

# Water in Confinement: a Spectroscopic Study of D<sub>2</sub>O Nano Clusters on a Graphene-Iridium Moiré Superstructure

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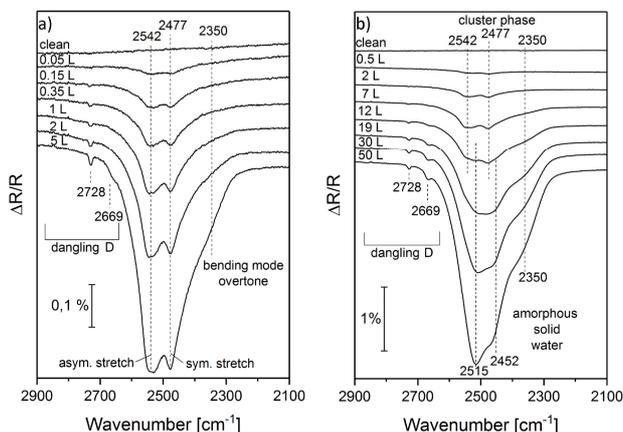
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Confined water is highly interesting due to its unique properties regarding the molecular arrangement, electronic structure and the interaction with its neighboring environment.[1,2] In this study, periodically arranged D<sub>2</sub>O nano droplets of about 1 nm size are generated on top of a graphene-iridium moiré superstructure and probed by a state-of-the-art Fourier transformation reflection absorption infrared spectrometer under UHV at 117 K. We found that the infrared bands of the heavy water clusters differ significantly from those observed for amorphous solid or crystalline phases, showing a characteristic gap at 2500 cm<sup>-1</sup> between two stretching bands.

At low exposures, water molecules adsorb on the surface and diffuse into minima of the potential landscape, i.e. the HCP areas with a preferred orientation facing the oxygen atom towards the graphene support. Michaelides et al. reported n-doping in graphene due to the adsorption of water, when the molecules adsorb from oxygen site to the graphene surface.[3] At higher D<sub>2</sub>O exposures, water molecules accumulate into clusters at the HCP areas of the moiré pattern. At this point two contrary effects occur: a) the molecules orientate the oxygen side to the partially positive deuterium terminated side of the initial molecules and b) the tendency to generate hydrogen bonds to neighboring molecules orient the molecules individually in order to maximize the coordination number of the molecules. At the surface of the clusters, threefold coordinated water molecules remain, directing dangling deuterium atoms towards the vacuum (2728 cm<sup>-1</sup>). For further water exposure, the droplets grow in size, resulting in coalescence and later the amorphous solid water forms with a lower degree of internal order.

There are two features of 'dangling' deuterium atoms originating from undercoordinated water molecules in the infrared spectrum. One of these features is located at noticeable lower wavenumbers than reported thus far, which is presumably the result of a rearrangement effect triggered by the coalescence of the droplets. The other feature originates from the threefold coordinated water molecules at the surface of the water clusters. [4, 5, 6]



**Fig. 1:** IR spectra of D<sub>2</sub>O on Gr/Ir(111).  
a) Exposures up to 5 L associated with heavy water nanoclusters.  
b) Exposures larger than 7 L associated with the presence of ASW.

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