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**Interaction of water with graphene/Ir(111) studied by
vibrational spectroscopy**

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Complete List of Authors:	Gleiszig, Robert; Deutsches Elektronen-Synchrotron, FS-NL Creutzburg, Marcus; Deutsches Elektronen-Synchrotron, DESY NanoLab Noei, Heshmat; Deutsches Elektronen-Synchrotron, Research Group X-ray Physics and Nanoscience Stierle, Andreas; Deutsches Elektronen-Synchrotron, FS-NL

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Vibrational fingerprint of graphene supported frozen water clusters

Robert Gleißner,^{†,‡} Marcus Creutzburg,^{†,‡} Heshmat Noei,^{*,†} and Andreas Stierle^{†,‡}

[†]*Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany*

[‡]*Fachbereich Physik, Universität Hamburg, Hamburg Germany*

E-mail: heshmat.noei@desy.de

Phone: +49 (0)40 8998 6011

Abstract

Water in confinement exhibits altered properties in molecular arrangement, bonding and interaction with its neighboring environment, as compared to its bulk counterpart. In this work, periodically arranged D₂O nano droplets of ~ 1 nm size on top of a graphene-iridium moiré superstructure were investigated by Fourier transformation reflection absorption infrared spectroscopy under ultrahigh vacuum conditions at ~ 120 K. The infrared bands of D₂O clusters differ significantly from those observed for bulk D₂O amorphous solid water or crystalline ice phases. Blue shifted symmetric and asymmetric stretching bands with narrower band widths and modified band intensity ratios were observed, pointing to an enhanced internal order and a reduced nearest neighbor distance. Furthermore, two IR bands of 'dangling' deuterium atoms were detected originating from threefold coordinated water molecules at the surface of the clusters and at their interface to the graphene layer. The latter arose only with the transition from the water clusters to an amorphous solid water layer. We propose that upon coalescence, opposing local dipoles trigger a hydrogen bond rearrangement

at the interface. Our results represent a first step towards an atomistic understanding of water in confinement.

Introduction

Water is the most fundamental substance for life, yet the understanding of the principal properties of water in its liquid and solid form, especially in nanometer confined geometries, is far from being complete. The understanding of the molecular structure and dynamics of bulk water and water in confinement is of fundamental importance for solvation science and biological as well as geological processes.¹⁻⁴ The motivation to study water in confinement is to gain a deeper understanding of the complex phase transitions of water and its local order⁵ by minimizing the amount of involved molecules, and furthermore to investigate interactions with the confining environment. Recent scientific work concerns water at various interfaces, where it forms patterns of molecular wetting layers. It was reported that water on surfaces can form half-dissociated adlayers,⁶ ordered structures as 2D stripes and patches⁷ or self-assembled nano sized clusters.⁸ The interaction with a substrate is reported to lead to a preferential orientation of the water molecules,⁹⁻¹³ which hence has impact on micro- to macroscopic properties of water, e.g. the flux through channels inside filtration membranes¹⁴ or other nano channels.¹⁵ As the surface-to-volume ratio is high for nanomaterials, a better understanding of the interplay between enhanced surface tension and hydrogen bonding properties inside water nanodroplets and nanopores is highly desirable.¹⁶

It was recently demonstrated that frozen water clusters of ~ 1 nm size can be periodically arranged on graphene/Ir(111).⁸ The arrangement of the water molecules inside the droplets is presumed to be amorphous, but their internal structure and phase has not been experimentally determined to this point. The moiré pattern of graphene on Ir(111) has a periodicity of 2.53 nm and provides an elegant way to decorate the surface with a high density of small nanoparticles with diameters up to 1.5 nm.^{17,18} At the so-called hexagonal closed packing

(HCP) sites, the graphene layer has the smallest distance to the Ir substrate and acts as a preferred location for the accumulation of adatoms and adsorbed molecules into clusters via interaction with the substrate.¹⁸ At higher coverages, the water clusters coalesce, and are supposed to form a layer of amorphous solid water (ASW).⁸ It was found that at 100 K an ASW film forms on a silica film grown on Mo(112) single crystal, while an ice monolayer film forms on the surface at 140-150 K.¹⁹ Previously we investigated the atomic structure of Pt and Ir nanoclusters on a graphene/Ir(111) support.^{20,21} As a key result, we found that the nanoclusters undergo a compression of up to 4.8% in the Pt case, triggered by the interaction with the graphene and the reduced geometry. The lattice compression can be translated to an effective pressure of ~ 100 MPa which, if also acting on water clusters, may result in interesting phase changes according to the water phase diagram. Such changes in the inter or intra molecular distances may have strong impact on water in solvation processes. Further on, density functional theory calculations for water molecules adsorbed on flat graphene supported by a Cu(111) surface as a weakly interacting metal (comparable to Ir (111)) resulted in slightly lower binding energies for water molecules with oxygen pointing downward to the graphene layer.⁹ For the water cluster phase, the same question of molecular water orientation at the interface arises.

To investigate the molecular water D₂O arrangement of the graphene/Ir(111) supported nanoclusters and their vibrational dynamics we utilized high resolution infrared reflection absorption spectroscopy (IRRAS). IR spectroscopy is the method of choice since the absorption band frequencies as well as their widths are strongly dependent on the water phase, pressure, temperature and sample history.^{19,22-24} The overall shape of the spectral regime between 2300-2650 cm⁻¹ serves as a fingerprint of specific phases and allows one to identify subtle structural changes, which is generally a challenge for nano-confined water.

Figure 1: Sample preparation and D₂O dosing procedure.

Experimental

All experiments are carried out at the DESY NanoLab.²⁵ The Ir(111) single crystal was mounted on a molybdenum sample holder by tantalum clips and introduced into a preparation chamber ($p_{\text{base}} < 10^{-10}$ mbar), which is part of an UHV transfer system. The sample was further prepared as depicted in Fig. 1 and described in the following. The crystal surface was cleaned by repeated Ar sputtering cycles (60 min, $p_{\text{Ar}} = 5 \cdot 10^{-6}$ mbar) and annealing in O₂ ($T = 1300$ K, $p_{\text{O}_2} = 5 \cdot 10^{-7}$ mbar) and vacuum ($T = 1500$ K). After cooling to room temperature, the sample was exposed to $1 \cdot 10^{-7}$ mbar ethylene (C₂H₄) for 45 s. Annealing for 10 min at 1400 K results in the dehydrogenation of the ethylene and formation of small graphene islands on the surface. The flakes orient at the elevated temperature in a R0° rotation with respect to the Ir(111) facet. Further exposure of C₂H₄ at 1200 K results in the growth of the graphene islands until a complete monolayer covers the iridium surface. Subsequent flash annealing was carried out to heal defects in the graphene layer. Low energy electron diffraction and Auger electron spectroscopy were carried out to probe the generation of the Gr/Ir(111) moiré structure (see Fig. S2 and S3). Shortly before the transfer, the samples are heated within the preparation chamber to at least 500 K at a base pressure better than $5 \cdot 10^{-11}$ mbar in order to remove captured adsorbates.

The infrared spectra were obtained by a FT-IRRAS, with capability to operate at ultrahigh vacuum conditions. The sample was transferred to the IR measurement chamber at a base pressure of $5 \cdot 10^{-10}$ mbar after cooling the sample station to 150 K by liquid N₂

cooling to avoid adsorption of residual molecules on the sample. The adsorption experiments were carried out at $T = 117$ K, as Ref. 8 found the water clusters to be stable under these conditions.

H₂O continuously adsorbs at the liquid N₂ cooled IR detector as ice. This is problematic, since it results in the formation of IR bands which overlap with those formed following the exposure of graphene to H₂O (see Fig. S5). The D₂O infrared bands are shifted to lower wavenumbers relative to H₂O, therefore by dosing D₂O instead of H₂O this overlap can be avoided, thus providing an unperturbed signal.

The D₂O was mounted in a glass vial on the gas supply line of the IR chamber. The gas line was previously heated to 120 °C whilst evacuating, in order to remove contaminants from the inside walls. Additionally, the gas line was flushed with argon and subsequently pumped to further remove residual gasses. Repeated freeze-pump-thaw cycles are carried out to remove dissolved gas from the water. Water was dosed via a leak valve into the chamber. The exposures were quantified in units of Langmuir (L) ($1 \text{ L} = 1.33 \cdot 10^{-6} \text{ mbar} \cdot \text{s}$). Details of the dosing are described in the supporting information (Table S1). Note that the obtained spectra are labeled with the total exposure (sum of all exposure steps).

Results and Discussion

In the following, we will present the FT-IR results as a function of the D₂O exposure. Details of the sample preparation and the experimental setup are summarized in the methodology section below and the supporting information (SI). Fig. 2 shows the IR spectra from the Gr/Ir(111) surface at 117 ± 3 K as a function of D₂O exposure between 0-50 Langmuir (L). The IR bands in this work are mainly originating from the D₂O molecules which are adsorbed perpendicular to the surface, as the detection of the flat-laying molecules on metal surfaces in IRRAS is difficult due to the so called surface selection rules.²⁷ According to Ref. 8, the ASW cluster phase is expected to form on the surface up to a coverage of about 2 L

Figure 2: IR spectra in dependence of D_2O exposure on the Gr/Ir(111) substrate. **a)** Exposures up to ~ 5 L result in stretching bands associated with the D_2O ASW cluster phase. **b)** Exposures larger than ~ 7 L result in stretching contributions at lower wavenumbers, which can be associated with the presence of an ASW film.

with 120 D_2O molecules per cluster. The spectra show the regime of the stretching bands (~ 2300 – 2650 cm^{-1}) and the bending mode overtone (2350 cm^{-1}) as well as two features of dangling deuterium atoms (2728 cm^{-1} , 2669 cm^{-1}), which we assign to under-coordinated water molecules.^{19,22,28–30} The dangling deuterium band at 2699 cm^{-1} was not reported in IR studies of the ASW on oxide and metal surfaces. Additionally, the bending mode fundamental and the association band are shown in Figure S1.

In Fig. 2a, the data for the exposure regime up to 5 L are plotted: the symmetric stretching band (ν_s) of D_2O is located at 2477 cm^{-1} , whereas the D_2O asymmetric stretching band (ν_{as}) is at 2542 cm^{-1} for this low coverage regime. The band positions are summarized in Table 1. These modes represent the most dominant vibrational bands in the spectrum. In Fig. 2b the data for an exposure up to 50 L are summarized. The rise of contributions at 2515 cm^{-1} and 2452 cm^{-1} are observed with increasing exposure above 5 L, at which the water clusters were observed by scanning tunneling microscopy to coalesce.⁸ Their line

shape and spectral position are in good agreement with bulk amorphous solid water (ASW film).^{23,24,28,29} Kaya et al. reported a long-range ordered structure of the ASW on the silica surface at 100 K by low energy electron diffraction showing a $c(2 \times 2)$ superstructure with respect to the silica substrate.¹⁹ This observation was further verified by IR spectra showing a broad IR band centered at 3400 cm^{-1} originating from ASW.¹⁹ In comparison with the signal from the ASW layer, generated for exposures larger than $\sim 5\text{-}7 \text{ L}$, the stretching modes of the ASW cluster phase forming at D_2O exposures below 5 L are blue shifted by $\sim 25 \text{ cm}^{-1}$. Also, a noticeable gap between the stretching contributions is present, which was not reported for ASW films, liquid water or crystalline ice so far.

The ASW cluster phase bands at 2542 cm^{-1} and 2477 cm^{-1} show narrower widths than the bands observed in bulk amorphous solid water spectra. The band width of water IR spectra is strongly dependent on the intermolecular distance distribution. An increased internal order reduces the distance distribution between the water molecules, decreasing the band width in IR spectra and thus explaining the gap between the two stretching modes. We can thus deduce that the ASW clusters show a higher degree of internal molecular order compared to ASW films, which may be attributed to the interaction with the graphene layer or the reduced number and nearest neighbors.

The $\sim 25 \text{ cm}^{-1}$ blue shift of the ASW cluster stretching modes compared to the stretching modes of the amorphous solid water film can be explained by an enhancement of intramolecular bond strength between O and D, as a result of the confined geometry. In contrast, the bending mode fundamental position at 1215 cm^{-1} was not changing over the whole exposure range up to 200 L (see Figure S1). This may be related to the fact that the water molecule bond angle does not change from the ASW cluster phase to the ASW film phase.

The development of the bending mode overtone sets in at exposures of $2\text{-}5 \text{ L}$, pointing to a reduction of the Fermi resonance between the symmetric stretch band and the bending mode overtone for the ASW cluster phase. An explanation for this observation can be found in the blue shift of the stretch bands. A Fermi resonance leads to a coupling between the

symmetric stretch mode and bending mode overtone which is possible because of nearly identical vibration frequencies and the same Mulliken symmetry. As a result of the coupling an enhancement of the bending mode overtone band together with a decrease in stretching vibration band intensity is expected, together with an enhanced splitting of the involved bands.^{31,32}

For the ASW cluster phase for exposures up to 5 L the intensity of the symmetric stretch mode at 2477 cm^{-1} is nearly identical to that one of the asymmetric stretch band at 2542 cm^{-1} . The symmetric stretch band was observed to get depopulated relative to the asymmetric stretch band with increasing exposure during cluster coalescence in conjunction with the ASW film formation, see Fig. 2b. At the same time, the bending mode overtone at 2350 cm^{-1} was observed to increase in intensity, supporting the hypothesis of an enhanced mode coupling for the ASW film phase at higher exposures.

In the obtained spectra, a small band was observed for all exposures at 2728 cm^{-1} . The position and intensity of this band suggests that it originates from threefold coordinated water molecules (one hydrogen donor bond, two hydrogen acceptor bonds) directing one 'dangling deuterium atom' (dD) towards the vacuum.^{29,30,33} A feature corresponding to twofold coordinated water molecules is not present in the spectrum, as it is expected to appear at higher wavenumbers (2748 cm^{-1}).³³ Since the band is present for all exposures, it is attributed to dD bonds at the nanocluster and ASW film surface.

Next we will discuss an atomic scale scenario for the ASW cluster and film formation based on the interpretation of our IR results (see Fig. 3): 1. at low exposures, water molecules adsorb on the surface and diffuse into minima of the potential landscape, i.e. the HCP sites (Fig. 3a) presumably with a preferred orientation facing the oxygen atom towards the graphene layer, because of the slight p doping of graphene on Ir(111).³⁴ 2. Upon further exposure of D_2O , the molecules accumulate into clusters at the HCP sites of the moiré pattern as observed by STM.⁸ A strong interaction of water with FCC and HCP rather than TOP domains was observed in the STM images of monolayer water molecules on moiré-structured

Figure 3: Proposed model of the molecular arrangement for different D_2O exposure regimes. a) Molecular adsorption and surface diffusion of D_2O molecules. b) Accumulation of molecules to water nanoclusters with an electrostatic net dipole and dangling deuterium atoms facing towards the vacuum. c) Amorphous solid water film after the coalescence of the clusters. Due to rearrangement, dangling deuterium atoms are facing towards the Gr/Ir(111) support. The net dipole is zero or negligible at this point. d) Close view on the dD atoms at the D_2O -Gr/Ir(111) interface. These features are not necessarily located at the HCP sites of the moiré pattern.

FeO film on Pt(111) by Merte et al.³⁵ The lower interaction of water with the TOP domain was attributed to the weaker electrostatic field above oxygen atoms at the TOP sites, resulting from the smaller rumpling of the FeO.³⁵ At this point two contrary effects may occur: a) the molecules orient the oxygen side to the partially positive deuterium terminated side of the initial molecules; b) the tendency to generate hydrogen bonds to neighboring molecules orients the molecules individually in order to maximize their coordination number. At the surface of the clusters, threefold coordinated water molecules remain, directing dangling deuterium atoms towards the vacuum (2728 cm^{-1}). As the available thermal energy is low, the orientations will not necessarily be thermodynamically favored. An electrical net dipole $\vec{p}$ remains in the clusters (Fig. 3b). The existence of a net dipole for small water clusters was reported by Su et al.,³⁶ investigating water clusters on Pt(111) surfaces at 120-137 K.

3. For further water exposure, the droplets grow in size. Just before coalescence sets in at $\sim 5\text{ L}$, the surfaces of neighboring nanoclusters are close and have local dipoles in opposing directions. Upon coalescence, a cascade of rearrangement by deuterium exchange sets in, in order to minimize the electrostatic repulsion and an amorphous solid water film is formed with a lower degree of internal order. Water molecules at the interface to the Gr/Ir(111) support find no neighboring molecules to bond with, remaining undercoordinated (Fig. 3c and 3d), facing dD to the substrate which are affected by the proximity of the surface (2669 cm^{-1}). Reorientation of hydrogen bonds was previously reported upon heating.³⁷ Here the reorientation is proposed to be triggered by the opposing net dipoles of the clusters as coalescence takes place. The reorientation process and the formation of dangling D bonds at the interface is further supported by the occurrence of a new band at 2669 cm^{-1} (see Figure 2b), which only started to appear at higher exposures for which the amorphous solid water film forms.

Finally we discuss the annealing behavior of the ASW cluster and film phases, demonstrating the power of FT-IR spectroscopy in the identification of adsorbed water phases on surfaces. By repeated IR measurements while increasing the sample temperature from

120 K to room temperature after the deposition of D₂O, irreversible annealing effects were observed, which provide insight into temperature dependent phase transitions.

In the first experiment, the clean sample was exposed to 5 L D₂O, generating the cluster phase (Fig. 4a). Afterwards, the sample was heated while continuing taking IR spectra. The annealing induced structural changes set in at about 140 K, indicated by a slight increase of the cluster phase symmetric stretch band at 2477 cm⁻¹, inline with an increased ordering.³⁸ At slightly higher temperatures, a new band was observed at 2440 cm⁻¹, indicating the onset of crystalline bulk ice I formation.³⁸ At the same time, the band at 2477 cm⁻¹ increased in intensity and the bending mode overtone band at 2350 cm⁻¹ got more pronounced, which may be explained by an enhanced Fermi resonance between the increased ASW cluster phase symmetric stretch band at 2477 cm⁻¹, as well as with the symmetric stretch bulk ice I band at 2440 cm⁻¹. Over all, this observations may be interpreted as a thermally induced structural rearrangement of water molecules in the ASW cluster phase during which also the dangling bond feature at 2669 cm⁻¹ got more pronounced.

Figure 4: IR spectra of the annealing of Gr/Ir(111) under UHV after a) dosing 5 L (ASW cluster phase) and b) 30 L (ASW film) of D₂O. The error bar of the temperatures given is ± 20 K.

With increasing temperature to about 194 K, the spectrum transformed completely: the asymmetric and symmetric stretch bands of ice I were observed at 2488 cm^{-1} and 2440 cm^{-1} , respectively, the latter being the most intense component in the spectrum due to the higher crystalline order of the bulk ice I phase. At higher temperatures, desorption started, which was complete at about 207 K, inline with Ref. 8. At the same time, the bending mode overtone band at 2350 cm^{-1} got more enhanced, which is related to the enhanced Fermi resonance with the symmetric stretch band of ice I, now positioned at lower wave numbers (2440 cm^{-1} as compared to 2477 cm^{-1} for the ASW cluster phase). Overall, also the integrated IR signal increased, which can have the possible cause that after annealing the water molecules in the crystalline ice I phase arrange in such a way, that they exhibit a larger net dipole moment perpendicular to the surface. The two dangling D features at 2728 cm^{-1} and 2669 cm^{-1} interestingly were present after the annealing process. This indicates, that even while rearranging the molecular orientation upon the crystallization process, a certain amount of water molecules stayed under coordinated.

For comparison, the annealing behavior of an amorphous solid water film formed after adsorption of 30 L D_2O at 120 K is presented in Fig. 4b). The onset of structural changes occurred again at about 156 K with a redshift of the stretching band frequencies to the values of crystalline bulk ice I, and a stronger increase of the symmetric stretch band signal, indicative for an increased ordering. With increased annealing temperature, the symmetric stretch band at 2440 cm^{-1} increased more strongly in intensity, inline with the formation of crystalline ice I. The O-D dangling bond signals at 2728 cm^{-1} and 2669 cm^{-1} were observed throughout the entire temperature cycle, inline with the interpretation given above. The desorption set also in at a temperature of 208 K. We can conclude that both the ASW cluster phase as well as the film phase exhibit a transition to crystalline ice I before desorption. No intermediate transition from the cluster phase to the layered ASW phase was identified during the annealing process.

Table 1: Summary of the vibration modes of D₂O observed by IRRAS. All values are given in cm⁻¹

	bending fundamental	bending overtone	stretching fundamentals	
ASW clusters	1215	2350	2477	2542
ASW film	1215	2350	2452	2515
Ice I ³⁸	1212	2355	2440	2488
dD:	towards vacuum: 2728		towards substrate: 2669	

Conclusion

In conclusion, we find that the adsorption of up to ~5 L of D₂O on a Gr/Ir(111) moiré structure at 117 K leads to the generation of a water phase with a unique infrared spectrum. This spectrum originates from water ASW nanoclusters self assembled on the Gr/Ir(111) superstructure. The stretching bands of the cluster phase exhibit a narrowing of the band width, in combination with an enhancement of the symmetric stretch band signal, as compared to the thin film ASW phase formed after higher exposures. Both point to an arrangement with a higher degree of molecular order compared to bulk amorphous solid water. Further on, we observed a blue shift of the stretching bands of the cluster phase relative to the ASW film phase which we attribute to a slightly enhanced intramolecular bond strength. Weak but sharp bands at 2728 cm⁻¹ are assigned to dangling deuterium atoms of threefold coordinated water molecules at the surface of the clusters, facing towards the vacuum. For exposures larger than ~5 L the water nanoclusters coalesce into a layer of ASW, evidenced by the corresponding IR fingerprint. Triggered by the opposing local net dipoles of the clusters, a rearrangement process of the hydrogen bond network takes place. As a result, the dangling D atoms present at the water-graphene interface, giving rise to a second, red shifted line at 2669 cm⁻¹. Furthermore, the IR results demonstrate that annealing of the cluster phase resulted in a transition to crystalline ice and an intermediate transition to thin film ASW was not observed. Our results show that the effect of net dipoles, as well as temperature dependent reorientation of the hydrogen bonds should be considered in order to understand

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3 phase transitions of water when interfaces are involved. In addition, they give evidence for a
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5 confinement induced compression of the ASW cluster phase, which is relevant for solvation
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7 and melting dynamics of water in reduced dimensions, as it occurs in biological or geolog-
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9 ical systems. Our experiments may trigger further experimental and theoretical studies to
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11 determine the atomic structure and dynamics of water in graphene supported nanoclusters.
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14 15 16 Conflicts of interest

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19 There are no conflicts to declare.
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31 32 33 Supporting Information Available

34 35 36 References

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Figure 1: Sample preparation and D₂O dosing procedure.

Figure 2: IR spectra in dependence of D_2O exposure on the $\text{Gr}/\text{Ir}(111)$ substrate. a) Exposures up to ~ 5 L result in stretching bands associated with the D_2O ASW cluster phase. b) Exposures larger than ~ 7 L result in stretching contributions at lower wavenumbers, which can be associated with the presence of an ASW film.

Figure 3: Proposed model of the molecular arrangement for different D₂O exposure regimes. a) Molecular adsorption and surface diffusion of D₂O molecules. b) Accumulation of molecules to water nanoclusters with an electrostatic net dipole and dangling deuterium atoms facing towards the vacuum. c) Amorphous solid water film after the coalescence of the clusters. Due to rearrangement, dangling deuterium atoms are facing towards the Gr/Ir(111) support. The net dipole is zero or negligible at this point. d) Close view on the dD atoms at the D₂O-Gr/Ir(111) interface. These features are not necessarily located at the HCP sites of the moiré pattern.

Figure 4: IR spectra of the annealing of Gr/Ir(111) under UHV after a) dosing 5 L (ASW cluster phase) and b) 30 L (ASW film) of D₂O. The error bar of the temperatures given is ± 20 K.

Figure 1: Exposure dependent D₂O adsorption on Gr/Ir(111): association bands and bending mode fundamental

Figure 2: Low energy electron diffraction pattern in reversed contrast. In the center, the backside of the electron gun covers the (00) reflex. Left: Diffraction pattern of the cleaned Ir(111) surface. Right: Diffraction pattern of the Gr/Ir(111) moiré structured surface.

Figure 4: Schematic image of the FT-IRRAS. The interferometer and detector compartment are evacuated to 3 mbar, whereas the sample environment is under UHV conditions. It is possible to cool the manipulator and thus the sample with liquid nitrogen (LN₂) flow to, and to heat the sample by filament heating. The lowest temperature obtained was 113 K. Via the transfer rod, it is possible to pick up samples in the UHV transfer system and introduce them into the sample compartment. The IR source is a silicon carbide globar. KBr windows are separating the UHV chamber from the other compartments.