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The crystal structure of ice under mesospheric conditions

Benjamin J. Murray [a,*], Tamsin L. Malkin [a], Christoph G. Salzmann [b]

[a] Institute for Climate and Atmospheric Science, School of Earth and Environment, University of Leeds, Woodhouse Lane, Leeds LS2 9JT, UK
[b] Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK

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ABSTRACT

Ice clouds form in the summer high latitude mesopause region, which is the coldest part of the Earth's atmosphere. At these very low temperatures (< 150 K) ice can exist in metastable forms, but the nature of these ices remains poorly understood. In this paper we show that ice which is grown at mesospherically relevant temperatures does not have a structure corresponding to the well-known hexagonal form or the metastable cubic form. Instead, the ice which forms under mesospheric conditions is a material in which cubic and hexagonal sequences of ice are randomly arranged to produce stacking disordered ice (ice I_{sd}). The structure of this ice is in the trigonal crystal system, rather than the cubic or hexagonal systems, and is expected to produce crystals with aspect ratios consistent with lidar observations.

1. Introduction

Mesospheric ice clouds exist in a region of the Earth's atmosphere characterised by extremes of temperature and saturation. They form and exist at temperatures between 100 and 150 K where the saturation ratio commonly exceeds 100 and may occasionally reach 10^8 (Lübken et al., 2009). These conditions contrast with the coldest clouds in the troposphere which form at temperatures of around 185 K and with saturation ratios of less than two (Jensen et al., 2013; Wilson et al., 2012). Under these extreme conditions we need to consider the possibility that mesospheric clouds are composed of metastable forms of ice.

Water can exist as 15 crystalline phases of ice (Salzmann et al., 2011) in addition to several low temperature amorphous solid forms (Loerting et al., 2011) and high viscosity liquid phases (Palmer et al., 2014). Under mesospheric conditions the only crystalline phase thought to form is ice I (phase ice one), but ice I can exist in two well-defined structural forms: the familiar hexagonal ice (ice I_h; ice one h), and metastable cubic ice (ice I_c; ice one c) (Hobbs, 1974).

More recently, it has been shown that ice I has a strong propensity to exist in a state in which cubic and hexagonal sequences are interlaced to produce stacking disordered ice (Kuhs et al., 2012; Malkin et al., 2015, 2012; Moore and Molinero, 2011). This material has a distinct crystal symmetry from either ice I_c and ice I_h and is referred to as ice I_{sd} (Malkin et al., 2012). In fact, it is suggested that all ice which was labelled ice I_c in the past is in fact ice I_{sd} (Hansen et al., 2008a, 2008b; Kuhs et al., 2012; Malkin et al., 2012, 2015).

In order to appreciate what stacking disorder is in the context of ice I, it is necessary to appreciate the structure of ice I_c and ice I_h. Both of these forms of ice I can be thought of as being made up of identical layers, but where the stacking of these layers differ in ice I_c and ice I_h. Each layer is made up of connected puckered six-membered rings of oxygen atoms, where the hydrogen atoms are positioned between the oxygen atoms. In ice I_h each successive layer is a mirror image of the preceding layer, whereas in ice I_c each successive layer is in the same orientation but shifted by one half of the width of the puckered hexagonal ring. However, what is commonly observed through diffraction studies is, particularly at low temperatures, that ice I has a mixture of sequences associated with both ice I_c and ice I_h, i.e. it is stacking disordered.

Satellite based spectroscopic measurements indicate that mesospheric clouds are predominantly composed of crystalline ice, but cannot rule out a small fraction of cloud mass being comprised of amorphous ice (Hervig and Gordley, 2010). Murray and Jensen (2010) suggested that amorphous ice nucleates, since the amorphous phase has a lower energy barrier to nucleation than crystalline ice, but may subsequently crystallise. This would suggest that amorphous ice may be a transient phase in the upper mesosphere, which rapidly crystallises. Hervig and Gordley (2010) state that they cannot distinguish between the different forms of crystalline ice in mesospheric clouds, therefore the nature of

* Corresponding author.
E-mail address: B.J.Murray@Leeds.ac.uk (B.J. Murray).

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mesospheric crystalline ice remains poorly constrained.

In this paper we report a sequence of experiments which show that crystalline ice grown at mesospherically relevant conditions is a form of stacking disordered ice.

2. Methods

In order to determine the crystal structure of ice grown under conditions pertinent to the mesopause region, we examine ice grown on a temperature controlled stage enclosed within an environmental chamber using X-ray diffraction. In these experiments we deposited ice from the vapour phase onto a glass substrate at 110 K as amorphous ice and the sample was then warmed at a rate of 1 K min^{-1} while recording detailed diffraction patterns over a range of temperatures relevant for mesospheric clouds.

We have used X-ray diffraction to study vapour deposited ice (Shilling et al., 2006) and ice crystallised from aqueous solution droplets (Malkin et al., 2012; Murray, 2008a, 2008b; Murray and Bertram, 2006, 2007; Murray et al., 2005; Wagner et al., 2012) in the past. The X-ray diffractometer (Bruker D8 Advance) used in these experiments was configured in a standard reflection geometry and was equipped with a Cu Kα X-ray source ($\lambda = 1.5418$ Å), a VÅNTEC detector and an Anton Paar TTK450 liquid nitrogen temperature-controlled stage. The stage is enclosed within an airtight chamber.

In order to prepare the ice film, the sample holder was cooled by liquid nitrogen to 110 K at a rate of 30 K min^{-1} with the chamber under vacuum. A diffraction pattern was taken to ensure no frosting had occurred during this process. If no detectable frosting of the sample support was detected, humidified nitrogen was admitted to the chamber. The pressure in the chamber was increased from 1×10^{-3} mbar to atmospheric pressure ($\sim$1 atm) in approximately 5 min and the ice film was then left to grow for about 25 min after which an observable ice deposit was evident in the X-ray diffraction patterns. The water content of the nitrogen gas was controlled using a water bubbler and successive dilution using mass flow metres in order that the maximum saturation ratio (with respect to ice I_h and the cold stage set to 110 K) was about 12. Vapour deposition of ice in this manner is expected to result in a porous ice film made up of nano-scaled amorphous ice particles (Murray and Plane, 2003a, 2003b, 2005). Once deposition was complete, the chamber was placed under vacuum and diffraction patterns ($2\theta = 10°$–$60°$) were recorded every 5 K as the sample was warmed continuously at 1 K min^{-1} from 110 K; warming the ice film in this way result in controlled and reproducible irreversible crystallisation.

3. Results and discussion

A sequence of diffraction patterns of ice which was initially deposited from the vapour phase at 110 K and then warmed at a rate of 1 K min^{-1}, together with the calculated ideal patterns of ice I_c and ice I_h, are shown in Fig. 1. The diffraction pattern of the ice which was initially deposited at 110 K has no sharp Bragg peaks, consistent with amorphous ice. The ice began to crystallise between 120 and 125 K as evidenced by the appearance of clear Bragg peaks. The intensity of the peaks in the patterns recorded between 125 and 160 K increase with increasing temperature as the amorphous ice crystallises. In the past, these patterns would have been identified as ice I_c on the basis that the three primary cubic peaks are present at 24°, 40° and 47.5° in the experimental patterns. However, closer inspection reveals a number of inconsistencies: the respective intensities of the 24°, 40° and 47.5° peaks are not a good match to the simulated pattern of ice I_c; there is a

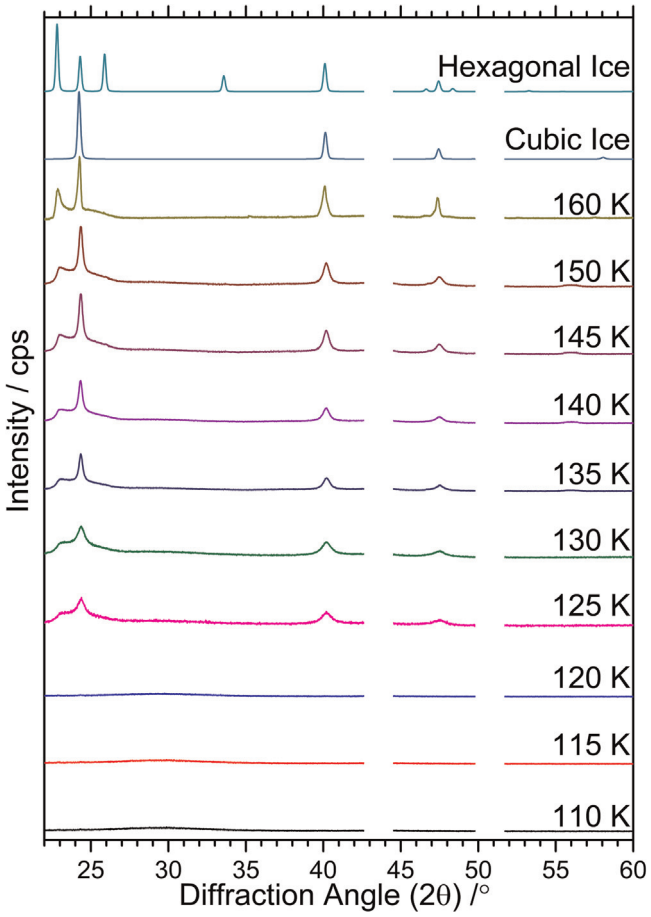

Fig. 1. X-ray diffraction patterns of deposited amorphous ice at 110 K (bottom), progressing to warmer temperatures (ascending patterns) with calculated pure ice I_c and pure ice I_h patterns at the top. The gaps in the pattern correspond to the positions of peaks from the cold stage. These patterns do not have the background subtracted. The *Y* axis is plotted as counts per second (cps).

peak at 23° at a position of a prominent peak in the simulated ice I_h pattern, but the absence of other ice I_h peaks (26° and 33.5°) shows that there is no bulk ice I_h present in the sample; finally, the region between 23° and 26° in the experimental patterns is raised above the background. In summary, the experimental patterns of crystalline ice over the mesospheric cloud temperature range are inconsistent with either ice I_h or ice I_c.

Instead, the features of these diffraction patterns are consistent with stacking disorder in ice I. In a study of the freezing of supercooled water droplets which froze around 233 K, showed that a diffraction pattern containing similar features was consistent with ice which had 50% cubic and 50% hexagonal sequences randomly arranged. The quantitative analysis was done using an algorithm for calculating diffraction patterns containing stacking disorder known as DIFFaX (Treacy et al., 1991). Subsequently we have used MCDIFFaX (Malkin et al., 2015; Salzmann, 2014) which incorporates the DIFFaX code in a Monte-Carlo based least square fitting routine which aids the analysis, especially in cases where stacking is complex.

MCDIFFaX can be used to model varying degrees of complexity of stacking disorder. In the simplest case, the probability of a particular layer appearing is independent of what came before. In this case we only need to define a single stacking probability, Φ_c which indicates the probability of cubic stacking expressed as %. The probability of hexagonal stacking, Φ_h, is simply $100 - \Phi_c$ and the stacking in ice which follows this model is said to be random. This simple model is a good description for ice nucleated