



Cite this: DOI: 10.1039/d5nr05194k

Spontaneously polarised crystalline water ice

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Received 10th December 2025,
Accepted 3rd February 2026

DOI: 10.1039/d5nr05194k

rsc.li/nanoscale

We describe a novel aspect of the structure of the hexagonal phase of crystalline water ice, using vacuum-ultraviolet absorption spectroscopy as a diagnostic tool. The key result is that hexagonal ice (I_h), prepared from condensation of pure water vapour, displays net molecular orientation. This reflects order in the disposition of the protons in ice I_h and our results require revision of the near century old conventional structure in which water molecular dipoles point in random directions in hexagonal ice. Orientation gives rise to spontaneous polarization and internal fields of $\sim 4 \times 10^6 \text{ V m}^{-1}$ in films of ice I_h tens of nanometres thick, condensed on an insulating MgF_2 substrate. Data are in the form of Stark shifts in absorption spectra, with no free charges or external electric fields introduced in the experiment.

Introduction

Electric fields can change the chemical structure, electronic behaviour and motion of molecules.¹ The effect of these fields has become a new frontier in areas ranging from catalysis, across biology, and to the engineering of electronic devices. For example, in biology, effects are often based on the natural ability of enzymes to generate local electric fields around molecular structures to catalyse specific processes. In the present work, we report on the inherent ability of nanoscale films of crystalline hexagonal water ice to spontaneously achieve a structure by which dipoles orient and produce an electric field internal to the solid.

Our results challenge the concept that solid crystalline water is always a proton disordered material. Hexagonal water ice, I_h , represents “ordinary” crystalline ice in our everyday experience. A central issue in the structure of ice I_h is the presence or absence of molecular dipole ordering.^{2–4} In ice I_h , molecules are positioned on an hexagonal array of O atoms with molecular dipoles directed along the C_2 rotation axes, conventionally pointing in random directions giving no dipole order, following the Bernal–Fowler ice rules.⁵ The spontaneous orientational order reported here, in crystalline ice, therefore represents a weak violation of the ice rules but does not involve sufficient translation of H atoms to form Bjerrum defects. The dipole moment of water in the solid is sufficiently

large, 3.0 D ,^{6,7} to create substantial internal electric fields despite the minor degree of order.

Spontaneous polarization in non-crystalline water ice, formed below 127.5 K , is a known proposition. Onsager *et al.* observed that condensing samples of pure water ice at 78 K , to form amorphous solid water (ASW), produced electrical effects.⁸ Subsequent Kelvin probe measurements concurred, and reported weak fields permeating ASW, formed by condensation on substrates at $\leq 125 \text{ K}$.^{6,7,9} These observations indicate a contribution from the presence of local fields of $>10^9 \text{ V m}^{-1}$, created through unbalanced dipoles in pores^{6,10} and sufficient to influence the hydrogen bond energy.^{11,12} Such fields can be recreated using molecular dynamics simulations.¹³

Previous observations of polarized crystalline water ice, as here, have been associated with injection of ions into the ice at the ice-substrate boundary. For example, Ice XI, prepared from dilute KOH, has been suggested as ferroelectric in ref. 14, though brought into doubt in ref. 15. Violation of the ice rules has also been observed in water ice in hetero-epitaxial ice films. Sum-frequency generation spectroscopy revealed spontaneous polarization,^{16,17} stabilized by the presence of hydronium (H_3O^+) ions at the interface with the ice film, where ions were formed through hole injection from a Pt(111) substrate. This leads to a strongly non-uniform field. Here by contrast, we use a substrate with a high band gap, MgF_2 , from which we may assume at our low temperatures that there is no injection of ions and thus we maintain pure water ice.

In the present work we report vacuum ultra-violet (VUV) absorption spectra for water ices condensed across a temperature range from 20 K to 140 K . This temperature range crosses the amorphous to crystalline phase transition for water ice at $\sim 127.5 \text{ K}$. Below the phase transition, the behaviour of VUV spectra concurs with what is known about the collapse of

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pores in films of ASW. Above the crystallisation temperature, films demonstrate an excitonic Stark effect,¹⁸ with absorption wavelengths showing correlation with deposition temperature. We have previously demonstrated, for films of carbon monoxide, nitrous oxide and ammonia, that this Stark effect in VUV spectroscopy can be used to quantify the rate of change in the degree of polarisation with condensation temperature. Moreover this rate of change can be understood by a model for the spontelectric effect.¹⁸ This model, introduced in more detail below, ascribes polarization to a metastable equilibrium established between water dipoles, which align with the intrinsic electric field that arises in condensed molecular films, and thermally induced disorder. In short, the spontelectric model describes spontaneous polarization as a homogeneous bulk effect. Hence, we report a metastable polarised phase of crystalline water ice.

Methods

Films of pure water ice were condensed, from a partial pressure of $\sim 10^{-7}$ mbar, onto a cold MgF_2 substrate maintained at a chosen fixed temperature and acting as a VUV window, held inside a chamber with a base pressure $< 2 \times 10^{-8}$ mbar. Deionised water was purified using multiple freeze–pump–thaw cycles prior to introduction to the vacuum measurement chamber, using a high precision variable leak valve attached to a tube of 6 mm diameter that lay 25 mm from the substrate. Film thicknesses were quantified using a laser interferometer technique.¹⁹ Note that a new film was laid down at each temperature and films were not heated or cooled before spectra were taken. Temperatures were measured using a Si-diode located close to the MgF_2 substrate and the temperature was controlled by heating the cryofinger *via* a resistive heater. Data were taken on the UV beamline on the ASTRID2 facility at Aarhus University, where the high stability of the VUV source allows for the very precise spectral measurements necessary for this experiment. The low VUV flux did not induce chemistry or affect the physical structure of the film.²⁰ Values of absorbance, $\log(I_0(\text{eV})/I(\text{eV}))$, *vs.* eV were recorded, where $I_0(\text{eV})$ is the transmitted intensity in the absence of a water film and $I(\text{eV})$ is the transmitted intensity through the film and substrate.

Results

The VUV spectrum for a water ice film grown at 130 K is shown in Fig. 1a. Earlier reports of VUV spectra of ice may be found in ref. 21–24. Representative spectra recorded of water ice films deposited at 125 K–140 K, in the spectral region of interest, are shown in Fig. 1b. Three gaussians were fitted to each spectrum in Fig. 1b: a background peak to account for an absorption with a maximum above the MgF_2 cut-off at 10.78 eV; a higher energy absorption peak around 8.65 eV and a lower energy absorption peak around 7.98 eV. Our working hypothesis is that these two absorptions arise from the $(1b_1)$

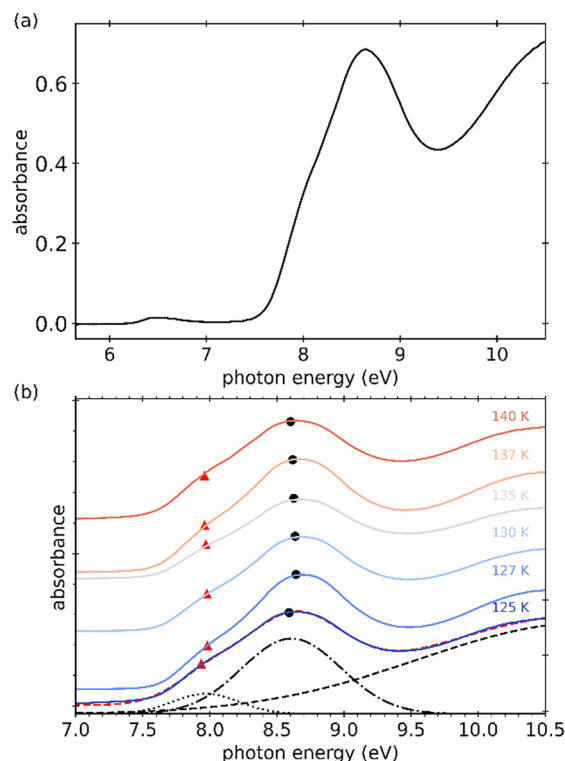


Fig. 1 (a) Absorption spectrum of an ~ 8 nm (~ 30 ML) water ice film grown at 130 K. (b) Spectra of ~ 8 nm (~ 30 ML) water ice films grown between $T = 125$ K and 140 K. Spectra are displaced on the vertical axis and all possess a maximum absorbance of ~ 0.6 . Transitions centred around the high energy (black circles) and low energy (red triangles) are discussed in the text. The dashed lines show the Gaussian fits to the spectrum at 125 K, with the resulting fit to the data shown in dashed red line as a typical example.

$(4a_1)A^1B_1 \leftarrow (1b_1)^2 X^1A_1$ transition, blue-shifted relative to the equivalent gas phase transition at 7.4 eV,^{25,26} in hexagonal I_h and cubic I_c ice respectively. Thus we take the view that over the full temperature range, ice films are composed of both hexagonal and cubic ice moieties giving stacking disordered ice, I_{sd} .^{27–30} Assuming the same oscillator strength for both hexagonal and cubic ice, films are $\sim 99\%$ hexagonal ice and 1% cubic ice. Below, we demonstrate that the shift in peak positions with temperature arises from the Stark effect, with the macroscopic electric field arising from the long-range ordered arrangement of dipoles within the condensed water ice film. Thus, our data refer to electric fields that are intrinsic to hexagonal I_h ice, with no contribution to these fields from cubic I_c ice, since spontaneous fields are created through the concerted effect of at least 5 to 10 ML of material.¹⁸ Thus I_c ice is subjected to the electric field generated within I_h ice, with no spontelectric field generated by I_c ice alone. Positions for the peak centred at 8.65 eV are shown as a function of sample deposition temperature in Fig. 2. Both peak positions for crystalline films are listed in Table 1.

Material is ASW for $T \leq 125$ K and crystalline for $T \geq 127.5$ K. Data for films deposited at 125 K were observed to evolve with time, representing the phase change from crystal-

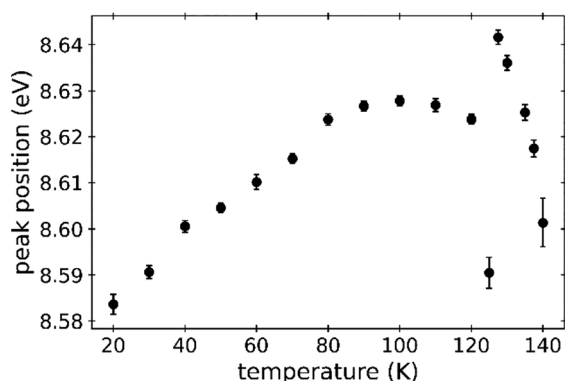


Fig. 2 Peak positions for the higher energy peak, attributed to I_h ice, marked with black dots in Fig. 1. Data indicate a phase change between 125 K and 127.5 K. Errors, marked as vertical lines, are 1 SD on the Gaussian fit and amount to systematic errors of up to 3.4 meV and 7 meV for the higher and lower energy peaks respectively.

line to amorphous ice films. The spectral evolution at $T = 125$ K, and spectra for all temperatures are shown in the Supplementary information (SI).

Data analysis

For I_{sd} with $T \geq 127.5$ K, the variation of transition energies with temperature, shown in Fig. 2 and columns 2 and 3 in Table 1, may be ascribed to temperature dependent Stark effects.¹⁸ The origin of the electric field responsible for the shift in the energy of the excitations, lies in the spontaneous orientation of dipoles and relates directly to the spontaneous partial ordering of protons in I_h ice. Similar shifts in energy to those in Fig. 1 and 2 have been observed in VUV absorption spectra of CO, nitrous oxide, ammonia and methanol and arise through the temperature dependence of the spontaneously created electric field – the “spontelectric field”.¹⁸ We show below that a well-established model for the spontelectric effect, coupled with a simple electrostatic model involving the influence of the spontelectric field on the exciton, reproduces these shifts for $T \geq 127.5$ K for both the higher and lower energy features in Fig. 1 and Table 1. We use these data to give a quantitative esti-

mate of the degree of orientational order and associated electric fields in the dominant I_h component of the ice films.

The spontelectric field, E_{sp} , acts on excitons, specifically Wannier–Mott electron–hole pairs, created in the A-state in the lattice of I_{sd} . If the ice is formed at higher temperature, say, the strength of the spontelectric field, E_{sp} , is lower and holds the hole and electron less far apart. This in turn causes the energy of the transition to decrease and is observed as the absorption peak red shifting. In the hypothetical absence of any intrinsic electric field in the ice film, the separation between the charge and hole within the exciton after excitation is represented by r . Dipoles orient at all temperatures for crystalline ice, and the resulting intrinsic electric fields produce coulombic effects that yield a Stark energy shift in the observed energy of the excitation. We describe this energy shift as, δ , and it is given by $2 E_{sp}$ times the physical displacement, Δr , from the unperturbed separation, r , where^{18,20}

$$\Delta r = r[(1 - 2E_{sp}\epsilon r^2)^{-1/2} - 1] \quad (1)$$

with ϵ as the relative permittivity of the medium, reported as 1.716.³¹ The spontelectric field, E_{sp} , is a positive quantity since the molecules are on average weakly oriented such that the O-atom points towards the film surface, giving a negative surface potential.^{9,13} Using (1), the strength of the intrinsic electric field may be expressed in terms of the energy shift observed in spectra, δ , as a solution of the equation:

$$\delta / \{2r[(1 - 2E_{sp}\epsilon r^2)^{-1/2} - 1]\} - E_{sp} = 0 \quad (2)$$

from which, by squaring both sides and solving the resulting cubic in E_{sp} , it follows that:

$$E_{sp} = -\frac{\delta}{3r} + \left(\frac{\delta}{3r}\right) \left[1 + \frac{6}{\delta\epsilon r}\right]^{\frac{1}{2}} \cos \left[\frac{1}{3} \arccos \left(\frac{1 - \frac{9}{2\delta\epsilon r}}{\left[1 + \frac{6}{\delta\epsilon r}\right]^{\frac{3}{2}}} \right) + \frac{2\pi k}{3} \right] \quad (3)$$

with $k = 0, 1, 2$. Only $k = 0$ gives a positive root, with $k = 1$ giving an unphysical negative value of E_{sp} and $k = 2$ no longer satisfying eqn (2). This arises from the sign ambiguity introduced by squaring.

Table 1 Peak positions and electric field strengths, calculated on the basis both of the exciton model, using an exciton size of $r = 9.75$ nm, and calculated on the basis of the spontelectric model, given a value of $E_A = -6.51449 \times 10^{10}$ V m⁻¹ (see eqn (4) et seq.)

Deposition T/K	Peak position/eV		Electric field strength			
	Higher energy peak	Lower energy peak	Higher energy peak/ 10^6 V m ⁻¹		Lower energy peak/ 10^6 V m ⁻¹	
			Exciton model	Spont. model	Exciton model	Spont. model
127.5	8.641(4)	7.980(7)	3.986	3.984	3.975	4.024
130.0	8.636(4)	7.978(7)	3.968	3.973	3.965	3.980
135.0	8.625(4)	7.970(7)	3.929	3.924	3.937	3.907
137.5	8.617(4)	7.960(7)	3.898	3.899	3.899	3.897
140.0	8.601(4)	7.959(7)	3.823	3.823	3.896	3.831

The numbers in parenthesis in columns 2 and 3 indicate the uncertainty in the last digit for the peak position.

Given values of r and δ , the latter as a function of temperature, and shown in Fig. 3, eqn (3) enables the evaluation of the change of E_{sp} with deposition temperature. Values of δ require knowledge of the shift in absorption energy relative to a limiting value in the absence of any intrinsic electric field in the ice film, λ_0 . Here, we constrain λ_0 , such that the absorption peak position occurs at the limit of an infinitely thin film.

The evaluation of E_{sp} and degrees of orientation *vs.* T represents an ill-posed problem, whose solution is to appeal to additional knowledge, so-called regularization. This is achieved using a well-established mean-field model of the spontelectric effect, which describes how E_{sp} changes with temperature.¹⁸ Thus we seek values of δ , *via* λ_0 and r , which simultaneously satisfy both eqn (3) and the mean-field model for spontelectrics, which we now briefly describe.

As a crystalline layer of water ice accumulates during deposition, incoming molecular dipoles tend spontaneously to orient as they settle into the film. Spontaneous dipole orientation creates a surface potential and an electric field in the film, noting the absence of any free charge. The resulting spatially averaged degree of dipole orientation is given by the ratio of the average net component of the dipole moment in the direction z , perpendicular to the plane of the film, relative to the total dipole moment of the species in the solid state, that is $\langle \mu_z \rangle / \mu$, henceforth m . The magnitude of m depends on the temperature of deposition, T , *i.e.*, the temperature of the surface. Dipole orientation is a bulk phenomenon and our analysis is therefore restricted to the I_h ice component of the film, as mentioned above. The mean-field Hamiltonian, $\mathcal{E}$, for the system is characterized by feedback, since m itself depends on the interaction of the molecular dipole with the field, which itself depends on m . We write:

$$\mathcal{E} = \mu E_z = \mu \{E_s[1 + \zeta m^2] - E_A m\} \quad (4)$$

where μ is the dipole moment of water in the solid state^{6,7} and E_z is the mean local field in the z -direction. In eqn (4), the parameter

E_s represents polarization, dispersion and both covalent and coulombic interactions within the ice, including hydrogen bonding. The term $\mu E_s \zeta m^2$ embodies the reluctance of molecules to rotate against one another, which is a determining trait in this strongly hydrogen bonded system. The term $E_A m$ gives the value of the spontelectric field in the bulk of the ice. E_s and ζ are free parameters to be determined by fitting to experimental data. Analysis³² shows that the model requires that $E_A = 4\pi\mu/\Omega$ where $\Omega = 17.35 \text{ \AA}^3$ is the molecular volume of water molecules in ice,³³ yielding $E_A = -6.514 \times 10^{10} \text{ V m}^{-1}$. The temperature of the substrate induces disorder into dipole orientation, and this is modelled using the standard Langevin relationship. Combining eqn (4) with the standard Langevin relationship³⁴ yields:

$$f(T, m) = m = \coth\{m[E_s[1 + \zeta m^2] - E_A m]/T\} - \{m[E_s[1 + \zeta m^2] - E_A m]/T\}^{-1}. \quad (5)$$

The task is therefore to find m and the corresponding spontelectric field, $E_{\text{sp}} = E_A m$, as a function of temperature. Thus, the two means of solving for E_{sp} , namely *via* the spontelectric model contained in eqn (5) and *via* the exciton model contained by eqn (3), provide for a regularized least squares approach. Values of E_s and ζ are found by fitting eqn (5), so that eqn (3) is simultaneously satisfied according to a least squares criterion for any chosen exciton size r and limiting value of transition energy, λ_0 . In order to facilitate this we employ the linear inverse form of the Langevin function.^{35,36} The parameter E_A is also allowed to vary since both μ and Ω have associated uncertainties, but we find that E_A becomes $-6.5144 \times 10^{10} \text{ V m}^{-1}$, remaining very close to the model value. The form of eqn (3)–(5) is such that values of r and λ_0 , and thus δ , cannot be established independently. However λ_0 is constrained, first by observations, such that λ_0 is lower in energy than E and such that δ (Fig. 3) is equal for both the high energy and low energy transitions, and also by regularization using the spontelectric model. Only values of δ that allow the spontelectric model to recreate a monotonic change with temperature are permissible.

These constraints and numerical experiments show that λ_0 lies at 8.475 eV for the higher energy line and 7.818 eV for the lower energy line. The corresponding values of δ are shown in Fig. 3 and the resulting fits are shown in Fig. 4, with values from the exciton model and the spontelectric model listed in Table 1. Values of r , which is the most influential parameter in this context, are restricted to $9.75 \pm 0.25 \text{ nm}$, a range which gives the best fit between the exciton model and the spontelectric model, see Fig. 4b. The exciton size is therefore found to be much greater than the molecular diameter (0.32 nm), consistent with a Wannier–Mott exciton. Associated values of parameters in the spontelectric model are $E_A = -6.5144 \times 10^{10} \text{ V m}^{-1}$ (see above), $E_s = 1.8975 \times 10^6 \text{ V m}^{-1}$, $\zeta = 2.8944 \times 10^8$. The degree of orientation, m , varies weakly over the temperature range between 127.5 K and 140 K and falls between -6.12×10^{-5} and -5.87×10^{-5} . Note that these values, and the value of E_A , are negative, due to the direction of orientation of the water molecules.

Values of m are very small, reflecting a rigid structure, commensurate with a strongly hydrogen bonded system. Very low

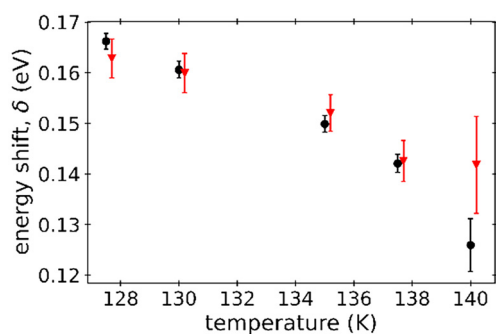


Fig. 3 Energy shifts, δ , in the higher energy peaks (black circles) and lower energy peaks (red triangles) as a function of deposition temperature, T , for $T \geq 127.5 \text{ K}$, relative to a zero, λ_0 , the peak position in the limit of an infinitely thin film, see text. The large uncertainty in δ for 140 K for the lower energy transition (red), is estimated from the Gaussian fit and stems from the experimental problem that material is continually sublimating at 140 K and that this spectral feature is $\sim 1\%$ of the higher energy feature (see Fig. 1).

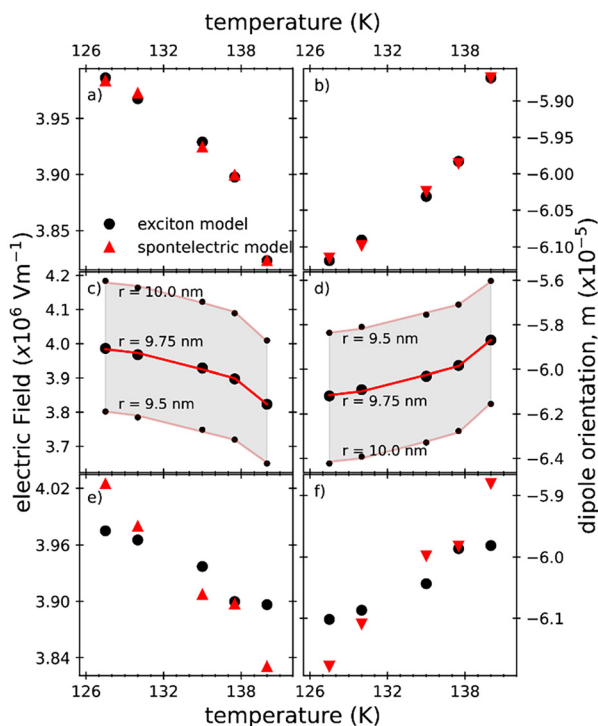


Fig. 4 Comparing the exciton model, eqn (1)–(3) (black circles), and the spontelectric model, eqn (4) and (5) (red triangles) for electric fields (left column), and dipole orientation (right column) arising in I_h . (a and b) Using data for the higher energy spectral line, with the fitted values of E_A , E_S and ζ given in the text and an exciton of size $r = 9.75$ nm. (c and d) Illustrating the sensitivity of results to values of exciton size between $r = 9.5$ nm and 10.0 nm. Beyond the range shaded in grey, consistency deteriorates establishing that the systematic error in the field is $\sim \pm 0.2 \times 10^5 \text{ V m}^{-1}$ and in m is $\sim \pm 0.2 \times 10^{-5}$. Solid red lines have been introduced to guide the eye. (e and f) as in (a) and (b) but for the lower energy spectral line relating to cubic ice, using the same values of E_A , E_S and ζ as in panels (a) and (b), recollecting that cubic ice is subjected to the field generated by hexagonal ice and does not itself generate a spontelectric field. The lower quality of the data, associated with the 1% proportion of cubic ice and sublimation at 140 K (see text), is reflected in the poorer consistency achieved between the exciton model and spontelectric model.

values of m nevertheless represent significant bound charge on the surface of the polarized ice, resulting from the high dipole moment of water moieties in ice and the small molecular volume of water. These together yield the large quoted value of E_A and give fields, $E_{sp} = mE_A$, of the order of $6 \times 10^{-5} \times 6.514 \times 10^{10} \text{ V m}^{-1}$ corresponding to 1.30 mV per ML. Thus, the surface of the 30 ML films studied here take on a negative potential of typically 39 mV or 0.039 C m^{-2} .

Discussion

Onsager *et al.*,⁸ in agreement with Kutzner,³⁷ ascribe the bulk polarization of water ice films wholly to dipole orientation, templated by the orientation that molecules achieve immediately after landing on the substrate. Subsequent work^{6,7,9,10} has shown that there is a significant contribution from pores in ice formed by deposition at 77 K . Be that as it may, the data of Onsager *et al.*⁸ based upon measurements of a thermally

stimulated current measured at a copper substrate, give an electric field of $3.95 \times 10^6 \text{ V m}^{-1}$ for ice deposited at liquid nitrogen temperature (77 K). At this temperature, for our data, there exists (i) the influence on the wavelength of absorption of very high local fields of the order of 10^9 V m^{-1} arising from pores in the ice and which affect the hydrogen bond energy^{11,12} and thus spectral transition energies and (ii) the presence of non-local spontelectric fields (termed in ref. 8 as a ‘natural electret’) affecting the energy of excitons, themselves arising from the nanocrystalline nature of ASW. Note that similar fields to the latter have been observed in low temperature ammonia ices which are nanocrystalline.³⁸ The spontelectric fields which we derive for I_{sd} ice at higher deposition temperatures relevant to crystalline ice, appear similar in value to the field derived at this one temperature of 77 K from the data of Onsager *et al.* collected by quite different means and relevant to ASW.

We note that the nature of the surface upon which spontelectric films are deposited has little or no bearing on the values of film polarization.³⁹ Thus, water ice deposited on substrates other than MgF_2 , for example, interstellar grains composed of silicates, would yield the same spontelectric fields as reported here. Turning specifically to the interstellar medium, polarization in ice can have an important impact on the rate of formation of young stellar objects, by reducing the degree of ionization in protostellar clouds, hastening the formation of magnetically supercritical cores and thus enhancing the rate of star formation.⁴⁰ This may be relevant to the formation of massive galaxies in the early Universe observed recently using the James Webb Space Telescope.⁴¹ It is known that water molecules in the ISM form *in situ* on the surface of cold dust grains, with temperatures of 10 K , *via* reactions between mobile H atoms and O atoms, and that this eventually leads to the build-up of water ice. On a timescale of $\sim 10^5$ years, these reactions can form a typical coverage of 100 monolayers.⁴² This first generation of ASW ice on grains in the ISM is created under very different conditions from those in our current experiment and is unlikely to be spontelectric. However, interstellar water ice is sublimated into the gas phase every $2 \pm 0.5 \text{ Myr}$ *via* interactions between dust grains and passing shocks.⁴⁰ This results in water concentrations $\sim 10^{-4}$ of the molecular hydrogen number density, several orders of magnitude greater than any yield from gas phase water production. These stochastic high gas phase abundances are, for example, required to account for both the brightness and range of frequencies of water masers found in star-forming regions and around late type stars.⁴³ Thus a second, and possible subsequent, generation of water ice may indeed be spontelectric, formed as water ice layers recondense on cold dust grains following the passage of a shock.

In addition, I_{sd} ice is posited to be found in the Earth’s mesosphere and stratosphere, in Mars, Venus and elsewhere in the Solar System.²⁹ Should such I_{sd} ices be spontelectric, the consequent bound charge at the surface of ice particles in the Solar System may inhibit particle coagulation and therefore rocky planet formation, and ice particle nucleation rates in general.^{44,45}

Although some crystalline water ice (*i.e.* at $T \gtrsim 125$ K) has been described as porous,^{46–49} the structural properties of water ice are highly sensitive to its formation conditions and thermal history. Even within a single formation method such as vapour deposition, parameters including deposition temperature,⁵⁰ dosing method,^{51–53} thermal history,⁵⁴ and film thickness^{50,54} can significantly affect porosity. These dependencies show that porosity cannot be generalised across vapour deposited ices without accounting for growth conditions and thermal history. Our deposition conditions and film thickness most closely match those of Kimmel *et al.*,⁵⁴ suggesting that our water ices grown above the transition temperature of 125 K are more likely non-porous crystalline ices, see SI. In contrast, porous crystalline ices have typically been produced *via* fundamentally different formation routes, such as freezing of liquid water,⁴⁷ or for much greater film thicknesses and different thermal histories.^{48,50,55}

Conclusion

With this report, we have described polarization in crystalline I_h ice as a bulk property that arises following the collective alignment of dipoles throughout the water film. Future work will aim at synthesising and characterising polarization in different ice polymorphs by controlling the temperature and pressure during film growth. The interest regarding the presence of spontaneous fields in crystalline ice is manifold. Polarization will affect ice particle nucleation rates,⁴⁴ and can impact the rate of formation of young stellar objects in the ISM. Electric fields in thin films might be also harnessed to separate charge carriers upon photoionization,⁵⁶ migrate solvated ions towards an interface or polarise bonds in solvated target molecules to affect the rate of chemical reactions.⁵⁷

Author contributions

RJ and DF carried out experiments; AC, DF and FP developed the theory and carried out numerical simulations; all authors contributed extensively to the interpretation of the data and the production of the manuscript.

Conflicts of interest

There are no conflicts to declare.

Data availability

Data for this article are available at the Zenodo database. See DOI: <https://doi.org/10.5281/zenodo.18699097>.

Supplementary information (SI) is available. SI contain VUV spectra between 20 K and 140 K; peak fitting details; time resolved data during the crystallisation process; and film density measurements. See DOI: <https://doi.org/10.1039/d5nr05194k>.

Acknowledgements

We acknowledge the Centre for Storage Ring Facilities at Aarhus (ISA) for granting access to the VUV beamline on the ASTRID2 storage ring. We also thank the staff at ISA for their technical assistance in performing our experiments, with special thanks to Nykola Jones and Søren Hoffmann. This work was supported by the Danish National Research Foundation through the Center of Excellence “InterCat” (Grant Agreement No. DNRF150), VILLUM FONDEN, through Grant No. VIL70175.

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