# Summary

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[-2010 Burke 18](#_Toc487109743)

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[-2009 Malenkov 19](#_Toc487109746)

[Liquid water and ices: understanding the structure and physical properties 19](#_Toc487109747)

[Structure & properties of condensed H2O, 15 ice modifications (9 (+ 1) crystalline), transition fields between structures, metastable modifications (Ic, IV, XII, & several ASW), diffusion coefficient of water molecules in dense regions of network is lower than in loose regions, but increase of density of entire network gives rise to an increase of diffusion coefficient 19](#_Toc487109748)

[-2001 Devlin 19](#_Toc487109749)

[Structure, spectra, and mobility of low-pressure ices: Ice I, amorphous solid water, and clathrate hydrates at T < 150 K 20](#_Toc487109750)

[Low-T behavior of ice I, (microporous) ASW & clathrate hydrates 20](#_Toc487109751)

[-2003 Baragiola 20](#_Toc487109752)

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[Characterisation 21](#_Toc487109755)

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[Spontaneous cracking of amorphous solid water films and the dependence on microporous structure 21](#_Toc487109757)

[Cracking of ASW: critical thickness increases with deposition T (10 – 50 K) & angle (0 – 55°) -> porosity dependent, modelling of tensile strength & stress, quartz crystal microbalance & optical interferometer & infrared spectrometer 21](#_Toc487109758)

[2016 Kouchi 21](#_Toc487109759)

[Matrix sublimation method for the formation of high-density amorphous ice 21](#_Toc487109760)

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[-2015 Parmentier 21](#_Toc487109762)

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[H-atom dynamics in several forms of ASW, inelastic neutron scattering, mean kinetic energies increase with increasing density (weaker H-bonds) vibrational potential energy surfaces get steeper, change in O-H stretching component with density stronger than suggested by e.g. Raman spectroscopy 22](#_Toc487109764)

[? 2015 Bu 22](#_Toc487109765)

[Effect of microstructure on spontaneous polarization in amorphous solid water films 22](#_Toc487109766)

[Surface voltages (Vs) of ASW (vapour deposited below 110 K), Kelvin probe measurements, Vs increases with film thickness &decreases with deposition T & angle, decreases by ≈ 80 % when annealed 30 K above deposition T, -> polarization in ASW is governed by incompletely coordinated water molecules, dangling with unbalanced dipoles at internal surface of pores 22](#_Toc487109767)

[? 2015 Silonov 22](#_Toc487109768)

[Amorphous Ice 23](#_Toc487109769)

[ASW only below glass transition @ 136 K, X-ray diffraction, 258 – 273 K, coexistence of ASW & hexagonal ice near melting point, radial distribution functions (near melting point first maximum of radial distribution function of ASW close to position of radius of first coordination sphere of hexagonal ice), isothermal changes of ice at 263 K 23](#_Toc487109770)

[-2015 Cazaux 23](#_Toc487109771)

[Pore evolution in interstellar ice analogues: Simulating the effects of temperature increase 23](#_Toc487109772)

[Porosity of ASW: Kinetic Monte Carlo simulations, thermal evolution of porosity & SSA, 10 – 120 K, accretion of gas-phase water & migration on surfaces (top layer & within bulk), with increasing T total surface of pores decreases to great extend while total volume decreases only slightly -> small pores connect and merge 23](#_Toc487109773)

[-2014 Isokoski 24](#_Toc487109774)

[Porosity and thermal collapse measurements of H2O, CH3OH, CO2, and H2O:CO2 ices 24](#_Toc487109775)

[Compaction of ice (H2O, CH3OH, CO2, mixed H2O:CO2 = 2:1) upon heating, astronomically relevant T-range, Laser interference & FTIR, for ASW the full loss of dangling OH bonds is not a proof for full compaction, for other ices thermal segregation benefits from higher degree of porosity 24](#_Toc487109776)

[-2013 Garrod 24](#_Toc487109777)

[Three-dimensional, off-lattice Monte Carlo kinetics simulations of interstellar grain chemistry and ice structure 24](#_Toc487109778)

[Monte Carlo kinetics model (using grain surface atom locations rather than fixed lattice structure), H & O atoms accrete onto grain to produce H2O, H2, O2, H2O2, porosity depends on gas density (2 × 104 cm−3 (dark interstellar clouds) produces fairly smooth & non-porous ice mantle), H2 formed collets in micropores, larger pores not filled with H2, direct deposition of water molecules onto grain indicates that amorphous ices formed this way may be significantly more porous than interstellar ices formed by surface chemistry 24](#_Toc487109779)

[-2013 Shephard 25](#_Toc487109780)

[Structural Relaxation of Low-Density Amorphous Ice upon Thermal Annealing 25](#_Toc487109781)

[LDA (prepared from HDA or vapour deposited) annealing, Raman & FTIR spectroscopy, structural relaxation -> increase of local and long-range order (starting before crystallisation and not finished at onset of crystallisation) -> contradicting findings on glass transition 25](#_Toc487109782)

[-2012 Maté 25](#_Toc487109783)

[A comparative study of the porosity and crystallization kinetics of compact and porous water ice 26](#_Toc487109784)

[Porosity and isothermal crystallization kinetics of ASW (vapour-deposited) & HGW (hyperquenched liquid droplets), ASW ≈ 7 x more porous than HGW, little difference in 150 K crystallisation between ASW & HGW (probably due to pore collapse in ASW, possible existence of different ASW phase at 14 K. 26](#_Toc487109785)

[-2012 Bossa 26](#_Toc487109786)

[Thermal collapse of porous interstellar ice 26](#_Toc487109787)

[ASW pore collapse, 20 -120 K, thickness (optical interference) & porosity/phase (FTIR) measurements, porous ASW: thickness decreases by (12 ± 1) % between 20 and 120 K, less porous ASW: smaller thickness decrease, crystalline ice: negligible thickness decrease 26](#_Toc487109788)

[-2012 Maté 26](#_Toc487109789)

[Morphology and crystallization kinetics of compact (HGW) and porous (ASW) amorphous water ice 27](#_Toc487109790)

[Porosity, SSA & Crystallisation of ASW & HGW: 14 – 150 K, CH4 adsorption -> SSA = 280 ± 30 m2 g-1 ( ASW) and SSA = 40 ± 12 m2 g-1 (HGW), crystallisation rate constant (≈ 7 x 10-4 s-1) independent of deposition T (14, 40, 90 K), hints towards different ASW structure at very low (14 K) T 27](#_Toc487109791)

[-2011 Wu 27](#_Toc487109792)

[Porosity and crystallization of water ice films studied by positron and positronium annihilation 27](#_Toc487109793)

[Porosity (< 1 nm) of ASW & crystalline ice, variable-energy positron annihilation spectroscopy (VEPAS), energetics of structural phase changes 27](#_Toc487109794)

[2010 Toburen 27](#_Toc487109795)

[Electron Emission from Amorphous Solid Water Induced by Passage of Energetic Protons and Fluorine Ions 28](#_Toc487109796)

[Doubly differential electron emission yields, ASW on copper (50 K), transmission of 6 MeV protons & 19 MeV fluorine ions, electron energies (time of flight), provide benchmark tests for Monte Carlo track structure codes (used for assessing effects of radiation on biological effectiveness) 28](#_Toc487109797)

[-2010 Wu 28](#_Toc487109798)

[Structural and Phase Changes in Amorphous Solid Water Films Revealed by Positron Beam Spectroscopy 28](#_Toc487109799)

[Positron beam spectroscopy, ASW (vapour deposited, 50 – 150 K, porosity & crystallisation, crystallisation occurs just below 140 K (topmost 80 nm crystallise at 90 – 100 K) 28](#_Toc487109800)

[2009 Winkler 28](#_Toc487109801)

[Relaxation effects in low density amorphous ice: Two distinct structural states observed by neutron diffraction 29](#_Toc487109802)

[Neutron diffraction on low density amorphous ice (produce from high density ASW by isobaric warming or very high density ASW by isothermal compression), -> two different forms of LDA (different compression behaviour & structures (atomistic modelling -> competition between short & intermediate order & disorder)) 29](#_Toc487109803)

[2008 Paschek 29](#_Toc487109804)

[Thermodynamic and Structural Characterization of the Transformation from a Metastable Low-Density to a Very High-Density Form of Supercooled TIP4P-Ew Model Water 29](#_Toc487109805)

[Liquid-liquid transition (TIP4P-Ew model water), 150 – 360 K, low/high/very high density transformations 29](#_Toc487109806)

[-2008 Gálvez 29](#_Toc487109807)

[Trapping and adsorption of CO2 in amorphous ice: A FTIR study 30](#_Toc487109808)

[SSA of ASW: Spectroscopy on CO2 ice (trapped in ASW pores), deposition at 95 K (simultaneously or sequentially), CO2 infrared bands shift & split in both cases (interaction with water molecules), larger amount of CO2 trapped in ASW in co-deposition, in sequential deposition most CO2 trapped in macropores of ASW, phase transition at 140 K -> CO2 molecules relocate -> similar bulk structure to co-deposited samples 30](#_Toc487109809)

[-2007 Raut 30](#_Toc487109810)

[Characterization of porosity in vapor-deposited amorphous solid water from methane adsorption 30](#_Toc487109811)

[Porosity of ASW via quartz crystal microgravimetry, UV-visible interferometry, and infrared reflectance spectrometry in tandem with methane adsorption: microporosity for all deposition methods, but collimated depositions show additional mesoporosity (up to 140 K (crystallization)), higher binding energy for collimated deposition, methane on dangling OH bonds -> no multilayer condensation inside micropores (methane coating the walls instead of filling the pore volume) 30](#_Toc487109812)

[-2007 Malyk 31](#_Toc487109813)

[Trapping and Release of CO2 Guest Molecules by Amorphous Ice 31](#_Toc487109814)

[Trapping and release of 13CO2 by porous ASW (13CO2 on top of/below/codeposited with ASW), TPD & FTIR, some 13CO2 becomes trapped when annealing ASW (amount depends on deposition method), two stage release of trapped 13CO2: 1. majority escapes at ASW-to-cubic transition (165 K), 2. rest desorbs together with cubic ice (185 K) -> must be trapped in cavities that do not open during crystallisation 31](#_Toc487109815)

[-2007 Cuppen 31](#_Toc487109816)

[Simulation of the formation and morphology of ice mantles on interstellar grains 31](#_Toc487109817)

[Simulations (continuous-time random-walk Monte Carlo), production rate & morphology of water dominated ice mantles containing CO & CO2, result: ice mantles only grow in denser regions 31](#_Toc487109818)

[? 2006 Laffon 32](#_Toc487109819)

[Radiation effects in water ice: A near-edge x-ray absorption fine structure study 32](#_Toc487109820)

[Structure and composition of vapour-deposited (porous amorphous solid water (p-ASW) & crystalline (Icryst)) ice films irradiated at 20 K with soft x-ray photons (3–900 eV), near-edge x-ray absorption fine structure spectroscopy (NEXAFS), 20 – 150 K, Icryst becomes amorphous, low-density p-ASW becomes high-density ASW (Iah), then (50 – 90 K) very high density ASW (Iavh), then partially crystallises (150 K) 32](#_Toc487109821)

[2006 Mason 32](#_Toc487109822)

[VUV spectroscopy and photo-processing of astrochemical ices: an experimental study 32](#_Toc487109823)

[VUV spectroscopy, morphology of various molecular ices 32](#_Toc487109824)

[? 2005 Souda 33](#_Toc487109825)

[Probing Surface Properties and Glass-Liquid Transition of Amorphous Solid Water: Temperature-Programmed TOF-SIMS and TPD Studies of Adsorption/Desorption of Hexane 33](#_Toc487109826)

[ASW-hexane interaction, 120 – 165 K, surface diffusion of molecules even below 120 K, abrupt dewetting at 165 K (glass-liquid transition), fluidity of supercooled liquid phase 33](#_Toc487109827)

[-2004 Manca 33](#_Toc487109828)

[Volumetric and infrared measurements on amorphous ice structure 33](#_Toc487109829)

[Adsorption isotherm volumetry & FTIR spectroscopy, ASW characterisation (porosity, SSA, crystallisation), annealing induced modifications, number of surface sites decreases before crystallisation, non-microporous ice can have large specific surface area 33](#_Toc487109830)

[-2003 Dohnálek 34](#_Toc487109831)

[The deposition angle-dependent density of amorphous solid water films 34](#_Toc487109832)

[ASW characterisation (laser optical interferometry): film thickness & density of ASW films (vapour deposited @ 22 K, collimated molecular beam, angle varied between normal & oblique incidence), normal incidence films presumed to be compact (0.94 g/cm3), glancing incidence ρ = 0.16 g/cm3 (> 80 % porosity), in agreement with ballistic deposition simulations 34](#_Toc487109833)

[? 2003 Maté 34](#_Toc487109834)

[Experimental Studies of Amorphous and Polycrystalline Ice Films Using FT-RAIRS 34](#_Toc487109835)

[ASW & crystalline H2O ice (vapour deposited), < 100 nm – 5 μm thickness, FT-RAIRS, Al & Au substrates (similar results for both), optical effects (surface suppression/vibrational mode enhancement) vary with thickness, spectral simulations (Fresnel model) 34](#_Toc487109836)

[2002 Finney 35](#_Toc487109837)

[Structure of a New Dense Amorphous Ice 35](#_Toc487109838)

[Neutron diffraction VHDA, double occupancy of stabilising interstitial found in HDA, VHDA to LDA transition is very sharp (thermal unlocking of interstitial) & kinetically controlled, VHDA better candidate for second putative liquid phase of H2O than HDA 35](#_Toc487109839)

[-2002 Parent 35](#_Toc487109840)

[Structure of the water ice surface studied by x-ray absorption spectroscopy at the O K-edge 35](#_Toc487109841)

[Vapour-deposited ASW & crystalline ice (38 – 150 K, UHV), NEXAFS (bulk sensitive) & PSD-NEXAFS (photon-stimulated desorption mode -> surface sensitive), ASW: 38 – 55 K: change from HDA to LDA, H2O-H2O molecular distance at surface always longer than in bulk 35](#_Toc487109842)

[? 2002 Tulk 36](#_Toc487109843)

[Structural Studies of Several Distinct Metastable Forms of Amorphous Ice 36](#_Toc487109844)

[High-density ASW annealing, neutron & X-ray diffraction, 5 distinct ASW forms – all metastable at each anneal T, structure evolves systematically between 4 – 8 K 36](#_Toc487109845)

[-2002 Manca 36](#_Toc487109846)

[Spectroscopic and volumetric characterization of a non-microporous amorphous ice 36](#_Toc487109847)

[Porosity & SSA of ASW & crystalline ice, N2, CH4 and Ar adsorption, adsorption isotherm volumetry & infrared spectroscopy, non-microporous ice can have large SSA 36](#_Toc487109848)

[2002 Finney 36](#_Toc487109849)

[Structures of High and Low Density Amorphous Ice by Neutron Diffraction 37](#_Toc487109850)

[Neutron diffraction, HDA & LDA, local similarities between LDA & Ih, path: HDA -> liquid -> LDA -> Ih (second shell radial order increases, spatial order decreases), reason: fifth first neighbour interstitial restricts orientation of first shell H2Os. 37](#_Toc487109851)

[-2000 Barker 37](#_Toc487109852)

[Voids in the H-bonded network of water and their manifestation in the structure factor 37](#_Toc487109853)

[oxygen-oxygen structure factor SOO(Q) peak of liquid water shows unusual doublet structure (shifting with pressure), limits correspond to peak positions of low/high density ASW -> polyamorphism of H2O, position determined by nearest-neighbour separation of voids in spatial distribution of oxygen atoms 37](#_Toc487109854)

[-2000b Sadtchenko 37](#_Toc487109855)

[Interactions of CCl4 with Thin D2O Amorphous Ice Films. 2. Variation of Desorption Kinetics with Ice Preparation Conditions and Evidence for Distinct Structures of Low-Density Amorphous Ice 37](#_Toc487109856)

[Three metastable forms of microporous ASW (D2O): Iμ, Iδ, and Iϵ, TPDMS, desorption kinetics of CCl4, that Iμ, Iδ, and Iϵ characterized by relative abundances of two-, three-, and four-coordinated D2O molecules at the ice surface respectively, barriers to diffusion of D2O on surface (EDδ = 5 ± 1 kcal/mol, EDϵ = 9 ± 2 kcal/mol), phase diagram for thin D2O ice films 37](#_Toc487109857)

[-2000a Sadtchenko 38](#_Toc487109858)

[Interactions of CCl4 with Thin D2O Amorphous Ice Films, Part I: A Nanoscale Probe of Ice Morphology 38](#_Toc487109859)

[Structure of vapour deposited ASW & solid (crystalline?) ice: TPDMS (TPD mass spectrometry), 500 ML D2O ASW, 95 – 190 K, adsorption of CCl4 on ASW, 95 K deposition: microporous amorphous ice (CCl4) clustering in ASW pores), 130 K deposition: pore-free solid ice, two structurally different forms of ice coexist at T between 95 and 130 K 38](#_Toc487109860)

[-1999 Stevenson 39](#_Toc487109861)

[Controlling the Morphology of Amorphous Solid Water 39](#_Toc487109862)

[Porosity of ASW depends on incident angle of H2O molecules 39](#_Toc487109863)

[1999 Paschek 39](#_Toc487109864)

[Simulation Study on the Diffusive Motion in Deeply Supercooled Water 39](#_Toc487109865)

[Molecular dynamics studies, diffusion process in supercooled liquid water (255 – 360 K), ST2 liquid shows no glass transition, hopping process controls reorientational & translational motions, activation energy: 115 kJ/mol 39](#_Toc487109866)

[1999 Klug 39](#_Toc487109867)

[Dynamics and Structural Details of Amorphous Phases of Ice Determined by Incoherent Inelastic Neutron Scattering 40](#_Toc487109868)

[Neutron scattering of HDA (from pressure0induced amorphisation), LDA (from annealing HDA, hyperquenched liquid water, Ih, & Ic, H-bond interaction in LDA differ from hyperquenched water & are stronger than in HDA 40](#_Toc487109869)

[-1996 Li 40](#_Toc487109870)

[Inelastic neutron scattering study of high density amorphous water ice 40](#_Toc487109871)

[ASW characterisation, inelastic neutron scattering (ISIS) & spectroscopy, high density amorphous ice & high T metastable phases (low density amorphous ice, cubic and hexagonal ices), 16 – 4025 cm-1, spectra of low density amorphous ice have similar features to cubic and hexagonal ices, spectrum of high density amorphous ice is significantly different in the translational and librational regions (< 150 meV) 40](#_Toc487109872)

[1996 Speedy 40](#_Toc487109873)

[The evaporation rate, free energy, and entropy of amorphous water at 150 K 40](#_Toc487109874)

[Free energy difference (ΔiaG (150 K) = 1100 J/mol) & residual entropy difference (ΔiaS (0) = 0.7 J/(K mol)) for ASW & crystalline ice, from evaporation rates, ΔiaS (0) allows connection of ASW with normal liquid H2O via reversible thermodynamic path (1 atm) 40](#_Toc487109875)

[-1995 Essmann 41](#_Toc487109876)

[Molecular dynamics simulation of vapor deposited amorphous ice 41](#_Toc487109877)

[Molecular dynamics simulation, vapour deposited ASW, compared to neutron scattering data from high & low density ASW (pressure induced transformation of crystalline ice), result: vapour deposited ASW between the other two, but closer to high density ASW, agreement with vapour deposited ASW neutron scattering & electron diffraction studies, ASW surface layer deeply fissured (-> high porosity of vapour deposited ice) 41](#_Toc487109878)

[-1995 Blake 41](#_Toc487109879)

[The metastable persistence of vapor-deposited amorphous ice at anomalously high temperatures 41](#_Toc487109880)

[Transmission Electron Microscope, structure of vapour-deposited astrophysical ice analogues as function of deposition (15 K, 0.05 μm thick), temperature history (1K/min) & composition (pure), 15 – 130 K: two amorphous to amorphous phase changes, 142 – 160 K: (time dependent) crystallisation (0.1 μm crystallites, stacking disorder (cubic/hexagonal/ amorphous)) 41](#_Toc487109881)

[-1994b Jenniskens 41](#_Toc487109882)

[Structural Transitions in Amorphous Water Ice and Astrophysical Implications 42](#_Toc487109883)

[Selected area electron diffraction (SAED), structure of vapour-deposited ASW (15 K, 18 μm/hr deposition rate, 1 – 3 K/min heating rate), 15 K: high density amorphous polymorph (Iah), 38 – 68 K: transition to low density amorphous polymorph (Ial), 131 K: onset to transformation to third amorphous polymorph (Iar), 148 – 188 K: metastable coexistence of cubic ice (Ic) with some (Iar) 42](#_Toc487109884)

[-1994a Jenniskens 42](#_Toc487109885)

[The structural changes of water ice I during warmup 42](#_Toc487109886)

[Selected area electron diffraction (SAED), structure of vapour-deposited ASW (15 K, 18 μm/hr deposition rate, 1 – 3 K/min heating rate), < 30 K: high density amorphous polymorph (Iah), 45 – 65 K: transition to low density amorphous polymorph (Ial), 131 – 142 K: onset to transformation to third amorphous polymorph (Iac), 142 – 161 K: crystallisation to cubic ice (Ic) with some (Iac) persisting, 225 K: crystallisation to hexagonal ice (Ih) 42](#_Toc487109887)

[1987 Giuère 42](#_Toc487109888)

[The bifurcated hydrogen-bond model of water and amorphous ice 42](#_Toc487109889)

[Two characteristic distances in (liquid?) H2O: bifurcated hydrogen bonds (BHB, between three molecules) = 1.85 Å, linear bonds (LHB) = 2.3 Å, few percent of H2O left with one “free” (non-H-bonded) OH group, ASW may also contain BHB (X-ray & neutron scattering 42](#_Toc487109890)

[1987 Bellisent-Funel 43](#_Toc487109891)

[Structure of high-density amorphous water. II. Neutron scattering study 43](#_Toc487109892)

[High-density & low-density ASW, neutron scattering, different (second/third) nearest-neighbour distances -> H-bond network strongly deformed (similar to H2O at high T), low-density ASW is closer to pair correlation functions of supercooled H2O 43](#_Toc487109893)

[1987 Bizid 43](#_Toc487109894)

[Structure of high-density amorphous water. I. X-ray diffraction study 43](#_Toc487109895)

[X-ray diffraction, high-density (from pressurised (2 GPa) Ih) & low-density (from heating high-density ASW) ASW, 77 K, 1 atm, both ices show different structures, low-density ASW very similar to vapour deposited (77 K) ASW 43](#_Toc487109896)

[1986 Floriano 44](#_Toc487109897)

[Structure of High-Density Amorphous Ice by Neutron Diffraction 44](#_Toc487109898)

[Neutron diffraction, HDA (from melting ice I @ 10.5 kbar & 77 K) @ 17 K & zero pressure, scaled pair distribution function similar to that of liquid D2O @ 9.8 kbar & 321 K -> HDA very similar to hypothetical glass that would be obtained by quenching water @ 10 kbar 44](#_Toc487109899)

[1986 Bosio 44](#_Toc487109900)

[X-Ray Study of High-Density Amorphous Water 44](#_Toc487109901)

[X-ray diffraction, 1 atm, 77 K, HDA (from 2 GPa pressurisation of Ih), structure at low-Q different from LDA, but nearest-neighbor distance & coordination number very similar, high density due to strong distortion of O-O-O angles from tetrahedral value. 44](#_Toc487109902)

[-1985 Eldrup 44](#_Toc487109903)

[Positronium formation and diffusion in crystalline and amorphous ice using a variable-energy positron beam 45](#_Toc487109904)

[Crystalline ice & ASW irradiated with positrons, Positronium formation -> detection when leaving the surface, probing electronic structure of ice, compare to Monte Carlo simulations, positron diffusion coefficients (ASW: 10-3 cm2/s, crystalline ice: 0.2 cm2/s), cavities of diameter > 17 Å in ASW (annealing out @ ≈ 100 K), crystallisation of ASW @ ≈ 135 K 45](#_Toc487109905)

[? 1974 Venkatesh 45](#_Toc487109906)

[Amorphous Solid Water: An X-ray Diffraction Study 45](#_Toc487109907)

[ASW (vapour deposited @ 10 K), density: 1.2 g/cm3, X-ray diffraction -> Oxygen-atom pair correlation functions 45](#_Toc487109908)

[Porosity 46](#_Toc487109909)

[2014 Bossa 46](#_Toc487109910)

[Porosity measurements of interstellar ice mixtures using optical laser interference and extended effective medium approximations 46](#_Toc487109911)

[Effect of contamination (CO2) on ASW structure and pore collapse: optical laser interference, IR spectroscopy (dangling OH) & extended effective medium approximations (EMAs), H2O:CO2 = 10:1, 4:1, and 2:1, CO2 premixed with water in the gas phase does not significantly affect ice morphology during omni-directional deposition, as long as physical conditions favourable to segregation not reached, CO2 diffuses on surface of growing ice sample and then fills the pores 46](#_Toc487109912)

[2013 Mispelaer 46](#_Toc487109913)

[Diffusion measurements of CO, HNCO, H2CO, and NH3 in amorphous water ice 46](#_Toc487109914)

[Thermal diffusion coefficients of HNCO, H2CO, NH3, and CO in porous ASW (10−15 to 10−11 cm2s−1, 35 – 140 K), bulk diffusion coefficient for compact ASW too low to be measured with FTIR (< 10−15 cm2s−1) 46](#_Toc487109915)

[2012 Accolla 47](#_Toc487109916)

[Morphology of the solid water synthesized through the pathway D + O2 studied by the sensitive TPD technique 47](#_Toc487109917)

[Formation of D2O on ASW from D + O2, TPD & IR spectroscopy, nascent ice mostly compact, underlying ice compacted during formation of D2O on surface (reaction heat), TPD more effective in probing ASW morphology, 47](#_Toc487109918)

[2011 Winkel 47](#_Toc487109919)

[Equilibrated High-Density Amorphous Ice and Its First-Order Transition to the Low-Density Form 48](#_Toc487109920)

[HDA-LDA transition (140 (H2O) and 143 K (D2O)), high pressures (0.07 – 0.2 GPa), X-ray diffraction, thermal stability of HDA against transformation to LDA at ambient pressure significantly increases with decreasing recovery pressure and reaches its maximum at 0.07 GPa 48](#_Toc487109921)

[2010 Herrero, 48](#_Toc487109922)

[Interaction of CH4 and H2O in ice mixtures 48](#_Toc487109923)

[Methane-water ice mixtures, IR spectroscopy: 14 – 60 K, dangling bonds of water, methane adsorbed on water micropores or trapped inside ASW structure, CH4 mobility depends on deposition method, CH4 fraction remains inside ASW after sublimation point (60 K) 48](#_Toc487109924)

[2010 Palumbo 49](#_Toc487109925)

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[Irradiation of ASW(-mixtures) with UV & ions: 12 – 16 K, ASW (pure/mixed with CO, CO2, O2, N2, H2O2, CH4, SO2, CH3OH), OH dangling bonds (intensity decreases) -> porosity decreases after irradiation 49](#_Toc487109927)

[? 2009 Fillion 49](#_Toc487109928)

[D2 desorption kinetics on amorphous solid water: from compact to porous ice films 49](#_Toc487109929)

[Desorptio of D2 from ASW of various porosities: 10 – 30 K / 120 K, < 1 – 20 monolayers, more energetic binding sites for porous ices, binding energy of D2 is primarily governed by the topological and morphological disorder of the surface at molecular scale 49](#_Toc487109930)

[2008 Raut 50](#_Toc487109931)

[Cosmic ray compaction of porous interstellar ices 50](#_Toc487109932)

[Compaction of microporous vapour deposited ice films under ion bombardment (80 – 400 keV), porosity decreases exponentially with irradiation, porous ice mantles on interstellar grains expected to compact by cosmic rays in 10 – 50 million years 50](#_Toc487109933)

[? 2007 Raut 50](#_Toc487109934)

[Compaction of microporous amorphous solid water by ion irradiation 50](#_Toc487109935)

[Ion impact compaction of ASW (vapour-deposited, 40 K), UV-VIS/IR spectroscopy & methane ad-/desorption, decrease in pore internal surface area (IR, dangling OH) precedes loss of pore volume 50](#_Toc487109936)

[-2007 Stähler 50](#_Toc487109937)

[Impact of Ice Structure on Ultrafast Electron Dynamics in D2O Clusters on Cu(111) 51](#_Toc487109938)

[Porous & compact ASW (D2O) structure, low-T scanning tunnelling microscopy & 2-photon photoemission spectroscopy, solvated electrons preferentially bind to D2O cluster surface but have different dynamics in both ices 51](#_Toc487109939)

[2005 Palumbo 51](#_Toc487109940)

[The morphology of interstellar water ice 51](#_Toc487109941)

[porosity of ASW decreases after ion-irradiation: 15 K, dangling OH-bonds, CO adsorption 51](#_Toc487109942)

[? 2004 Souda 51](#_Toc487109943)

[Hydrophobic hydration of alkanes: Its implication for the property of amorphous solid water 51](#_Toc487109944)

[nonporous ASW below 100 K: secondary ion mass spectrometry to measure incorporation of alkanes (butane/hexane) in ASW, glass transition: 136 K, liquid water above 165 K ( surface tension) 51](#_Toc487109945)

[SSA 52](#_Toc487109946)

[? 2013 Bag 52](#_Toc487109947)

[Probing Molecular Solids with Low-Energy Ions 52](#_Toc487109948)

[Method review (low energy ion-surface collisions, 1 – 100 eV), probing properties of condensed molecular solids (e.g. processes on ice surface) 52](#_Toc487109949)

[Wetting of ASW 52](#_Toc487109950)

[? 2011 May 52](#_Toc487109951)

[Probing the interaction of amorphous solid water on a hydrophobic surface: dewetting and crystallization kinetics of ASW on carbon tetrachloride 52](#_Toc487109952)

[Dewetting and crystallisation of ASW on CCl4 underlayer on graphene, mobility of water molecules increases with ASW deposition temperature, when ASW completely covers the underlayer, CCl4 desorption is delayed until crystallisation of H2O (cracking -> molecular volcano) 52](#_Toc487109953)

[? 2008 Souda 53](#_Toc487109954)

[Dewetting of Thin Amorphous Solid Water Films and Liquid-Cubic Ice Coexistence in Droplets Studied Using Infrared-Absorption and Secondary-Ion-Mass Spectroscopy 53](#_Toc487109955)

[Coupled & decoupled OH/OD bonds in ASW (4 mol% HOD in 20-monolayer H2O), 150 – 160 K, spontaneous nucleation at 160 K is bypassed when amorphous solid water is deposited on a crystallized water film; the crystals grow around nuclei at ca. 150 K, crystal grains behave like viscous droplets (morphology changes continuously after completion of crystallization), coexisting liquid-like water is indistinguishable from cubic ice in local structure 53](#_Toc487109956)

[? 2007 Kimmel 53](#_Toc487109957)

[Crystalline ice growth on Pt(111) and Pd(111): Nonwetting growth on a hydrophobic water monolayer 53](#_Toc487109958)

[temperature programmed desorption (rare gases adsorbed on H2O), substrates: Pt(111) & Pd(111), 20 – 155 K, ice films grown above 135 K do not wet first monolayer (similar results for D2O and H2O), ASW films crystallise and dewet when annealed. Typical distances between initial crystallites: 14 nm or more, results consistent with no dangling OH bonds at surface 53](#_Toc487109959)

[Dangling OH bonds characterization 54](#_Toc487109960)

[2015 Coussan 54](#_Toc487109961)

[Inhomogeneity of the amorphous solid water dangling bonds 54](#_Toc487109962)

[Behaviour of surface and immediate sublayers upon mid-infrared irradiation of ASW, selective IR irradiations of surface water molecules induces modification of surface and production of new monomer species (bonding to surface via its two electronic doublets), characterise two dH dangling bonds -> selective irradiation reveals inhomogeneity of these surface modes, irradiation induced surface reorientation -> max photoinduced isomerisation yield ≈ 15 % 54](#_Toc487109963)

[2014b Noble 54](#_Toc487109964)

[IR Selective Irradiations of Amorphous Solid Water Dangling Modes: Irradiation vs Annealing Effects 55](#_Toc487109965)

[Surface chemistry driven by dangling OH bonds (other molecules binding to them), thermal and irradiation processing of ASW (affects bulk and surface structure) -> irradiation processing pathway clearly distinct from thermal processing (irradiation produces water monomer interacting with surface -> new trapping sites/new catalytic properties, thermal effect: global reorganisation of ice structure) 55](#_Toc487109966)

[2014a Noble 55](#_Toc487109967)

[Unveiling the Surface Structure of Amorphous Solid Water via Selective Infrared Irradiation of OH Stretching Modes 55](#_Toc487109968)

[ASW dangling OH bonds, irradiation effects: surface H2O molecules reorganise, form monomer-like water mode on surface -> reduced range of binding sites -> altered catalytic capacity 55](#_Toc487109969)

[2004 Fraser 56](#_Toc487109970)

[Using laboratory studies of CO–H2O ices to understand the non-detection of a 2152 cm-1 (4.647 μm) band in the spectra of interstellar ices 56](#_Toc487109971)

[CO-H2O-ice system: lab experiments, dangling OH bonds exist in interstellar ices, but are blocked by other species -> no CO feature observed 56](#_Toc487109972)

[??? 2004 Al-Halabi 56](#_Toc487109973)

[Adsorption of CO on amorphous water-ice surfaces 56](#_Toc487109974)

[Classical trajectory calculations, adsorption of thermal CO on surface of compact ASW, 90 K, no diffusion of CO inside ice or into surface valley, maximum potential energy when CO interacts with dangling OH group, relatively few dangling OH groups present on ASW surface -> might explain lack of astronomical observations of this feature, CO also interacts with bonded OH groups, 10 K: lifetime of CO on surface longer than age of universe, 90 K: lifetime = 300 ns 56](#_Toc487109975)

[-2002 Mitlin 57](#_Toc487109976)

[Film Growth of Ice by Vapor Deposition at 128-185 K Studied by Fourier Transform Infrared Reflection-Absorption Spectroscopy: Evolution of the OH Stretch and the Dangling Bond with Film Thickness 57](#_Toc487109977)

[Vapour deposited H2O ice (poly- and non-crystalline): 128 – 185 K, grazing-angle Fourier transform Infrared Reflection-Absorption Spectroscopy (RAS), polycrystalline ice above 155 K, non-crystalline below 145 K, OH stretching band changes as function of film thickness (< 10 – 1500 nm), changes similar for poly- and non-crystalline ice -> dangling OH bonds are integral part of surfaces of both ices for thick films (> 700 nm), non-crystalline ice contains larger amount of dangling OH bonds -> bonds are on tracery external surface for non-crystalline ice and on crystal grain boundaries & surface for polycrystalline ice. 57](#_Toc487109978)

[? 2001 Devlin 58](#_Toc487109979)

[Infrared Spectra of Large H2O Clusters:  New Understanding of the Elusive Bending Mode of Ice 58](#_Toc487109980)

[1400−1700 cm-1 spectral range (annealed ASW & crystalline cubic ice at 10 K) characterized by broad absorption (water bending vibrations) lacking distinct features, bend-mode frequency & band intensity depend on strength & tetrahedrality of hydrogen bonding, significant decrease of librational-mode frequency (when hydrogen bonding is reduced relative to ice I) reduces overlap of bending mode with librational overtone 58](#_Toc487109981)

[2000 Manca 58](#_Toc487109982)

[Quantum study of the adsorption of small molecules on ice: The infrared frequency of the surface hydroxyl group and the vibrational stark effect 59](#_Toc487109983)

[Quantum calculation, adsorption of small nonpolar model systems (C2H2, C2H4, O3, CO, N2, Ar) on ice, IR shift of dangling surface hydroxyls (OH) largely governed by vibrational stark effect 59](#_Toc487109984)

[Chemistry of ASW 59](#_Toc487109985)

[2015 Smith 59](#_Toc487109986)

[Desorption Kinetics of Ar, Kr, Xe, N2, O2, CO, Methane, Ethane, and Propane from Graphene and Amorphous Solid Water Surfaces 59](#_Toc487109987)

[Desorption kinetics for Ar, Kr, Xe, N2, O2, CO, methane, ethane & propane from graphene-covered Pt(111) & ASW surfaces, TPD, results: desorption energies and prefactors for desorption 59](#_Toc487109988)

[? 2009 Oba 59](#_Toc487109989)

[Formation of compact amorphous H2O ice by codeposition of Hydrogen atoms with Oxygen molecules on grain surfaces 60](#_Toc487109990)

[H2O formation by co-deposition, IR spectroscopy: 10 – 40 K, H2O and H2O2 continuously formed, ratio varies with deposition conditions (H/O2-ratio, T), H2O-ice is amorphous but compact (no dangling OH-bonds observable) 60](#_Toc487109991)

[? 2008 Burke 60](#_Toc487109992)

[Thermally induced mixing of water dominated interstellar ices 60](#_Toc487109993)

[Adsorption and desorption of C2H5OH deposited on top/underneath/concurrently with ASW: TPD & RAIRS, 98 K, thermally induced mixing between C2H5OH and H2O observed for all deposition methods, C2H5OH modifies H2O desorption and ASW-Ic phase transition 60](#_Toc487109994)

[2008 Coupeaud 61](#_Toc487109995)

[Experimental and Theoretical Investigation of HC5N Adsorption on Amorphous Ice Surface: Simulation of the Interstellar Chemistry 61](#_Toc487109996)

[HC5N adsorbed on ASW (@ 10 K) interacts with ice surface and induces restructuring of bulk, desorption between 120 – 160 K, desorption energy: 90 kJ/mol -> ASW surface is essentially dynamic, HC5N moiety presents curvature and is stabilized by two strong N· · ·H bonds (2.09 and 2.29 Å) and one H· · ·O bond (1.84 Å) 61](#_Toc487109997)

[2008 Hidaka 61](#_Toc487109998)

[Structural effects of ice grain surfaces on the hydrogenation of CO at low temperatures 61](#_Toc487109999)

[Hydrogenation of CO on crystalline ice & ASW @ 15 K, CO-coverage on ice surfaces dominates effective reaction rate (rather than surface structure), larger depletion of CO on crystalline ice than on ASW 61](#_Toc487110000)

[2007 Cyriac 61](#_Toc487110001)

[Probing Difference in Diffusivity of Chloromethanes through Water Ice in the Temperature Range of 110-150 K 62](#_Toc487110002)

[Diffusive mixing of chloromethanes in different molecular solids H2O, D2O, and CH3OH by monitoring their chemical sputtering spectra due to the impact of Ar+ ions (focus ASW), no effect of ice crystallinity on diffusivity of water molecules (when deposited below chloromethanes), effect of substrate was insignificant, rise in temperature increased diffusive mixing wherever process was observed at lower T, CCl4 diffusion hindered under conditions where e.g. CHCl3 and CH2Cl2 undergo diffusive mixing, 4 – 600 monolayers 62](#_Toc487110003)

[? 2005 Kumi 62](#_Toc487110004)

[Amorphous Solid Water Films: Transport and Guest-Host Interactions with CO2 and N2O Dopants 62](#_Toc487110005)

[ASW interaction with CO2/N2O dopants, deposition @ 90 K, FTIR spectroscopy & TPD, top-layer of dopant desorbs above 105 K, some dopants residing within ASW remain until crystallisation @ 155 K (then all of it expelled), no differences between CO2 & N2O, annealing ASW to 130 K lowers capacity for dopant inclusion by factor ≈ 3, but no differences visible in ASW spectral feature @ ≈ 3250 cm-1, dangling OH bonds observed (redshift ≈ 50 cm-1 by dopant interaction) 62](#_Toc487110006)

[2004 Herring 63](#_Toc487110007)

[Stimulated Desorption of Cations from Pristine and Acidic Low-Temperature Water Ice Surfaces 63](#_Toc487110008)

[Electron-impact ionization of low-temperature water ice leads to H+, H2+, and H+(H2O)n=1–8 desorption. Cation yields probe surface acidity 63](#_Toc487110009)

[2004 Grecea 63](#_Toc487110010)

[Mobility of haloforms on ice surfaces 63](#_Toc487110011)

[TPD & RAIRS: CHCl3 does not diffuse over the crystalline ice surface (below its desorption T @ 140 K), CHBr3 is mobile at low temperatures (85 K) 63](#_Toc487110012)

[2004 Borodin 64](#_Toc487110013)

[Electron spectroscopy (UPS(HeI and II) and metastable impact electron spectroscopy (MIES)) applied to molecular surfaces: the interaction of atoms and molecules with solid water 64](#_Toc487110014)

[Interaction of atoms & molecules with ASW (80 K deposition), photoelectron spectroscopy, UPS, metastable impact electron spectroscopy (MIES), 1. Na atoms: 3s-electron is delocalised from Na core & trapped between Na & H2O of surrounding water shell, 2. NaCl: no interpenetration of H2O & NaCl @ 90 K, but ionic dissociation happens when H2O & NaCl in direct contact, solvation of Cl- & Na+ becomes significant @ 105 K, H2O desorption from mixed films between 145 & 170 K (species bound ionically to Na+ and Cl- are removed last), 3. Chlorobenzene & chlorophenyl: different mobilities w.r.t. H2O, annealing to 200 K 64](#_Toc487110015)

[? 2003 Collings 64](#_Toc487110016)

[Laboratory studies of the interaction of carbon monoxide with water ice 65](#_Toc487110017)

[Interaction of CO with ASW, TPD & FT-RAIRS, astrophysically relevant temperatures, model (including CO desorption, migration, and entrapment in ice matrix & H2O crystallisation) 65](#_Toc487110018)

[2003 Souda 65](#_Toc487110019)

[Hydrogen bonding between water and methanol studied by temperature-programmed time-of-flight secondary ion mass spectrometry 65](#_Toc487110020)

[CH3OH – D2O isotope exchange & H-bonding: 15 – 200 K, CH3OH adsorbed on D2O, proton-transfer, 100 – 150 K: sputtering of D+(CH3OH) ions, secondary ion mass spectrometry 65](#_Toc487110021)

[2003 Manca 65](#_Toc487110022)

[Comparative Study of Gas Adsorption on Amorphous Ice: Thermodynamic and Spectroscopic Features of the Adlayer and the Surface 66](#_Toc487110023)

[Adsorption on ASW (N2, CO, Ar, Kr, CH4, CF4), adsorption isotherm volumetry & IR spectroscopy, adsorption energies & capacities, N2 & CO: H-bonding with surface dangling OH 66](#_Toc487110024)

[2002b Martin 66](#_Toc487110025)

[Adsorption of small molecules on amorphous ice: volumetric and FT-IR isotherm co-measurements - Part II. The case of CO 66](#_Toc487110026)

[Volumetric & spectroscopic isothermal measurements, CO adsorption on ASW preferentially on dangling OH bonds, CO-CO interactions cause peak at 2139 cm-1 66](#_Toc487110027)

[2002a Martin 66](#_Toc487110028)

[Adsorption of small molecules on amorphous ice: volumetric and FT-IR isotherm co-measurements Part I. Different probe molecules 66](#_Toc487110029)

[Ar, Kr, CH4, N2, CO and CF4 adsorption on ASW, FTIR spectroscopy & volumetric isotherm measurements, different types of wetting, net heat of adsorption (1 – 2.6 kJ/mol), shift of dangling OH bond (7 – 60 cm-1), coverage: submonolayer to bulk 66](#_Toc487110030)

[2002 Haq 67](#_Toc487110031)

[Adsorption and Solvation of HCl into Ice Surfaces 67](#_Toc487110032)

[Kinetics of HCl adsorption & incorporation into crystalline ice & ASW, FTIR & RAIRS, 85 – 145 K, adsorption becomes less favorable with increasing HCl coverage, saturating with one HCl adsorbed for each surface H2O molecule, independent of ice thickness for T ≤ 120 K, above 125 K, HCl is incorporated into the ice film, ASW shows similar behaviour (but greater H2O density in surface and easier HCl transport into film) 67](#_Toc487110033)

[2001 Manca 67](#_Toc487110034)

[Experimental and Theoretical Reinvestigation of CO Adsorption on Amorphous Ice 67](#_Toc487110035)

[Quantum calculations & volumetric isotherm & IR experiments CO adsorption on ASW, multilayer formation, site specific (3 surface sites) & nonselective (similar energies) adsorption process 67](#_Toc487110036)

[2000 Borget 68](#_Toc487110037)

[Experimental and Quantum Study of Adsorption of Ozone (O3) on Amorphous Water Ice Film 68](#_Toc487110038)

[O3 ad-/desorption on ASW, FTIR & TPD, desorption between 70 – 90 K, desorption energy: 20 kJ/mol (agreeing with periodic Hartree-Fock (PHF) & density functional theory (DFT) estimates), OH vibration al frequency shifts by 60 cm-1, small amount of O3 is incorporated into bulk (desorbs at onset of crystallisation @ 145 K) 68](#_Toc487110039)

[2000 Manca 68](#_Toc487110040)

[Volumetric and infrared co-measurements of CH4 and CO isotherms on microporous ice 68](#_Toc487110041)

[CH4 & CO adsorption volumetric isotherms (-> SSA) & IR spectrometry (nature of physical/chemical bonding), microporous ice, 50 – 80 K, result: both methods well correlated & provide info on adsorption sites 68](#_Toc487110042)

[1997 Allouche 69](#_Toc487110043)

[CO Adsorption Isotherms on Ice by Fourier Transform Infrared Spectroscopy and New Insights of the Ice Surface from Quantum ab Initio Investigations 69](#_Toc487110044)

[Ice samples are prepared from highly concentrated H2O/Ar matrixes (various stages of order - amorphous to nanocrystalline clusters), 43 – 48 K, 0.1 – few monolayers, absorbance of CO, FTIR spectroscopy & quantum modelling, CO orients perpendicular to surface (no preference for CO or OC arrangement) by hydrogen bonding, adsorption dynamic process insensitive to presence of surface defects 69](#_Toc487110045)

[Crystallisation of ASW 69](#_Toc487110046)

[? 2016 Heidorn 69](#_Toc487110047)

[The fractal dimension of ice on the nanoscale 69](#_Toc487110048)

[Heterogeneous ice nucleation, formation of fractal ice structures, real-space observations, 89 – 119 K, fractal dimension changes linearly from 5/3 to ≈ 1 (equal-sided hexagon), shape dependent sticking coefficient of mobile ice clusters to fractal islands 69](#_Toc487110049)

[2012 May 70](#_Toc487110050)

[The Molecular Volcano Revisited: Determination of Crack Propagation and Distribution During the Crystallization of Nanoscale Amorphous Solid Water Films 70](#_Toc487110051)

[Length distribution of cracks forming in ASW during crystallisation: TPD & RAIRS, ASW deposited on top of O2, sufficiently thick overlayers of H2O trap O2 (second desorption peak at higher T), preponderance of cracks propagate down from outer surface of ASW 70](#_Toc487110052)

[2007 Kondo 70](#_Toc487110053)

[Deposition and crystallization studies of thin amorphous solid water films on Ru(0001) and on CO-precovered Ru(0001) 70](#_Toc487110054)

[Crystallisation occurs through random nucleation events in bulk material, followed by homogeneous growth (on both substrates), ≈50 layers thick ASW film, helium atom scattering, infrared reflection absorption spectroscopy, isothermal temperature-programmed desorption 70](#_Toc487110055)

[-1999 Sieger 71](#_Toc487110056)

[Probing low-temperature water ice phases using electron stimulated desorption 71](#_Toc487110057)

[Porous ASW (D2O) crystallises differently when annealed rather than deposited as crystalline D2O, 90 – 155 K deposition, Pt(111) substrate, low T depositions sinter between 120 – 140 K, ASW deposited on crystalline D2O crystallises into the same structure like substrate (surface nucleates) when annealed 71](#_Toc487110058)

[1999 Dohnálek 71](#_Toc487110059)

[Substrate induced crystallization of amorphous solid water at low temperatures 71](#_Toc487110060)

[N2 monolayer desorption from ice surfaces (quantitative, highly sensitive method for following surface crystallization kinetics at low T), vapour deposited substrate (< 110 K) ASW on crystalline ice crystallises faster than on Pt(111) -> crystalline substrate acts as 2D crystallisation nucleus 71](#_Toc487110061)

[1997 Jenniskens 72](#_Toc487110062)

[Liquid water in the domain of cubic crystalline ice Ic 72](#_Toc487110063)

[ASW (vapour deposited), 120 – 210 K, above glass transition (120 – 140 K) viscous liquid, coexists with cubic ice up to 210 K, transmission electron microscopy (TEM): morphology of water ice on non-wetting surface changes at 175 K, TPD: binding energy of H2O molecules changes, RAIRS: shape of 3.07 μm absorption band (O-H stretch) changes (change in selection rules), -> this form of liquid water must be common in comets/planets/sattelites 72](#_Toc487110064)

[1997 Smith 72](#_Toc487110065)

[The Molecular Volcano: Abrupt CCl4 Desorption Driven by the Crystallization of Amorphous Solid Water 72](#_Toc487110066)

[Desorption kinetics of ultrathin films of CCl4 & ASW, abrupt desorption of CCl4 at onset of crystallisation (through connected pathways formed in water overlayer during nucleation & crystallisation of ASW) -> episodic release 72](#_Toc487110067)

[1992 Moore 73](#_Toc487110068)

[Far infrared spectral studies of phase changes in water ice induced by proton irradiation 73](#_Toc487110069)

[Phase change between ASW and crystalline ice induced by proton irradiation, far-IR spectroscopy to distinguish ice phase, 13 – 77 K: irradiated crystalline ice becomes amorphous, 36 – 125 K: irradiated amorphous ice does not change, 13 K & dose > 2 eV/molecule: cyclic conversions between amorphous & crystalline + H2, H2O, O2 release. 73](#_Toc487110070)

[Crystalline H2O 73](#_Toc487110071)

[2014 Massey 73](#_Toc487110072)

[The role of lattice parameter in water adsorption and wetting of a solid surface 73](#_Toc487110073)

[Wetting of crystalline ice and ice nucleation depends on substrate structure, pseudomorphic surfaces (form ordered template that matches arrangement of water in bulk ice Ih(0001) bilayer: M(111) surfaces (M = Pt, Pd, Rh, Cu and Ni) form a (√3 x √3)R30° Sn substitutional alloy surface), only PtSn surface, with lattice parameter ≈ 7% greater than for bulk ice forms stable water layer, all other surfaces non-wetting (forming multilayer ice clusters) => repeat spacing of surface should ideally match O–O spacing in ice 73](#_Toc487110074)

[2014 Karssemeijer 74](#_Toc487110075)

[Diffusion-desorption ratio of adsorbed CO and CO2 on water ice (Research Note) 74](#_Toc487110076)

[Monte Carlo (simulations) diffusion/desorption barriers for CO & CO2 adsorbed on crystalline water surfaces 74](#_Toc487110077)

[2014 Geiger 74](#_Toc487110078)

[Proton Ordering of Cubic Ice Ic: Spectroscopy and Computer Simulations 75](#_Toc487110079)

[Proton ordering of ice, FTIR (librational band), cubic ice only partially proton orders under procedure where hexagonal ice would fully proton order, proton ordered structures are ferroelectric 75](#_Toc487110080)

[2014 Townrow 75](#_Toc487110081)

[Structure and sublimation of water ice films grown in vacuo at 120–190 K studied by positron and positronium annihilation 75](#_Toc487110082)

[Crystalline structure of H2O ice films (165 – 182 K), smaller deposition rate -> less lattice defects, films less disordered when grown > 172 K 75](#_Toc487110083)

[2012 McBride 75](#_Toc487110084)

[Strain relief and disorder in commensurate water layers formed on Pd(111) 76](#_Toc487110085)

[Water adsorbs and desorbs intact on Pd(111), forming H-bonded wetting layer, low energy electron diffraction (LEED) & He atom scattering (HAS) structural characterisation, H2O forms (√3 x √3)R30° clusters, but remains disorderes on local (≈ 10 Å) scale, flat domains, disordered coundaries, mostly H-down water (stress relief mechanism) 76](#_Toc487110086)

[2009 Kimmel 76](#_Toc487110087)

[No Confinement Needed: Observation of a Metastable Hydrophobic Wetting Two-Layer Ice on Graphene 76](#_Toc487110088)

[Special stacking of hexagonal bilayers for crystalline H2O ice grown on graphene on Pt(111), nontetrahedral geometry with weakened hydrogen bonds 76](#_Toc487110089)

[2007 Kondo 76](#_Toc487110090)

[The distinct vibrational signature of grain-boundary water in nano-crystalline ice films 77](#_Toc487110091)

[OD spectral feature (2500 cm-1) attributed to grain-boundary increases with decreasing crystal domain size (nm-range) 77](#_Toc487110092)

[? 2007b Michaelides 77](#_Toc487110093)

[Ice nanoclusters at hydrophobic metal surfaces 77](#_Toc487110094)

[Heterogeneous ice nucleation, metal-supported H2O hexamers & hydrated nanoclusters (hepta-/octa-/nonamers), low-T scanning tunnelling microscopy & first-principle electronic structure calculations, cyclic H2O hexamer (smallest piece of ice), competition between ability of H2O molecules to simultaneously bond to substrate and accept H-bonds 77](#_Toc487110095)

[2007a Michaelides 77](#_Toc487110096)

[Simulating ice nucleation, one molecule at a time, with the ‘DFT microscope’ 77](#_Toc487110097)

[Heterogeneous ice nucleation, density functional theory (DFT) calculations & scanning tunnelling microscopy, clusters of 2 – 6 H2O molecules adsorbed on Cu(111) surface 77](#_Toc487110098)

[2005 Kimmel 78](#_Toc487110099)

[Crystalline Ice Growth on Pt(111): Observation of a Hydrophobic Water Monolayer 78](#_Toc487110100)

[rare gas physisorption on H2O, substrate Pt(111) &, 20 – 155 K, ice films grown above 135 K do not wet first monolayer, results consistent with no dangling OH bonds at surface 78](#_Toc487110101)

[2005 Zimbitas 78](#_Toc487110102)

[The morphology of thin water films on Pt(111) probed by chloroform adsorption 78](#_Toc487110103)

[Wetting of crystalline H2O ice and ASW: probe molecule (chloroform), (√39 x √39)R16° wetting layer, individual crystallites for < 40 layers, restructuring into oriented bulk ice for > 50 layers 78](#_Toc487110104)

[2002 Haq 78](#_Toc487110105)

[Growth of thin crystalline ice films on Pt(111) 78](#_Toc487110106)

[1992 Bellisent-Funel 79](#_Toc487110107)

[X-ray and neutron scattering studies of the structure of hyperquenched glassy water 79](#_Toc487110108)

[X-ray & neutron diffraction, hyperquenched water droplets (on cryoplate), structure factors & radial distribution functions nearly identical to ASW (formed either by 77 K vapour deposition or heating HDA) 79](#_Toc487110109)

# Review

## -2010 Burke

21 January , Brown

### Ice in space: surface science investigations of the thermal desorption of model interstellar ices on dust grain analogue surfaces

#### Overview of the current level of understanding of the adsorption and desorption of astrophysically relevant molecules from a range of dust grain analogue surfaces, 10 – 20 K, TPD & RAIRS

More than 140 different molecules have been identified in the interstellar medium (ISM) to date. Dust grain particles are also found in the ISM, and some of these molecules freeze out at the cold temperatures (10–20 K) to form molecular ices. Understanding the adsorption and desorption of these ices is crucially important in understanding the processes that lead to star and planet formation, and may even help to lead to an understanding of the origin of life itself. High sensitivity surface science techniques, including temperature programmed desorption (TPD) and reflection absorption infrared spectroscopy (RAIRS), are being increasingly used to investigate the interactions between dust grains and interstellar ices. This perspective provides an overview of the current level of understanding of the adsorption and desorption of astrophysically relevant molecules from a range of dust grain analogue surfaces. Whilst the focus of this review is on interstellar ices, the results discussed are equally valid to discussions of cometary and planetary ices.

## -2009 Malenkov

18 June

### Liquid water and ices: understanding the structure and physical properties

#### Structure & properties of condensed H2O, 15 ice modifications (9 (+ 1) crystalline), transition fields between structures, metastable modifications (Ic, IV, XII, & several ASW), diffusion coefficient of water molecules in dense regions of network is lower than in loose regions, but increase of density of entire network gives rise to an increase of diffusion coefficient

A review of the structure and some properties of condensed phases of water is given. Since the discovery of the polymorphism of crystalline ice (beginning of the twentieth century), 15 ice modifications have been found and their structures have been determined. If we do not take into consideration proton ordering or disordering, nine distinct crystalline ice modifications in which water molecules retain their individuality are known. In the tenth, ice X, there are no H2O molecules. It contains ions (or atoms) of oxygen and hydrogen. The structure of all these modifications is described and information about their fields of stability and about the transition between them is given. It is emphasized that there are ice modifications which are metastable at any temperature and pressure (ices Ic, IV and XII), and many modifications can exist as metastable phases beyond their fields of stability. The ability of water to exist in metastable states is one of its remarkable properties. Several amorphous ice modifications (all of them are metastable) are known. Brief information about their properties and transitions between them is given. At the end of the 1960s the conception of the water structure as a three-dimensional hydrogen-bonded network was conclusively formed. Discovery of the polymorphism of amorphous ices awakened interest in the heterogeneity of the water network. Structural and dynamical heterogeneity of liquid water is discussed in detail. Computer simulation showed that the diffusion coefficient of water molecules in dense regions of the network is lower than in the loose regions, while an increase of density of the entire network gives rise to an increase of diffusion coefficient. This finding contradicts the conceptions associated with the primitive two-state models and can be explained from pressure dependences of melting temperature and of homogeneous nucleation temperature. A brief discussion of the picture of molecular motions in liquid water based on experiment and on computer simulation is given. This picture is still very incomplete. The most fascinating idea that was put forward during the last 20 years was the second critical point conjecture. It is still not clear whether this conjecture corresponds to reality.

## -2001 Devlin

1 December

### Structure, spectra, and mobility of low-pressure ices: Ice I, amorphous solid water, and clathrate hydrates at T < 150 K

#### Low-T behavior of ice I, (microporous) ASW & clathrate hydrates

Recent advances in the study of low-pressure water ices, including clathrate hydrates, are examined, highlighting aspects of modern science possibly related to the behavior of water ices in extraterrestrial environments. An effort has been made to identify properties of ice that are likely to be important in the conditions that exist in such environments and to review advances in understanding these properties. The basic science of crystalline ice I is relatively mature, but attention is given to concepts, such as point defects, which continue to evolve and which relate in an important manner to the low-temperature behavior of ice I as well as of amorphous ice and the clathrate hydrates. A concept of amorphous and microporous amorphous ice, developed in the early 1980s, is presented, but more recent characterizations are emphasized. Similarly, fundamental properties of clathrate hydrates are summarized and used in discussions of more recently appreciated characteristics that may be important in space science. Particular emphasis is placed on the formation, infrared spectroscopy, and behavior of clathrate hydrates in vacuo at temperatures below 150 K. The review closes with a section on the properties of ice nanoparticles, which have only recently emerged as a subject of molecular science. Modern experimental and theoretical studies of ice particles have focused on the infrared spectra and structure of the ice surface, and the interaction of the surface with molecular adsorbates. Since, with the exception of high-energy radiation, ice normally interacts with its environment through surface processes, such research may enlighten future studies.

## -2003 Baragiola

12 May

### Water ice on outer solar system surfaces: Basic properties and radiation effects

#### Properties of vapour-deposited H2O ice, emphasis on ASW & microporosity, irradiation effects (sputtering, phase change, chemistry, cracking), growth & irradiation effects on optical properties

This paper reviews the properties of vapor-deposited water ice in connection with icy surfaces in the outer solar system. The emphasis is on knowledge gained during the last decade, and on the properties of the amorphous phase, especially those affected by the presence of microporosity. The paper discusses the role played by the properties of different phases of ice and the effect of irradiation on the icy surfaces of satellites in the outer solar system: sputtering, phase transformation, the production and trapping of molecular radiation products, and stress induced cracking. The understanding of how growth and irradiation processes affect the optical properties of ice will lead to extract better information from optical remote sensing than is possible today. It is argued that cracks in ice induced by stresses are the main reason causing low-temperature ices to be strongly scattering.

# Characterisation

## -2016 Bu

23 October , Dukes, Baragiola

### Spontaneous cracking of amorphous solid water films and the dependence on microporous structure

#### Cracking of ASW: critical thickness increases with deposition T (10 – 50 K) & angle (0 – 55°) -> porosity dependent, modelling of tensile strength & stress, quartz crystal microbalance & optical interferometer & infrared spectrometer

Vapor-deposited, porous, amorphous, water-ice films, also called amorphous solid water (ASW), crack spontaneously during growth when the film thickness exceeds a critical value (Lc). We measured the Lc during growth of ASW films as a function of growth temperature (Tg = 10 K, 30 K, and 50 K) and deposition angle (θ = 0°, 45°, and 55°) using a quartz crystal microbalance, an optical interferometer, and an infrared spectrometer. The critical thickness, 1–5 μm under our experimental conditions, increases with Tg and θ, an indication of film porosity. We suggest that ASW films undergo tensile stress due to the mismatch between substrate adhesion and contracting forces derived from the incompletely coordinated molecules on the surfaces of the pores. We provide a model to explain the observed dependences of Lc on the Tg and h in the context of Griffith theory and estimate the tensile strength of low-temperature ASW to be ≈ 25 – 40 MPa. Our model can be applied more generally to describe fracture of other solids with microporous structures, such as metallic or ceramic materials with voids.

## 2016 Kouchi

23 June , Hama, Kimura, Hidaka, Escribano, Watanabe

### Matrix sublimation method for the formation of high-density amorphous ice

#### Co-deposition of CO and H2O @ 8 – 10 K, then evaporation of CO matrix => remaining ice is highly porous, density similar to high-density ice, crystallisation to cubic ice happens suddenly @ 140 K, ASW stable below 140 K (unlike conventional vapour deposited ASW)

A novel method for the formation of amorphous ice involving matrix sublimation has been developed. A CO-rich CO:H2O mixed ice was deposited at 8–10 K under ultra-high vacuum condition, which was then allowed to warm. After the sublimation of matrix CO at 35 K, amorphous ice remained. The amorphous ice formed exhibits a highly porous microscale texture; however, it also rather exhibits a density similar to that of high-density amorphous ice formed under high pressure. Furthermore, unlike conventional vapor-deposited amorphous ice, the amorphous ice is stable up to 140 K, where it transforms directly to cubic ice Ic.

## -2015 Parmentier

12 May , Shephard, Romanelli, Senesi, Salzmann, Andreani

### Evolution of Hydrogen Dynamics in Amorphous Ice with Density

#### H-atom dynamics in several forms of ASW, inelastic neutron scattering, mean kinetic energies increase with increasing density (weaker H-bonds) vibrational potential energy surfaces get steeper, change in O-H stretching component with density stronger than suggested by e.g. Raman spectroscopy

The single-particle dynamics of hydrogen atoms in several of the amorphous ices are reported using a combination of deep inelastic neutron scattering (DINS) and inelastic neutron scattering (INS). The mean kinetic energies of the hydrogen nuclei are found to increase with increasing density, indicating the weakening of hydrogen bonds as well as a trend toward steeper and more harmonic hydrogen vibrational potential energy surfaces. DINS shows much more pronounced changes in the O−H stretching component of the mean kinetic energy going from low- to high-density amorphous ices than indicated by INS and Raman spectroscopy. This highlights the power of the DINS technique to retrieve accurate ground-state kinetic energies beyond the harmonic approximation. In a novel approach, we use information from DINS and INS to determine the anharmonicity constants of the O−H stretching modes. Furthermore, our experimental kinetic energies will serve as important benchmark values for path-integral Monte Carlo simulations.

## ? 2015 Bu

1 April , Shi, Raut, Mitchell, Baragiola

### Effect of microstructure on spontaneous polarization in amorphous solid water films

#### Surface voltages (Vs) of ASW (vapour deposited below 110 K), Kelvin probe measurements, Vs increases with film thickness &decreases with deposition T & angle, decreases by ≈ 80 % when annealed 30 K above deposition T, -> polarization in ASW is governed by incompletely coordinated water molecules, dangling with unbalanced dipoles at internal surface of pores

Amorphous solid water (ASW) films grown by vapor deposition below 110 K develop negative surface voltages Vs with respect to the substrate. This polarization is due to a partial alignment of the water molecules during condensation. Kelvin probe measurements show that the magnitude of the surface potential, |Vs|, increases linearly with film thickness at a rate that decreases with increasing deposition temperature. |Vs| decreases with increasing deposition temperature and increasing incidence angle of the vapor source. After film growth, |Vs| decreases irreversibly by 80% when the ice film is heated to ∼30 K above the deposition temperature. The measurements of |Vs| as a function of film porosity indicate that polarization in ASW is governed by incompletely coordinated water molecules, dangling with unbalanced dipoles at the internal surface of the pores and weakly aligned by the anisotropic film-vacuum interface. This idea is supported by the strikingly similar behaviour of |Vs| and the infrared absorption due to the most pliable, two-coordinated surface molecules with annealing temperature.

## ? 2015 Silonov

20 April , Chubarov

### Amorphous Ice

#### ASW only below glass transition @ 136 K, X-ray diffraction, 258 – 273 K, coexistence of ASW & hexagonal ice near melting point, radial distribution functions (near melting point first maximum of radial distribution function of ASW close to position of radius of first coordination sphere of hexagonal ice), isothermal changes of ice at 263 K

The detailed analysis of published data was carried out for amorphous ices. It is shown that on modern representations the amorphous ice exists in different states only at the temperature below the glass transition temperature 136K. The X-ray diffraction method was used for studying of structure formation, because this method is the basic way of producing the direct information about structure of investigated object. For researching the X-ray scattering by ices near the melting point the precision low-temperature devices for X-ray diffractometer were elaborated. The improved device provides virtually unlimited in time maintaining of temperature of investigated sample in the range from 0°C to -25°C with precision ±0.1°C. For the first time, as a result of researches, the coexistence of amorphous structure and crystalline hexagonal structure of ice was established near melting point. The one diffuse maximum was able to identify on one of the diffractional pattern of ice, obtained from distillated water, with the almost complete absence of structural reflexes. There is the sign of completely amorphous state. The radial distribution functions were calculated from obtained diffractional patterns. They are shown that near the melting point the first maximums of radial distribution function of amorphous ice close in positions to first radii of coordination spheres of hexagonal ice. The revealed splitting of first maximum of radial distribution function can be explained by increasing of interatomic distances of neighbor atoms lying on different levels. On prolonged exposure the permanent reallocation on diffractional patterns of diffuse scattering maxima was revealed on ice sample at the constant temperature -10°C.

## -2015 Cazaux

22 October 2014 , Bossa, Linnartz, Tielens

### Pore evolution in interstellar ice analogues: Simulating the effects of temperature increase

#### Porosity of ASW: Kinetic Monte Carlo simulations, thermal evolution of porosity & SSA, 10 – 120 K, accretion of gas-phase water & migration on surfaces (top layer & within bulk), with increasing T total surface of pores decreases to great extend while total volume decreases only slightly -> small pores connect and merge

*Context*. The level of porosity of interstellar ices, largely comprised of amorphous solid water (ASW), contains clues about the trapping capacity of other volatile species and determines the surface accessibility that is needed for solid-state reactions to take place.

*Aims*. Our goal is to simulate the growth of amorphous water ice at low temperature (10 K) and to characterise the evolution of the porosity (and the specific surface area) as a function of temperature (from 10 to 120 K).

*Methods*. Kinetic Monte Carlo simulations are used to mimic the formation and the thermal evolution of pores in amorphous water ice. We follow the accretion of gas-phase water molecules as well as their migration on surfaces with different grid sizes, both at the top growing layer and within the bulk.

*Results*. We show that the porosity characteristics change substantially in water ice as the temperature increases. The total surface of the pores decreases to a great extend while the total volume decreases only slightly for higher temperatures. This will decrease the overall reaction efficiency, but in parallel, small pores connect and merge, which allows trapped molecules to meet and react within the pores network and provides a pathway to increase the reaction efficiency. We introduce pore coalescence as a new solid-state process that may boost the solid-state formation of new molecules in space, and which has not been considered so far.

## -2014 Isokoski

5 December 2013 , Bossa, Triemstra, Linnartz

### Porosity and thermal collapse measurements of H2O, CH3OH, CO2, and H2O:CO2 ices

#### Compaction of ice (H2O, CH3OH, CO2, mixed H2O:CO2 = 2:1) upon heating, astronomically relevant T-range, Laser interference & FTIR, for ASW the full loss of dangling OH bonds is not a proof for full compaction, for other ices thermal segregation benefits from higher degree of porosity

The majority of astronomical and laboratory based studies of interstellar ices have been focusing on ice constituents. Ice structure is a much less studied topic. Particularly the amount of porosity is an ongoing point of discussion. A porous ice offers more surface area than a compact ice, for reactions that are fully surface driven. In this paper we discuss the amount of compaction for four different ices – H2O, CH3OH, CO2 and mixed H2O:CO2 = 2 : 1 – upon heating over an astronomically relevant temperature regime. Laser interference and Fourier transform infrared spectroscopy are used to confirm that for amorphous solid water the full signal loss of dangling OH bonds is not a proof for full compaction. These data are compared with the first compaction results for pure CH3OH, pure CO2 and mixed H2O:CO2 = 2 : 1 ice. Here we find that thermal segregation benefits from a higher degree of porosity.

## -2013 Garrod

13 November

### Three-dimensional, off-lattice Monte Carlo kinetics simulations of interstellar grain chemistry and ice structure

#### Monte Carlo kinetics model (using grain surface atom locations rather than fixed lattice structure), H & O atoms accrete onto grain to produce H2O, H2, O2, H2O2, porosity depends on gas density (2 × 104 cm−3 (dark interstellar clouds) produces fairly smooth & non-porous ice mantle), H2 formed collets in micropores, larger pores not filled with H2, direct deposition of water molecules onto grain indicates that amorphous ices formed this way may be significantly more porous than interstellar ices formed by surface chemistry

The first off-lattice Monte Carlo kinetics model of interstellar dust grain surface chemistry is presented. The positions of all surface particles are determined explicitly, according to the local potential minima resulting from the pair-wise interactions of contiguous atoms and molecules, rather than by a pre-defined lattice structure. The model is capable of simulating chemical kinetics on any arbitrary dust grain morphology, as determined by the user-defined positions of each individual dust grain atom. A simple method is devised for the determination of the most likely diffusion pathways and their associated energy barriers for surface species. The model is applied to a small, idealized dust grain, adopting various gas densities and using a small chemical network. Hydrogen and oxygen atoms accrete onto the grain to produce H2O, H2, O2, and H2O2. The off-lattice method allows the ice structure to evolve freely; the ice mantle porosity is found to be dependent on the gas density, which controls the accretion rate. A gas density of 2 × 104 cm−3, appropriate for dark interstellar clouds, is found to produce a fairly smooth and non-porous ice mantle. At all densities, H2 molecules formed on the grains collect within the crevices that divide nodules of ice and within micropores (whose extreme inward curvature produces strong local potential minima). The larger pores produced in the high-density models are not typically filled with H2. Direct deposition of water molecules onto the grain indicates that amorphous ices formed in this way may be significantly more porous than interstellar ices that are formed by surface chemistry.

## -2013 Shephard

14 October , Evans, Salzmann

### Structural Relaxation of Low-Density Amorphous Ice upon Thermal Annealing

#### LDA (prepared from HDA or vapour deposited) annealing, Raman & FTIR spectroscopy, structural relaxation -> increase of local and long-range order (starting before crystallisation and not finished at onset of crystallisation) -> contradicting findings on glass transition

Despite the importance of low-density amorphous ice (LDA) in critical cosmological processes and its prominence as one of the polyamorphs of water there is still an incomplete picture of the processes that take place upon thermal annealing. Using Raman and Fourier transform infrared (FT-IR) spectroscopy, we show that a gradual structural relaxation process takes place upon heating vapor-deposited LDA, also called amorphous solid water, and LDAs obtained from several different states of high-density amorphous ice. The relaxation leads to an increase in structural order on local and more extended length scales as the average O−O distance shortens and the O−O distance distribution narrows. The relaxation process is separate from crystallization, and it does not seem to reach completion before crystallization sets in. Our findings are difficult to reconcile with the postulated glass transition of LDA to the supercooled and highly viscous liquid prior to crystallization.

## -2012 Maté

, Rodríguez-Lazcano, Herrero

### A comparative study of the porosity and crystallization kinetics of compact and porous water ice

#### Porosity and isothermal crystallization kinetics of ASW (vapour-deposited) & HGW (hyperquenched liquid droplets), ASW ≈ 7 x more porous than HGW, little difference in 150 K crystallisation between ASW & HGW (probably due to pore collapse in ASW, possible existence of different ASW phase at 14 K.

An investigation of porosity and isothermal crystallization kinetics of amorphous ice produced either by background water vapour deposition (ASW) or by hyperquenching of liquid droplets (HGW) is presented. ASW samples are found to be ~ 7 times more porous than their HGW counterparts, but little difference is found in the 150 K crystallization of the two types of samples due probably to pore collapse in ASW with growing temperature. Both the HGW and ASW data support the possible existence of a previously suggested different amorphous ice phase for ices generated at very low temperature (14 K).

## -2012 Bossa

27 July , Isokoski, de Valois, Linnartz

### Thermal collapse of porous interstellar ice

#### ASW pore collapse, 20 -120 K, thickness (optical interference) & porosity/phase (FTIR) measurements, porous ASW: thickness decreases by (12 ± 1) % between 20 and 120 K, less porous ASW: smaller thickness decrease, crystalline ice: negligible thickness decrease

*Aims*. This article aims at a quantitative characterization of the phase transition of porous amorphous solid water (ASW) to a nonporous, i.e., more compact structure over an astronomically relevant temperature regime.

*Methods*. A new laboratory based method is described that monitors the ice thickness decrease by combining optical interference with Fourier transform infrared spectroscopy. Three different water ice morphologies are studied; porous ASW as primary target, and less-porous ASW as well as crystalline solid water for comparison.

*Results*. The thickness of the porous ASW sample is found to decrease by 12 ± 1% upon heating from 20 to 120 K. The thickness decrease of less-porous ASW is smaller, and negligible for crystalline solid water.

*Conclusions*. Porous ASW, if formed under interstellar conditions, is expected to become less porous with increasing temperature. The thermally induced structural collapse affects the diffusion of the interstellar ice components, and therefore the catalytic properties of the ice.

## -2012 Maté

11 June , Rodríguez-Lazcano, Herrero

### Morphology and crystallization kinetics of compact (HGW) and porous (ASW) amorphous water ice

#### Porosity, SSA & Crystallisation of ASW & HGW: 14 – 150 K, CH4 adsorption -> SSA = 280 ± 30 m2 g-1 ( ASW) and SSA = 40 ± 12 m2 g-1 (HGW), crystallisation rate constant (≈ 7 x 10-4 s-1) independent of deposition T (14, 40, 90 K), hints towards different ASW structure at very low (14 K) T

An investigation of porosity and isothermal crystallization kinetics of amorphous ice produced either by background water vapour deposition (ASW) or by hyperquenching of liquid droplets (HGW) is presented. These two types of ice are relevant for astronomical ice research (Gálvez et al., Astrophys. J., 2010, 724, 539) and are studied here for the first time under comparable experimental conditions. From CH4 isothermal adsorption experiments at 40 K, surface areas of 280 ± 30 m2 g-1 for the ASW deposits and of 40 ± 12 m2 g-1 for comparable HGW samples were obtained. The crystallization kinetics was studied at 150 K by following the evolution of the band shape of the OD stretching vibration in HDO doped ASW and HGW samples generated at 14 K, 40 K and 90 K. Comparable rate constants of ≈ 7 x 10-4 s-1 were obtained in all cases. However a significant difference was found between the *n* Avrami parameter of the samples generated at 14 K (*n* ≈ 1) and that of the rest (*n* > 2). This result hints at the possible existence of a structurally different form of amorphous ice for very low generation temperatures, already suggested in previous literature works.

## -2011 Wu

29 August , Jiang, Wang, Kallis, Coleman

### Porosity and crystallization of water ice films studied by positron and positronium annihilation

#### Porosity (< 1 nm) of ASW & crystalline ice, variable-energy positron annihilation spectroscopy (VEPAS), energetics of structural phase changes

The growth, evolution, and annealing of closed and interconnected pores in amorphous and crystalline films of water ice grown under a range of conditions have been studied by variable-energy positron annihilation spectroscopy (VEPAS). By measuring positron and positronium-related annihilation parameters as a function of time and film temperature it is shown that VEPAS has the capacity to yield a wealth of depth-dependent information on film morphology, with particularly promising results on the evolution and annealing of subnanometer closed pores—inaccessible to other techniques—and the study of the energetics of structural and phase changes.

## 2010 Toburen

, S. McLawhorn, R. McLawhorn, Carnes, Dingfelder, Shinpaugh

### Electron Emission from Amorphous Solid Water Induced by Passage of Energetic Protons and Fluorine Ions

#### Doubly differential electron emission yields, ASW on copper (50 K), transmission of 6 MeV protons & 19 MeV fluorine ions, electron energies (time of flight), provide benchmark tests for Monte Carlo track structure codes (used for assessing effects of radiation on biological effectiveness)

Absolute doubly differential electron emission yields were measured from thin films of amorphous solid water (ASW) after the transmission of 6 MeV protons and 19 MeV (1 MeV/nucleon) fluorine ions. The ASW films were frozen on thin (1- mm) copper foils cooled to approximately 50 K. Electrons emitted from the films were detected as a function of angle in both the forward and backward direction and as a function of the film thickness. Electron energies were determined by measuring the ejected electron time of flight, a technique that optimizes the accuracy of measuring low-energy electron yields, where the effects of molecular environment on electron transport are expected to be most evident. Relative electron emission yields were normalized to an absolute scale by comparison of the integrated total yields for proton-induced electron emission from the copper substrate to values published previously. The absolute doubly differential yields from ASW are presented along with integrated values, providing single differential and total electron emission yields. These data may provide benchmark tests of Monte Carlo track structure codes commonly used for assessing the effects of radiation quality on biological effectiveness.

## -2010 Wu

5 August , Kallis, Jiang, Coleman

### Structural and Phase Changes in Amorphous Solid Water Films Revealed by Positron Beam Spectroscopy

#### Positron beam spectroscopy, ASW (vapour deposited, 50 – 150 K, porosity & crystallisation, crystallisation occurs just below 140 K (topmost 80 nm crystallise at 90 – 100 K)

The evolution and annealing of pores in, and the crystallization of, vapor-deposited films of amorphous solid water have been studied by using variable-energy positron annihilation spectroscopy for temperatures in the range 50–150 K. Both positron and positronium annihilation provide insight to the nature of the grown-in pores and their evolution with temperature. Crystallization of the films was observed at just below 140 K, in agreement with earlier studies, with the topmost 80 nm undergoing a transition consistent with crystallization at 90–100 K.

## 2009 Winkler

28 April , Bowron, Loerting, Mayer, Finney

### Relaxation effects in low density amorphous ice: Two distinct structural states observed by neutron diffraction

#### Neutron diffraction on low density amorphous ice (produce from high density ASW by isobaric warming or very high density ASW by isothermal compression), -> two different forms of LDA (different compression behaviour & structures (atomistic modelling -> competition between short & intermediate order & disorder))

Neutron diffraction with H/D isotopic substitution is used to investigate the structure of low density amorphous ice produced from (1) high density amorphous ice by isobaric warming and (2) very high density amorphous ice by isothermal decompression. Differences are found in the scattering patterns of the two low density amorphous ices that correlate with structural perturbations on intermediate length scales in the hydrogen bonded water network. Atomistic modeling suggests that the structural states of the two samples may relate to a competition between short range and intermediate range order and disorder. This structural difference in two low density amorphous (LDA) ices is also evident when comparing their compression behavior. In terms of the energy landscape formalism this finding implies that we have produced and characterized the structural difference of two different basins within the LDA-megabasin corresponding to identical macroscopic densities.

## 2008 Paschek

, Rüppert, Geiger

### Thermodynamic and Structural Characterization of the Transformation from a Metastable Low-Density to a Very High-Density Form of Supercooled TIP4P-Ew Model Water

#### Liquid-liquid transition (TIP4P-Ew model water), 150 – 360 K, low/high/very high density transformations

We explore the phase diagram of the metastable TIP4P-Ew liquid model water from 360 K down to 150 K at densities ranging from 0.950 to 1.355 g/cm3. In addition to the low-density/high-density (LDL/HDL) liquid–liquid transition, we observe a structural highdensity/very high-density (HDL/VHDL) transformation for the lowest temperatures at 1.30 g/cm3. The characteristics of the isobars and isotherms suggest the presence of a stepwise HDL/VHDL transition with first-order-like appearance. In addition, we also identify an apparent pretransition at 1.24 g/cm3, which suggests that the experimentally detected LDA/VHDA transformation might evolve into a multiple-step process with different local structures representing local minima in the free-energy landscape. Such a scenario is supported by a pronounced correlation between the isothermal density dependence of the pressure, with a stepwise increase of the oxygen coordination number, due to the appearance of interstitial water molecules.

## -2008 Gálvez

6 June , Maté, Herrero, Escribano

### Trapping and adsorption of CO2 in amorphous ice: A FTIR study

#### SSA of ASW: Spectroscopy on CO2 ice (trapped in ASW pores), deposition at 95 K (simultaneously or sequentially), CO2 infrared bands shift & split in both cases (interaction with water molecules), larger amount of CO2 trapped in ASW in co-deposition, in sequential deposition most CO2 trapped in macropores of ASW, phase transition at 140 K -> CO2 molecules relocate -> similar bulk structure to co-deposited samples

The interaction of carbon dioxide and amorphous water ice at 95 K is studied using transmission infrared spectroscopy. Samples are prepared in two ways: co-deposition of the gases admitted simultaneously or sequential deposition, in which amorphous water ice (ASW) is grown first and CO2 vapor is added subsequently. In either case, a fraction of the CO2 molecules is found to interact with water in a way that gives rise to shifts and splittings in the infrared bands with respect to those of a pure CO2 solid. In co-deposition experiments, a larger amount of carbon dioxide is trapped within the amorphous water than in sequential deposition samples, where a substantial proportion of molecules appears to be trapped in macropores of the ASW. The specific surface area of sequential samples is evaluated and compared to previous literature results. When the sequential samples are heated to 140 K, beyond the onset temperature at which water ice undergoes a phase transition, the CO2 molecules at the pores relocate inside the bulk in a structure similar to that found in co-deposited samples, as deduced by changes in the shape of the CO2 infrared bands.

## -2007 Raut

30 November , Famá, Teolis, Baragiola

### Characterization of porosity in vapor-deposited amorphous solid water from methane adsorption

#### Porosity of ASW via quartz crystal microgravimetry, UV-visible interferometry, and infrared reflectance spectrometry in tandem with methane adsorption: microporosity for all deposition methods, but collimated depositions show additional mesoporosity (up to 140 K (crystallization)), higher binding energy for collimated deposition, methane on dangling OH bonds -> no multilayer condensation inside micropores (methane coating the walls instead of filling the pore volume)

We have characterized the porosity of vapor-deposited amorphous solid water ice films deposited at 30–40 K using several complementary techniques such as quartz crystal microgravimetry, UV-visible interferometry, and infrared reflectance spectrometry in tandem with methane adsorption. The results, inferred from the gas adsorption isotherms, reveal the existence of microporosity in all vapor-deposited films condensed from both diffuse and collimated water vapor sources. Films deposited from a diffuse source show a step in the isotherms and much less adsorption at low pressures than films deposited from a collimated source with the difference increasing with film thickness. Ice films deposited from a collimated vapor source at 77° incidence are mesoporous, in addition to having micropores. Remarkably, mesoporosity is retained upon warming to temperatures as high as 140 K where the ice crystallized. The binding energy distribution for methane adsorption in the micropores of ice films deposited from a collimated source peaks at 0.083 eV for deposition at normal incidence and at 0.077 eV for deposition at 45° incidence. For microporous ice, the intensity of the infrared bands due to methane molecules on dangling OH bonds on pore surfaces increases linearly with methane uptake, up to saturation adsorption. This shows that the multilayer condensation of methane does not occur inside the micropores. Rather, filling of the core volume results from coating the pore walls with the first layer of methane, indicating pore widths below a few molecular diameters. For ice deposited at 77° incidence, the increase in intensity of the dangling bond absorptions modified by methane adsorption departs from linearity at large uptakes.

## -2007 Malyk

20 September , Kumi, Reisler, Wittig

### Trapping and Release of CO2 Guest Molecules by Amorphous Ice

#### Trapping and release of 13CO2 by porous ASW (13CO2 on top of/below/codeposited with ASW), TPD & FTIR, some 13CO2 becomes trapped when annealing ASW (amount depends on deposition method), two stage release of trapped 13CO2: 1. majority escapes at ASW-to-cubic transition (165 K), 2. rest desorbs together with cubic ice (185 K) -> must be trapped in cavities that do not open during crystallisation

Interactions of 13CO2 guest molecules with vapor-deposited porous H2O ices have been examined using temperature-programmed desorption (TPD) and Fourier transform infrared (FTIR) techniques. Specifically, the trapping and release of 13CO2 by amorphous solid water (ASW) has been studied. The use of 13CO2 eliminates problems with background CO2. Samples were prepared by (i) depositing 13CO2 on top of ASW, (ii) depositing 13CO2 underneath ASW, and (iii) codepositing 13CO2 and H2O during ASW formation. Some of the deposited 13CO2 becomes trapped when the ice film is annealed. The amount of 13CO2 trapped in the film depends on the deposition method. The release of trapped molecules occurs in two stages. The majority of the trapped 13CO2 escapes during the ASW-to-cubic ice phase transition at 165 K, and the rest desorbs together with the cubic ice film at 185 K. We speculate that the presence of 13CO2 at temperatures up to 185 K is due to 13CO2 that is trapped in cavities within the ASW film. These cavities are similar to ones that trap the 13CO2 that is released during crystallization. The difference is that 13CO2 that remains at temperatures up to 185 K does not have access to escape pathways to the surface during crystallization.

## -2007 Cuppen

8 June , Herbst

### Simulation of the formation and morphology of ice mantles on interstellar grains

#### Simulations (continuous-time random-walk Monte Carlo), production rate & morphology of water dominated ice mantles containing CO & CO2, result: ice mantles only grow in denser regions

Although still poorly understood, the chemistry that occurs on the surfaces of interstellar dust particles profoundly affects the growth of molecules in the interstellar medium. An important set of surface reactions produces icy mantles of many monolayers in cold and dense regions. The monolayers are dominated by water ice, but also contain CO, CO2, and occasionally methanol, as well as minor constituents. In this paper, the rate of production of water-ice-dominated mantles is calculated for different physical conditions of interstellar clouds and for the first time images of the morphology of interstellar ices are presented. For this purpose, the continuous-time random-walk Monte Carlo simulation technique has been used. The visual extinction, density, and gas and grain temperatures are varied. It is shown that our stochastic approach can reproduce the important observation that ice mantles only grow in the denser regions.

## ? 2006 Laffon

29 November , Lacombe, Bournel, Parent

### Radiation effects in water ice: A near-edge x-ray absorption fine structure study

#### Structure and composition of vapour-deposited (porous amorphous solid water (p-ASW) & crystalline (Icryst)) ice films irradiated at 20 K with soft x-ray photons (3–900 eV), near-edge x-ray absorption fine structure spectroscopy (NEXAFS), 20 – 150 K, Icryst becomes amorphous, low-density p-ASW becomes high-density ASW (Iah), then (50 – 90 K) very high density ASW (Iavh), then partially crystallises (150 K)

The changes in the structure and composition of vapor-deposited ice films irradiated at 20 K with soft x-ray photons (3–900 eV) and their subsequent evolution with temperatures between 20 and 150 K have been investigated by near-edge x-ray absorption fine structure spectroscopy (NEXAFS) at the oxygen K edge. We observe the hydroxyl OH, the atomic oxygen O, and the hydroperoxyl HO2 radicals, as well as the oxygen O2 and hydrogen peroxide H2O2 molecules in irradiated porous amorphous solid water (p-ASW) and crystalline (Icryst) ice films. The evolution of their concentrations with the temperature indicates that HO2, O2, and H2O2 result from a simple step reaction fuelled by OH, where O2 is a product of HO2 and HO2 a product of H2O2. The local order of ice is also modified, whatever the initial structure is. The crystalline ice Icryst becomes amorphous. The high-density amorphous phase (Iah) of ice is observed after irradiation of the p-ASW film, whose initial structure is the normal low-density form of the amorphous ice (Ial). The phase Iah is thus peculiar to irradiated ice and does not exist in the as-deposited ice films. A new “very high density” amorphous phase—we call Iavh—is obtained after warming at 50 K the irradiated p-ASW ice. This phase is stable up to 90 K and partially transforms into crystalline ice at 150 K.

## 2006 Mason

13 February , Dawes, Holtom, Mukerji, Davis, Sivaraman, Kaiser, Hoffmann, Shaw

### VUV spectroscopy and photo-processing of astrochemical ices: an experimental study

#### VUV spectroscopy, morphology of various molecular ices

In order to understand much of the chemistry that underpins astronomical phenomena (e.g. star and planet formation) it is essential to probe the physico-chemistry of ice surfaces under astronomical conditions. The physical properties and chemical reactivity of such icy surfaces depends upon its morphology. Thus it is necessary to explore how the morphology of astrochemical ices is influenced by their local environment (e.g. temperature and pressure) and the mechanisms by which they are processed. In this paper we report the results of a series of experiments to explore the morphology of a variety of molecular ices using VUV spectroscopy. Spectral signatures are found that may allow the morphology of such ices to be identified.

## ? 2005 Souda

21 September

### Probing Surface Properties and Glass-Liquid Transition of Amorphous Solid Water: Temperature-Programmed TOF-SIMS and TPD Studies of Adsorption/Desorption of Hexane

#### ASW-hexane interaction, 120 – 165 K, surface diffusion of molecules even below 120 K, abrupt dewetting at 165 K (glass-liquid transition), fluidity of supercooled liquid phase

The interaction of hexane with amorphous solid water has been investigated in terms of the surface diffusion, hydrogen bond imperfections, hydrophobic hydration, crystallization, and glass-liquid transition. The hexane exhibits two main peaks in temperature-programmed desorption: one is ascribed to a complex formed at the surface or subsurface sites (135 K) and the other is caused by a bulk complex (165 K). The latter is associated with the presence of frozen-in imperfections in hydrogen bonds and formed provided that the annealing temperature of the film is below 130 K, whereas the former is created even when the film is annealed up to 150 K. Thus, the hexane-water interaction is hardly characterized by simple physisorption. The hexane is incorporated in the bulk during reorganization of hydrogen bonds due to rotational and translational diffusions of water molecules above 120-140 K, whereas the surface complex is formed even below 120 K due to the surface diffusion of molecules. The film undergoes abrupt dewetting at 165 K as a consequence of the glass-liquid transition. The slow evolution of the fluidity in the supercooled liquid phase may be responsible for the delay of the structural relaxation (165 K) relative to the onset of the translational molecular diffusion (135-140 K).

## -2004 Manca

6 January , Martin, Roubin

### Volumetric and infrared measurements on amorphous ice structure

#### Adsorption isotherm volumetry & FTIR spectroscopy, ASW characterisation (porosity, SSA, crystallisation), annealing induced modifications, number of surface sites decreases before crystallisation, non-microporous ice can have large specific surface area

We have simultaneously used adsorption isotherm volumetry and Fourier transform infrared spectroscopy in order to take the investigations on amorphous ice structure a step further, especially concerning porosity and annealing-induced modifications. We have studied surface reorganization during annealing and found that the number of surface sites decreases before crystallization, their relative ratios being different for amorphous and crystalline ice. We also present results confirming that ice can have a large specific surface area and nevertheless be non-microporous.

## -2003 Dohnálek

7 October , Kimmel, Ayotte, Smith, Kay

### The deposition angle-dependent density of amorphous solid water films

#### ASW characterisation (laser optical interferometry): film thickness & density of ASW films (vapour deposited @ 22 K, collimated molecular beam, angle varied between normal & oblique incidence), normal incidence films presumed to be compact (0.94 g/cm3), glancing incidence ρ = 0.16 g/cm3 (> 80 % porosity), in agreement with ballistic deposition simulations

The index of refraction and thickness of amorphous solid water (ASW) films are determined using laser optical interferometry. From the film thickness, the density of ASW can be calculated directly since the molecular beam flux and the H2O condensation coefficient are both known. From the index of refraction the ASW density can also be determined using the Lorentz–Lorenz relationship. The densities determined via both methods agree within experimental uncertainty. For films deposited at 22 K using a collimated molecular beam, the index of refraction and density decrease monotonically as the deposition angle is varied from normal to oblique incidence. At normal incidence the films have an index of refraction of 1.285 and are presumed to be fully dense (0.94 g/cm3). At glancing incidence (86°) the film has a refractive index of 1.05 and a density of 0.16 g/cm3, indicating a porosity exceeding 80%. The angle-dependent film density is in semiquantitative agreement with the results of ballistic deposition simulations of ASW film growth.

## ? 2003 Maté

2 July , Medialdea, Moreno, Escribano, Herrero

### Experimental Studies of Amorphous and Polycrystalline Ice Films Using FT-RAIRS

#### ASW & crystalline H2O ice (vapour deposited), < 100 nm – 5 μm thickness, FT-RAIRS, Al & Au substrates (similar results for both), optical effects (surface suppression/vibrational mode enhancement) vary with thickness, spectral simulations (Fresnel model)

A systematic investigation of amorphous and crystalline vapor deposited ice layers with thickness ranging from less than 100 nm to more than 5 μm has been performed using Fourier transform (FT) reflection-absorption infrared spectroscopy (RAIRS). Al and Au surfaces were used for the vapor deposition and very similar results were obtained on both. The spectra were recorded both with polarized and nonpolarized radiation and simulated with a simple Fresnel reflection model and empirical optical indices from the literature. Optical effects peculiar to this technique like surface suppression or enhancement of vibrational modes, saturation of intense absorptions, and IR interferences, are found to distort the spectra to a greater or lesser extent over the whole thickness range investigated. The diverse spectral band shapes and intensities are globally well reproduced with the mentioned Fresnel model. Some noteworthy discrepancies are, however, observed in the most intense peaks of the polarized spectra, which are affected by larger distortions. Whenever possible, the present measurements have been compared with published spectra recorded under similar conditions and a good accordance has been found. This comparison and the spectral simulations can reconcile seeming discrepancies in the previous literature data.

## 2002 Finney

29 October , Bowron, Soper, Loerting, Mayer, Hallbrucker

### Structure of a New Dense Amorphous Ice

#### Neutron diffraction VHDA, double occupancy of stabilising interstitial found in HDA, VHDA to LDA transition is very sharp (thermal unlocking of interstitial) & kinetically controlled, VHDA better candidate for second putative liquid phase of H2O than HDA

The detailed structure of a new dense amorphous ice, VHDA, is determined by isotope substitution neutron diffraction. Its structure is characterized by a doubled occupancy of the stabilizing interstitial location that was found in high density amorphous ice, HDA. As would be expected for a thermally activated unlocking of the stabilizing ‘‘interstitial,’’ the transition from VHDA to LDA (low-density amorphous ice) is very sharp. Although its higher density makes VHDA a better candidate than HDA for a physical manifestation of the second putative liquid phase of water, as for the HDA case, the VHDA to LDA transition also appears to be kinetically controlled.

## -2002 Parent

12 September , Laffon, Mangeney, Bournel, Tronc

### Structure of the water ice surface studied by x-ray absorption spectroscopy at the O K-edge

#### Vapour-deposited ASW & crystalline ice (38 – 150 K, UHV), NEXAFS (bulk sensitive) & PSD-NEXAFS (photon-stimulated desorption mode -> surface sensitive), ASW: 38 – 55 K: change from HDA to LDA, H2O-H2O molecular distance at surface always longer than in bulk

Vapor-deposited H2O ice films grown between 38 and 150 K under ultrahigh vacuum conditions have been investigated using near-edge x-ray absorption fine structure (NEXAFS) spectroscopy at the oxygen K-edge, in conventional mode—which is bulk sensitive-, and using the photon-stimulated desorption mode (PSD-NEXAFS), which is surface sensitive. By recording simultaneously those two signals, we have evidenced the differences between the surface and bulk electronic and atomic structures, for both amorphous porous ice condensed at 40 K and crystalline ice condensed at 150 K. We have also followed the bulk and surface evolutions of an amorphous ice film annealed from 38 to 147 K. A steep change in the local atomic structure of the bulk is observed, likely related to the high-density amorphous ice -> low-density amorphous ice phase transition between 38 and 55 K. We have shown that the surface of crystalline ice is well ordered, but this order is different from that of the bulk. We have evidenced that the H2O–H2O intermolecular distance at the surface of ice is always longer than in the bulk, and that this difference increases with temperature, as the thermally induced reordering of the surface proceeds. SCF-Xα multiple scattering calculations allow us to figure out those structural differences, both in the bulk and at the surface of amorphous ice, but further calculations are necessary for crystalline ice. We have shown that the PSD-NEXAFS signal is sensitive to the surface morphology that changes with temperature because of the micropores collapse. We have used a model [E. Vichnevetski, A. D. Bass, and L. Sanche, J. Chem. Phys. 113, 3874 (2000)] that quantitatively describes the effect of the surface porosity on the ion yield. The surface of ice at 38 K is well described by a network of vertical cylindrical pores of 20 Å of diameter, separated by 6 Å, collapsing when annealing the film. This model also properly accounts of the peculiar temperature evolution of the PSD signal at the O1s-14a1+1 excitation, and therefore, allows to establish the relation between the PSD-NEXAFS signal and the surface porosity.

## ? 2002 Tulk

23 August , Benmore, Urquidi, Klug, Neuefeind, Tomberli, Egelstaff

### Structural Studies of Several Distinct Metastable Forms of Amorphous Ice

#### High-density ASW annealing, neutron & X-ray diffraction, 5 distinct ASW forms – all metastable at each anneal T, structure evolves systematically between 4 – 8 K

Structural changes during annealing of high-density amorphous ice were studied with both neutron and X-ray diffraction. The first diffraction peak was followed from the high- to the low-density amorphous form. Changes were observed to occur through a series of intermediate forms that appear to metastable at each anneal temperature. Five distinct amorphous forms were studied with neutron scattering, and many more forms may be possible. Radial distribution functions indicate that the structure evolves systematically between 4 and 8 angstroms. The phase transformations in low-temperature liquid water may be much more complex than currently understood.

## -2002 Manca

22 July , Martin, Roubin

### Spectroscopic and volumetric characterization of a non-microporous amorphous ice

#### Porosity & SSA of ASW & crystalline ice, N2, CH4 and Ar adsorption, adsorption isotherm volumetry & infrared spectroscopy, non-microporous ice can have large SSA

The aim of this Letter is to re-investigate the characterization of ice porosity. N2, CH4 and Ar adsorption on amorphous ice has been compared to that on crystalline ice at low temperatures, using adsorption isotherm volumetry and infrared spectroscopy simultaneously. Here we show that amorphous ice can present a large specific surface area and nevertheless be non-microporous; this provides new ways for the understanding of interstellar reactivity.

## 2002 Finney

17 May , Hallbrucker, Kohl, Soper, Bowron

### Structures of High and Low Density Amorphous Ice by Neutron Diffraction

#### Neutron diffraction, HDA & LDA, local similarities between LDA & Ih, path: HDA -> liquid -> LDA -> Ih (second shell radial order increases, spatial order decreases), reason: fifth first neighbour interstitial restricts orientation of first shell H2Os.

Neutron diffraction with isotope substitution is used to determine the structures of high (HDA) and low (LDA) density amorphous ice. Both “phases” are fully hydrogen bonded, tetrahedral networks, with local order similarities between LDA and ice Ih, and HDA and liquid water. Moving from HDA, through liquid water and LDA to ice Ih, the second shell radial order increases at the expense of spatial order. This is linked to a fifth first neighbor “interstitial” that restricts the orientations of first shell waters. This “lynch pin” molecule which keeps the HDA structure intact has implications for the nature of the HDA-LDA transition that bear on the current metastable water debate.

## -2000 Barker

8 February , Wilson, Madden, Medvedev, Geiger

### Voids in the H-bonded network of water and their manifestation in the structure factor

#### oxygen-oxygen structure factor SOO(Q) peak of liquid water shows unusual doublet structure (shifting with pressure), limits correspond to peak positions of low/high density ASW -> polyamorphism of H2O, position determined by nearest-neighbour separation of voids in spatial distribution of oxygen atoms

The main peak of the oxygen-oxygen structure factor SOO(Q) of liquid water shows an unusual doublet structure. The low-Q feature of the doublet shifts appreciably with pressure, between limits which correspond to the position of the first peak in the low- and high-density forms of amorphous ice. This pressure dependence has been cited as evidence of polyamorphism in water. It is shown that this feature is analogous to the ‘‘prepeak,’’ or ‘‘first-sharp-diffraction peak’’ which is well known in network-forming ionic liquids, like SiO2, and that its position is determined by the nearest-neighbor separation of *voids* in the spatial distribution of oxygen atoms.

## -2000b Sadtchenko

10 January , Knutsen, Giese, Gentry

### Interactions of CCl4 with Thin D2O Amorphous Ice Films. 2. Variation of Desorption Kinetics with Ice Preparation Conditions and Evidence for Distinct Structures of Low-Density Amorphous Ice

#### Three metastable forms of microporous ASW (D2O): Iμ, Iδ, and Iϵ, TPDMS, desorption kinetics of CCl4, that Iμ, Iδ, and Iϵ characterized by relative abundances of two-, three-, and four-coordinated D2O molecules at the ice surface respectively, barriers to diffusion of D2O on surface (EDδ = 5 ± 1 kcal/mol, EDϵ = 9 ± 2 kcal/mol), phase diagram for thin D2O ice films

High sensitivity temperature-programmed desorption mass spectrometry (TPDMS) was employed in order to investigate the desorption kinetics of CCl4 from thin (≈ 500 ML (ML: monolayer)) amorphous D2O ice films. TPDMS experiments demonstrate that at low coverages CCl4 is trapped in the pores near the surface of microscopically rough ice. Three distinct desorption features, μ-, δ-, and ϵ-CCl4, consistent with the release of trapped CCl4 were observed. The μ-, δ-, and ϵ-CCl4 desorption yields demonstrate high sensitivity to the temperature and rate of ice film deposition. We interpret these results as evidence of the existence of three metastable forms of microporous amorphous ice, Iμ, Iδ, and Iϵ. Measurements of the relative desorption yields from CCl4 species trapped at the surface of ice films prepared at different temperatures and deposition rates were used in order to estimate the barriers to the diffusion of D2O on the surface of Iδ (EDδ) and Iϵ (EDϵ). The values obtained were EDδ = 5 ± 1 kcal/mol and EDϵ = 9 ± 2 kcal/mol. We suggest that Iμ, Iδ, and Iϵ can be characterized respectively by the relative abundances of two-, three-, and four-coordinated D2O molecules at the ice surface. A proposed phase diagram for thin D2O ice films is presented.

## -2000a Sadtchenko

15 December , Knutsen, Giese, Gentry

### Interactions of CCl4 with Thin D2O Amorphous Ice Films, Part I: A Nanoscale Probe of Ice Morphology

#### Structure of vapour deposited ASW & solid (crystalline?) ice: TPDMS (TPD mass spectrometry), 500 ML D2O ASW, 95 – 190 K, adsorption of CCl4 on ASW, 95 K deposition: microporous amorphous ice (CCl4) clustering in ASW pores), 130 K deposition: pore-free solid ice, two structurally different forms of ice coexist at T between 95 and 130 K

High sensitivity temperature-programmed desorption mass spectrometry (TPDMS) was used in order to investigate the adsorption of carbon tetrachloride on thin (≈ 500 ML) amorphous D2O ice films at 95 K. The TPDMS experiments demonstrate that the desorption kinetics of CCl4 are extremely sensitive to the ice morphology. At submonolayer coverages, the adsorption of CCl4 on ice films prepared by vapor deposition at 130 K results in TPD spectra which consist of a single desorption feature α-CCl4 at 133-140 K. The TPD spectrum of CCl4 from ice films vapor-deposited at 95 K, however, consists of three desorption peaks labelled σ-, δ-, and ϵ-CCl4 at 145, 180, and 190 K, respectively. We attribute the observed differences in the TPD spectra of CCl4 from the two types of ice to differences in the microstructure of the ice surface. D2O vapor deposition at 95 K apparently results in the formation of microporous amorphous ice, while deposition at 130 K results in the formation of pore-free, solid ice. Analysis of the TPD spectra demonstrates that CCl4 adsorption on ice prepared at 130 K results in the formation of metastable, two-dimensional islands. CCl4 adsorption on ice prepared at 95 K, however, proceeds through formation of three-dimensional clusters in the pores of microscopically rough ice. At very low coverages, small CCl4 clusters are trapped at the ice surface during TPD. Trapped CCl4 evolves into the gas phase at two different temperatures giving rise to δ- and ϵ-CCl4 desorption states. The dependence of δ- and ϵ-CCl4 yields on the temperature of ice film deposition indicates that two structurally different forms of ice coexist at temperatures between 95 and 130 K.

## -1999 Stevenson

5 March , Kimmel, Dohnálek, Smith, Kay

### Controlling the Morphology of Amorphous Solid Water

#### Porosity of ASW depends on incident angle of H2O molecules

The morphology of amorphous solid water grown by vapor deposition was found to depend strongly on the angular distribution of the water molecules incident from the gas phase. Systematic variation of the incident angle during deposition using a collimated beam of water led to the growth of nonporous to highly porous amorphous solid water. The physical and chemical properties of amorphous solid water are of interest because of its presence in astrophysical environments. The ability to control its properties in the laboratory may shed light on some of the outstanding conflicts related to this important material.

## 1999 Paschek

25 February , Geiger

### Simulation Study on the Diffusive Motion in Deeply Supercooled Water

#### Molecular dynamics studies, diffusion process in supercooled liquid water (255 – 360 K), ST2 liquid shows no glass transition, hopping process controls reorientational & translational motions, activation energy: 115 kJ/mol

The diffusion process in supercooled liquid water has been studied by a series of molecular dynamics simulations using systems of 216 ST2-model molecules in the temperature range between 255 and 360 K. In contrast to SPC/E water (Phys. ReV. E 1996, 54, 6331), the ST2 liquid does not show the appearance of a kinetic glass transition with structural arrest. Instead, we observe a significant change of the diffusion mechanism in the deeply supercooled region. The high-temperature microstep diffusion mechanism transforms continuously into a jump-diffusive behavior at low temperatures. By analyzing the intermediate incoherent structure factor of the center of mass motion we can characterize the hopping process by an average residence time τ0. The hopping process is found to control reorientational and translational motions, leading to a second region of apparent Arrhenius behavior with a high activation energy of about 115 kJ/mol. The change in the dynamic behavior occurs in parallel to the structural and thermodynamical transformation to a low-density liquid form of ST2 water.

## 1999 Klug

16 February , Tulk, Svensson, Loong

### Dynamics and Structural Details of Amorphous Phases of Ice Determined by Incoherent Inelastic Neutron Scattering

#### Neutron scattering of HDA (from pressure0induced amorphisation), LDA (from annealing HDA, hyperquenched liquid water, Ih, & Ic, H-bond interaction in LDA differ from hyperquenched water & are stronger than in HDA

Incoherent-inelastic neutron scattering data are obtained over the energy range of lattice and internal vibrations of water molecules in phases of ice prepared by pressure-induced amorphization (highdensity amorphous ice, hda), by thermal annealing of hda (low-density amorphous ice, lda), and by rapidly cooling water, as well as in ice Ih and Ic. Hydrogen bonding interactions in lda differ significantly from those in the glass obtained by rapid quenching, which has hydrogen-bond interactions characteristic of highly supercooled water. Hydrogen-bond interactions in hda are weaker than in the low-density phases.

## -1996 Li

16 September , Jenniskens

### Inelastic neutron scattering study of high density amorphous water ice

#### ASW characterisation, inelastic neutron scattering (ISIS) & spectroscopy, high density amorphous ice & high T metastable phases (low density amorphous ice, cubic and hexagonal ices), 16 – 4025 cm-1, spectra of low density amorphous ice have similar features to cubic and hexagonal ices, spectrum of high density amorphous ice is significantly different in the translational and librational regions (< 150 meV)

The various forms of amorphous ices with trapped impurities play an important role in astrophysics. Such ices observed spectroscopically as frost on interstellar dust in dense molecular clouds and in comets require a detailed understanding of the spectroscopic properties in laboratory conditions. Using the neutron inelastic scattering technique on ISIS at Rutherford-Appleton Laboratory, the recovered high density amorphous ice is measured along with its subsequent high temperature metastable phases: low density amorphous ice, cubic and hexagonal ices under the same conditions in the energy transfer region from 2 to 5OO meV (i.e. 16 – 4025 cm-1). The results show that the spectra of low density amorphous ice have similar features to cubic and hexagonal ices. However, the spectrum for the high density amorphous ice is significantly different from the others in the translational and librational regions (< 150 meV).

## 1996 Speedy

27 March , Debenedetti, Smith, Huang, Kay,

### The evaporation rate, free energy, and entropy of amorphous water at 150 K

#### Free energy difference (ΔiaG (150 K) = 1100 J/mol) & residual entropy difference (ΔiaS (0) = 0.7 J/(K mol)) for ASW & crystalline ice, from evaporation rates, ΔiaS (0) allows connection of ASW with normal liquid H2O via reversible thermodynamic path (1 atm)

Measurement of the rates of evaporation of amorphous water (a) and ice (i) near 150 K can be interpreted as giving a measure of their free energy difference, ΔiaG (150 K) = 1100 ± 100 J/mol, which, together with the known enthalpy difference and heat capacity data, suggests a residual entropy difference of ΔiaS (0) = 0.7 ± 2.2 J/(K mol) at absolute zero. Previous theoretical estimates of ΔiaS (0), which are much larger, did not allow the amorph to be connected with normal liquid water by a reversible thermodynamic path at atmospheric pressure. The present value allows such a connection.

## -1995 Essmann

27 April , Geiger

### Molecular dynamics simulation of vapor deposited amorphous ice

#### Molecular dynamics simulation, vapour deposited ASW, compared to neutron scattering data from high & low density ASW (pressure induced transformation of crystalline ice), result: vapour deposited ASW between the other two, but closer to high density ASW, agreement with vapour deposited ASW neutron scattering & electron diffraction studies, ASW surface layer deeply fissured (-> high porosity of vapour deposited ice)

We report a molecular dynamics simulation of the vapor deposition of amorphous ice on a cold surface. We compare the obtained structure with neutron scattering data of high and low density amorphous ice formed by pressure induced transformation of crystalline ice. The structure of our vapor deposited ice is intermediate between these two, although closer to high density amorphous ice. Its radial distribution functions resemble the results of a simulation of cluster formation in the gas phase as well as of a recent neutron scattering experiment on vapor deposited amorphous ice. The occurrence of an intermediate structure is also in agreement with a recent electron diffraction study. Structural differences are discussed in terms of the hydrogen-bond network. The amorphous surface layer is deeply fissured, suggesting a high porosity of vapor deposited ice.

## -1995 Blake

, Jenniskens

### The metastable persistence of vapor-deposited amorphous ice at anomalously high temperatures

#### Transmission Electron Microscope, structure of vapour-deposited astrophysical ice analogues as function of deposition (15 K, 0.05 μm thick), temperature history (1K/min) & composition (pure), 15 – 130 K: two amorphous to amorphous phase changes, 142 – 160 K: (time dependent) crystallisation (0.1 μm crystallites, stacking disorder (cubic/hexagonal/ amorphous))

CONFERENCE ABSTRACT

## -1994b Jenniskens

5 August , Blake

### Structural Transitions in Amorphous Water Ice and Astrophysical Implications

#### Selected area electron diffraction (SAED), structure of vapour-deposited ASW (15 K, 18 μm/hr deposition rate, 1 – 3 K/min heating rate), 15 K: high density amorphous polymorph (Iah), 38 – 68 K: transition to low density amorphous polymorph (Ial), 131 K: onset to transformation to third amorphous polymorph (Iar), 148 – 188 K: metastable coexistence of cubic ice (Ic) with some (Iar)

Selected area electron diffraction is used to monitor structural changes of vapor-deposited water ice in vacuum during warm-up from 15 to 188 K. A progression of three amorphous forms of water ice is found with well-defined transitions. The formation of a high-density amorphous form (lah) at 15 K is confirmed, and the transition to the more familiar low- density form (lal) occurs gradually over the range 38 to 68 K. At 131 K, the ice transforms into a third amorphous form (lar), which precedes the crystallization of cubic ice (Ic) and coexists metastably with lc from 148 K until at least 188 K. These structural transformations of amorphous water ice can be used to explain hitherto anomalous properties of astrophysical ices. The structural transition from lah to lal is responsible for the diffusion and recombination of radicals in ultraviolet-photolyzed interstellar ices at low temperatures. The occurrence and persistence of lar explains anomalous gas retention and gas release from water-rich ices at temperatures above 150 K.

## -1994a Jenniskens

, Blake

### The structural changes of water ice I during warmup

#### Selected area electron diffraction (SAED), structure of vapour-deposited ASW (15 K, 18 μm/hr deposition rate, 1 – 3 K/min heating rate), < 30 K: high density amorphous polymorph (Iah), 45 – 65 K: transition to low density amorphous polymorph (Ial), 131 – 142 K: onset to transformation to third amorphous polymorph (Iac), 142 – 161 K: crystallisation to cubic ice (Ic) with some (Iac) persisting, 225 K: crystallisation to hexagonal ice (Ih)

CONFERENCE ABSTRACT

## 1987 Giuère

14 July

### The bifurcated hydrogen-bond model of water and amorphous ice

#### Two characteristic distances in (liquid?) H2O: bifurcated hydrogen bonds (BHB, between three molecules) = 1.85 Å, linear bonds (LHB) = 2.3 Å, few percent of H2O left with one “free” (non-H-bonded) OH group, ASW may also contain BHB (X-ray & neutron scattering

The existence of bifurcated hydrogen bonds (BHB) between three molecules as a major feature of the structure of liquid water was postulated recently to account for the remarkable effect of temperature on the O-H stretching bands in the Raman spectra. As a corollary, there should be two kinds of H∙∙∙O distances in water: one, 1.85 Å, for the well-known linear bonds (LHB), prevalent in cold water, the other, 2.3 Å, for the weaker BHB. This is evident in the neutron diffraction studies of heavy water, which reveal important structural changes with temperature. For instance, the atom pair correlation functions, both in the first-order difference, and the isochoric temperature derivative methods, show two peaks at 1.8 and 2.3 Å, with inverse temperature dependence similar to that of the Raman bands at 3220 (LHB) and 3420 cm-1 (BHB). In the BHB the nearest-neighbor O∙∙∙O distances are the same as in the LHB, but the apex angle is much smaller than the tetrahedral, between 95° and 100°. This allows slightly shorter second neighbour O∙∙∙O distances, and a closer packing of the molecules. The increased average coordination of the H and O atoms creates an imbalance in the stoichiometry of hydrogen bonding. As a result, a few percent of the water molecules are left with one “free”, i.e., nonhydrogen-bonded OH group (NHB). The energy of the BHB is estimated at 2.5 kcal/mol, i.e., half that of the LHB, and its proportion in the liquid, at nearly 30 % at 0°C. Amorphous ice prepared from the vapor may also contain BHB according to x-ray and neutron diffraction data. The BHB appears as a common feature of hydroxylic compounds; e.g., hydrogen peroxide, alcohols, etc.

## 1987 Bellisent-Funel

30 April , Teixeira, Bosio

### Structure of high-density amorphous water. II. Neutron scattering study

#### High-density & low-density ASW, neutron scattering, different (second/third) nearest-neighbour distances -> H-bond network strongly deformed (similar to H2O at high T), low-density ASW is closer to pair correlation functions of supercooled H2O

High-density amorphous water is studied by neutron scattering in a Q range extending to 16 Å-1. The low-density form of amorphous water is also analysed and compared with previous results. There are very important differences in the composite pair correlation functions of the two forms of amorphous ice, in particular beyond the first nearest-neighbors distance. We conclude that the hydrogen bond network is strongly deformed in a manner analogous to that found in water at high temperature. This is in contrast with the behaviour of the pair correlation function of low-density amorphous water, which is closer to that of supercooled water.

## 1987 Bizid

30 April , Bosio, Defrain, Oumezzine

### Structure of high-density amorphous water. I. X-ray diffraction study

#### X-ray diffraction, high-density (from pressurised (2 GPa) Ih) & low-density (from heating high-density ASW) ASW, 77 K, 1 atm, both ices show different structures, low-density ASW very similar to vapour deposited (77 K) ASW

X-ray diffraction measurements up to momentum transfer q = 16 Å-1 were performed at atmospheric pressure on both the high-density form of amorphous ice obtained from pressurization of crystalline ice Ih at 77 K up to 2 GPa and the low-density form obtained by further heating. These two amorphous phases exhibit significant differences at the level of the second- and third-nearest neighbors which involve a decrease of the O-O-O angle on compression at high pressure. Moreover it is found that the low-density form is quite similar to that obtained by vapor deposition on cooled substrates at 77 K.

## 1986 Floriano

21 August , Whalley, Svensson, Sears

### Structure of High-Density Amorphous Ice by Neutron Diffraction

#### Neutron diffraction, HDA (from melting ice I @ 10.5 kbar & 77 K) @ 17 K & zero pressure, scaled pair distribution function similar to that of liquid D2O @ 9.8 kbar & 321 K -> HDA very similar to hypothetical glass that would be obtained by quenching water @ 10 kbar

The static structure factor and pair distribution function of high-density amorphous D2O ice, which is made by apparently melting ice I at 10.5 kbar and 77 K, have been determined by neutron diffraction at 17 K and zero pressure. The pair distribution function, scaled to 10 kbar, is compared with the same function for D2O liquid at 9.8 kbar and 321 K. The functions are very similar, which suggests that the structure of the high-density amorph is very similar to that of the, as yet hypothetical, glass that would be obtained by the quenching of water of 10 kbar.

## 1986 Bosio

12 November 1985 , Johari, Teixeira

### X-Ray Study of High-Density Amorphous Water

#### X-ray diffraction, 1 atm, 77 K, HDA (from 2 GPa pressurisation of Ih), structure at low-Q different from LDA, but nearest-neighbor distance & coordination number very similar, high density due to strong distortion of O-O-O angles from tetrahedral value.

X-ray diffraction measurements were performed at atmospheric pressure on a high-density form of amorphous ice obtained by pressurization of crystalline ice Ih at 77 K, up to 2 GPa. The low-momentum-transfer region of the determined structure factor is quite different from that corresponding to the low-density form of amorphous ice. However, the nearest-neighbor distance and coordination number are almost unchanged. The high density of this form of amorphous ice is explained by the strong distortion of the O-O-O angles from the ideal tetrahedral value.

## -1985 Eldrup

2 May , Vehanen, Schultz, Lynn,

### Positronium formation and diffusion in crystalline and amorphous ice using a variable-energy positron beam

#### Crystalline ice & ASW irradiated with positrons, Positronium formation -> detection when leaving the surface, probing electronic structure of ice, compare to Monte Carlo simulations, positron diffusion coefficients (ASW: 10-3 cm2/s, crystalline ice: 0.2 cm2/s), cavities of diameter > 17 Å in ASW (annealing out @ ≈ 100 K), crystallisation of ASW @ ≈ 135 K

The behavior of positrons in crystalline and amorphous ice has been studied with a beam of monoenergetic positrons with incident energies 0—4.5 keV. Positronium (Ps) is formed in the bulk ice and diffuses until it annihilates or escapes from the surface. Measurements were carried out on the fraction of ortho-Ps leaving the surface and of the Doppler broadening of the 511-keV γ annihilation line. For incident energies 0—60 eV the Ps formation probability shows large variations. These variations are associated with Ps formation in the so-called Ore gaps and reflect the electronic structure of ice as demonstrated by Monte Carlo simulations of the positron slowing-down process. At higher energies, up to about 1 keV, the total Ps yield increases from about 50 to 75%, which is attributed to Ps formation via spur processes. A large difference is found between the Ps diffusion coefficient in crystalline ice (about 0.2 cm2/sec) and in amorphous ice (roughly 10-3 cm2/sec). From the red shift of the 511-keV annihilation line the Ps work function (affinity) in the crystalline ice is estimated to be -2 ± 1 eV. Evidence for low-energy-positron diffraction in the crystalline ice is found with scattered intensities higher than 25 %. Sputtering of the crystalline ice creates surface damage which strongly reduces the yield of Ps escaping the surface. Cavities of average diameter larger than about 17 Å are found in the as-grown amorphous ice. They anneal out at about 100 K, which is below the crystallization temperature of about 135 K.

## ? 1974 Venkatesh

6 December , Rice, Narten

### Amorphous Solid Water: An X-ray Diffraction Study

#### ASW (vapour deposited @ 10 K), density: 1.2 g/cm3, X-ray diffraction -> Oxygen-atom pair correlation functions

Water vapor that condenses on a metal surface at 10 K forms a non-crystalline phase of estimated density 1.2 grams per cubic centimeter. X-ray diffraction data of high precision and resolution have been analyzed to yield oxygen atom pair correlation functions. The positional correlation in amorphous solid water extends over only a few molecular radii, and the radial distribution of near-neighbor oxygen atoms in amorphous solid water is qualitatively different from that found in the low-pressure ice modifications. Amorphous solid water is a useful material for liquid water models because it can be studied under conditions such that the effects of static disorder and thermal excitation can be separated.

# Porosity

## 2014 Bossa

29 November 2013 , Isokoski, Paardekooper, Bonnin, van der Linden, Triemstra, Cazaux, Tielens, Linnartz

### Porosity measurements of interstellar ice mixtures using optical laser interference and extended effective medium approximations

#### Effect of contamination (CO2) on ASW structure and pore collapse: optical laser interference, IR spectroscopy (dangling OH) & extended effective medium approximations (EMAs), H2O:CO2 = 10:1, 4:1, and 2:1, CO2 premixed with water in the gas phase does not significantly affect ice morphology during omni-directional deposition, as long as physical conditions favourable to segregation not reached, CO2 diffuses on surface of growing ice sample and then fills the pores

*Aims*. This article aims to provide an alternative method of measuring the porosity of multi-phase composite ices from their refractive indices and of characterising how the abundance of a premixed contaminant (e.g., CO2) affects the porosity of water-rich ice mixtures during omni-directional deposition.

*Methods*. We combine optical laser interference and extended effective medium approximations (EMAs) to measure the porosity of three astrophysically relevant ice mixtures: H2O:CO2 = 10:1, 4:1, and 2:1. Infrared spectroscopy is used as a benchmarking test of this new laboratory-based method.

*Results*. By independently monitoring the O-H dangling modes of the different water-rich ice mixtures, we confirm the porosities predicted by the extended EMAs. We also demonstrate that CO2 premixed with water in the gas phase does not significantly affect the ice morphology during omni-directional deposition, as long as the physical conditions favourable to segregation are not reached. We propose a mechanism in which CO2 molecules diffuse on the surface of the growing ice sample prior to being incorporated into the bulk and then fill the pores partly or completely, depending on the relative abundance and the growth temperature.

## 2013 Mispelaer

2 May , Theulé, Aouididi, Noble, Duvernay, Danger, Roubin, Morata, Hasegawa, Chiavassa

### Diffusion measurements of CO, HNCO, H2CO, and NH3 in amorphous water ice

#### Thermal diffusion coefficients of HNCO, H2CO, NH3, and CO in porous ASW (10−15 to 10−11 cm2s−1, 35 – 140 K), bulk diffusion coefficient for compact ASW too low to be measured with FTIR (< 10−15 cm2s−1)

*Context*. Water is the major component of the interstellar ice mantle. In interstellar ice, chemical reactivity is limited by the diffusion of the reacting molecules, which are usually present at abundances of a few percent with respect to water.

*Aims*. We want to study the thermal diffusion of H2CO, NH3, HNCO, and CO in amorphous water ice experimentally to account for the mobility of these molecules in the interstellar grain ice mantle.

*Methods*. In laboratory experiments performed at fixed temperatures, the diffusion of molecules in ice analogues was monitored by Fourier transform infrared spectroscopy. Diffusion coefficients were extracted from isothermal experiments using Fick’s second law of diffusion.

*Results*. We measured the surface diffusion coefficients and their dependence with the temperature in porous amorphous ice for HNCO, H2CO, NH3, and CO. They range from 10−15 to 10−11 cm2s−1 for HNCO, H2CO, and NH3 between 110 K and 140 K, and between 5–8 × 10−13 cm2s−1 for CO between 35 K and 40 K. The bulk diffusion coefficients in compact amorphous ice are too low to be measured by our technique and a 10−15 cm2s−1 upper limit can be estimated. The amorphous ice framework reorganization at low temperature is also put in evidence.

*Conclusions*. Surface diffusion of molecular species in amorphous ice can be experimentally measured, while their bulk diffusion may be slower than the ice mantle desorption kinetics.

## 2012 Accolla

22 October , Congiu, Manicò, Dulieu, Chaabouni, Lemaire, Pirronello

### Morphology of the solid water synthesized through the pathway D + O2 studied by the sensitive TPD technique

#### Formation of D2O on ASW from D + O2, TPD & IR spectroscopy, nascent ice mostly compact, underlying ice compacted during formation of D2O on surface (reaction heat), TPD more effective in probing ASW morphology,

We report on an experimental study on the formation of water, through the D + O2 pathway, on a sample of amorphous solid water, i.e. a realistic analogue of the surface of the interstellar grains of dense clouds. For improving our experimental conditions we use deuterium instead of hydrogen. We obtain, using both Temperature-Programmed Desorption Spectroscopy and Infrared Spectroscopy, that the morphology of the nascent water ice is mostly compact. We compare our results with those obtained previously by Oba et al. and show that the first technique is more effective in probing the morphology of amorphous water ice. We propose that the formation of compact ice is due to the heat of reactions which lead to the formation of water molecules. Water is synthesized, through the D + O2 pathway, on a film of compact amorphous solid water and on a porous substrate for comparison purposes. We show that in this latter case a gradual compaction of the sample takes place upon formation of new water molecules. We compare this reduction of water ice porosity with that one obtained by Accolla et al., due to recombination of deuterium atoms sent on the surface of an amorphous porous ice sample, and show that the compaction of the sample as a consequence of the water formation appears clearly more efficient.

## 2011 Winkel

12 July , Mayer, Loerting

### Equilibrated High-Density Amorphous Ice and Its First-Order Transition to the Low-Density Form

#### HDA-LDA transition (140 (H2O) and 143 K (D2O)), high pressures (0.07 – 0.2 GPa), X-ray diffraction, thermal stability of HDA against transformation to LDA at ambient pressure significantly increases with decreasing recovery pressure and reaches its maximum at 0.07 GPa

We investigate the downstroke transition from high- (HDA) to low-density amorphous ice (LDA) at 140 (H2O) and 143 K (D2O). The visual observation of sudden phase separation at 0.07 GPa is evidence of the first-order character of the transition. Powder X-ray diffractograms recorded on chips recovered from the propagating front show a double halo peak indicative of the simultaneous presence of LDA and HDA. By contrast, chips picked from different parts of the sample cylinder show either HDA or LDA. Growth of the low-density form takes place randomly somewhere inside of the high-density matrix. The thermal stability of HDA against transformation to LDA at ambient pressure significantly increases with decreasing recovery pressure and reaches its maximum at 0.07 GPa. A sample decompressed to 0.07 GPa is by ∼17 K more stable than an unannealed HDA sample. An increasingly relaxed nature of the sample is also evident from the progressive disappearance of the broad calorimetric relaxation exotherm, preceding the sharp transition to LDA. Finally, we show that two independent thermodynamic paths lead to a very similar state of (relaxed) HDA at 140 K and 0.2 GPa. We argue that these observations imply an equilibrated nature of the amorphous sample in the pressure range of p <≈ 0.2 GPa and speculate that the observation of macroscopic phase separation involves two ultraviscous liquid phases at 140 K. This supports the scenario of a firstorder liquid–liquid transition in bulk water.

## 2010 Herrero,

18 January , Gálvez, Maté, Escribano

### Interaction of CH4 and H2O in ice mixtures

#### Methane-water ice mixtures, IR spectroscopy: 14 – 60 K, dangling bonds of water, methane adsorbed on water micropores or trapped inside ASW structure, CH4 mobility depends on deposition method, CH4 fraction remains inside ASW after sublimation point (60 K)

Ice mixtures of methane and water are investigated by means of IR spectroscopy in the 14–60 K range. The spectroscopic research is focused on the symmetry-forbidden n1 band of CH4 and the dangling bond bands of water. The n1 band is visible in the spectra of the mixtures, revealing a distorted methane structure which co-exists with the normal crystalline methane. The water dangling bond bands are found to increase their intensity and appear at red-shifted frequency when distorted methane is present. Methane adsorbed on water micropores or trapped inside the amorphous solid water structure is assumed to be responsible for these effects. CH4 mobility in water ice depends on the deposition method used to prepare the samples and on the temperature. After warming the samples to 60 K, above the methane sublimation point, a fraction of CH4 is retained in the water ice. An adsorption isotherm analysis is performed yielding the estimation of the desorption energy of CH4 on H2O amorphous surfaces.

## 2010 Palumbo

5 December 2009 , Baratta, Leto, Strazzulla

### H bonds in astrophysical ices

#### Irradiation of ASW (-mixtures) with UV & ions: 12 – 16 K, ASW (pure/mixed with CO, CO2, O2, N2, H2O2, CH4, SO2, CH3OH), OH dangling bonds (intensity decreases) -> porosity decreases after irradiation

We have studied, by infrared absorption spectroscopy, the profile (shape and peak position) of the OH dangling bond feature in pure porous amorphous solid water (ASW) and in mixtures of water with other species (CO, CO2, O2, N2, H2O2, CH4, SO2, and CH3OH) at 12–16 K. Furthermore, we have investigated the effects of ion and UV irradiation on the morphology/porosity of amorphous water ice. Thin films (about 0.25–1 lm) of porous amorphous water ice were irradiated with 200 keV H+, 30 keV He+, and 10.2 eV Lyman alpha photons at 12–16 K. We have found that the profile of the OH dangling bond feature depends on the mixture considered and that the intensity of the OH dangling bond feature decreases after irradiation. This latter result indicates that the porosity of amorphous water ice decreases after both ion and UV irradiation.

## ? 2009 Fillion

2 March , Amiaud, Congiu, Dulieu, Momeniz, Lemaire

### D2 desorption kinetics on amorphous solid water: from compact to porous ice films

#### Desorption of D2 from ASW of various porosities: 10 – 30 K / 120 K, < 1 – 20 monolayers, more energetic binding sites for porous ices, binding energy of D2 is primarily governed by the topological and morphological disorder of the surface at molecular scale

The desorption kinetics of D2 from amorphous solid water (ASW) films have been studied by the temperature-programmed desorption (TPD) technique in the 10–30 K temperature range. Compact (and nonporous) films were grown at 120 K over a copper substrate. Ultra-thin porous films were additionally grown at 10 K over the compact base. The TPD spectra from compact and from up to 20 monolayers (ML) porous films were compared. The simulation of the TPD experimental traces provides the corresponding D2 binding-energy distributions. As compared to the compact case, the binding-energy distribution found for the 10 ML porous film clearly extends to higher energies. To study the transition from compact to porous ice, porous films of intermediate thicknesses (< 10 ML), including ultra-thin films (< 1 ML), were grown over the compact substrate. The thermal D2 desorption peak was found to shift to higher temperatures as the porous ice network was progressively formed. This behavior can be explained by the formation of more energetic binding sites related to porous films. TPD spectra were also modelled by using a combination of the two energy distributions, one associated to a bare compact ice and the other associated to a 10 ML porous ice film. This analysis reveals a very fast evolution of the binding-energy distribution towards that of porous ice. Our results show that few ML of additional porous film are sufficient to produce a sample for which the D2 adsorption can be described by the energy distribution found for the 10 ML porous film. These experiments then provide evidence that the binding energy of D2 on ASW ice is primarily governed by the topological and morphological disorder of the surface at molecular scale.

## 2008 Raut

28 July , Famá, Loeffler, Baragiola

### Cosmic ray compaction of porous interstellar ices

#### Compaction of microporous vapour deposited ice films under ion bombardment (80 – 400 keV), porosity decreases exponentially with irradiation, porous ice mantles on interstellar grains expected to compact by cosmic rays in 10 – 50 million years

We studied the compaction of microporous vapor-deposited ice films under irradiation with different ions in the 80 – 400 keV energy range. We found that porosity decreases exponentially with irradiation fluence, with a mean compaction area per ion that scales linearly with the stopping power of the projectile S above a threshold St = 4 eV Å-1. The experiments roughly follow a universal dependence of ion-induced compaction with restricted dose (eV/molecule). This behavior can be used to extrapolate our results to conditions of the interstellar medium. Relating our results to ionization rates of interstellar H2, we estimate that porous ice mantles on grains in dense molecular clouds are compacted by cosmic rays in ≈ 10 – 50 million years.

## ? 2007 Raut

28 June , Teolis, Loeffler, Vidal, Famá, Baragiola

### Compaction of microporous amorphous solid water by ion irradiation

#### Ion impact compaction of ASW (vapour-deposited, 40 K), UV-VIS/IR spectroscopy & methane ad-/desorption, decrease in pore internal surface area (IR, dangling OH) precedes loss of pore volume

We have studied the compaction of vapor-deposited amorphous solid water by energetic ions at 40 K. The porosity was characterized by ultraviolet-visible spectroscopy, infrared spectroscopy, and methane adsorption/desorption. These three techniques provide different and complementary views of the structural changes in ice resulting from irradiation. We find that the decrease in internal surface area of the pores, signaled by infrared absorption by dangling bonds, precedes the decrease in the pore volume during irradiation. Our results imply that impacts from cosmic rays can cause compaction in the icy mantles of the interstellar grains, which can explain the absence of dangling bond features in the infrared spectrum of molecular clouds.

## -2007 Stähler

15 May , Mehlhorn, Bovensiepen, Meyer, Kusmierek, Morgenstern, Wolf

### Impact of Ice Structure on Ultrafast Electron Dynamics in D2O Clusters on Cu(111)

#### Porous & compact ASW (D2O) structure, low-T scanning tunnelling microscopy & 2-photon photoemission spectroscopy, solvated electrons preferentially bind to D2O cluster surface but have different dynamics in both ices

The structure of D2O clusters on a Cu(111) surface and the femtosecond dynamics of photoexcited excess electrons are investigated by low-temperature scanning tunneling microscopy and two-photon photoemission spectroscopy. Two types of amorphous ice clusters, porous and compact, which exhibit characteristic differences in electron dynamics, are identified. By titration with Xe we show that in both structures solvated electrons preferentially bind on the cluster surface.

## 2005 Palumbo

### The morphology of interstellar water ice

#### porosity of ASW decreases after ion-irradiation: 15 K, dangling OH-bonds, CO adsorption

We have studied, by infrared absorption spectroscopy, the effects of ion irradiation (with 200 keV protons) on the morphology/porosity of thin amorphous water ice (H2O) samples at 15 K. We have found that the intensity of the OH dangling bond feature decreases after ion irradiation and that the amount of carbon monoxide (CO) absorbed in water ice decreases as the fluence of impinging ions increases. These results indicate that the porosity of amorphous water ice decreases after ion irradiation. Here we present the experimental results and suggest that because of cosmic ray bombardment water ice in interstellar grain mantles is compact in structure.

## ? 2004 Souda

16 September

### Hydrophobic hydration of alkanes: Its implication for the property of amorphous solid water

#### nonporous ASW below 100 K: secondary ion mass spectrometry to measure incorporation of alkanes (butane/hexane) in ASW, glass transition: 136 K, liquid water above 165 K ( surface tension)

We measured the incorporation of adsorbed alkanes in and their desorption from the amorphous solid water ASW by means of secondary ion mass spectroscopy and temperature programmed desorption. The heavier alkanes such as butane and hexane are incorporated completely in the bulk of the *nonporous* ASW layer below 100 K probably due to the preferential formation of ice structures around the solute molecules. The self-diffusion of water molecules occurs above the glass transition temperature 136 K. The liquid water emerges above 165 K, as evidenced by simultaneous occurrence of the dehydration of alkanes and the morphological change of the water layer induced by the surface tension.

# SSA

## ? 2013 Bag

14 March , Bhuin, Natarajan, Pradeep

### Probing Molecular Solids with Low-Energy Ions

#### Method review (low energy ion-surface collisions, 1 – 100 eV), probing properties of condensed molecular solids (e.g. processes on ice surface)

Ion/surface collisions in the ultralow- to low-energy (1–100-eV) window represent an excellent technique for investigation of the properties of condensed molecular solids at low temperatures. For example, this technique has revealed the unique physical and chemical processes that occur on the surface of ice, versus the liquid and vapor phases of water. Such instrument dependent research, which is usually performed with spectroscopy and mass spectrometry, has led to new directions in studies of molecular materials. In this review, we discuss some interesting results and highlight recent developments in the area. We hope that access to the study of molecular solids with extreme surface specificity, as described here, will encourage investigators to explore new areas of research, some of which are outlined in this review.

# Wetting of ASW

## ? 2011 May

31 July , Smith, Kay

### Probing the interaction of amorphous solid water on a hydrophobic surface: dewetting and crystallization kinetics of ASW on carbon tetrachloride

#### Dewetting and crystallisation of ASW on CCl4 underlayer on graphene, mobility of water molecules increases with ASW deposition temperature, when ASW completely covers the underlayer, CCl4 desorption is delayed until crystallisation of H2O (cracking -> molecular volcano)

Desorption of carbon tetrachloride from beneath an amorphous solid water (ASW) overlayer is explored utilizing a combination of temperature programmed desorption and infrared spectroscopy. Otherwise inaccessible information about the dewetting and crystallization of ASW is revealed by monitoring desorption of the CCl4 underlayer. The desorption maximum of CCl4 on graphene occurs at ≈ 140 K. When ASW wets the CCl4 no desorption below 140 K is observed. However, the mobility of the water molecules increases with ASW deposition temperature, leading to a thermodynamically driven dewetting of water from the hydrophobic CCl4 surface. This dewetting exposes some CCl4 to the ambient environment, allowing unhindered desorption of CCl4 below 140 K. When ASW completely covers the underlayer, desorption of CCl4 is delayed until crystallization induced cracking of the ASW overlayer opens an escape path to the surface. The subsequent rapid episodic release of CCl4 is termed a ‘‘molecular volcano’’. Reflection absorption infrared spectroscopy (RAIRS) measurements indicate that the onset and duration of the molecular volcano is directly controlled by the ASW crystallization kinetics.

## ? 2008 Souda

25 July

### Dewetting of Thin Amorphous Solid Water Films and Liquid-Cubic Ice Coexistence in Droplets Studied Using Infrared-Absorption and Secondary-Ion-Mass Spectroscopy

#### Coupled & decoupled OH/OD bonds in ASW (4 mol% HOD in 20-monolayer H2O), 150 – 160 K, spontaneous nucleation at 160 K is bypassed when amorphous solid water is deposited on a crystallized water film; the crystals grow around nuclei at ca. 150 K, crystal grains behave like viscous droplets (morphology changes continuously after completion of crystallization), coexisting liquid-like water is indistinguishable from cubic ice in local structure

The infrared absorption band of decoupled OD stretching vibration (4 mol% HOD in 20-monolayer H2O) of amorphous solid water is red-shifted and sharpened at around 160 K because of spontaneous nucleation. The crystal grows in a fluidized liquid that forms droplets on a Ni(111) substrate. The shape change and red-shift of a coupled OH band during crystallization are elucidated by a Mie particle scattering model, indicating that nanometer-size droplets are formed preferentially. The spontaneous nucleation at 160 K is bypassed when amorphous solid water is deposited on a crystallized water film; the crystals grow around nuclei at ca. 150 K, resulting in larger crystal grains that do not cause Mie scattering. However, the crystal grains behave like viscous droplets because their morphology changes continuously after the completion of crystallization. The coexisting liquid-like water is indistinguishable from cubic ice in local structure. This behavior resembles that of a quasiliquid formed during premelting.

## ? 2007 Kimmel

16 March , Petrik, Dohnálek, Kay

### Crystalline ice growth on Pt(111) and Pd(111): Nonwetting growth on a hydrophobic water monolayer

#### temperature programmed desorption (rare gases adsorbed on H2O), substrates: Pt(111) & Pd(111), 20 – 155 K, ice films grown above 135 K do not wet first monolayer (similar results for D2O and H2O), ASW films crystallise and dewet when annealed. Typical distances between initial crystallites: 14 nm or more, results consistent with no dangling OH bonds at surface

The growth of crystalline ice films on Pt(111) and Pd(111) is investigated using temperature programed desorption of the water films and of rare gases adsorbed on the water films. The water monolayer wets both Pt(111) and Pd(111) at all temperatures investigated e.g., 20–155 K for Pt(111) . However, crystalline ice films grown at higher temperatures e.g., *T* 135 K do not wet the monolayer. Similar results are obtained for crystalline ice films of D2O and H2O. Amorphous water films, which initially wet the surface, crystallize and dewet, exposing the water monolayer when they are annealed at higher temperatures. Thinner films crystallize and dewet at lower temperatures than thicker films. For samples sputtered with energetic Xe atoms to prepare ice crystallites surrounded by bare Pt(111) , subsequent annealing of the films causes water molecules to diffuse off the ice crystallites to reform the water monolayer. A simple model suggests that, for crystalline films grown at high temperatures, the ice crystallites are initially widely separated with typical distances between crystallites of 14 nm or more. The experimental results are consistent with recent theory and experiments suggesting that the molecules in the water monolayer form a surface with no dangling OH bonds or lone pair electrons, giving rise to a hydrophobic water monolayer on both Pt(111) and Pd(111) .

# Dangling OH bonds characterization

## 2015 Coussan

3 March , Roubin, Noble

### Inhomogeneity of the amorphous solid water dangling bonds

#### Behaviour of surface and immediate sublayers upon mid-infrared irradiation of ASW, selective IR irradiations of surface water molecules induces modification of surface and production of new monomer species (bonding to surface via its two electronic doublets), characterise two dH dangling bonds -> selective irradiation reveals inhomogeneity of these surface modes, irradiation induced surface reorientation -> max photoinduced isomerisation yield ≈ 15 %

Amorphous solid water (ASW) is one of the most widely studied molecular systems because of its importance in the physics and chemistry of the interstellar medium and the upper layers of the Earth’s atmosphere. Although the global structure of this material, i.e. the bulk and the surface, is well characterised, we are far from having an overall understanding of the changes induced upon chemical or physical perturbation. More specifically, the behaviour of the surface and the immediate sublayers upon mid-infrared irradiation must be understood due to its direct effect on the adsorption capacities of the ASW surface. Small molecules can accrete or form at the surface, adsorbed on the dangling OH groups of surface water molecules. This behaviour allows further reactivity which, in turn, could lead to more complex molecular systems. We have already demonstrated that selective IR irradiations of surface water molecules induce a modification of the surface and the production of a new monomer species which bonds to the surface via its two electronic doublets. However, we did not probe the structure of the dangling bands, namely their homogeneity or inhomogeneity. The structure and orientation of these surface molecules are closely linked to the way the surface can relax its vibrational energy. In this work, we have focussed our attention on the two dH dangling bonds, carrying out a series of selective irradiations which reveal the inhomogeneity of these surface modes. We have also studied the effects of irradiation duration on the surface reorientation, determining that the maximum photoinduced isomerisation yield is ≈15%.

## 2014b Noble

29 July , Martin, Fraser, Roubin, Coussan

### IR Selective Irradiations of Amorphous Solid Water Dangling Modes: Irradiation vs Annealing Effects

#### Surface chemistry driven by dangling OH bonds (other molecules binding to them), thermal and irradiation processing of ASW (affects bulk and surface structure) -> irradiation processing pathway clearly distinct from thermal processing (irradiation produces water monomer interacting with surface -> new trapping sites/new catalytic properties, thermal effect: global reorganisation of ice structure)

Amorphous solid water (ASW) is one of the most widely studied molecular systems. Ubiquitous in the interstellar medium (ISM) and potentially present in the upper layers of the Earth’s atmosphere, ASW plays a major role in heterogeneous physical chemistry. Small molecules form or accrete at the ice surface, bonding to water molecules with an OH bond projecting from the surface, so-called “dangling bonds”. These dangling OH are of crucial importance in the quest to identify and quantify surface reactions. Water ices in the ISM or Earth’s atmosphere undergo constant processing by thermal and irradiation effects, which can significantly affect both the bulk and surface structures and therefore the catalytic properties of the surface. In this work we have studied thermal and irradiation processing of ASW and determine that there is a photochemical processing pathway of the ice surface which is clearly distinct from purely thermal effects. Selective IR irradiations of each of the surface water modes led to the observation of a “hole-burning” at the irradiation frequency, counterbalanced by the production of a new band, identified as a water monomer interacting with the surface. The thermal effects, meanwhile, led to a global decrease of all the dangling modes due to global reorganization of the water ice structure. It is thus obvious that, depending on the processing history of an ice, its catalytic properties will not be affected in the same way. The fact that we observe an IR selective irradiation effect illustrates that some fraction of the vibrational energy, rather than being relaxed through the H-bonded network of the bulk ice, is trapped at the surface; this energy induces a reorganization of the surface structure, forming new trapping sites, and thus generating new catalytic properties.

## 2014a Noble

11 February , Martin, Fraser, Roubin, Coussan

### Unveiling the Surface Structure of Amorphous Solid Water via Selective Infrared Irradiation of OH Stretching Modes

#### ASW dangling OH bonds, irradiation effects: surface H2O molecules reorganise, form monomer-like water mode on surface -> reduced range of binding sites -> altered catalytic capacity

In the quest to understand the formation of the building blocks of life, amorphous solid water (ASW) is one of the most widely studied molecular systems. Indeed, ASW is ubiquitous in the cold interstellar medium (ISM), where ASW-coated dust grains provide a catalytic surface for solid phase chemistry, and is believed to be present in the Earth’s atmosphere at high altitudes. It has been shown that the ice surface adsorbs small molecules such as CO, N2, or CH4, most likely at OH groups dangling from the surface. Our study presents completely new insights concerning the behavior of ASW upon selective infrared (IR) irradiation of its dangling modes. When irradiated, these surface H2O molecules reorganize, predominantly forming a stabilized monomer-like water mode on the ice surface. We show that we systematically provoke “hole-burning” effects (or net loss of oscillators) at the wavelength of irradiation and reproduce the same absorbed water monomer on the ASW surface. Our study suggests that all dangling modes share one common channel of vibrational relaxation; the ice remains amorphous but with a reduced range of binding sites, and thus an altered catalytic capacity.

## 2004 Fraser

18 May , Collings, Dever, McCoustra

### Using laboratory studies of CO–H2O ices to understand the non-detection of a 2152 cm-1 (4.647 μm) band in the spectra of interstellar ices

#### CO-H2O-ice system: lab experiments, dangling OH bonds exist in interstellar ices, but are blocked by other species -> no CO feature observed

We present results from laboratory experiments on layered CO–H2O-ice systems, carried out from sub-monolayer to multilayer CO coverages, and review recent experimental data, as published by the authors. Under certain specific laboratory conditions the 2152 cm−1 feature, associated with CO molecules adsorbed at dangling-OH bonds at the ice surface, is ‘missing’. A detailed analysis is used to understand why the same feature is not detected in spectra of interstellar ices. We conclude that the dangling-OH sites do exist in interstellar ices but that the sites are blocked by another species. The astronomical implications of this deduction are discussed.

## ??? 2004 Al-Halabi

4 March , Fraser, Kroes, van Dishoeck

### Adsorption of CO on amorphous water-ice surfaces

#### Classical trajectory calculations, adsorption of thermal CO on surface of compact ASW, 90 K, no diffusion of CO inside ice or into surface valley, maximum potential energy when CO interacts with dangling OH group, relatively few dangling OH groups present on ASW surface -> might explain lack of astronomical observations of this feature, CO also interacts with bonded OH groups, 10 K: lifetime of CO on surface longer than age of universe, 90 K: lifetime = 300 ns

We present the results of classical trajectory calculations of the adsorption of thermal CO on the surface of compact amorphous water ice, with a view to understanding the processes governing the growth and destruction of icy mantles on dust grains in the interstellar medium and interpreting solid CO infrared spectra. The calculations are performed at normal incidence, for Ei = 0.01 eV (116 K) and surface temperature Ts = 90 K. The calculations predict high adsorption probabilities (∼1), with the adsorbed CO molecules having potential energies ranging from −0.15 to −0.04 eV with an average energy of −0.094 eV. In all the adsorbing trajectories, CO sits on top of the surface. No case of CO diffusion inside the ice or into a surface valley with restricted access was seen. Geometry minimizations suggest that the maximum potential energy of adsorbed CO (−0.155 eV) occurs when CO interacts with a “dangling OH” group, associated with the 2152 cm-1 band seen in laboratory solid-state CO spectra. We show that relatively few “dangling OH” groups are present on the amorphous ice surface, potentially explaining the absence of this feature in astronomical spectra. CO also interacts with “bonded OH” groups, which we associate with the 2139 cm-1 infrared feature of solid CO. Our results for CO adsorption on amorphous ice are compared with those previously obtained for CO adsorption to crystalline ice. The implications of the spectroscopic assignments are discussed in terms of the solid-CO infrared spectra observed in interstellar regions. Using the Frenkel model, the lifetime τ for which CO may remain adsorbed at the surface is calculated. At temperatures relevant to the interstellar medium, i.e. 10 K, it is longer than the age of the universe, but decreases dramatically with increasing Ts, such that at Ts = 90 K, τ = 300 ns. The pre-exponential factor τν used in the Frenkel model is found to be 0.95 ± 0.02 ps. These data are compared to recent experimental results. The astrophysical implications of these calculations are discussed, with particular reference to the CO binding sites identified on amorphous ice surfaces, their adsorption energies, probabilities and lifetimes.

## -2002 Mitlin

10 April , Leung

### Film Growth of Ice by Vapor Deposition at 128-185 K Studied by Fourier Transform Infrared Reflection-Absorption Spectroscopy: Evolution of the OH Stretch and the Dangling Bond with Film Thickness

#### Vapour deposited H2O ice (poly- and non-crystalline): 128 – 185 K, grazing-angle Fourier transform Infrared Reflection-Absorption Spectroscopy (RAS), polycrystalline ice above 155 K, non-crystalline below 145 K, OH stretching band changes as function of film thickness (< 10 – 1500 nm), changes similar for poly- and non-crystalline ice -> dangling OH bonds are integral part of surfaces of both ices for thick films (> 700 nm), non-crystalline ice contains larger amount of dangling OH bonds -> bonds are on tracery external surface for non-crystalline ice and on crystal grain boundaries & surface for polycrystalline ice.

The polycrystalline and noncrystalline ice films vapor-deposited at 128-185 K were investigated by grazing-angle Fourier transform Infrared Reflection-Absorption Spectroscopy (RAS). In particular, the polycrystalline ice phase was found above 155 K, whereas the noncrystalline phase was formed below 145 K. The nature of the polycrystalline and noncrystalline ice phases can be differentiated by comparing the respective RA spectra with spectral simulations based on the Fresnel reflection and Mie scattering methods. Furthermore, the OH stretching band (3800-2800 cm-1) exhibits complex behavior as a function of film thickness (from less than 10 nm to 1500 nm), which can be simulated and attributed primarily to the physics of absorption-reflection based on the Fresnel equations for reflection coefficients for parallel- and perpendicular-polarized light in a vacuum-dielectric film-metal system. The spectral evolution of the OH stretch with the film thickness is found to be similar for both polycrystalline and noncrystalline phases. In addition, spectral features of the incompletely coordinated OH groups at 3700-3690 cm-1 have been observed for a majority of noncrystalline and polycrystalline ice samples grown under different conditions (e.g., at 185 K), which shows that these OH dangling bonds are an integral part of the surfaces of both noncrystalline and polycrystalline ice phases. For thin films less than 200 nm thick, both kinds of ice are found to have a comparable amount of OH dangling bonds. In contrast, the thicker films (with thicknesses greater than 700 nm) of the noncrystalline phase contain a noticeably larger amount of OH dangling bonds than the polycrystalline films of comparable thickness. This thickness dependence of the OH dangling bond feature suggests that the OH dangling bonds are located most likely on the external surfaces of the crystalline grains and/or of the ice film itself at larger thicknesses for polycrystalline phase and on the tracery external surface in the case of noncrystalline phase.

## ? 2001 Devlin

23 January , Sadlej, Buch

### Infrared Spectra of Large H2O Clusters:  New Understanding of the Elusive Bending Mode of Ice

#### 1400−1700 cm-1 spectral range (annealed ASW & crystalline cubic ice at 10 K) characterized by broad absorption (water bending vibrations) lacking distinct features, bend-mode frequency & band intensity depend on strength & tetrahedrality of hydrogen bonding, significant decrease of librational-mode frequency (when hydrogen bonding is reduced relative to ice I) reduces overlap of bending mode with librational overtone

Infrared spectroscopic data for large water clusters, ranging from ∼100 to 64 000 molecules, have been extended to the O−H stretch and bending mode regions of H2O. The stretch-mode spectra and analysis parallel results reported recently for D2O large clusters. Ambiguities in the current understanding of the bending region of the spectra of amorphous and crystalline ice are addressed using insights derived from the cluster infrared spectra and ab initio reduced-dimensionality models of ice and of the ice surface. The 1400−1700 cm-1 spectral range, for *annealed* amorphous ice and crystalline cubic ice at 10 K, is characterized by a broad absorption lacking distinct features assignable to water bending vibrations. The spectra suggest that the bend-mode intensity of the bulk ices is either inherently very weak, diffused through interaction with the librational overtone, or both. However, this is not the case for large water clusters, which display distinct and relatively narrow bands attributed to the bending modes of subsets of *surface* water molecules. The new computational results suggest a strong but irregular dependence of the bend-mode frequency and band intensity on the strength and tetrahedrality of the hydrogen bonding. The computed intensity does decrease substantially for 4-coordinated vs lower-coordinated waters, but the highest frequency corresponds to double-donor 3-coordinated surface water molecules. A significant decrease of the *librational-mode* frequency, for those cases for which hydrogen bonding is reduced relative to ice I, is known to reduce the overlap of the bending mode with the librational overtone. Thus, for liquid water, *microporous* amorphous ice and the ice surface, which deviate strongly from tetrahedral bonding and for which the hydrogen bonding is diminished, the bend-mode absorption assumes a more normal intensity and bandwidth. From this basis a qualitative interpretation is presented of the infrared spectra for the region from ∼500 to ∼2400 cm-1.

## 2000 Manca

17 October , Allouche

### Quantum study of the adsorption of small molecules on ice: The infrared frequency of the surface hydroxyl group and the vibrational stark effect

#### Quantum calculation, adsorption of small nonpolar model systems (C2H2, C2H4, O3, CO, N2, Ar) on ice, IR shift of dangling surface hydroxyls (OH) largely governed by vibrational stark effect

A periodic Hartree–Fock quantum calculation has been developed for the adsorption of small nonpolar model systems (C2H2, C2H4, O3, CO, N2, and Ar) on ice in order to determine the physical variables responsible for the large infrared frequency shifts of the surface hydroxyls. It is shown that the correlation between these shifts and the corresponding interaction energies is not quite convincing. On the contrary it appears that the frequency shifts are tightly correlated to the variation with adsorption of the local electric field along the OH bond thus demonstrating that the dangling hydroxyl frequency is largely governed by the vibrational stark effect.

# Chemistry of ASW

## 2015 Smith

23 November , May, Kay

### Desorption Kinetics of Ar, Kr, Xe, N2, O2, CO, Methane, Ethane, and Propane from Graphene and Amorphous Solid Water Surfaces

#### Desorption kinetics for Ar, Kr, Xe, N2, O2, CO, methane, ethane & propane from graphene-covered Pt(111) & ASW surfaces, TPD, results: desorption energies and prefactors for desorption

The desorption kinetics for Ar, Kr, Xe, N2, O2, CO, methane, ethane, and propane from graphene-covered Pt(111) and amorphous solid water (ASW) surfaces are investigated using temperature-programmed desorption (TPD). The TPD spectra for all of the adsorbates from graphene have well-resolved first, second, third, and multilayer desorption peaks. The alignment of the leading edges is consistent the zero-order desorption for all of the adsorbates. An Arrhenius analysis is used to obtain desorption energies and prefactors for desorption from graphene for all of the adsorbates. In contrast, the leading desorption edges for the adsorbates from ASW do not align (for coverages < 2 ML). The nonalignment of TPD leading edges suggests that there are multiple desorption binding sites on the ASW surface. Inversion analysis is used to obtain the coverage dependent desorption energies and prefactors for desorption from ASW for all of the adsorbates.

## ? 2009 Oba

10 August , Miyauchi, Hidaka, Chigai, Watanabe, Kouchi

### Formation of compact amorphous H2O ice by codeposition of Hydrogen atoms with Oxygen molecules on grain surfaces

#### H2O formation by co-deposition, IR spectroscopy: 10 – 40 K, H2O and H2O2 continuously formed, ratio varies with deposition conditions (H/O2-ratio, T), H2O-ice is amorphous but compact (no dangling OH-bonds observable)

Formation of H2O molecules through the codeposition of oxygen molecules and hydrogen atoms is examined in situ using IR spectroscopy at 10–40 K under various O2 and H fluxes. It is found that H2O and H2O2 are continuously formed by reaction, even at 40 K. The H2O ice formed is amorphous, but has a compact (not microporous) structure compared to vapor-deposited amorphous H2O ice, because dangling OH bonds are not observed in the IR spectrum. This is consistent with astronomical observations in molecular clouds and theoretical predictions, which suggest that hydrogenation of O2 is one of the potential routes for reproducing these IR spectral characteristics. The composition of the ice formed by codeposition varies with the O2/H ratio and temperature. Although no data are available at present for the H2O/H2O2 ratio of ice in molecular clouds, this study suggests that hydrogenation of O2 has a potential to yield a H2O/H2O2 ratio of 5 or more in molecular clouds.

## ? 2008 Burke

1 July , Wolff, Edridge, Brown

### Thermally induced mixing of water dominated interstellar ices

#### Adsorption and desorption of C2H5OH deposited on top/underneath/concurrently with ASW: TPD & RAIRS, 98 K, thermally induced mixing between C2H5OH and H2O observed for all deposition methods, C2H5OH modifies H2O desorption and ASW-Ic phase transition

Despite considerable attention in the literature being given to the desorption behaviour of smaller volatiles, the thermal properties of complex organics, such as ethanol (C2H5OH), which are predicted to be formed within interstellar ices, have yet to be characterized. With this in mind, reflection absorption infrared spectroscopy (RAIRS) and temperature programmed desorption (TPD) have been used to probe the adsorption and desorption of C2H5OH deposited on top of water (H2O) films of various thicknesses grown on highly oriented pyrolytic graphite (HOPG) at 98 K. Unlike many other molecules detected within interstellar ices, C2H5OH has a comparable sublimation temperature to H2O and therefore gives rise to a complicated desorption profile. RAIRS and TPD show that C2H5OH is incorporated into the underlying ASW film during heating, due to a morphology change in both the C2H5OH and H2O ices. Desorption peaks assigned to C2H5OH co-desorption with amorphous, crystalline (CI) and hexagonal H2O-ice phases, in addition to C2H5OH multilayer desorption are observed in the TPD. When C2H5OH is deposited beneath ASW films, or is co-deposited as a mixture with H2O, complete co-desorption is observed, providing further evidence of thermally induced mixing between the ices. C2H5OH is also shown to modify the desorption of H2O at the ASW-CI phase transition. This behaviour has not been previously reported for more commonly studied volatiles found within astrophysical ices. These results are consistent with astronomical observations, which suggest that gas-phase C2H5OH is localized in hotter regions of the ISM, such as hot cores.

## 2008 Coupeaud

1 July , Piétri, Allouche, Aycard, Couturier-Tamburelli

### Experimental and Theoretical Investigation of HC5N Adsorption on Amorphous Ice Surface: Simulation of the Interstellar Chemistry

#### HC5N adsorbed on ASW (@ 10 K) interacts with ice surface and induces restructuring of bulk, desorption between 120 – 160 K, desorption energy: 90 kJ/mol -> ASW surface is essentially dynamic, HC5N moiety presents curvature and is stabilized by two strong N· · ·H bonds (2.09 and 2.29 Å) and one H· · ·O bond (1.84 Å)

HC5N adsorbed on amorphous water ice at 10 K presents an interaction with the ice surface and induces the restructuring of the ice amorphous bulk. Warming up the sample induces the HC5N desorption from the H2O ice film, between 120 and 160 K, and the associated desorption energy is 90 kJ/mol. This value is in good agreement with that calculated Ed (80 kJ/mol) and gives evidence that the amorphous ice surface is essentially dynamic. From theoretical calculations, it is shown that the HC5N moiety presents a curvature and is no more linear and stabilized by two strong N· · ·H bonds (2.09 and 2.29 Å) and one H· · ·O bond (1.84 Å).

## 2008 Hidaka

5 March , Miyauchi, Kouchi, Watanabe

### Structural effects of ice grain surfaces on the hydrogenation of CO at low temperatures

#### Hydrogenation of CO on crystalline ice & ASW @ 15 K, CO-coverage on ice surfaces dominates effective reaction rate (rather than surface structure), larger depletion of CO on crystalline ice than on ASW

Experiments on the hydrogenation of CO on crystalline and amorphous ice at 15 K were carried out to investigate the structural effects of the ice surface. The effective rate of H atom addition to CO on the amorphous ice was found to be larger than that on the crystalline ice, while CO depletion on crystalline ice became larger after long exposure. We demonstrated that the CO-coverage on the ice surfaces dominates the effective reaction rate rather than the surface structure. The larger depletion of CO on crystalline ice, as compared to amorphous ice, suggests easier desorption of CO and/or products by the heat of the reaction.

## 2007 Cyriac

30 March , Pradeep

### Probing Difference in Diffusivity of Chloromethanes through Water Ice in the Temperature Range of 110-150 K

#### Diffusive mixing of chloromethanes in different molecular solids H2O, D2O, and CH3OH by monitoring their chemical sputtering spectra due to the impact of Ar+ ions (focus ASW), no effect of ice crystallinity on diffusivity of water molecules (when deposited below chloromethanes), effect of substrate was insignificant, rise in temperature increased diffusive mixing wherever process was observed at lower T, CCl4 diffusion hindered under conditions where e.g. CHCl3 and CH2Cl2 undergo diffusive mixing, 4 – 600 monolayers

In this work, we have examined the diffusive mixing of chloromethanes in different molecular solids H2O, D2O, and CH3OH by monitoring their chemical sputtering spectra due to the impact of Ar+ ions in the collision energy range of 3-60 eV, focusing on amorphous solid water. The chemical sputtering spectra have been monitored over the temperature window accessible by liquid nitrogen, and the coverages of the molecules of interest and ice have been varied from one to several hundred monolayers. Instrumentation and sensitivity of the technique have been discussed. It is found that while the diffusion of CCl4 in the molecular solids investigated is hindered, other chloromethanes such as CHCl3 and CH2Cl2 undergo diffusive mixing over the same temperature range. Quantitatively, while ≈ 4 monolayers (ML) of ice are found to block CCl4 diffusion, the numbers are ≈ 250 and ≈ 600 ML for CHCl3 and CH2Cl2, respectively. Crystallinity of ice does not have any effect on the diffusivity of water molecules when it is deposited below the chloromethanes. The effect of substrate was insignificant, and the rise in temperature increased diffusive mixing wherever the process was observed at a lower temperature.

## ? 2005 Kumi

12 December , Malyk, Hawkins, Reisler, Wittig

### Amorphous Solid Water Films: Transport and Guest-Host Interactions with CO2 and N2O Dopants

#### ASW interaction with CO2/N2O dopants, deposition @ 90 K, FTIR spectroscopy & TPD, top-layer of dopant desorbs above 105 K, some dopants residing within ASW remain until crystallisation @ 155 K (then all of it expelled), no differences between CO2 & N2O, annealing ASW to 130 K lowers capacity for dopant inclusion by factor ≈ 3, but no differences visible in ASW spectral feature @ ≈ 3250 cm-1, dangling OH bonds observed (redshift ≈ 50 cm-1 by dopant interaction)

Guest-host interactions have been examined experimentally for amorphous solid water (ASW) films doped with CO2 or N2O. The main diagnostics are Fourier transform infrared (FTIR) spectroscopy and temperature programmed desorption (TPD). ASW films deposited at 90 K are exposed to a dopant, and the first molecules that attach to a film enter its bulk until it is saturated with them. Subsequent dopant adsorption results in crystal growth atop the ASW film. There are distinct spectral signatures for these two cases: LO and TO vibrational modes for the crystal overlayer, and an easily distinguished peak for dopant molecules that reside within the ASW film. Above 105 K, the dopant surface layer desorbs fully. Some dopants residing within the ASW film remain until 155 K, at which point the ASW-to-crystalline-ice transition occurs, expelling essentially all of the dopant. No substantial differences are observed for CO2 versus N2O. It is shown that annealing an ASW film to 130 K lowers the film’s capacity to include dopants by a factor of ≈ 3, despite the fact that the ASW spectral feature centred at ≈ 3250 cm-1 shows no discernible change. Sandwiches were prepared: ASW-dopant-ASW etc., with the dopant layer displaying crystallinity. Raising these samples past 105 K resulted in the expulsion of essentially all of the crystalline dopant. What remained displayed the same spectral signature as the molecules that entered the bulk following adsorption at the surface. It is concluded that the adsorption sites, though prepared differently, have a lot in common. Dangling OH bonds were observed. When they interacted with a dopant, they underwent a red shift of ≈ 50 cm-1. This is in qualitative agreement with studies that have been carried out with weakly bound binary complexes. As a result of this study, a fairly complete, albeit qualitative, picture is in place for the adsorption, binding, and transport of CO2 and N2O in ASW films.

## 2004 Herring

7 May , Aleksandrov, Orlando

### Stimulated Desorption of Cations from Pristine and Acidic Low-Temperature Water Ice Surfaces

#### Electron-impact ionization of low-temperature water ice leads to H+, H2+, and H+(H2O)n=1–8 desorption. Cation yields probe surface acidity

Electron-impact ionization of low-temperature water ice leads to H+, H2+, and H+(H2O)n=1–8 desorption. The 22 eV H+ desorption threshold is correlated with localized 2-hole 1-electron and 2-hole final states which Coulomb explode, while the 22 eV H2+ threshold is due to H2O+ unimolecular dissociation. The 70 eV primary cluster ion threshold is consistent with holes in the 2a1 level and secondary ionization channels. All cation yields are sensitive to local structural changes and probe surface acidity. The cluster size distribution indicates hole-hole screening distances of 1–2 nm.

## 2004 Grecea

22 December 2003 , Backus, Fraser, Pradeep, Kleyn, Bonn

### Mobility of haloforms on ice surfaces

#### TPD & RAIRS: CHCl3 does not diffuse over the crystalline ice surface (below its desorption T @ 140 K), CHBr3 is mobile at low temperatures (85 K)

We have investigated the mobility of bromoform (CHBr3) and chloroform (CHCl3) on amorphous solid water and crystalline ice surfaces, by monitoring their adsorption and desorption behavior using temperature programmed desorption spectroscopy and reflection absorption infrared spectroscopy. Up to its desorption temperature, of 140 K, CHCl3 does not diffuse over the crystalline ice surface, whereas CHBr3 is found to be mobile at temperatures as low as 85 K. The results demonstrate distinct differences between the surface mobility of structurally similar haloform molecules on crystalline ice surfaces, which may have implications to the halocarbon chemistry occurring on atmospheric ice particles.

## 2004 Borodin

1 December , Höfft, Kahnert, Kempter, Allouche

### Electron spectroscopy (UPS(HeI and II) and metastable impact electron spectroscopy (MIES)) applied to molecular surfaces: the interaction of atoms and molecules with solid water

#### Interaction of atoms & molecules with ASW (80 K deposition), photoelectron spectroscopy, UPS, metastable impact electron spectroscopy (MIES), 1. Na atoms: 3s-electron is delocalised from Na core & trapped between Na & H2O of surrounding water shell, 2. NaCl: no interpenetration of H2O & NaCl @ 90 K, but ionic dissociation happens when H2O & NaCl in direct contact, solvation of Cl- & Na+ becomes significant @ 105 K, H2O desorption from mixed films between 145 & 170 K (species bound ionically to Na+ and Cl- are removed last), 3. Chlorobenzene & chlorophenyl: different mobilities w.r.t. H2O, annealing to 200 K

We report studies of the interaction of atoms and molecules with solid molecular surfaces, water in particular, by combining photoelectron spectroscopy, UPS with HeI and II, and metastable impact electron spectroscopy (MIES). In MIES charge exchange processes of the Auger-type taking place between metastable He atoms and the surface under study are utilized to gain information on their electronic structure. The MIES spectra give a rather direct image of the surface DOS. We concentrate on the following processes taking place on water films produced at 80 K:

(1) Interaction of Na Atoms with Amorphous Solid H2O Films: emphasis was on the role of the 3sNa electrons in the water dissociation process. In order to make a detailed comparison with density functional theory (DFT), DOS (density of states) information is compared with the MIES spectra. Our results are consistent with the theoretical prediction that the 3s-electron is delocalized from the Na-core and trapped (solvated) between the Na-core and water molecules of the surrounding water shell.

(2) Ionization and Solvation of NaCl Interacting with Amorphous Solid Water: at 90K there is no interpenetration of H2O and NaCl. However, ionic dissociation of NaCl takes place when H2O and NaCl are in direct contact. At 105K the solvation of the ionic species Cl- and Na+ becomes significant. The desorption of H2O from the mixed film takes place between 145 and 170 K; those species bound ionically to Na+ and Cl- are removed last.

(3) The Interaction of PBTs (persistent, bio-accumulative, and toxic substances), chlorobenzene and chlorophenyl, with amorphous solid water: the organic layers produced at 80K were annealed up to 200K under in situ control of MIES and UPS. The different behaviour of the interfaces for the three studied cases is traced back to the different mobilities of the molecules with respect to that of water. The interaction between H2O and the benzene derivatives is discussed on the basis of qualitative free energy profiles.

## ? 2003 Collings

, Dever, Fraser, McCoustra

### Laboratory studies of the interaction of carbon monoxide with water ice

#### Interaction of CO with ASW, TPD & FT-RAIRS, astrophysically relevant temperatures, model (including CO desorption, migration, and entrapment in ice matrix & H2O crystallisation)

The interaction of carbon monoxide (CO) with vapour-deposited water (H2O) ices has been studied using temperature programmed desorption (TPD) and Fourier transform reflection-absorption infrared spectroscopy (FT-RAIRS) over a range of astrophysically relevant temperatures. Such measurements have shown that CO desorption from amorphous H2O ices is a much more complex process than current astrochemical models suggest. Re-visiting previously reported laboratory experiments (Collings et al., 2003), a rate model has been constructed to explain, in a phenomenological manner, the desorption of CO over astronomically relevant timescales. The model presented here can be widely applied to a range of astronomical environments where depletion of CO from the gas phase is relevant. The model accounts for the two competing processes of CO desorption and migration, and also enables the entrapment of some of the CO in the ice matrix and its subsequent release as the water ice crystallises and then desorbs. The astronomical implications of this model are discussed.

## 2003 Souda

25 June , Kawanowa, Kondo, Gotoh

### Hydrogen bonding between water and methanol studied by temperature-programmed time-of-flight secondary ion mass spectrometry

#### CH3OH – D2O isotope exchange & H-bonding: 15 – 200 K, CH3OH adsorbed on D2O, proton-transfer, 100 – 150 K: sputtering of D+(CH3OH) ions, secondary ion mass spectrometry

The interactions between condensed molecules at cryogenic temperatures 15–200 K have been investigated on the basis of secondary ion mass spectrometry. It is demonstrated that the protonated molecular ions, emitted via the proton transfer reactions, provide us unique information about the reorganization of hydrogen-bonded molecules. From the CH3OH molecules adsorbed on the D2O–ice surface, the D+(CH3OH) ions are sputtered predominantly in the temperature range between 100 and 150 K since most of the CH3OH molecules are bound to the D2O layer via hydrogen bonds. A rapid and almost complete H/D exchange, yielding the D+(CH3OD) species, occurs above 150 K due to the enhanced mobility of the surface D2O molecules. Up to the desorption temperature of 180 K, a considerable amount of methanol exists on the surface without mixing with the heavy-water layer due to hydrophobicity of the methyl group. On the methanol–ice surface, the adsorbed D2O molecules form hydrogen bonds preferentially with the CH3OH molecules and tend to be incorporated in the thin-layer bulk of methanol above 120 K.

## 2003 Manca

16 May , Martin, Roubin

### Comparative Study of Gas Adsorption on Amorphous Ice: Thermodynamic and Spectroscopic Features of the Adlayer and the Surface

#### Adsorption on ASW (N2, CO, Ar, Kr, CH4, CF4), adsorption isotherm volumetry & IR spectroscopy, adsorption energies & capacities, N2 & CO: H-bonding with surface dangling OH

The features of adsorption on amorphous ice are compared for N2, CO, Ar, Kr, CH4, and CF4, studied by both adsorption isotherm volumetry and infrared spectroscopy. The analysis of the two types of experimental results is consistent, allowing us to distinguish different behaviors according to the strength of the bonding with the ice surface sites. Adsorption energies and capacities have been estimated, and hydrogen bonding with surface dangling O-H has been evidenced for N2 and CO. Infrared isotherms have been obtained for the three surface sites of ice and are compared with that of the adsorbate in the case of CH4.

## 2002b Martin

, Manca, Roubin

### Adsorption of small molecules on amorphous ice: volumetric and FT-IR isotherm co-measurements - Part II. The case of CO

#### Volumetric & spectroscopic isothermal measurements, CO adsorption on ASW preferentially on dangling OH bonds, CO-CO interactions cause peak at 2139 cm-1

The aim of this paper is to deepen the investigation of vibrational properties of CO adsorbed on amorphous ice, by using the combination of volumetric and spectroscopic isothermal measurements as presented in part I. CO is found to be one of the more interactive molecules that can be physisorbed on ice, as proved by the sharp increase in the adsorbed amount at the monolayer formation. The analysis of the evolution of the infrared signals as a function of equilibrium pressure, for both ice and CO, allows us to elucidate the origin of the peak at 2139 cm-1 as due to CO–CO interactions and to characterize the evolution of the three ice surface signals. Pre-adsorbing CF4 or CH4 enables site selectivity to be evidenced, CO being preferentially associated to dangling O–H bonds.

## 2002a Martin

, Manca, Roubin

### Adsorption of small molecules on amorphous ice: volumetric and FT-IR isotherm co-measurements Part I. Different probe molecules

#### Ar, Kr, CH4, N2, CO and CF4 adsorption on ASW, FTIR spectroscopy & volumetric isotherm measurements, different types of wetting, net heat of adsorption (1 – 2.6 kJ/mol), shift of dangling OH bond (7 – 60 cm-1), coverage: submonolayer to bulk

Ar, Kr, CH4, N2, CO and CF4 adsorption on amorphous ice has been studied by using a combination of volumetric isotherm measurements and FT-IR spectroscopy. We have been able to characterize the modifications in the three vibrational surface modes of ice throughout the adlayer formation and to observe different types of wetting. For these gases, we have measured the net heat of adsorption within a range of 1–2.6 kJ/mol, showing the weakness of surface interaction and conversely, we have measured the shift of the dangling OH bond within a range of 7–60 cm-1, showing its high sensitivity to the adsorption process. We have succeeded in correlating both techniques by measuring the evolution of vibrational surface modes as a function of the relative pressure, from submonolayer to bulk.

## 2002 Haq

17 January , Harnett, Hodgson

### Adsorption and Solvation of HCl into Ice Surfaces

#### Kinetics of HCl adsorption & incorporation into crystalline ice & ASW, FTIR & RAIRS, 85 – 145 K, adsorption becomes less favorable with increasing HCl coverage, saturating with one HCl adsorbed for each surface H2O molecule, independent of ice thickness for T ≤ 120 K, above 125 K, HCl is incorporated into the ice film, ASW shows similar behaviour (but greater H2O density in surface and easier HCl transport into film)

The kinetics of HCl adsorption and incorporation into crystalline and amorphous ice were studied by using a thermal molecular beam, with FTIR spectroscopy to characterize the products. Thin films of hexagonal ice were grown on Pt(111) to provide a highly ordered surface on which to test models for HCl adsorption. Absolute HCl uptakes, product H2O:HCl stoichiometries, and sticking probabilities were measured as a function of HCl exposure and temperature between 85 and 145 K. Adsorption proceeds via a trapping mechanism, with the barrier to HCl adsorption into the final state being 7 kJ/mol lower than for desorption at low coverages. Adsorption becomes less favorable with increasing HCl coverage, saturating with one HCl adsorbed for each surface H2O molecule, independent of the ice thickness for T ≤ 120 K. Above 125 K, HCl is incorporated into the ice film, absorption showing a complex exposure and flux dependence. HCl absorption disrupts the ice lattice, causing the rate of HCl uptake to increase as adsorption proceeds. At high HCl fluxes, the creation of favorable adsorption sites on the ice surface is limited by the rate of HCl transport into the film and the sticking probability drops. The saturation product for 130 ≤ T ≤ 140 K is the amorphous trihydrate HCl●(3.1 ± 0.3)H2O and RAIR spectra for this, and for the surface-adsorbed monohydrate species, showed no bands due to molecular HCl. Amorphous ice films show a similar behavior, but with a greater density of water in the surface and more facile HCl transport into the film.

## 2001 Manca

27 September , Martin, Allouche, Roubin

### Experimental and Theoretical Reinvestigation of CO Adsorption on Amorphous Ice

#### Quantum calculations & volumetric isotherm & IR experiments CO adsorption on ASW, multilayer formation, site specific (3 surface sites) & nonselective (similar energies) adsorption process

We have performed new quantum calculations based on density functional theory, using plane waves and ultrasoft pseudopotentials to deal with the problem of modeling CO adsorption on a water ice surface and to obtain a theoretical understanding on the physical mechanisms involved during the monolayer formation. We have also done a new series of experiments, using the combination of volumetric adsorption isotherm and infrared spectroscopy measurements to study the different stages of CO adsorption on amorphous ice, from submonolayer to solid condensation. The multilayer formation has been evidenced by volumetric measurements, and its contribution has been characterized in the low-frequency part of the CO infrared spectrum. Three surface sites have been identified by spectroscopy, and their intensities have been controlled throughout the whole monolayer formation, showing a site specific, though nonselective, adsorption process. Calculations have consistently succeeded in determining three adsorption configurations whose energies are similar. Finally, the geometry of the complete monolayer has been fully described, and its high compacity has been explained by analyzing the balance between vertical and lateral interactions.

## 2000 Borget

28 July , Chiavassa, Allouche, Aycard

### Experimental and Quantum Study of Adsorption of Ozone (O3) on Amorphous Water Ice Film

#### O3 ad-/desorption on ASW, FTIR & TPD, desorption between 70 – 90 K, desorption energy: 20 kJ/mol (agreeing with periodic Hartree-Fock (PHF) & density functional theory (DFT) estimates), OH vibration al frequency shifts by 60 cm-1, small amount of O3 is incorporated into bulk (desorbs at onset of crystallisation @ 145 K)

Ozone (O3) adsorption and desorption on amorphous water ice film is monitored by Fourier transform infrared spectroscopy (FTIR) using the temperature-programmed desorption (TPD) method. A single type of site is observed between O3 and ice which involves the dangling OH bonds of the amorphous ice. The O3 desorption occurs between 70 and 90 K and the associated desorption energy is 20 kJ/mol. This value is in good agreement with that estimated from Periodic Hartree-Fock (PHF) calculations using a density functional theory (DFT) evaluation of the electronic correlation energy. These calculations confirmed the electrostatic nature of the interaction forces. The dangling OH vibrational frequency shift is also calculated and is close to the 60 cm-1 experimental value. A small amount of ozone is incorporated into the bulk and desorbs at the onset of the ice crystallization near 145 K.

## 2000 Manca

24 July , Roubin, Martin

### Volumetric and infrared co-measurements of CH4 and CO isotherms on microporous ice

#### CH4 & CO adsorption volumetric isotherms (-> SSA) & IR spectrometry (nature of physical/chemical bonding), microporous ice, 50 – 80 K, result: both methods well correlated & provide info on adsorption sites

CH4 and CO adsorption isotherms on microporous ice surfaces have been performed simultaneously by pressure measurements and infrared spectrometry in the 50 – 80 K temperature range in order to compare the two techniques: volumetric isotherms allow evaluation of the surface area of the ice and the net heat of adsorption by the BET model, while infrared spectrometry gives complementary information on the nature of the chemical or physical bonding interaction. Our results show that the two methods are well correlated and that their comparison provides valuable information on the different adsorption sites.

## 1997 Allouche

13 October , Verlaque, Pourcin

### CO Adsorption Isotherms on Ice by Fourier Transform Infrared Spectroscopy and New Insights of the Ice Surface from Quantum ab Initio Investigations

#### Ice samples are prepared from highly concentrated H2O/Ar matrixes (various stages of order - amorphous to nanocrystalline clusters), 43 – 48 K, 0.1 – few monolayers, absorbance of CO, FTIR spectroscopy & quantum modelling, CO orients perpendicular to surface (no preference for CO or OC arrangement) by hydrogen bonding, adsorption dynamic process insensitive to presence of surface defects

Various ice samples are prepared from highly concentrated H2O/Ar matrixes submitted to various annealing treatments. Each of these samples corresponds to a different stage in the solid organization from amorphous to nanocrystalline clusters. The type II isotherms are drawn from a 0.1 to a few monolayers surface coverage in the 43-48 K temperature range as a function of the integrated absorbance of the carbon monoxide (CO) vibrational mode, measured by FTIR spectroscopy, vs the CO equilibrium pressure. In the frame of the Brunauer, Emmett, and Teller (BET) model the mean enthalpy of adsorption of the first CO mono layer is evaluated to be about 10 kJ/mol and is independent of the history of the ice surfaces. The quantum modelling on a perfect ice surface leads to adsorption energies in good agreement with experimental results for an isolated admolecule as well as for the monolayer. The CO adsorbs perpendicularly to the surface plane, and the two orientations of CO or OC are energetically equivalent. Adsorption on a surface defect modeled as a hole indicates hydrogen bonding between the admolecule and the substrate. Comparing experimental and quantum results, we may conclude that the CO molecule sees the ice surface as covered by protons that make the adsorption dynamic process insensitive to the presence of surface defects.

# Crystallisation of ASW

## ? 2016 Heidorn

24 September , Bertram, Morgenstern

### The fractal dimension of ice on the nanoscale

#### Heterogeneous ice nucleation, formation of fractal ice structures, real-space observations, 89 – 119 K, fractal dimension changes linearly from 5/3 to ≈ 1 (equal-sided hexagon), shape dependent sticking coefficient of mobile ice clusters to fractal islands

Studies of supported water clusters provide a means for understanding the initial stages of heterogeneous ice nucleation in diverse areas as atmospheric chemistry and astrophysics. Despite the importance of non-perfect ice structures in these fields, research focused on crystalline ice structures. Here, we report real-space observations of fractal ice islands grown between 89 K and 119 K. The island shape changes linearly from the most fractal dimension of 5/3 to the fractal dimension close to the one of an equalsided hexagon. The mere linear increase is assigned to a shape dependent sticking coefficient of mobile ice clusters to the fractal islands. Our study reveals the complexity involved in formation of fractal ice structures.

## 2012 May

11 January , Smith, Kay

### The Molecular Volcano Revisited: Determination of Crack Propagation and Distribution During the Crystallization of Nanoscale Amorphous Solid Water Films

#### Length distribution of cracks forming in ASW during crystallisation: TPD & RAIRS, ASW deposited on top of O2, sufficiently thick overlayers of H2O trap O2 (second desorption peak at higher T), preponderance of cracks propagate down from outer surface of ASW

Temperature programmed desorption (TPD) is utilized to determine the length distribution of cracks formed through amorphous solid water (ASW) during crystallization. This distribution is determined by monitoring how the thickness of an ASW overlayer alters desorption of an underlayer of O2. As deposited, ASW prevents desorption of O2. During crystallization, cracks form through the ASW and open a path to vacuum, which allows O2 to escape in a rapid episodic release known as the “molecular volcano”. Sufficiently thick ASW overlayers further trap O2 resulting in a second, higher temperature, O2 desorption peak. The evolution of this trapping peak with overlayer thickness is the basis for determining the length distribution of crystallization-induced cracks spanning the ASW. Reflection absorption infrared spectroscopy (RAIRS) and TPD of multicomponent parfait structures of ASW, O2, and Kr indicate that a preponderance of these cracks propagate down from the outer surface of the ASW.

## 2007 Kondo

17 July , Kato, Bonn, Kawai

### Deposition and crystallization studies of thin amorphous solid water films on Ru(0001) and on CO-precovered Ru(0001)

#### Crystallisation occurs through random nucleation events in bulk material, followed by homogeneous growth (on both substrates), ≈50 layers thick ASW film, helium atom scattering, infrared reflection absorption spectroscopy, isothermal temperature-programmed desorption

The deposition and the isothermal crystallization kinetics of thin amorphous solid water (ASW) films on both Ru(0001) and CO-precovered Ru(0001) have been investigated in real time by simultaneously employing helium atom scattering, infrared reflection absorption spectroscopy, and isothermal temperature-programmed desorption. During ASW deposition, the interaction between water and the substrate depends critically on the amount of preadsorbed CO. However, the mechanism and kinetics of the crystallization of ≈50 layers thick ASW film were found to be independent of the amount of preadsorbed CO. We demonstrate that crystallization occurs through random nucleation events in the bulk of the material, followed by homogeneous growth, for solid water on both substrates. The morphological change involving the formation of three-dimensional grains of crystalline ice results in the exposure of the water monolayer just above the substrate to the vacuum during the crystallization process on both substrates.

## -1999 Sieger

10 November , Orlando

### Probing low-temperature water ice phases using electron stimulated desorption

#### Porous ASW (D2O) crystallises differently when annealed rather than deposited as crystalline D2O, 90 – 155 K deposition, Pt(111) substrate, low T depositions sinter between 120 – 140 K, ASW deposited on crystalline D2O crystallises into the same structure like substrate (surface nucleates) when annealed

Low-energy electron-stimulated desorption (ESD) of D+ from D2O has been used to examine the phase and growth behavior of nanoscale vapor-deposited ice films grown on Pt(111) between 90–155 K. The D+ yield from porous amorphous solid water (deposited at 90 K) shows evidence for sintering near 120 K, increases between 120 and 140 K, and then drops at the amorphous–crystalline phase transition near 155 K. Ice deposited at 155 K forms an epitaxial crystalline film, with a D+ yield nearly one-third larger than the yield from crystalline films prepared by annealing the amorphous phase. This suggests that the film formed by annealing may have a different crystalline ordering or morphology than the epitaxial film deposited between 150 and 155 K. Ice deposited at 90 K on top of the epitaxial film is amorphous, but it crystallizes to a form similar to that of the underlying crystalline ice substrate. This suggests that, in this case, the buried two-dimensional interface nucleates the crystallization.

## 1999 Dohnálek

20 January , Ciolli, Kimmel, Stevenson, Smith, Kay

### Substrate induced crystallization of amorphous solid water at low temperatures

#### N2 monolayer desorption from ice surfaces (quantitative, highly sensitive method for following surface crystallization kinetics at low T), vapour deposited substrate (< 110 K) ASW on crystalline ice crystallises faster than on Pt(111) -> crystalline substrate acts as 2D crystallisation nucleus

We show that N2 monolayer desorption from ice surfaces is a quantitative, highly sensitive method for following the surface crystallization kinetics at low temperatures. Vapor deposited water films on a crystalline ice substrate exhibit amorphous growth at temperatures below ≈ 110 K. The rate of crystallization for these amorphous films is dramatically accelerated compared to the rate of crystallization observed for the amorphous films deposited directly on Pt(111). We find that the crystalline ice substrate acts as a two-dimensional nucleus for the growth of the crystalline phase, thereby accelerating the crystallization kinetics.

## 1997 Jenniskens

6 April , Banham, Blake, McCoustra

### Liquid water in the domain of cubic crystalline ice Ic

#### ASW (vapour deposited), 120 – 210 K, above glass transition (120 – 140 K) viscous liquid, coexists with cubic ice up to 210 K, transmission electron microscopy (TEM): morphology of water ice on non-wetting surface changes at 175 K, TPD: binding energy of H2O molecules changes, RAIRS: shape of 3.07 μm absorption band (O-H stretch) changes (change in selection rules), -> this form of liquid water must be common in comets/planets/sattelites

Vapor-deposited amorphous water ice, when warmed above the glass transition temperature (120–140 K), is a viscous liquid which exhibits a viscosity vs temperature relationship different from that of liquid water at room temperature. New studies of thin water ice films now demonstrate that viscous liquid water persists in the temperature range 140–210 K, where it coexists with cubic crystalline ice. The liquid character of amorphous water above the glass transition is demonstrated by (1) changes in the morphology of water ice films on a nonwetting surface observed in transmission electron microscopy (TEM) at around 175 K during slow warming, (2) changes in the binding energy of water molecules measured in temperature programmed desorption (TPD) studies, and (3) changes in the shape of the 3.07 μm absorption band observed in grazing angle reflection-absorption infrared spectroscopy (RAIRS) during annealing at high temperature, whereby the decreased roughness of the water surface is thought to cause changes in the selection rules for the excitation of O–H stretch vibrations. Because it is present over such a wide range of temperatures, we propose that this form of liquid water is a common material in nature, where it is expected to exist in the subsurface layers of comets and on the surfaces of some planets and satellites.

## 1997 Smith

3 March , Huang, Wong, Kay

### The Molecular Volcano: Abrupt CCl4 Desorption Driven by the Crystallization of Amorphous Solid Water

#### Desorption kinetics of ultrathin films of CCl4 & ASW, abrupt desorption of CCl4 at onset of crystallisation (through connected pathways formed in water overlayer during nucleation & crystallisation of ASW) -> episodic release

The desorption kinetics of molecular beam deposited ultrathin films of CCl4 and amorphous solid water (ASW) are studied. Overlayers of ASW impede CCl4 desorption until the onset of crystallization, whereupon the CCl4 desorbs abruptly. The abrupt desorption occurs through connected pathways that are formed in the water overlayer during the nucleation and growth of crystalline ice from ASW. The onset of the abrupt desorption corresponds to the threshold for dynamic percolation. As the crystallization proceeds, the number of connected pathways rapidly increases, giving rise to the episodic release of CCl4.

## 1992 Moore

16 June , Hudson

### Far infrared spectral studies of phase changes in water ice induced by proton irradiation

#### Phase change between ASW and crystalline ice induced by proton irradiation, far-IR spectroscopy to distinguish ice phase, 13 – 77 K: irradiated crystalline ice becomes amorphous, 36 – 125 K: irradiated amorphous ice does not change, 13 K & dose > 2 eV/molecule: cyclic conversions between amorphous & crystalline + H2, H2O, O2 release.

Far-infrared spectra form 20 μm (500 cm-1) to 100 μm (100 cm-1) of water ice have been measured over the temperature range of 13 – 155 K. Amorphous and crystalline water ice are easily identified in far-infrared spectra since amorphous ice has one broad absorption peak near 45 μm (220 cm-1) and crystalline ice has absorptions near 44 μm (229 cm-1) and 62 μm (162cm-1).

We have observed radiation induces phase changes in both amorphous and crystalline ice. Crystalline ice converts to an amorphous phase when irradiated at temperatures between 77 and 13 K. The conversion rate increases as the temperature is decreased and the converted fraction is dose dependent. No radiation-induced changes are detected in amorphous ice between 125 and 36 K. However, far-infrared spectra of proton-irradiated ices near 13 K show interconversion between the amorphous and crystalline ice phases beginning at doses near 2 eV/molecule and continuing cyclically with increased dose. A quadrupole mass spectrometer was used to detect H2, H2O, and O2 releases associated with the cyclic phase conversions.

Radiation-induces phase changes in these two forms will be discussed in relation to interstellar ices, and ices in comets.

# Crystalline H2O

## 2014 Massey

26 September , McBride, Darling, Nakamura, Hodgson

### The role of lattice parameter in water adsorption and wetting of a solid surface

#### Wetting of crystalline ice and ice nucleation depends on substrate structure, pseudomorphic surfaces (form ordered template that matches arrangement of water in bulk ice Ih(0001) bilayer: M(111) surfaces (M = Pt, Pd, Rh, Cu and Ni) form a (√3 x √3)R30° Sn substitutional alloy surface), only PtSn surface, with lattice parameter ≈ 7% greater than for bulk ice forms stable water layer, all other surfaces non-wetting (forming multilayer ice clusters) => repeat spacing of surface should ideally match O–O spacing in ice

Ice formation is a complex cooperative process that is almost invariably catalysed by the presence of an interface on which ice crystals nucleate. As yet there is no clear picture of what factors make a surface particularly good at nucleating ice, but the importance of having a template with a suitable lattice parameter has often been proposed. Here we report the contrasting wetting behaviour of a series of pseudomorphic surfaces, designed to form an ordered template that matches the arrangement of water in a bulk ice Ih(0001) bilayer. The close-packed M(111) surfaces (M = Pt, Pd, Rh, Cu and Ni) form a (√3 x √3)R30° Sn substitutional alloy surface, with Sn atoms occupying sites that match the symmetry of an ice bilayer. The lattice constant of the alloy changes from 4% smaller to 7% greater than the lateral spacing of ice across the series. We show that only the PtSn surface, with a lattice parameter some 7% greater than that of a bulk ice layer, forms a stable water layer, all the other surfaces being non-wetting and instead forming multilayer ice clusters. This observation is consistent with the idea that the repeat spacing of the surface should ideally match the O–O spacing in ice, rather than the bulk ice lattice parameter, in order to form a continuous commensurate water monolayer. We discuss the role of the lattice parameter in stabilising the first layer of water and the factors that lead to formation of a simple commensurate structure rather than an incommensurate or large unit cell water network. We argue that lattice match is not a good criteria for a material to give low energy nucleation sites for bulk ice, and that considerations such as binding energy and mobility of the surface layer are more relevant.

## 2014 Karssemeijer

10 September , Cuppen

### Diffusion-desorption ratio of adsorbed CO and CO2 on water ice (Research Note)

#### Monte Carlo (simulations) diffusion/desorption barriers for CO & CO2 adsorbed on crystalline water surfaces

*Context*. Diffusion of atoms and molecules is a key process for the chemical evolution in star-forming regions of the interstellar medium. Accurate data on the mobility of many important interstellar species is often not available, however, which seriously limits the reliability of models describing the physical and chemical processes in molecular clouds.

*Aims*. Here we aim to provide the astrochemical modeling community with reliable data on the ratio between the energy barriers for diffusion and desorption for adsorbed CO and CO2 on water ices.

*Methods*. To this end, we used a fully atomistic, off-lattice kinetic Monte Carlo technique to generate dynamical trajectories of CO and CO2 molecules on the surface of crystalline ice at temperatures relevant for the interstellar medium.

*Results*. The diffusion-to-desorption barrier ratios are determined to be 0.31 for CO and 0.39 for CO2. These ratios can be directly used to improve the accuracy of current gas-grain chemical models.

## 2014 Geiger

29 April , Dellago, Macher, Franchini, Kresse, Bernard, Stern, Loerting

### Proton Ordering of Cubic Ice Ic: Spectroscopy and Computer Simulations

#### Proton ordering of ice, FTIR (librational band), cubic ice only partially proton orders under procedure where hexagonal ice would fully proton order, proton ordered structures are ferroelectric

Several proton-disordered crystalline ice structures are known to proton order at sufficiently low temperatures, provided that the right preparation procedure is used. For cubic ice, ice Ic, however, no proton ordering has been observed so far. Here, we subject ice Ic to an experimental protocol similar to that used to proton order hexagonal ice. In situ FT-IR spectroscopy carried out during this procedure reveals that the librational band of the spectrum narrows and acquires a structure that is observed neither in protondisordered ice Ic nor in ice XI, the proton-ordered variant of hexagonal ice. On the basis of vibrational spectra computed for ice Ic and four of its proton-ordered variants using classical molecular dynamics and ab initio simulations, we conclude that the features of our experimental spectra are due to partial proton ordering, providing the first evidence of proton ordering in cubic ice. We further find that the proton-ordered structure with the lowest energy is ferroelectric, while the structure with the second lowest energy is weakly ferroelectric. Both structures fit the experimental spectral similarly well such that no unique assignment of proton order is possible based on our results.

## 2014 Townrow

3 February , Coleman

### Structure and sublimation of water ice films grown in vacuo at 120–190 K studied by positron and positronium annihilation

#### Crystalline structure of H2O ice films (165 – 182 K), smaller deposition rate -> less lattice defects, films less disordered when grown > 172 K

The crystalline structure of ≈ 5–20 μm water ice films grown at 165 and 172 K has been probed by measuring the fraction of positrons forming ortho-positronium (ortho-Ps) and decaying into three gamma photons. It has been established that films grown at slower rates (water vapour pressure ≥ 1 mPa) have lower concentrations of lattice defects and closed pores, which act as Ps traps, than those grown at higher rates (vapour pressure ≈ 100 mPa), evidenced by ortho-Ps diffusion lengths being approximately four times greater in the former. By varying the growth temperature between 162 and 182 K it was found that films become less disordered at temperatures above ≈ 172 K, with the ortho-Ps diffusion length rising by ≈ 60%, in this range. The sublimation energy for water ice films grown on copper has been measured to be 0.462(5) eV using the time dependence of positron annihilation parameters from 165 to 195 K, in agreement with earlier studies and with no measurable dependence on growth rate and thermal history.

## 2012 McBride

31 October , Omer, Clay, Cummings, Darling, Hodgson

### Strain relief and disorder in commensurate water layers formed on Pd(111)

#### Water adsorbs and desorbs intact on Pd(111), forming H-bonded wetting layer, low energy electron diffraction (LEED) & He atom scattering (HAS) structural characterisation, H2O forms (√3 x √3)R30° clusters, but remains disorderes on local (≈ 10 Å) scale, flat domains, disordered coundaries, mostly H-down water (stress relief mechanism)

Water adsorbs and desorbs intact on Pd(111), forming a hydrogen-bonded wetting layer whose structure we examine by low energy electron diffraction (LEED) and He atom scattering (HAS). LEED shows that water forms commensurate (√3 x √3)R30° clusters that aggregate into a partially ordered, approximately (7 x 7) superstructure as the layer completes. HAS indicates that the water layer remains disordered on a local (approximately 10 Å) scale. Based on workfunction measurements and density functional theory simulations we propose that water forms small, flat domains of a commensurate (√3 x √3)R30° by disordered domain boundaries containing largely H-down water. This arrangement allows the water layer to adapt its density and relieve the lateral strain associated with adsorbing water in the optimum flat atop adsorption site. We discuss different possibilities for the structure of these domain walls and compare this strain relief mechanism to the highly ordered, large unit cell structures formed on surfaces such as Pt(111).

## 2009 Kimmel

9 June , Matthiesen, Baer, Mundy, Petrik, Smith, Dohnálek, Kay

### No Confinement Needed: Observation of a Metastable Hydrophobic Wetting Two-Layer Ice on Graphene

#### Special stacking of hexagonal bilayers for crystalline H2O ice grown on graphene on Pt(111), nontetrahedral geometry with weakened hydrogen bonds

The structure of water at interfaces is crucial for processes ranging from photocatalysis to protein folding. Here, we investigate the structure and lattice dynamics of two-layer crystalline ice films grown on a hydrophobic substrate, graphene on Pt(111), with low energy electron diffraction, reflection-absorption infrared spectroscopy, rare-gas adsorption/desorption, and ab initio molecular dynamics. Unlike hexagonal ice, which consists of stacks of puckered hexagonal “bilayers”, this new ice polymorph consists of two flat hexagonal sheets of water molecules in which the hexagons in each sheet are stacked directly on top of each other. Such two-layer ices have been predicted for water confined between hydrophobic walls, but not previously observed experimentally. Our results show that the two-layer ice forms even at zero pressure at a single hydrophobic interface by maximizing the number of hydrogen bonds at the expense of adopting a nontetrahedral geometry with weakened hydrogen bonds.

## 2007 Kondo

24 September , Kato, Kawai, Bonn

### The distinct vibrational signature of grain-boundary water in nano-crystalline ice films

#### OD spectral feature (2500 cm-1) attributed to grain-boundary increases with decreasing crystal domain size (nm-range)

We have characterized the vibrational response of grain-boundary water in crystalline ice films consisting of nanometer-sized crystalline domains. The crystalline ice is grown isothermally on Ru(0001), and the crystalline domain size is controlled by varying the crystallization temperature. A distinct vibrational feature in the OD stretching region is observed, which we attribute to grain-boundary water. The relative contribution of the grain-boundary vibrational response to the overall spectrum increases with decreasing crystal domain size. Its central frequency is located around 2500 cm-1, between that of amorphous solid water and crystalline ice.

## ? 2007b Michaelides

17 June , Morgenstern

### Ice nanoclusters at hydrophobic metal surfaces

#### Heterogeneous ice nucleation, metal-supported H2O hexamers & hydrated nanoclusters (hepta-/octa-/nonamers), low-T scanning tunnelling microscopy & first-principle electronic structure calculations, cyclic H2O hexamer (smallest piece of ice), competition between ability of H2O molecules to simultaneously bond to substrate and accept H-bonds

Studies of the structure of supported water clusters provide a means for obtaining a rigorous molecular-scale description of the initial stages of heterogeneous ice nucleation: a process of importance to fields as diverse as atmospheric chemistry, astrophysics and biology. Here, we report the observation and characterization of metal-supported water hexamers and a family of hydrated nanoclusters — heptamers, octamers and nonamers — through a combination of low-temperature scanning tunnelling microscopy experiments and first-principles electronic-structure calculations. Aside from achieving unprecedented resolution of the cyclic water hexamer — the so-called smallest piece of ice — we identify and explain a hitherto unknown competition between the ability of water molecules to simultaneously bond to a substrate and to accept hydrogen bonds. This competition also rationalizes previous structure predictions for water clusters on other substrates.

## 2007a Michaelides

1 February

### Simulating ice nucleation, one molecule at a time, with the ‘DFT microscope’

#### Heterogeneous ice nucleation, density functional theory (DFT) calculations & scanning tunnelling microscopy, clusters of 2 – 6 H2O molecules adsorbed on Cu(111) surface

Few physical processes are as ubiquitous as the nucleation of water into ice. However, ice nucleation and, in particular, heterogeneously catalysed nucleation remains poorly understood at the atomic level. Here, we report an initial series of density functional theory (DFT) calculations aimed at putting our understanding of ice nucleation and water clustering at metallic surfaces on a firmer footing. Taking a prototype hydrophobic metal surface, Cu(111), for which scanning tunneling microscopy measurements of water clustering have recently been performed, possible structures of adsorbed clusters comprised of 2–6 H2O molecules have been computed. How the water clusters in this size regime differ from those in the gas phase is discussed, as is the nature of their interaction with the substrate.

## 2005 Kimmel

11 October , Petrik, Dohnálek, Kay

### Crystalline Ice Growth on Pt(111): Observation of a Hydrophobic Water Monolayer

#### rare gas physisorption on H2O, substrate Pt(111) &, 20 – 155 K, ice films grown above 135 K do not wet first monolayer, results consistent with no dangling OH bonds at surface

The growth of crystalline water films on Pt(111) is investigated using rare gas physisorption. The water monolayer wets Pt(111) at all temperatures investigated (20–155 K). At low temperatures (T 120 K), additional water layers kinetically wet the monolayer surface. However, crystalline ice films grown at higher temperatures (T > 135 K) do not wet the water monolayer. These results are consistent with recent theory and experiments suggesting that the molecules in the water monolayer form a surface with no dangling OH bonds or lone pair electrons, giving rise to a hydrophobic water monolayer on Pt(111).

## 2005 Zimbitas

21 September , Hodgson

### The morphology of thin water films on Pt(111) probed by chloroform adsorption

#### Wetting of crystalline H2O ice and ASW: probe molecule (chloroform), (√39 x √39)R16° wetting layer, individual crystallites for < 40 layers, restructuring into oriented bulk ice for > 50 layers

We have investigated water adsorption on Pt(111) using chloroform to probe the structure and binding sites available on the ice surface. A stable adsorption site appears, associated with growth of ice crystallites on the (√39 x √39)R16° wetting layer, and disappears slowly as the film grows and loses its registry to the wetting layer. The √39 multilayer consists of ordered crystalline ice nuclei which aggregate progressively into a continuous incommensurate ice as the film grows to ≈ 40 layers, the entire film and wetting layer restructuring into an oriented bulk ice only for films more than 50 layers thick.

## 2002 Haq

7 January , Harnett, Hodgson

### Growth of thin crystalline ice films on Pt(111)

Adsorption of water on Pt(111) at 135 K or above proceeds by a Stranski–Krastanov mechanism to form crystalline ice films. The structure of thin films reflects a conflict between maximising the binding to the surface and minimising the stress in the multilayer film. The first bilayer of water forms an ordered hexagonal overlayer which shows a (√39 x √39)R16.1° LEED pattern. Water condensation on this overlayer is initially slow, accelerating as second layer nucleation sites form and allow multilayer growth. Adsorption continues to grow the (√39 x √39)R16.1° structure until the film reaches a thickness of 5 bilayers at 137 K, after which further adsorption reorients the overlayer to form an incommensurate hexagonal film aligned at 30° to the Pt(111) close packed direction. Thermal desorption measurements reveal a change in the water desorption rate as the multilayer re-crystallises during heating, formation of the hexagonal R30° structure stabilising the multilayer film at the cost of reducing the binding of the first layer of water to the Pt(111) surface. The (√39 x √39)R16.1° overlayer becomes increasingly unstable to electron exposure as its thickness increases towards five bilayers, the ice rapidly restructuring to form islands with the R30° structure and exposing bare Pt.

## 1992 Bellisent-Funel

10 April , Bosio, Hallbrucker, Mayer, Sridi-Dorbez

### X-ray and neutron scattering studies of the structure of hyperquenched glassy water

#### X-ray & neutron diffraction, hyperquenched water droplets (on cryoplate), structure factors & radial distribution functions nearly identical to ASW (formed either by 77 K vapour deposition or heating HDA)

X-ray and neutron diffraction measurements were performed on glassy water prepared by rapid cooling of water droplets on a cryoplate. Structure factors and radial distribution functions were found to be nearly identical to those obtained from amorphous ice formed either by vapor deposition onto substrates cooled at 77 K or after heating the high-density amorphous ice.