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Fathoming ice

Using non-linear ultrafast spectroscopy to look at interfacial properties

Sudera, P.

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Summary

Water has a 71% coverage on Earth, of which only 0.001% is present in the atmosphere in the form of small droplets, ice crystals, and water vapour. Despite a small fraction, water in its condensed states in the atmosphere has implications in heterogeneous photochemical reactions, most notable being the catalysis of ozone hole formation on crystalline ice surfaces. Understanding molecular structure, dynamics and energy transfer pathways at water interfaces, which are the immediate reaction sites, are thus a gateway to understanding fundamentally relevant physical, chemical and biological processes. Vibrational spectroscopy is a suitable method to study the dynamic cohesive three-dimensional hydrogen bond network of water in its liquid and solid states. The vibrational modes of water are sensitive to the hydrogen bond environment and provide information on the hydrogen bond strength and types. By using the second-order non-linear technique Sum Frequency Generation (SFG) spectroscopy in the Infrared frequency range, vibrational properties of specifically the interface can be obtained. This thesis is a comprehensive study of the interfacial vibrational properties of water in its solid and liquid states, to answer fundamental questions on the microscopic differences we observe for the two states.

The first experimental chapter is centred on probing the spectral region around 1600 cm^{-1} where we perform the first H-O-H vibrational bend mode measurements of interfacial ice. From isotopic dilution measurements on water, it is known that the vibrational bend mode is less influenced by intermolecular coupling compared to the stretch region, making it interesting to study systems without spectral complications due to intermolecular coupling effects. The bend mode is also important for vibrational relaxation mechanisms, acting as an intermediate between the high-frequency stretch, and the low-frequency librational and rotational bands. Surprisingly, the interfacial vibrational bend mode of ice is considerably wider in comparison to liquid water. In contrast, the vibrational stretch band of ice is considerably narrower for ice than water. Moreover, the vibrational stretch mode in its intensity and central frequency is strongly temperature dependent, while hardly any temperature effects were observed for the bend mode. Our measurements reveal that the ice bend mode is primarily homogeneously broadened. This is an interesting result, pointing towards ultrafast pure dephasing of the bend mode, thereby asserting the importance of the bend mode region for energy transfer mechanisms. Further comparison of the bend mode for ice and water, and differences to the stretch mode shed more light on the structure of interfacial ice.

The second experimental chapter explores the possibility of proton order at the ice interface. It is known that the bulk of ice, although having an ordered crystalline arrangement of oxygen atoms, has a disordered hydrogen arrangement throughout the entire temperature range till absolute zero. At the surface however, due to different electrostatics than in the bulk, reconstruction of the proton arrangement is proposed to occur. We measure the -OH stretch vibrational SFG spectra of ice, ranging from the low-frequency strongly hydrogen-bonded, to the high-frequency free-OH region, as a function of temperature. The low-frequency 3200 cm^{-1} stretch region, being sensitive to relative orientation of dipoles, is a potential measure of the orientational disorder of water molecules at the ice surface. Experimental measurements are correlated to calculated SFG spectra in an attempt to unravel the nature and mechanism of proton ordering on the surface of ice. Estimations of the enthalpic and entropic contributions of differently proton-ordered surfaces are performed to complement the simulation models and experimental data. Our understanding is far from complete, and through our thorough analysis we hope to be able to encourage further experimental and

theoretical work in this direction. Specifically, simple entropic and enthalpic contributions do not sustain in the temperature range of our experimental study; the data however could be described by a simple disordered to ordered transition, with an associated reaction enthalpy.

The third experimental chapter uses an advanced pump-probe scheme of SFG spectroscopy to perform time-resolved measurements in the vibrational stretch region of interfacial ice. We employed the pump-probe method on both ice and water, in the hydrogen-bonded and the free-OH stretch region, to elucidate vibrational relaxation dynamics of the two systems. We find a faster relaxation time constant for ice in the hydrogen-bonded region compared to water, but surprisingly a rather slow time constant in the free-OH region. These differences in dynamics can point towards differences in photochemical reaction mechanisms for ice and water. Specifically, our results potentially shed light on the efficient catalytic properties of ice, possibly explained due to better adsorption of species on the ice surface because of slower re-orientation of the free-OH species, when compared to water.

Finally, the last experimental chapter is focussed on understanding if the molecular structure or the structural order is majorly accountable for the ice nucleation efficiency of a substance. We looked at the water-cholesterol interface, combining SFG experiments, ice nucleation assay experiments, and MD simulations to understand the ice nucleating activities of cholesterol in its crystalline and monolayer forms. From a comparison of the different physical forms explored of the same ice nucleating agent cholesterol, varying in structure flexibility and order, we conclude that order outweighs molecular structure, as the ordering of the monolayer directly impacts the ice nucleating efficiency. This work may provide some guidelines into designing of next-generation ice-nucleating agents, especially focussing on its supra-molecular chemistry.

Samenvatting

71% van de aarde is bedekt met water. Slechts 0,001% daarvan is aanwezig in de atmosfeer in de vorm van kleine druppels, ijskristallen en waterdamp. Ondanks zijn kleine fractie heeft water in gecondenseerde toestand in de atmosfeer belangrijke implicaties in heterogene fotochemische reacties, met als meest opmerkelijke de katalyse van de vorming van ozongaten aan kristallijne ijsoppervlakken. Inzicht in de moleculaire structuur van en de dynamica en energieoverdracht aan wateroppervlakken, is dus belangrijk om fysische, chemische en biologische processen te begrijpen. Vibratiespectroscopie is een geschikte methode om het dynamische driedimensionale waterstofbruggennetwerk van water in zijn vloeibare en vaste toestand te bestuderen. De trillingsmodes van water zijn gevoelig voor de waterstofbrug omgeving en geven informatie over de waterstofbrug sterkte en types. Door gebruik te maken van de tweede-orde niet-lineaire techniek somfrequentiegeneratie (SFG) spectroscopie in het infrarode frequentiegebied, kunnen vibratie-eigenschappen van specifiek het oppervlak worden verkregen. Dit proefschrift gebruikt de vibratie-eigenschappen van water aan een oppervlak in zijn vaste en vloeibare toestand, om fundamentele vragen te beantwoorden over de microscopische verschillen die we waarnemen voor de twee toestanden.

Het eerste experimentele hoofdstuk is gericht op het spectrale gebied rond 1600 cm^{-1} waar we voor de eerste keer de H-O-H buigvibratie van het oppervlak van ijs hebben kunnen meten. Uit isotopische verdunningsmetingen aan water is bekend dat de buigvibratie minder wordt beïnvloed door intermoleculaire koppeling dan de strekvibratie; deze vibratie maakt het dus mogelijk water te bestuderen bijna zonder spectrale complicaties als gevolg van intermoleculaire koppelingseffecten. De buigvibratie is ook belangrijk voor trillingsrelaxatiemechanismen, omdat deze vibratie fungeert als een intermediair tussen de hoogfrequente strekband en de laagfrequente libratorische en rotationele banden. Onze data laten zien dat de buigmodus van ijs aan het ijs-lucht grensvlak aanzienlijk breder is in vergelijking met vloeibaar water. Daarentegen is de strekvibratieband van ijs aanzienlijk smaller dan die van water. Bovendien is de intensiteit en de centrale frequentie van de strekvibratieband sterk afhankelijk van de temperatuur, terwijl er nauwelijks temperatuureffecten zijn waargenomen bij de buigvibratieband. Onze metingen laten zien dat de buigmodus van ijs voornamelijk homogeen verbreed is. Dit is een interessant resultaat, dat wijst op ultrasnelle pure dephasing van de buigmodus, waarmee het belang van de buigmodus voor energieoverdracht wordt bevestigd. Verdere vergelijking van de buigmodus voor ijs en water, en verschillen met de strekmodus werpen meer licht op de structuur van oppervlakte-ijs.

Het tweede experimentele hoofdstuk onderzoekt de mogelijkheid van protonorde aan het grensvlak van ijs. Hoewel in bulk ijs de zuurstofatomen volgens het kristalrooster zeer geordend zijn, zijn de waterstofatomen over het gehele temperatuurbereik tot aan het absolute nulpunt zeer ongeordend. Aan het oppervlak echter, als gevolg van een andere elektrostatica dan in de bulk, zou een reconstructie van de protonorde plaats moeten kunnen vinden. Met SFG hebben we de O-H strekvibratie van ijs, in het waterstofgebonden en het vrije O-H gebied, als functie van de temperatuur gemeten. Het signaal bij 3200 cm^{-1} van de waterstofgebrugde molekulen is gevoelig voor de relatieve oriëntatie van dipolen en dus een potentiële maat voor de oriëntatie van watermoleculen aan het ijsoppervlak. De experimenten worden gecorrigeerd aan berekende SFG spectra in een poging om de aard en het mechanisme van proton ordening aan het oppervlak van ijs te ontrafelen. Schattingen van de enthalpische en entropische bijdragen van verschillend protongeordende oppervlakken worden uitgevoerd om de simulatiemodellen en experimentele gegevens aan te vullen. Ons inzicht is verre van volledig. Door onze grondige analyse hopen we toekomstig experimenteel en

theoretisch werk in deze richting te kunnen aanmoedigen. In het bijzonder, de eenvoudige entropische en enthalpische bijdragen laten zien dat pas in de buurt van het absolute nulpunt protonorde aan het oppervlak plaats zou vinden. De experimenten kunnen beschreven worden door een eenvoudige ongeordende naar geordende overgang, met een bijbehorende reactie-enthalpie.

Het derde experimentele hoofdstuk maakt gebruik van een geavanceerd pomp-probe schema van SFG spectroscopie om tijdsopgeloste metingen uit te voeren in het strekvibratie gebied van het ijsoppervlak. We hebben de pomp-probe methode toegepast op zowel ijs als water, in het waterstof-gebonden en het vrije-OH strekgebied, om de dynamica van de trillingsrelaxatie van de twee systemen op te helderen. We vinden een snellere relaxatie voor ijs in het waterstof-gebonden gebied dan voor water, maar verrassend genoeg een eerder trage relaxatie in het vrije-OH gebied. Deze verschillen in dynamica kunnen wijzen op verschillen in fotochemische reactiemechanismen voor ijs en water. Meer specifiek, onze resultaten werpen mogelijk licht op de efficiënte katalytische eigenschappen van ijs, mogelijk te verklaren door betere adsorptie van molekulen aan het ijsoppervlak als gevolg van langzamere reoriëntatie van de molekulen met een vrije OH, vergeleken met water.

Het laatste experimentele hoofdstuk is gericht op de vraag of de moleculaire structuur of de ordening van de molekulen in belangrijke mate verantwoordelijk is voor de ijsvormingsefficiëntie van een stof. We hebben gekeken naar het grensvlak tussen water en cholesterol, waarbij we SFG-experimenten, ijsvormingsexperimenten en MD-simulaties hebben gecombineerd om te onderzoeken wat bepalende factoren zijn voor de formatie van ijs. We hebben cholesterol in twee verschillende fysische vormen, kristallijn en als monolaag vergeleken. We concluderen dat ordening zwaarder weegt dan moleculaire structuur, omdat de ordening van de monolaag direct van invloed is op de efficiëntie van ijsformatie. Dit werk kan een aantal richtlijnen geven voor het ontwerpen van de volgende generatie ijs-nucleatiemiddelen, waarbij de aandacht vooral uitgaat naar de supramoleculaire chemie.

Publications covered in the thesis

1. Sudera, P., Cyran, J.D., Deiseroth, M., Backus, E.H.G., Bonn, M. Interfacial Vibrational Dynamics of Ice Ih and Liquid Water. *J. Am. Chem. Soc.* 2020, 142, 28, 12005–12009.
2. Sudera, P., Cyran, J.D., Bonn, M., Backus, E.H.G., Interfacial Vibrational Spectroscopy of the Water Bending Mode on Ice Ih. Just *Published*, *J. Phys. Chem. C* (2021). DOI: 10.1021/acs.jpcc.1c08046
3. Sosso, G.C., Sudera, P., Kunert, A.T., Whale, T.F., Fröhlich-Nowoisky, J., Bonn, M., Michaelides, A., Backus, E.H.G., Molecular Structure versus Structural Order: Understanding Heterogeneous Ice Nucleation. *Submitted*.

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