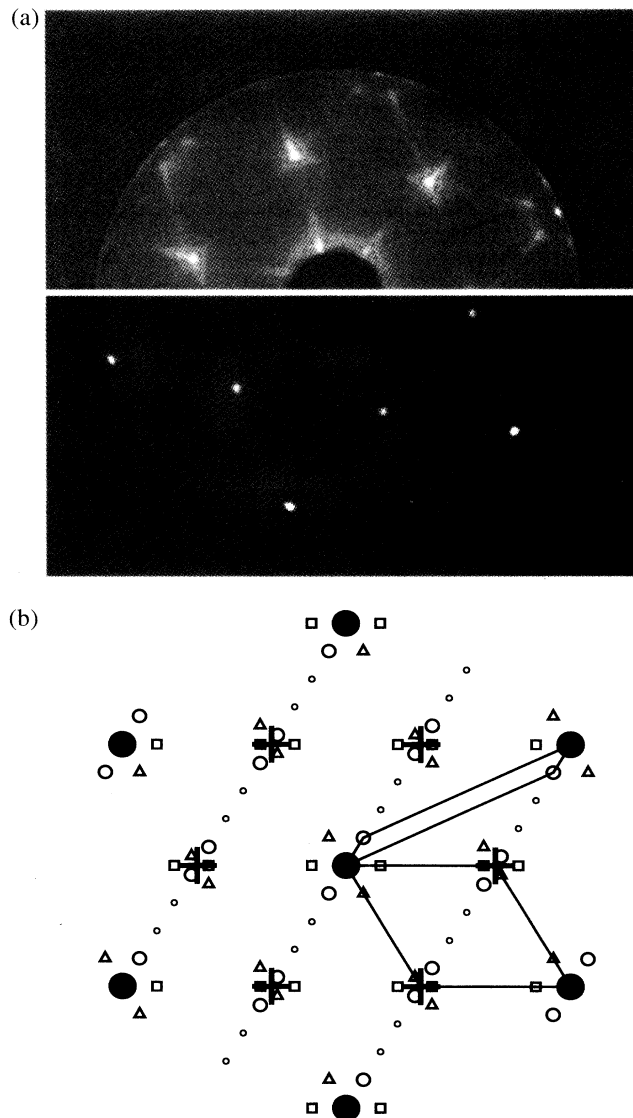


FIG. 1. (a) LEED patterns seen for the H_2O (at 50 eV, upper half) and D_2O (52 eV, lower half) bilayers on Ru(001). (b) Sketch of their main features, without indication of streaking. Circles, squares, and triangles correspond to the three different rotational domains of H_2O ; the crosses mark the positions of the $\sqrt{3}$ beams, the only ones seen for the D_2O bilayer. The positions of H_2O superstructure spots not seen because of the local $\sqrt{3}$ order are marked by small circles, for one of the rotational domains only.

widths (>100 Å) for D_2O , and arranged in a domain structure for H_2O .

The observation of anisotropic broadening of the superstructure spots along the direction between the (0,0) and (1,0) spots and symmetry related directions shows that the N_1 structure consists of striped domains describable by the matrices

$$\begin{pmatrix} 1 & 2 \\ 0 & 13 \end{pmatrix} \text{ or } \begin{pmatrix} 1 & 2 \\ -7 & -1 \end{pmatrix},$$

in contrast to the triangular domains suggested earlier [7] (see also Ref. [9]). The N_1 unit mesh extends along the

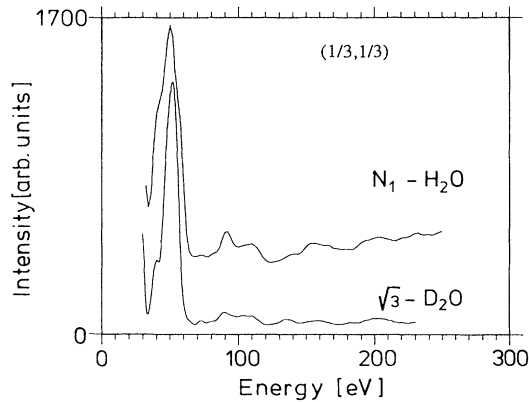


FIG. 2. Comparison of the LEED IV curves for the first superstructure spots (integrating over all satellites for H_2O), for the two structures. Most differences seen are explainable by small differences in integration and background subtraction procedures.

[010] direction for 6.5 substrate lattice constants and is $\sqrt{3}$ substrate lattice constants wide; its area corresponds to 13 substrate unit meshes as calculated from the determinant of its matrix. On the grounds of the local geometry being equal to that of the commensurate bilayer structure with coverage $\Theta = \frac{2}{3}$ and the layer being saturated, the N_1 unit mesh can contain either eight ($\Theta = \frac{8}{13} = 0.62$) or nine molecules ($\Theta = \frac{9}{13} = 0.69$). This together with the Bernal-Fowler-Pauling rules [8] leads to the two domain structures of Fig. 3, with light and heavy domain walls, respectively. Unfortunately, accurate coverage information, which would allow us to decide between them, is not available; for various reasons, neither x-ray photoemission spectroscopy (XPS) data for H_2O [11] nor the ratio of our TDS integrals allows a definite conclusion. Arguments can be advanced for either one (for details, see Ref. [9]). However this may be, the main point here is that, while the D_2O bilayer can fully adjust to the substrate spacing, the H_2O bilayer does not do so, but must react by the introduction of periodic domain boundaries. It is obvious, then, that the misfit between the Ru(001) and the ice spacings ($\sqrt{3} \times 2.71 = 4.69 \text{ \AA}$ vs 4.49 \AA for the projected ice lattice constant) cannot be the only cause for the domain structure of H_2O as originally suggested [7], because almost the same misfit exists for D_2O . Also, while essentially no structural isotopic effect exists in ice (see above), it is obviously turned on by the situation in the bilayer structure. The explanation comes from an analysis of the latter in connection with the Ubbelohde ideas [3,4].

Ubbelohde and Gallagher have examined the structural isotope effect in hydrogen-bonded systems, expressed by the change of the O-H-O bond length upon isotopic substitution, $\Delta_{HD}d$, as a function of this length d . They found that for d values smaller than that of ice (2.76 \AA) an elongation occurs upon substitution of H by D (positive Ubbelohde effect); for larger ones, a contraction results (negative Ubbelohde effect); and for ice the change is negligible ($\approx 0.001 \text{ \AA}$). The explanation rests on the anharmonicity

of the bonding potential for the hydrogen atom between the two oxygen atoms, and the mass-dependent zero point motion of the hydrogen atom in it. The mass change produces two opposing effects which cancel for water (see Ref. [4] for details). For the small d range 2.49 to 2.76 \AA , a linear relation holds [4]: $\Delta_{HD}d = 0.16 (2.77 \text{ \AA} - d)$. Our structure analysis for the D_2O bilayer [6] has shown that in reaction to the surface forces, the O-D-O distance therein is changed from the ice value of 2.76 \AA to 2.71 \AA . This shifts water from the situation of $\Delta_{HD}d \approx 0$ to a finite change. Application of the formula above leads to $\Delta_{HD}d$ of somewhat more than 0.01 \AA , which is not only higher by a factor of 7 more than for ice at atmospheric pressure but also leads to a stronger misfit to the substrate for H_2O compared to D_2O . In addition, the effects leading to the vertical bilayer compression very likely cause an increase of the anharmonicity of the O-H-O bond which further increases the Ubbelohde effect. The bond length change just estimated is then only a lower bound on the actual increase of misfit by isotopic substitution. Changes of this order of magnitude can lead to a breakup of the adjusted superstructure into domains. The formation of stripes rather than of triangular or hexagonal domains results from their relatively fewer edge molecules and their maximization of the hydrogen bond number. The misfit will lead to small displacements of the molecules relative to the commensurate structure which must be at a maximum at the domain boundaries; there they must be shifted from their ideal on-top positions by at least 0.04 \AA . Since the adjustment of the water bilayer, compressed by the surface interaction, to the Ru(001) lattice is the driving force of the fit or misfit, there may also be a contribution of the different force constants in the H_2O and D_2O layers.

These considerations give a self-consistent explanation of the structural changes occurring in the formation of a water bilayer on a metal surface and, in particular, of the finding that a structural isotope effect is turned on by it which does not exist for bulk ice. Since this Ubbelohde effect depends sensitively on the O-H-O distance and its change upon adsorption, it could be tested using other substrates for which $p(\sqrt{3} \times \sqrt{3})R30^\circ$ structures have also been seen or can be expected. Obviously, on the basis of this qualitative model, a quantitative theoretical analysis would be highly desirable.

In conclusion, we have found a structural isotope effect in adsorbed water bilayers. This deviation from the behavior of bulk water, where no such effect exists, can be explained on the basis of the structural changes induced in the water bilayers by their interaction with the metal substrate (bond-induced changes, dipole-image dipole interactions, and lattice misfit) which lead to a change of the H-bond length and its isotopic dependence in the sense described by Ubbelohde and Gallagher. More generally, our work has shown that the long range order of an adsorbate layer not only depends on the chemical species but can also be influenced by the isotopes involved, in particular, in hydrogen-bonded networks. Since the adsorbate lattice

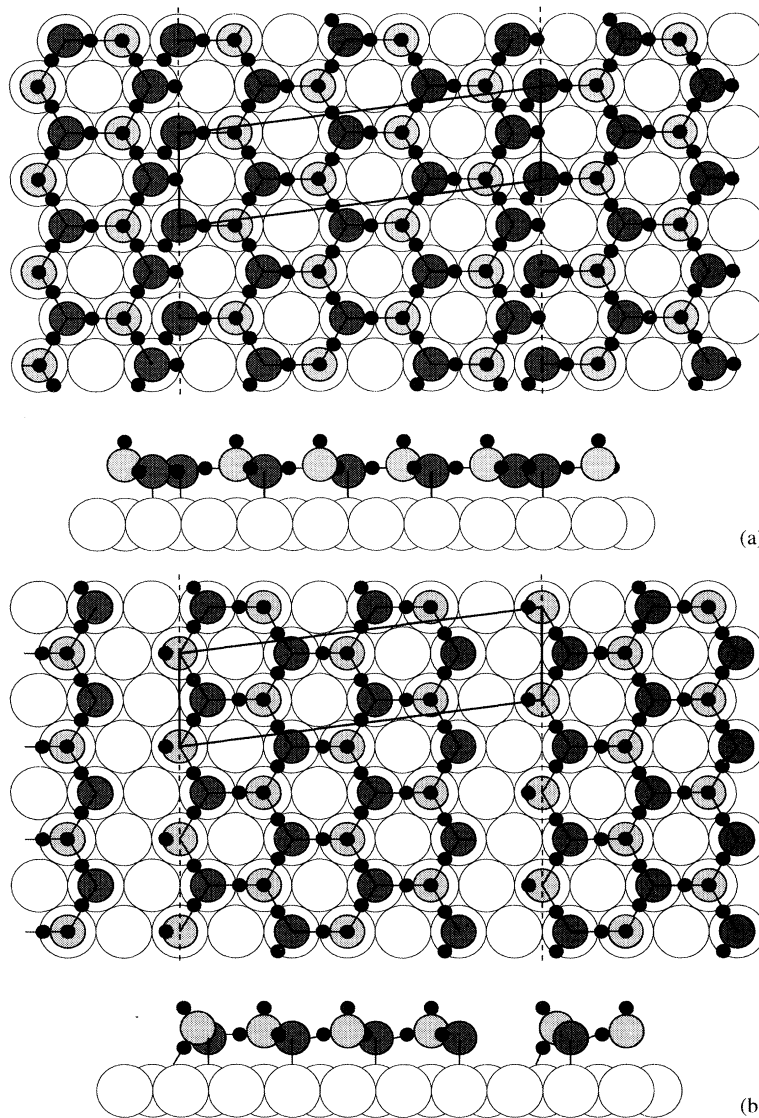


FIG. 3. Real space N_1 structures discussed in the text (one rotational domain each), viewed from above and from the side; (a) $\frac{9}{13}$ structure; (b) $\frac{8}{13}$ structure. Dark circles: oxygen atoms of lower water molecules bonded to the surface. Shaded circles: O atoms of upper water molecules. Black dots: hydrogen atoms. The commensurate $p(\sqrt{3} \times \sqrt{3})R30^\circ$ structure of D_2O fills the whole surface with the layer corresponding to the central parts of both N_1 structures.

cannot respond to small isotopic differences in the bonding as a whole by adjusting the lattice constants, it has to relax in other ways—in our case by breaking up into domains. In more practical terms, such possibilities have to be considered when isotopic substitution is used, e.g., for the assignment of vibrational modes.

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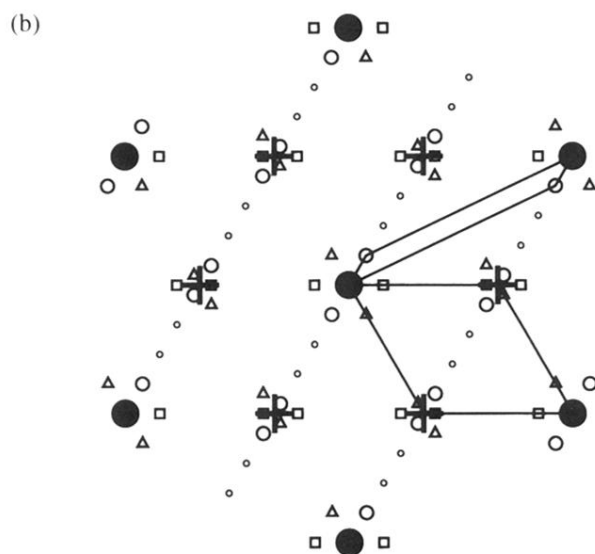
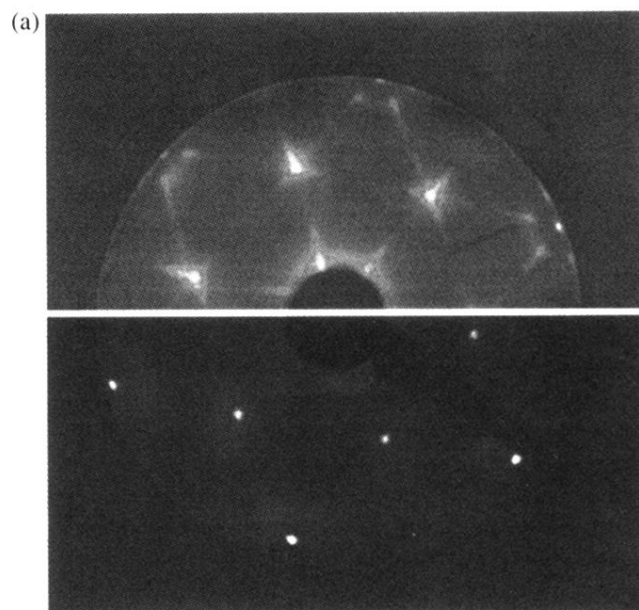


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