

## Supporting Information: On the Nature of the Excess Electron in Ice $I_h$

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### Abstract

In this document we provide further details concerning the results presented in the main manuscript.

## I. DEFECT STRUCTURES

The proton-disordered ice  $I_h$  crystal structure is of the Wurtzite type in which each water molecule takes part in 4 hydrogen bonds (HB), with each water molecule donating and receiving precisely 2 HBs, respectively, and such that there is no long-range order in the HB orientations. This arrangement is described in terms of the two Bernal-Fowler ice rules<sup>1</sup> which state that (1), each oxygen atom is covalently bonded to precisely 2 protons and, (2) there is precisely one proton between each nearest-neighbor oxygen-oxygen pair. These rules imply that ice consists of water molecules and that all HBs are saturated. To visualize these it is useful to consider the hypothetical 2-dimensional square ice,<sup>1</sup> shown schematically in Fig. S1.

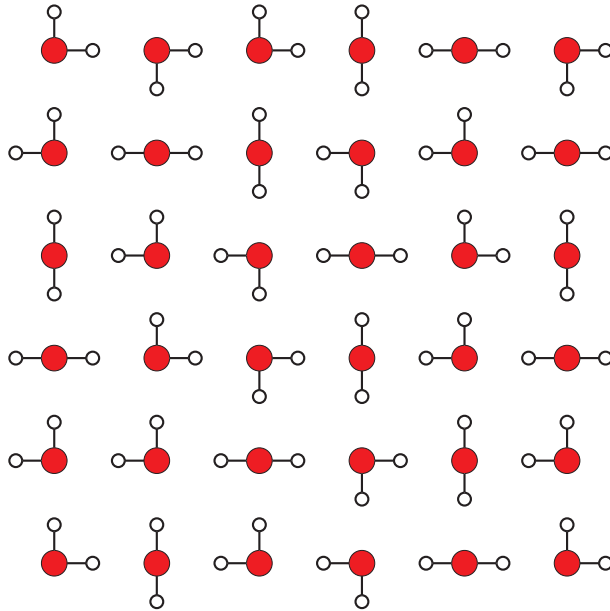


Figure S1. (Color online) Hydrogen-bond topology of square ice

In the context of trapping sites for the excess electron (EE) the presence of dangling HBs is fundamental, leading to the consideration of crystal defects. The first defect structure considered is the Bjerrum defect pair<sup>1</sup>, which is formed by rotating a molecule about one of its covalent O-H bonds by an angle close to the tetrahedral angle such that one oxygen-oxygen nearest-neighbor pair has two protons between it, referred to as the D-defect, and another has none, called the L-defect. Successive molecular rotations can then separate both defects. The Bjerrum defect pair represents a violation of the second ice rule and the according HB topology change for the square ice is shown in schematically Fig. S2 a). The molecular

structure of the D-defect is quite different from the schematic shown in Fig S2a), however, as was shown previously using both empirical force fields<sup>2</sup> as well as DFT calculations<sup>3</sup>. Due to the strong electrostatic interaction the two covalently bonded protons tend to repel, such that one of the protons rotates away from the O-O axis, leaving an unsaturated HB, as shown in Fig S2b). In this fashion, the D-defect is an intrinsic lattice defect characterized by a single dangling HB. In the calculations, the D-L defect pair has been separated by a

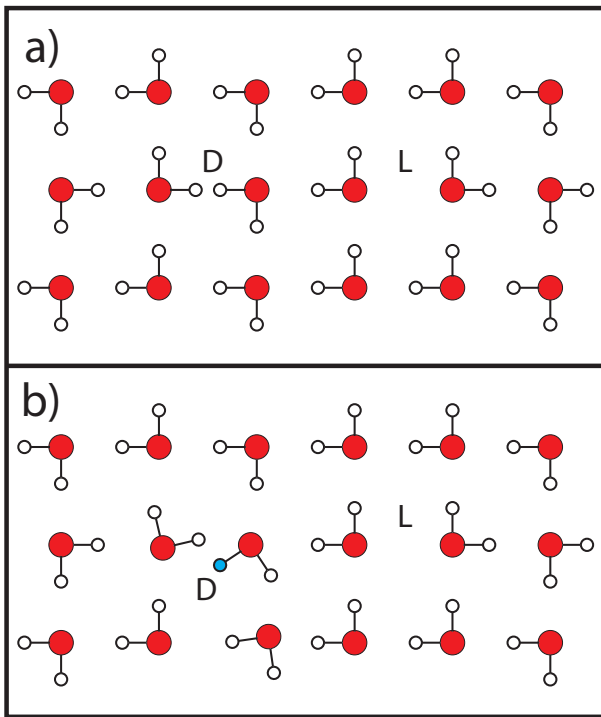


Figure S2. (Color online) Bjerrum defect pair in square ice. a) Definition of D and L defects. D-defect is characterized by presence of two protons between neighboring O-O pair. L-defect is located on nearest-neighbor O-O pair without any protons in between. b) Schematic representation of molecular structure of D-defect. Due to electrostatic repulsion two protons do not remain aligned and one of them rotates away, leaving a dangling HB. Dangling proton shown in light blue

number of molecular rotations such that the distance between them is  $11 \text{ \AA}$  and maximal within the used 96-molecule periodic cell<sup>3</sup>.

A lattice defect that introduces two dangling HBs is the simple molecular vacancy, as shown in Fig. S3a) The removal of a water molecule breaks four HBs, of which the two donated by nearest-neighbor molecules become unsaturated, leaving two dangling protons pointing toward the center of a cavity. The number of dangling protons can be further

increased by creating defect complexes combining the molecular vacancy with one or two D-type Bjerrum defects, which lead to configurations with 3 and 4 dangling HBs, respectively, as shown schematically for square ice in Fig. S3 b) and c).

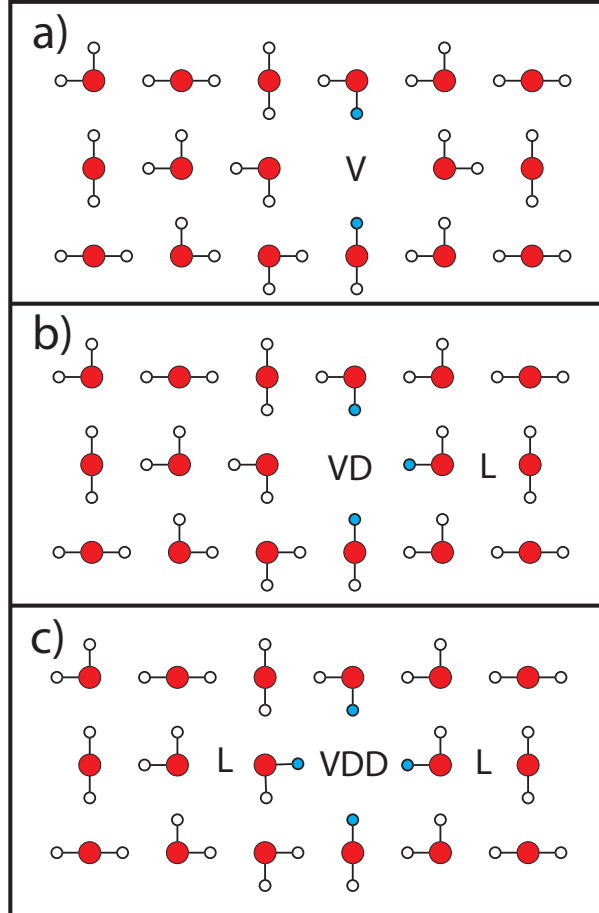


Figure S3. (Color online) Molecular vacancy and its complexes with D-type Bjerrum defects. Dangling protons are shown in light blue. a) Molecular vacancy leaves 2 dangling HBs point toward center of cavity. b) Complex formed by molecular vacancy and D-defect (VD) leaves 3 dangling HBs. c) Complex formed by molecular vacancy and 2 D-type Bjerrum defects (VDD) leaves 4 dangling HBs pointing toward center of cavity.

## II. DEFECT-FREE ICE $I_h$

Figure S4 shows a charge-density contour profile associated with the Kohn-Sham (KS) level occupied by the EE. It is spread out throughout the entire cell, which is reflected in its large Participation Ratio (PR) value of  $V/1.7$ , with  $V = 3127.95 \text{ \AA}^3$  the volume of the

computational cell. This means that the effective volume participating in this level is of the same order of magnitude as the volume of the cell itself.

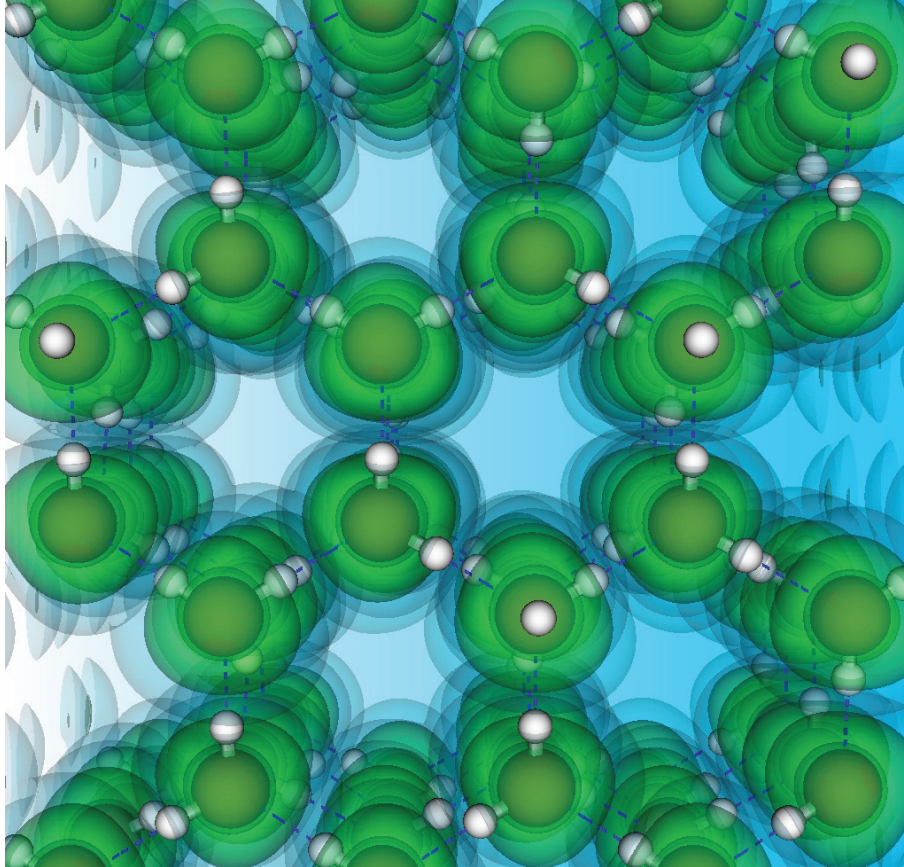


Figure S4. (Color online) Charge-density profile associated with the KS level occupied by the EE in defect-free ice  $I_h$  for  $3 \times 3 \times 3$  Brillouin-zone sampling and the PBE functional. Contours depict density levels of  $6.4 \times 10^{-4}$  and  $3.2 \times 10^{-4} e/\text{\AA}^3$ .

### III. VDD DEFECT

As detailed in Sec. I, the addition of a second D-type Bjerrum defect to a VD complex leads to the VDD defect structure, which is characterized by a vacancy cage with four inward-pointing dangling HBs. Figure S4 displays a typical charge-density profile and absorption signatures for the EE in this defect structure. The EE charge density is more strongly localized in this cavity compared to the VD center, with the PR giving effective volumes of

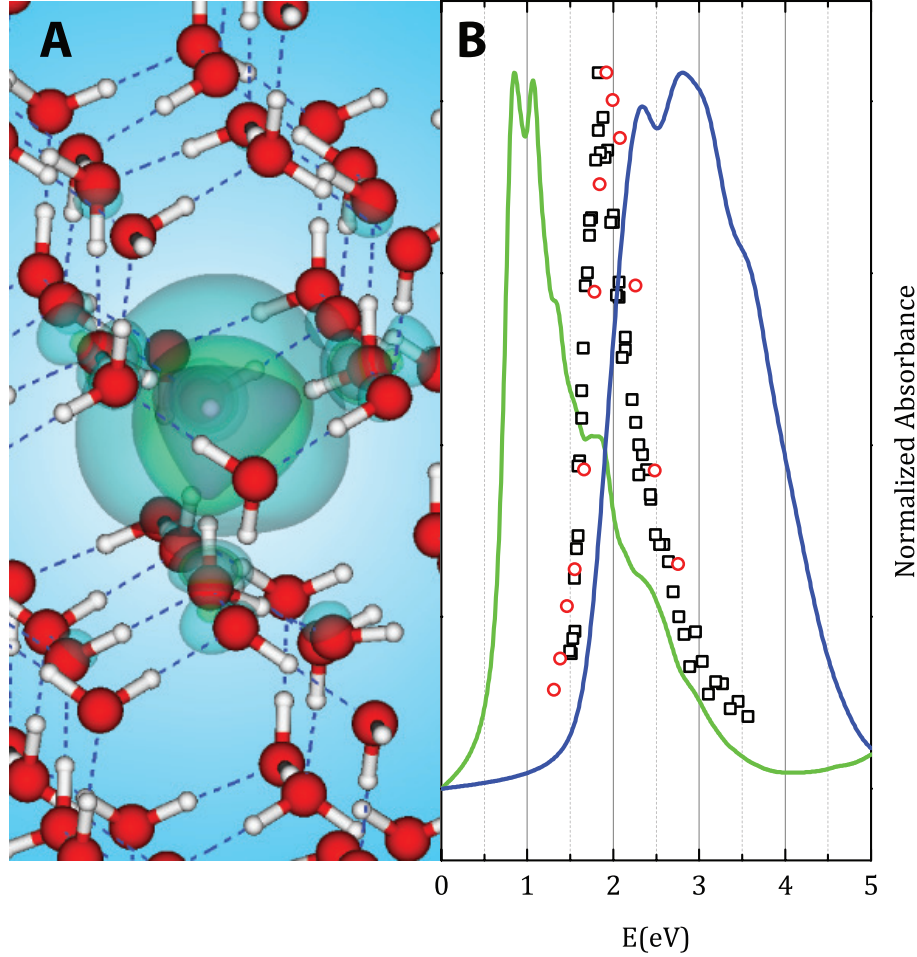


Figure S5. (Color online) Typical charge-density profile and absorption signals for the EE in the presence of a VDD defect complex. **(A)** shows PBE charge-density profile for  $5 \times 5 \times 5$  Brillouin-zone sampling obtained by subtracting both spin-component total electron densities. Three contours depict density levels of  $5.2 \times 10^{-2}$ ,  $2.9 \times 10^{-2}$ , and  $7.0 \times 10^{-3} e/\text{\AA}^3$ . **(B)** shows normalized absorption profiles for PBE and PBE0 functionals, as well as experimental data. Green line represents spin-polarized  $5 \times 5 \times 5$  PBE absorptions. Blue curve shows  $3 \times 3 \times 3$  PBE0 result. Squares and circles depict the experimental results from Refs. 4 and 5, respectively.

0.7 and 0.5 12-molecule cages, or radii of 2.4 and 2.1 Å for the PBE and PBE0 functionals, respectively. Furthermore, as for the VD trapping center (See main text), the EE density for the VDD structure is spin polarized. The computed absorption profiles show the same asymmetric shape as that seen for the VD defect in Fig. 2 of the main text, again emerging

from contributions of transitions between the EE level and unoccupied states. However, although the peak position of the PBE absorption profile is now closer to the experimental position, the corresponding PBE0 result is centered around an energy  $\sim 1$  eV higher than the experimental peak center. This suggests that the VDD defect is unlikely to be involved in the experimental absorption signal. Indeed, the binding energy of a second D-defect to the VD complex is negative,  $\sim -0.3$  eV,<sup>6</sup> implying that the VDD defect is unstable with respect to dissociation into separated VD and D-type Bjerrum defects. Accordingly, it is not expected to play an important role in ice  $I_h$ .

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