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Chemical Physics Letters 376 (2003) 618–624

**CHEMICAL
PHYSICS
LETTERS**www.elsevier.com/locate/cplett

Interfacial structure of water on Ru(001) investigated by vibrational spectroscopy

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Received 20 May 2003; in final form 16 June 2003

Abstract

In light of the controversial discussion of the interfacial structure of water on metal surfaces, adsorption of D₂O on Ru(001) is investigated using sum-frequency generation vibrational spectroscopy. In contrast to a recent theoretical study claiming partial dissociation of the first bilayer of water on Ru(001) [Science 295 (2002) 99], clear spectroscopic evidence is found that the adsorbed molecules remain intact. In the context of all experimental data available, a bilayer structure where every second water molecule exhibits a hydrogen–metal bond with a comparably large, proton-disordered unit cell seems most plausible.

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1. Introduction

The interaction of water with solid surfaces is of key importance for electrochemistry, heterogeneous catalysis and corrosion. Despite this relevance and numerous studies on the structure of the first layers of water on solid surfaces [1], this interface is not yet well understood. The understanding of thin water layers on comparably simple single crystal surfaces would be an important step towards a convergence of surface science

theory and experiment [2]. The prototype system for this interaction with the most comprehensive structural knowledge available to date is water (D₂O) adsorbed on Ru(001).

The Ru(001) surface closely matches the basal plane of ice *I*_h [3], so that for the first layers of water the picture depicted in Fig. 1a had been originally accepted: the first two layers forming essentially an epitaxial bilayer (BL) of intact molecules in an arrangement derived from crystalline bulk ice (ice *I*_h), with the O atoms binding to the substrate [1]. However, careful studies by low energy electron diffraction (LEED) revealed serious discrepancies [4]: all O atoms were observed to be nearly coplanar, as if the water BL was vertically compressed ('H-up' in Fig. 1b). This

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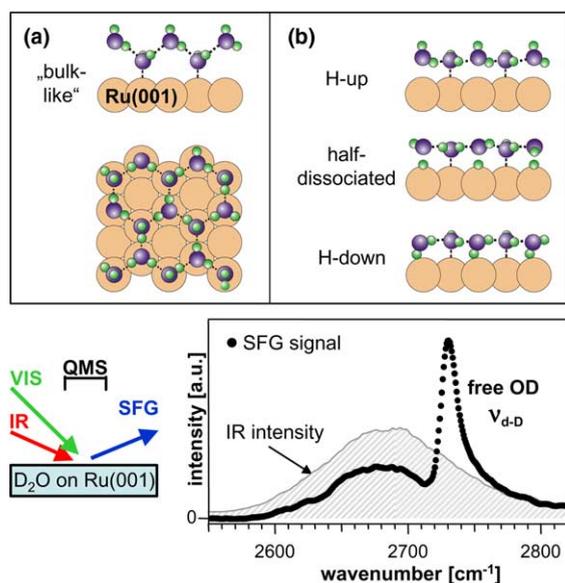


Fig. 1. (a) Buckled BL derived from bulk ice I_h , (b) proposed structures with the nearly coplanar oxygen geometry observed in LEED; note that the atomic positions are illustrative only. Bottom: sketch of the SFG geometry and exemplary broadband-IR-VIS SFG spectrum of the free OD vibration for 2.0 BL D_2O on Ru(001).

could not be accounted for theoretically, until recently Feibelman based on elaborate density functional theory (DFT) calculations [5,6] proposed that only a half-dissociated structure (Fig. 1b) with the observed near-coplanar O atom geometry is wetting the surface at all (corroborated by another DFT study [7]). Even though experimental reinvestigations have already been published [8,9], this proposal could neither be confirmed nor dismissed.

In this Letter, the hydrogen bonding of up to 10 BL D_2O on Ru(001) is investigated by vibrational spectroscopy and compared to predictions for the half-dissociated structure [6]: the vibrational properties are found to be very similar to bulk ice I_h for *all* coverages, which implies that the first BL of water on Ru(001) is not half-dissociated but consists of intact D_2O molecules. Instead, we propose that the molecules are most likely arranged in a 'H-down' fashion (Fig. 1b), which has also been proposed very recently for $H_2O/Pt(111)$ [10].

2. Broadband SFG vibrational spectroscopy and experimental details

Vibrational spectroscopy is an extremely valuable probe allowing for the identification of chemical species and their local binding geometry. Here, vibrational sum-frequency generation (SFG) is applied [11], which has been successfully used to probe the interfacial structure also for water [12] and ice [13]. SFG is a second-order nonlinear process forbidden in media with inversion symmetry [11], thus intrinsically sensitive to interfaces of centrosymmetric media. The SFG intensity is proportional to the second-order nonlinear polarization $\mathbf{P}^{(2)}(\omega_{SFG} = \omega_{IR} + \omega_{VIS})$ induced by frequency mixing in the interfacial region: $I_{SFG} \propto |\mathbf{P}^{(2)}(\omega_{SFG})|^2 \propto |\chi_S^{(2)}(\omega_{IR})|^2 I_{IR} I_{VIS}$, where $\chi_S^{(2)}$ is the interface nonlinear susceptibility (proportional to the number density of interfacial molecules [11,12]), and I_{IR} and I_{VIS} are the intensities of the laser beams at frequencies ω_{IR} and ω_{VIS} , respectively. To lowest order, $\chi_S^{(2)}$ can be described as the sum of a nonresonant term $\chi_{NR}^{(2)}(\theta)$ and a resonant term describing the probed vibrations as Lorentzians [11,12]

$$\chi_S^{(2)}(\theta, \omega_{IR}) = \chi_{NR}^{(2)}(\theta) + \sum_q \frac{A_q e^{i\phi_q}}{\omega_{IR} - \omega_q + i\Gamma_q}, \quad (1)$$

where A_q , ϕ_q , ω_q and Γ_q are the strength, relative phase, resonance frequency and damping constant of the q th mode. The nonresonant part $\chi_{NR}^{(2)}(\theta)$ originates from the nonlinear response of the metal electrons near the surface, which depends crucially on the electronic structure at the interface, i.e., varies with adsorbate coverage θ [14].

For SFG spectroscopy, a broadband IR pulse (~ 150 fs, 20–30 μJ) with a bandwidth of ~ 120 cm^{-1} (FWHM) is used together with a narrow-band visible (VIS) up-conversion pulse of 7.5 μJ at $\omega_{VIS} = 800$ nm. Both beams are p-polarized under grazing incidence of $\sim 75^\circ$ and the resulting SFG signal is spectrally dispersed and detected by an intensified CCD camera. Thus, the SFG spectrum is recorded within the IR bandwidth without tuning the IR frequency. Further experimental details are given in [15].

The Ru(001) single crystal is mounted on a liquid helium cryostat in an ultrahigh vacuum (UHV) chamber (base pressure $< 1 \times 10^{-10}$ mbar). The

sample temperature is digitally controlled by resistive heating and constant sweep rates can be performed at 3 K/min. D₂O (Sigma–Aldrich, isotopic purity >99.9%) is dosed with low flux onto the sample at 140 K via a retractable pinhole doser. Great care is taken to ensure high purity of the D₂O adlayer and growth as crystalline ice I_h – controlled by temperature programmed desorption (TPD); for explicit TPD data and preparation details see [9].

The experiments are performed as follows: after adsorption of 3–10 BL of D₂O, the sample surface is brought in a position facing the ionization volume of a quadrupole mass spectrometer (QMS) while also being optically accessible for SFG spectroscopy. During a slow temperature ramp of 3 K/min, the amount of desorbing D₂O is recorded by the QMS to calibrate the water coverage θ , while simultaneously SFG spectra are taken. The temperature change only decreases the water coverage, which has been verified by comparing the spectra recorded during the temperature ramp to such obtained at corresponding smaller D₂O coverages at 140 K.

3. Results and discussion

The lower part of Fig. 1 shows an exemplary SFG spectrum of 2.0 BL D₂O/Ru(001). The resonance of the free OD stretch mode at 2729 cm⁻¹ can be clearly identified superimposed on the nonresonant background. According to Eq. (1), the SFG intensity is directly proportional to the incident IR intensity $I_{\text{IR}}(\omega_{\text{IR}})$ if no resonances are present within the IR bandwidth. Thus, the relative intensity $I_{\text{IR}}(\omega_{\text{IR}})$ can always be determined from the SFG signal of the bare surface after all water has desorbed at 250 K, i.e., from the nonresonant contribution at $\theta = 0$.

An overview spectrum for 2.0 BL D₂O/Ru(001) is shown in Fig. 2. In order to record the SFG spectrum for such a broad frequency range, the ultrashort IR pulse has to be tuned to adjacent frequency windows (top panel). The data are then analyzed by fitting Eq. (1) to derive the resonance values. To obtain the coverage dependence of the nonresonant contribution $\chi_{\text{NR}}^{(2)}(\theta)$ in Eq. (1), the SFG signal is measured as a function of water

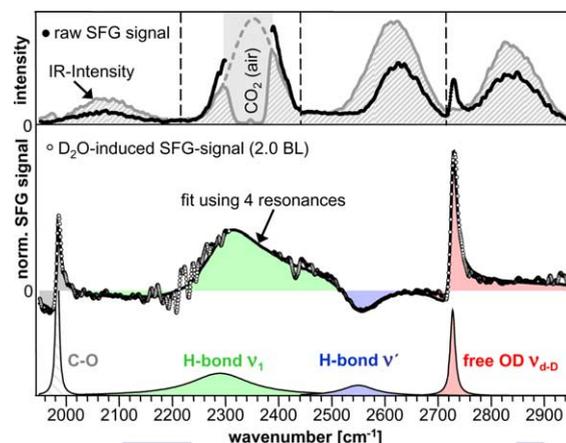


Fig. 2. SFG spectrum of 2.0 BL of D₂O/Ru(001). Top: raw data and corresponding IR intensity for four adjacent frequency windows. Around 2349 cm⁻¹ the asymmetric CO₂ stretch vibration in air absorbs all IR intensity. Bottom: normalized D₂O-induced SFG intensity. The fit using four Lorentzian resonances (real part of the Lorentzians normalized to A_q^2 depicted below) nicely models the data. The different line-shapes originate from the relative phases of $\phi_q = 0.45, -1.75$ and 0.6 for the ν_1, ν' and ν_{d-D} resonance (with respect to the nonresonant contribution). Note: The CO stretch resonance is measured with the nonresonant background on *clean* Ru(001) due to the extreme sensitivity for a minute CO contamination; with water adsorbed no CO is detected.

coverage in a spectral region without any resonant contributions (here >2800 cm⁻¹), from which the amplitude variation $\chi_{\text{NR}}^{(2)}(\theta) = A_{\text{NR}}(\theta) \cdot \chi_{\text{NR}}^{(2)}(\theta = 0)$ is extracted as plotted in Fig. 4. To visualize the adsorbate contributions to the SFG spectrum, the lower part of Fig. 2 depicts the normalized SFG signal induced by the D₂O resonances. This is derived from the overall SFG signal [16] by (i) subtraction of the nonresonant contribution of the SFG signal at the corresponding coverage and (ii) subsequent normalization to the IR intensity. Note that the analysis is performed using the raw data, and only for visualization purposes both, the raw data and its theoretical model using Eq. (1), are transformed as described above.

The coverage dependence of the SFG spectra in the region of interest is shown in Fig. 3 (data were acquired in the whole spectral region depicted in Fig. 2, but, as also visible there, only the region 2200–2750 cm⁻¹ exhibits D₂O vibrational resonances). As can be seen from the agreement with

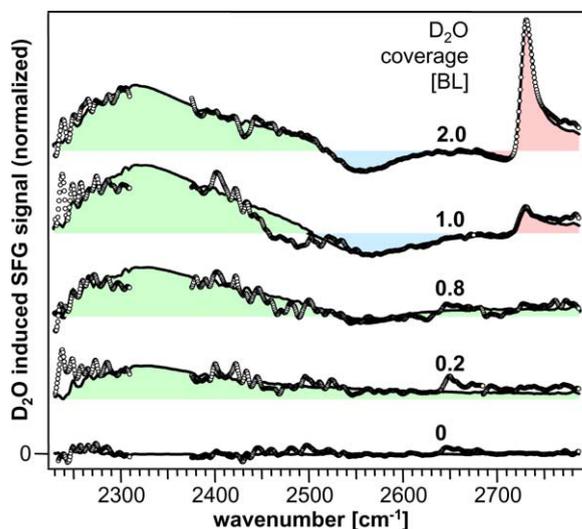


Fig. 3. SFG spectrum and theoretical model as a function of D_2O coverage. The simultaneously recorded TPD was used for coverage calibration, the error in coverage is estimated to be $\leq 10\%$. At 1.0 ± 0.1 BL the free OD mode vanishes.

the fits for all coverages, the data are accounted for by the three D_2O resonances depicted explicitly in Fig. 2; their positions are given in Table 1. With changing D_2O coverage θ , only the amplitudes of the resonances and the nonresonant contribution vary, which are all plotted as a function of θ in Fig. 4. The fact that even for coverages below 1 BL the vibrational spectrum does not change is consistent with the LEED finding of shrinking islands of BL structure [4].

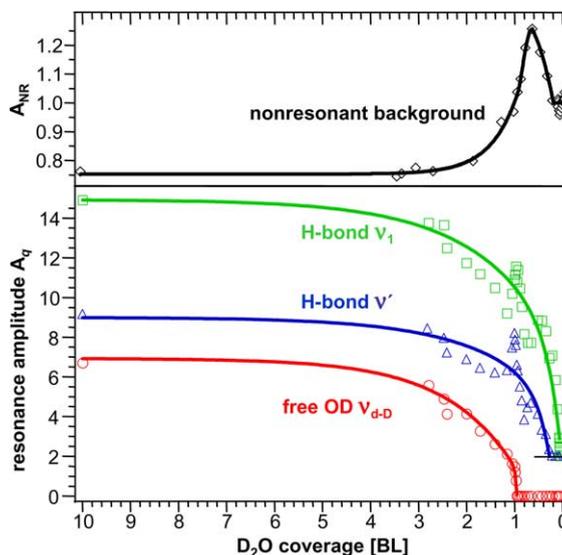


Fig. 4. Coverage dependence of the amplitudes of the nonresonant contribution (topmost), and the three vibrational modes for $D_2O/Ru(001)$ extracted by fits to the data as shown in Fig. 3; lines are a guide to the eye, $A_{v_1, v'}$ are offset for clarity.

The assignment of the three resonances to vibrational modes of D_2O ice I_h is as follows: the most obvious mode is $\nu_{d-D} = 2729 \text{ cm}^{-1}$, the unperturbed dangling-D oscillators (referred to as free OD) at the surface [18,19]. The coverage dependence in Fig. 4 reveals that up to $\theta = 1$ BL no free OD moiety is present, but appears above 1 BL and reaches saturation at ~ 4 BL. In the hydrogen-bonded region ($2200\text{--}2600 \text{ cm}^{-1}$), the strong peak

Table 1

Vibrational resonances of the O–D stretch mode obtained by SFG for D_2O on $Ru(001)$ and $Pt(111)$, compared to theoretical results from DFT calculations (in cm^{-1})

Reference	$\nu(\text{OD})$	$\nu_1(D_2O)$	ν'	$\nu_{\text{DOD} \rightarrow \text{metal}}$	ν_{d-D}
This work, 0.2–10 BL $D_2O/Ru(001)$	–	2290	~ 2550	–	2729^a
[17] 140 BL $D_2O/Pt(111)^b$	–	2300	2540	–	$_{-}^b$
[6] DFT, half-dissociated BL ^c	~ 2000	–	2590	–	–
Intact ‘H-up’ BL	–	2260	~ 2450	–	2706
[24] DFT, ^d intact ‘H-up’ BL	–	~ 2320	~ 2580	–	~ 2790
Intact ‘H-down’ BL	–	~ 2290	~ 2530	$\sim 2600^e$	–

^a Present for >1 BL only.

^b Fig. 4b in [17], 140 BL D_2O ; free OD below detection threshold.

^c Calculated dipole active modes for the $3 \times 3\sqrt{3}$ unit cell.

^d Calculated for $H_2O/Pt(111)$ with an $(\sqrt{3} \times \sqrt{3})R30^\circ$ unit cell; values have been converted to reflect D_2O using an isotope factor of 1.35.

^e (Weak) O–H stretch vibration of the $\text{HOH} \cdots \text{Pt}$ bonded molecules (Fig. 2 and Table II in [24]).

centered at $\nu_1(\text{D}_2\text{O}) = 2290 \text{ cm}^{-1}$ is attributed to the O–D stretch vibrations of D_2O in the hydrogen bonding lattice of ice I_h [20–22]. The assignment of the weaker resonance at $\nu' \sim 2550 \text{ cm}^{-1}$ is less clear. It originates most probably from D_2O molecules at/near the surface lacking the ideal tetrahedral coordination of bulk ice,¹ and thus exhibiting distorted hydrogen bonding (e.g., molecules at the surface with either a ‘dangling-D’ [24] or ‘dangling-O’ [19] atom).

Both hydrogen-bonded modes share roughly the same coverage dependence, saturating at ~ 4 BL (Fig. 4). This means that a net proton-ordering is only present for about 4 BL (additional layers will not contribute to the SFG intensity if they are proton disordered and thus centrosymmetric, like bulk ice I_h [3]).

The implications for the bilayer structure of D_2O on Ru(001) are as follows: the presence of the free OD species only for >1 BL rules out any configuration with unbound D atoms pointing up from the surface (such as ‘bulk-like’ and compressed ‘H-up’, compare Fig. 1). At first glance, this appears to be compatible with the half-dissociated structure [5], and our free OD data have been interpreted accordingly in Feibelman’s study on vibrations of water adlayers on Ru(001) [6]. The latter work finds that the hydrogen-bonded vibrational spectrum between 1950 and 2650 cm^{-1} differs significantly for the half-dissociated BL and the compressed ‘H-up’ BL of intact D_2O molecules (see Fig. 7 in [6]; Table 1): For the half-dissociated BL, a mode at $\sim 2000 \text{ cm}^{-1}$ is predicted, while the $\nu_1(\text{D}_2\text{O})$ -mode at $\sim 2300 \text{ cm}^{-1}$ should be completely absent due to the replacement of every second D_2O molecule in the hydrogen-bonded network by an OD fragment. However, our data clearly show that the collective $\nu_1(\text{D}_2\text{O})$ -mode characteristic for a hydrogen-bonded network of intact D_2O molecules is present at *all* coverages

(0.2–10 BL) investigated, while the vibrational resonance predicted by DFT for the OD species around $\sim 2000 \text{ cm}^{-1}$ is never observed.² Furthermore, our data are in good agreement with previous experimental and theoretical results for intact water molecules: SFG studies of intact D_2O on Pt(111) and Mica [17,23], and also DFT findings for $\text{H}_2\text{O}/\text{Pt}(111)$ [24] (see also Table 1). Therefore, it can only be concluded that the structure of the first D_2O bilayer on Ru(001) is not half-dissociated, but consists of intact D_2O molecules (with the upper limit for an eventual half-dissociated minority species being some percent).

This finding is further corroborated by isotopic scrambling experiments. At coverages just below 1 BL, the water adsorption structure forms islands [4,16]. If the water were partially dissociated it should be possible to titrate the OD species by coadsorption of H on the remaining bare Ru(001) surface sites. However, studies of ~ 0.7 BL total D_2O coverage show no isotopic scrambling with coadsorbed H [16], i.e., in thermal desorption no HOD is formed (instead all D_2O is found to desorb prior to the H_2 recombination reaction).

4. Conclusions for the bilayer structure

What conclusions can now be drawn for the real structure of the first bilayer of D_2O on Ru(001)? A strong boundary condition is the very detailed structural information from Held and Menzel’s LEED study [4], which yields the O atom positions with a small $\sqrt{3} \times \sqrt{3}$ O-atom unit cell. As discussed above, we find that the water molecules are all intact and no free OD species are present in the first BL. Thus, the D atoms have to be arranged with respect to the O-lattice found in LEED such that hydrogen bonds between intact water molecules are formed – with the constraint

¹ In addition to the good agreement with theoretical calculations ([24]; see also Table 1) this is corroborated by the fact that in the interface-specific SFG studies always a strong $\sim 2550 \text{ cm}^{-1}$ feature is reported [17,23]. However, when considering studies of bulk ice, other possible assignments include combination modes [20] or the second overtone of the bending mode [21].

² The calculated vibrational resonances in [6] are very sharp due to the small unit cell employed, implying a highly ordered structure. They should broaden considerably in larger, less proton-ordered unit cells, nevertheless the contradiction to the experimental data remains unchanged.

of no free OD species present. Therefore, the only remaining possibility is the ‘H-down’ structure (Fig. 1b), where every second water molecule exhibits a hydrogen–Ru bond. It should be noted though, that in Fig. 1b a perfectly proton-ordered H-down structure is shown for reasons of clarity, equivalent to a $(\sqrt{3} \times \sqrt{3})R30^\circ$ unit cell for the overall adsorption structure including the D-atom positions. However, such perfect proton-ordering seems highly unlikely, implying that the unit cell including all hydrogen atoms should be much larger, which might also be the origin of the discrepancy between DFT and experiment. Furthermore, as indicated in Fig. 1b, the geometry of the H-down structure would be in line with the atomic positions as observed by LEED [4], when the $\text{DOD} \cdots \text{Ru}$ bond is not taken to be perpendicular to the substrate surface.

For the ‘H-down’ structure one would expect the appearance of a characteristic O–D stretch resonance in the $\text{DOD} \cdots \text{Ru}(001)$ bond. For the according mode, DFT calculations in the case of $\text{H}_2\text{O}/\text{Pt}(111)$ predict a weak vibrational feature ([24], around $\sim 2600 \text{ cm}^{-1}$ when converted to reflect D_2O ; see also Table 1), which suggests that in our experiment this mode can not be identified due to the small intensity, a possibly broad resonance width and overlapping with the ν' mode.

The ‘H-down’ geometry has also been proposed recently for 1 BL $\text{H}_2\text{O}/\text{Pt}(111)$ from the analysis of X-ray scattering results in conjunction with DFT theory [10], and the vibrational properties of ‘H-down’ and ‘H-up’ were studied theoretically [24] (note, however, that the $\text{H}_2\text{O}/\text{Pt}(111)$ $(\sqrt{3} \times \sqrt{3})R30^\circ$ unit cell on which both studies [10,24] base their DFT-modeling is not observed experimentally [25]). Previously, SFG data similar to that presented here revealed that H_2O ice grows on $\text{Pt}(111)$ with some degree of substrate induced net proton-ordering (or ferroelectricity) for up to ~ 30 BL [26,17]. However, the absolute amount of proton-ordering has to be rather small, as otherwise the workfunction would change significantly with every dipole-aligned water layer [27]. In contrast, Fig. 4 shows that for D_2O on $\text{Ru}(001)$ only a maximum of ~ 4 BL are proton ordered to some extent. This is consistent with results for ice nanocrystals [19] and molecular dynamics simulations

of ice [28], which find a transition region of 2–3 BL from crystalline ice to a quite disordered surface layer (with relatively few free OD species). Furthermore, the workfunction data are compatible with this: the significant reduction in workfunction for the first BL of $\sim 1.3 \text{ eV}$ is a consequence of the chemisorption, whereas only a slight further decrease of $\sim 0.1 \text{ eV}$ is observed with the subsequent layers [4,16]. This is once more contradictory to the half-dissociated structure, for which a workfunction change of only 0.3 eV has been computed [5].

5. Summary

Summarizing, our studies show that the first bilayer of D_2O adsorbed on $\text{Ru}(001)$ (i) does not exhibit any free OD species, (ii) consists of intact water molecules forming hydrogen bonds very similar to those of bulk ice I_h and (iii) induces proton-ordering for $\lesssim 3$ successive layers in which the transformation to the UHV/ice interface occurs. Thus from an experimental point of view, the half-dissociated structure as predicted by state-of-the-art DFT [5–7] has to be discarded. Instead, a proton-disordered ‘H-down’ structure with a comparably large unit cell seems most likely; however, the DFT analysis anticipates that this structure does not even wet the surface [5].

This discrepancy points either to basic problems of DFT for hydrogen-bonded systems or a lack in our physical understanding of this prototype system [2]. For example, it cannot be ruled out that the experimentally accessible states are metastable, while the DFT calculations yield the absolute energetic minimum structure, unaccessible due to a barrier which cannot be overcome at the low water adsorption temperatures.³ Hence, it remains a

³ This is supported by the DFT finding of a reaction pathway for water dissociation with a barrier height not allowing for appreciable dissociation rates at the water adsorption temperatures $\lesssim 150 \text{ K}$ [7]. On the other hand, the results of [7] can nicely account for the different degrees of dissociation observed at higher temperatures *during* thermal desorption of D_2O and H_2O [9], due to the significantly different highest desorption temperatures of D_2O and H_2O ($\ll 200 \text{ K}$ and $\gg 200 \text{ K}$, respectively).

challenge to achieve convergence of surface science theory and experiment on this fundamental issue.

Acknowledgements

We thank P.J. Feibelman, G. Held and C. Gahl for helpful discussions and sharing their preprints. This work was supported in part by the Deutsche Forschungsgemeinschaft.

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