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The Cold Ice Surface, and a Warm Heart - Victoria Buch (1954-2009)

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ITALY

THE COLD ICE SURFACE, AND A WARM HEART --VICTORIA BUCH--(1954-2009)

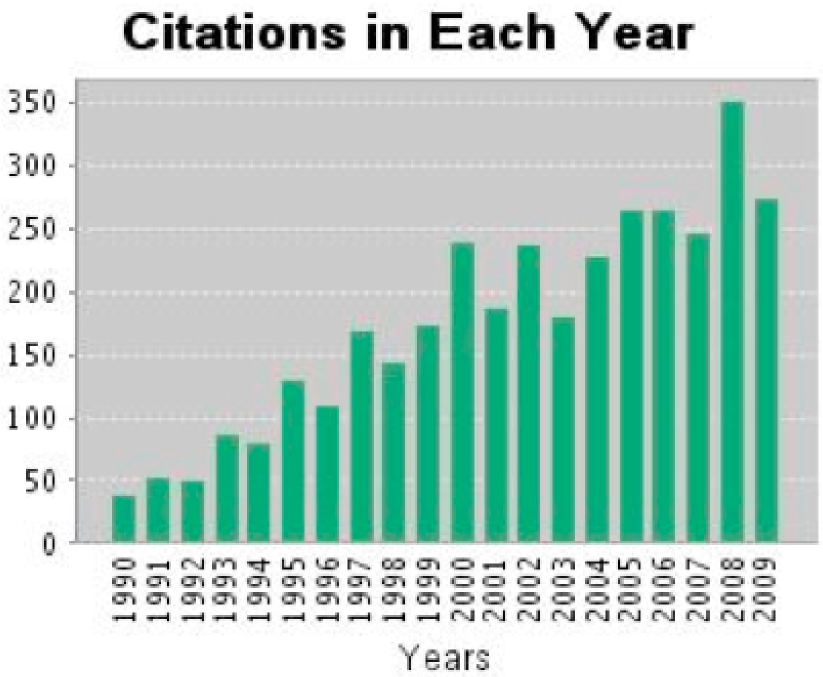
ICTP, 26/ 10/ 2009

Born in Poland to a Jewish, russian-speaking family. Emigrated to Israel 1968, at age 14.

She was a very gifted child. She started to study chemistry in the Hebrew University when she was 17 years old and finished her PhD by 30 with 16 articles. Benny Gerber was her supervisor then, and he remained her scientific collaborator and her friend until her final days.

She continued her academic career in Theoretical Chemistry in the United States, where she lived for 8 years with Ron Elber, her erstwhile husband and Dassi`s father.

SCIENCE: strong well established theoretical physical chemist, specializing in ice, nanoparticles, surfaces, clusters, reactions,…



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Militant against Israeli occupation of Palestinian territories. Founded the Occupation Magazine.

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In Memory of Prof. Victoria Buch, Occupation Magazine`s Founder (a statement and an article)

Victoria

PROTON ORDER AT THE ICE SURFACE

Victoria BUCH

Hebrew University, Jerusalem

PNAS 105, 5947 (2008); and unpublished

H. GROENZIN	Tufts University, Medford, MA
I. LI	“
M.J. SHULTZ	“
E. T.	SISSA, ICTP, Democritos, Trieste

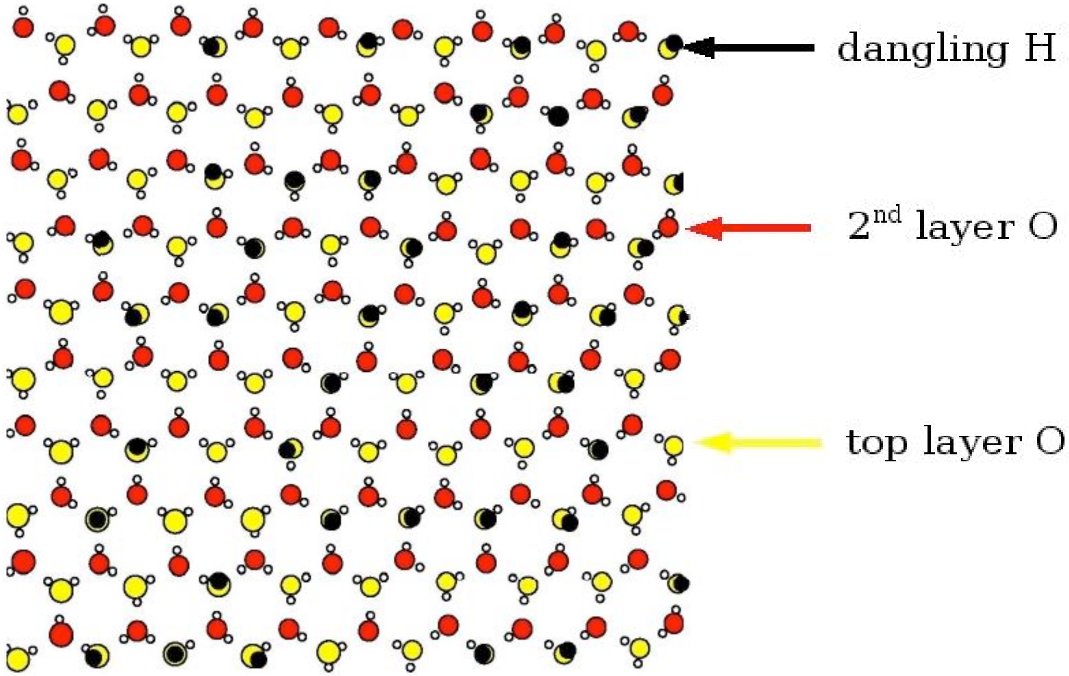
HEXAGONAL ICE, T< 273 K

BULK: OXYGENS ARE ORDERED
PROTONS ARE DISORDERED

(0001) BASAL SURFACE

WHAT IS THE SURFACE STRUCTURE???

(top view)



TOPMOST OXYGENS FORM YELLOW TRIANGULAR LATTICE, WELL ORDERED UP TO ~180 K

HALF COVERAGE OF PROTONS--ONE OXYGEN OUT OF TWO HAS A “DANGLING HYDROGEN” ON TOP

FRUSTRATION+ BULK DISORDER=EXPECT SURFACE TO BE PROTON DISORDERED TOO!

He-atom scattering
GLEBOV et al JCP (2000)

1. Perfect triangular surface lattice of oxygens (integer peaks)

2. Unexplained fractional "2.1x2.1" peaks (a), (b).

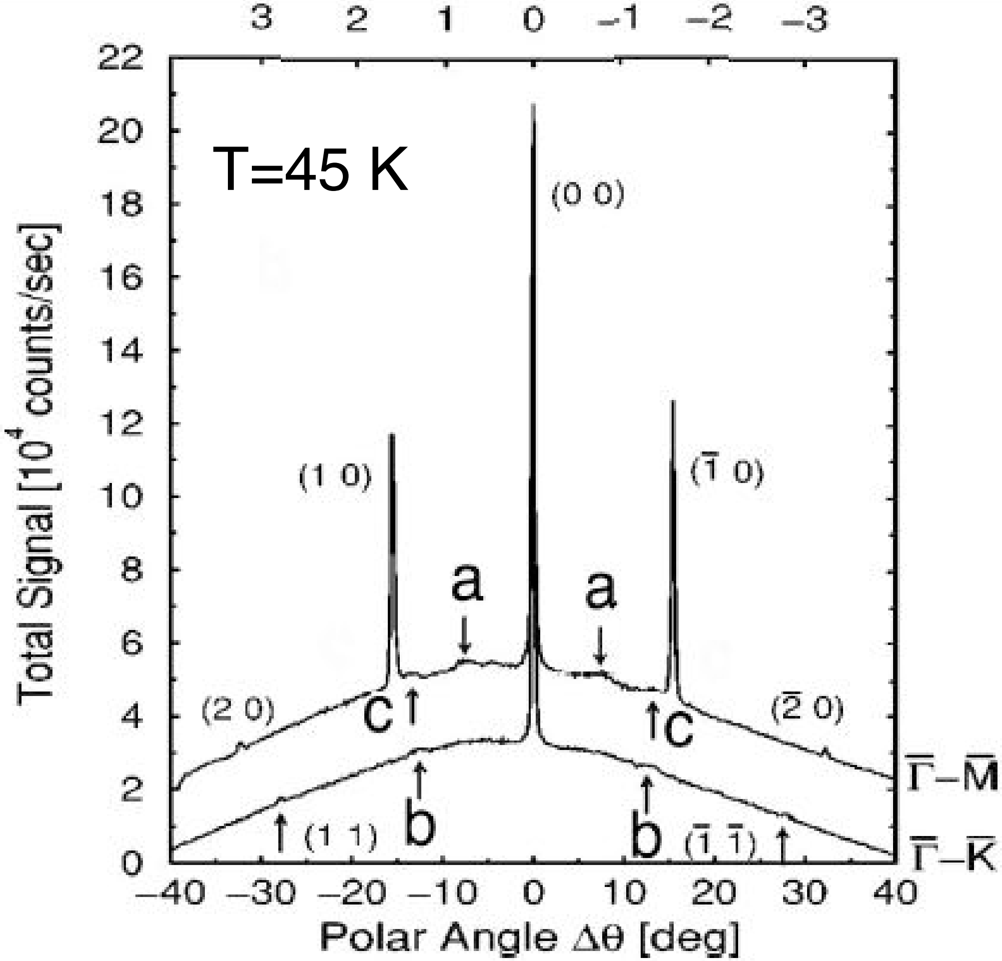
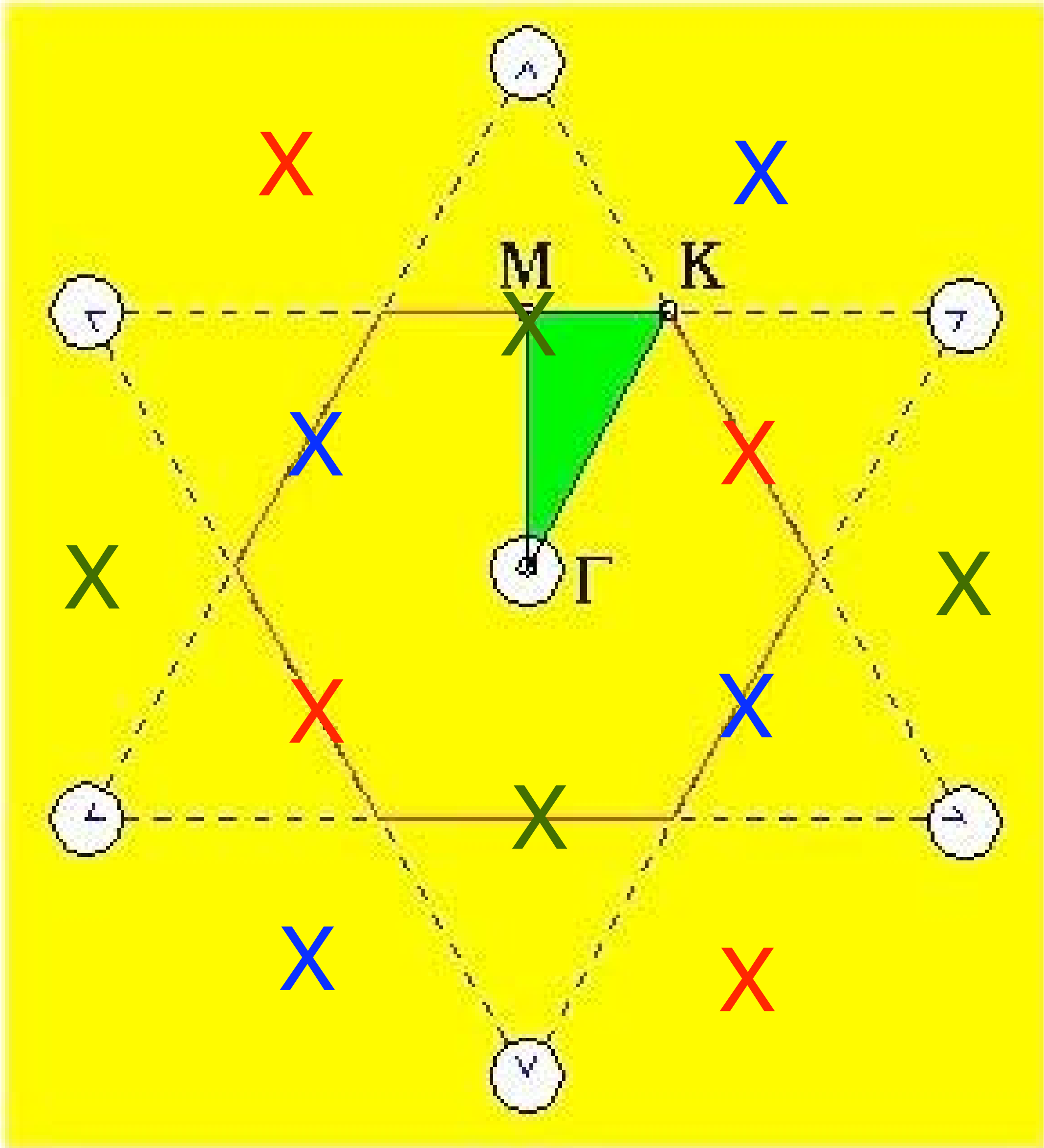
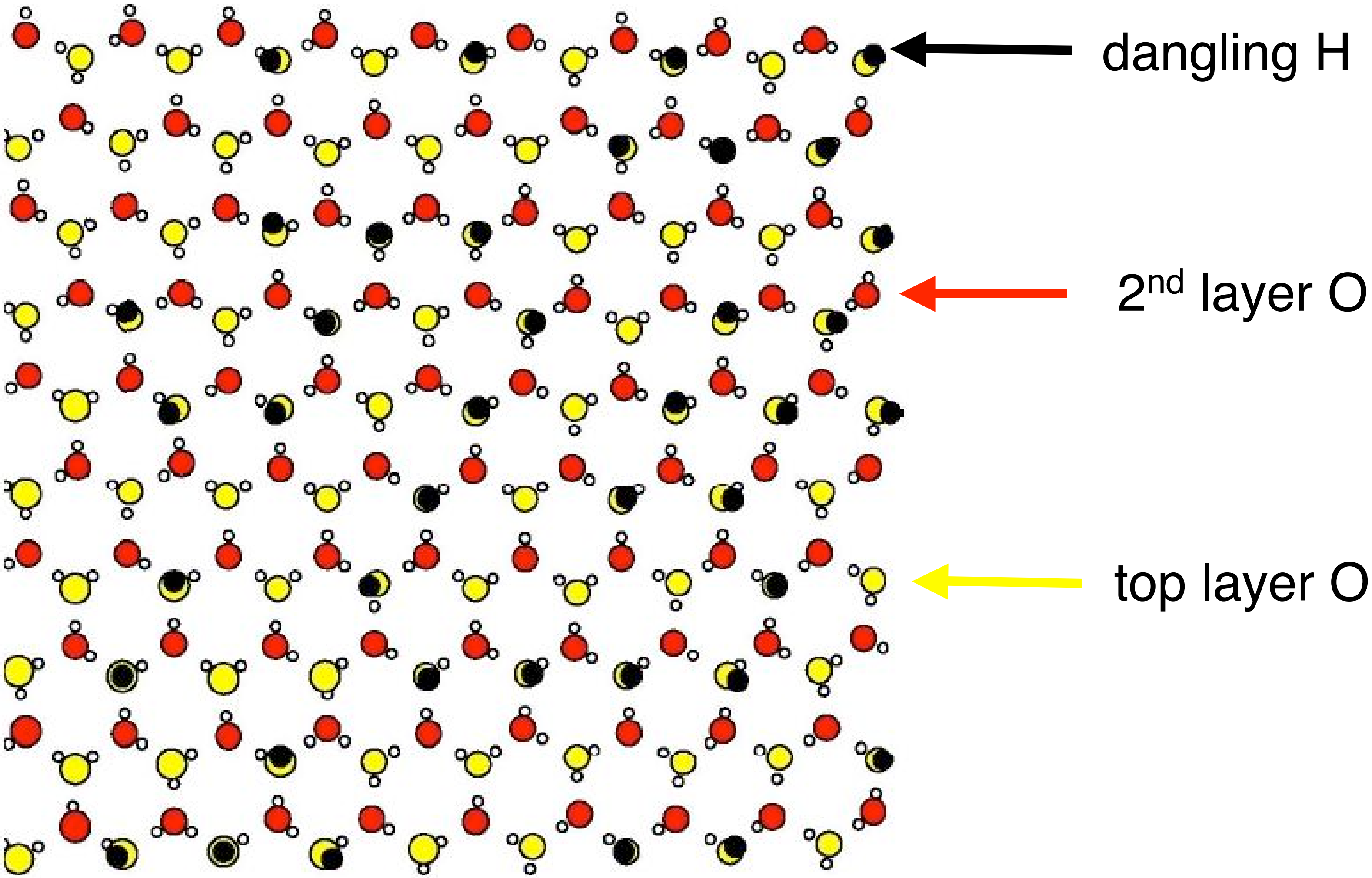


Fig. 4. Helium diffraction pattern from the basal ice surface [reproduc with permission from ref. 8 (Copyright 2000, American Institute of Physic Angular distributions along the ice surface $\bar{\Gamma} - \bar{M}$ (upper curve) and $\bar{\Gamma}$ - azimuths (lower curve) for an incident energy of 10.5 meV and a surf temperature $T_s = 45$ K. Sharp, first-order diffraction peaks from the hexago ice surface are observed along the $\bar{\Gamma} - \bar{M}$ azimuths, along with weak seco order peaks along both the $\bar{\Gamma} - \bar{M}$ and $\bar{\Gamma} - \bar{K}$ azimuths. Additional broad, we features (indicated by arrows) can be seen for both directions. Calcula



COULD THREE 2x1's BE MISTAKEN FOR A 2x2?



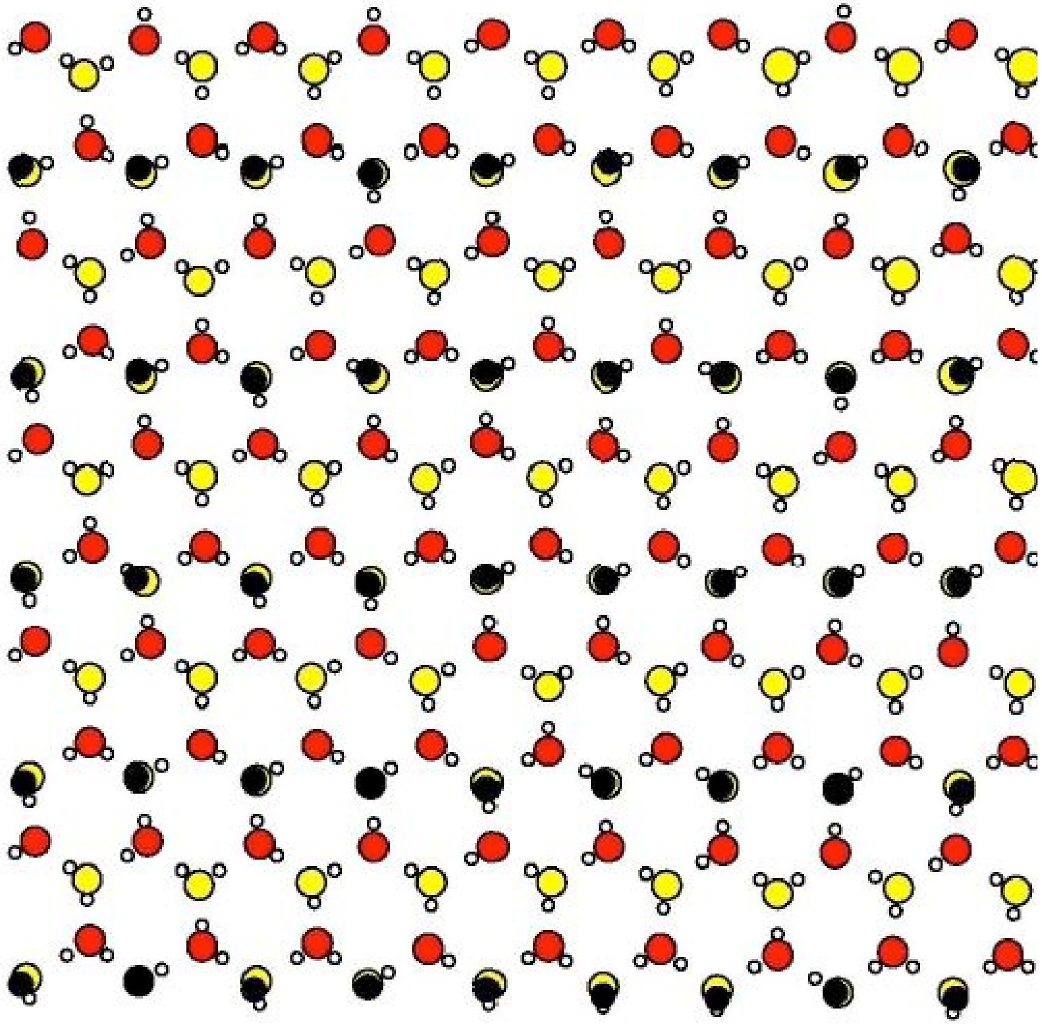
(A) proton disordered surface (TOP VIEW)

SURFACE PROTONS
"DANGLING HYDROGENS"
REPEL EACH OTHER DUE,
e.g., TO DIPOLE-DIPOLE
INTERACTIONS.

WILL STAY AS MUCH AS
POSSIBLE APART.

IN HALF FILLED TRIANGULAR
LATTICE, THERE IS
FRUSTRATION.

FLETCHER (1992):
BEST SOLUTION COULD
BE A STRIPED 2x1 PHASE



(B) striped phase

(TOP VIEW)

SIMULATIONS (CLASSICAL) V. Buch

a) Molecular Dynamics; or

b) Monte Carlo configuration sampling

-- Potentials: TIP4P-ice; EMP.

-- Slabs, up to 10 bilayers, or ~5,000 H_2O molecules

SIMULATIONS (CLASSICAL) V. Buch

Oxygens: start in ideal crystalline positions and a) free to move (MD); (b) frozen (MC);

Protons: always disordered in bulk ; lower surface, disordered; top surface: various types of order.

All configurations compatible with ice rule.

MD: oxygen lattice stable for T<180

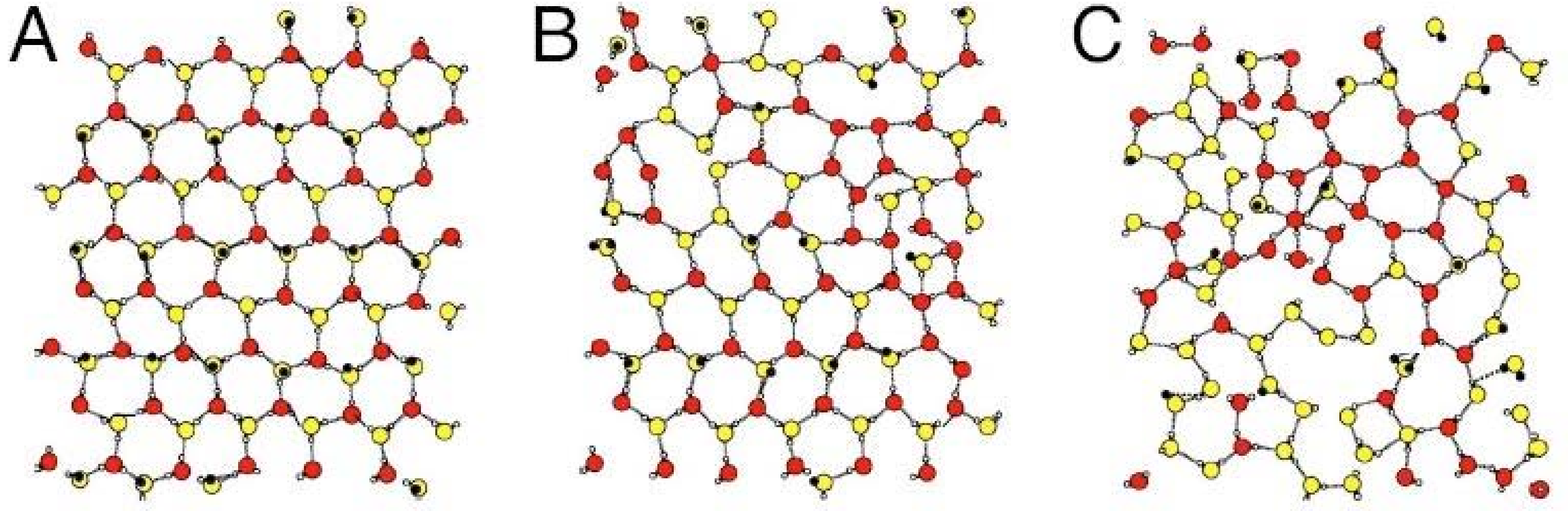


Fig. 6. Final snapshots of MD simulations of the initially striped ice surface at 150 K (*A*), 200 K (*B*), and 250 K (*C*). The simulation slab contained 960 molecules arranged in 10 bilayers, with all molecules fully mobile; only the top 96 molecules are displayed. The snapshots correspond to 2-ns-long simulations at 150 K and 200 K and 1 ns at 250 K. O atoms belonging to the four-coordinated molecules are in red; O atoms belonging to the three-coordinated molecules are in yellow; d-H atoms are in black.

180 K ~ " Tammann temperature" of ice(0001)

LOW T: LATTICE MONTE CARLO ENERGY DISTRIBUTION CURVES

6 BILAYERS OF 180 MOLECULES EACH
OXYGENS RIGIDLY ORDERED
PROTONS DISORDERED IN BULK (+ICE RULE)

SETS OF ABOUT 200 CONFIGURATIONS EACH

EACH SET WITH A DIFFERENT TOP SURFACE ORDER: STRIPED, HONEYCOMB, DISORDERED

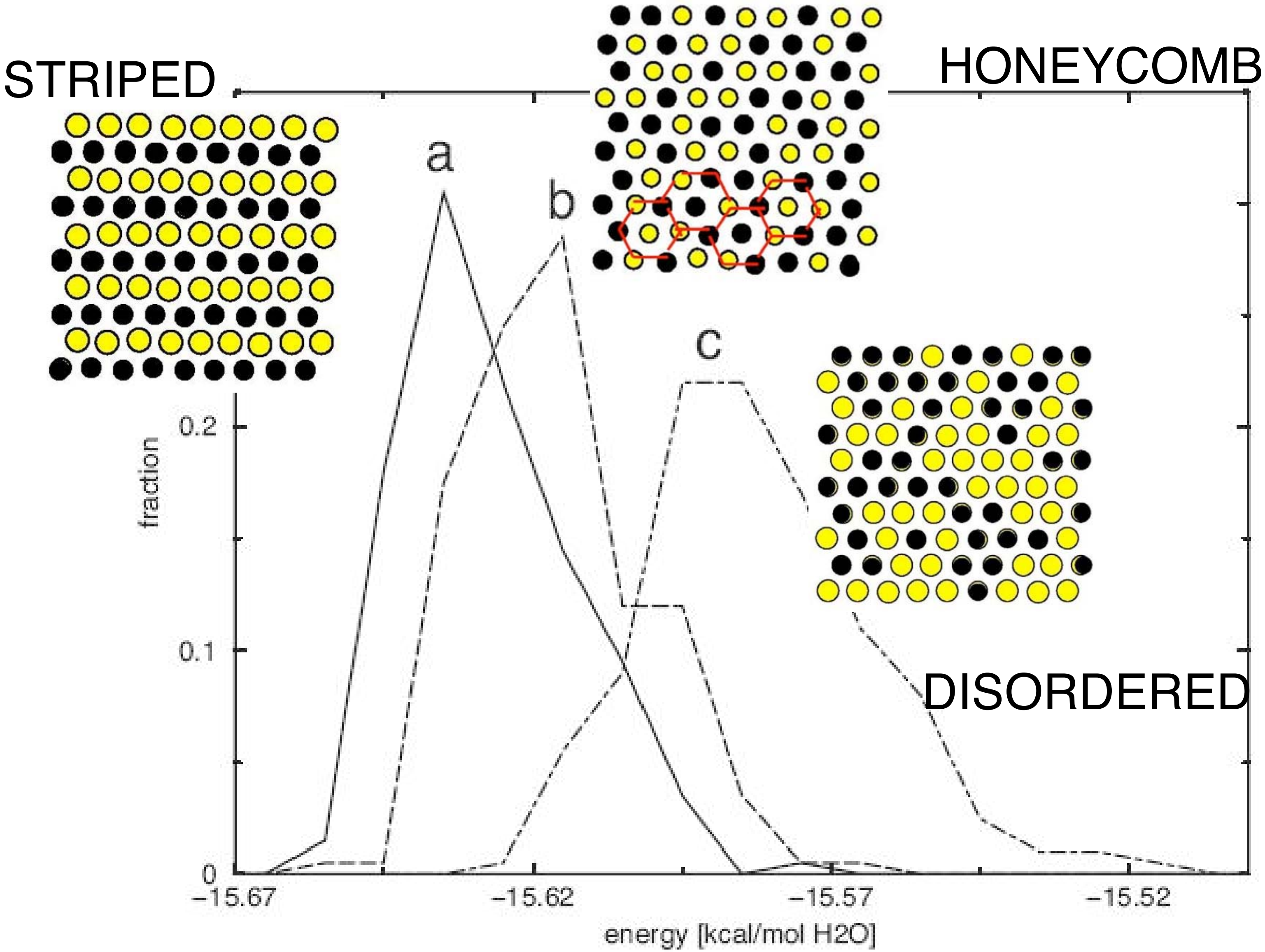
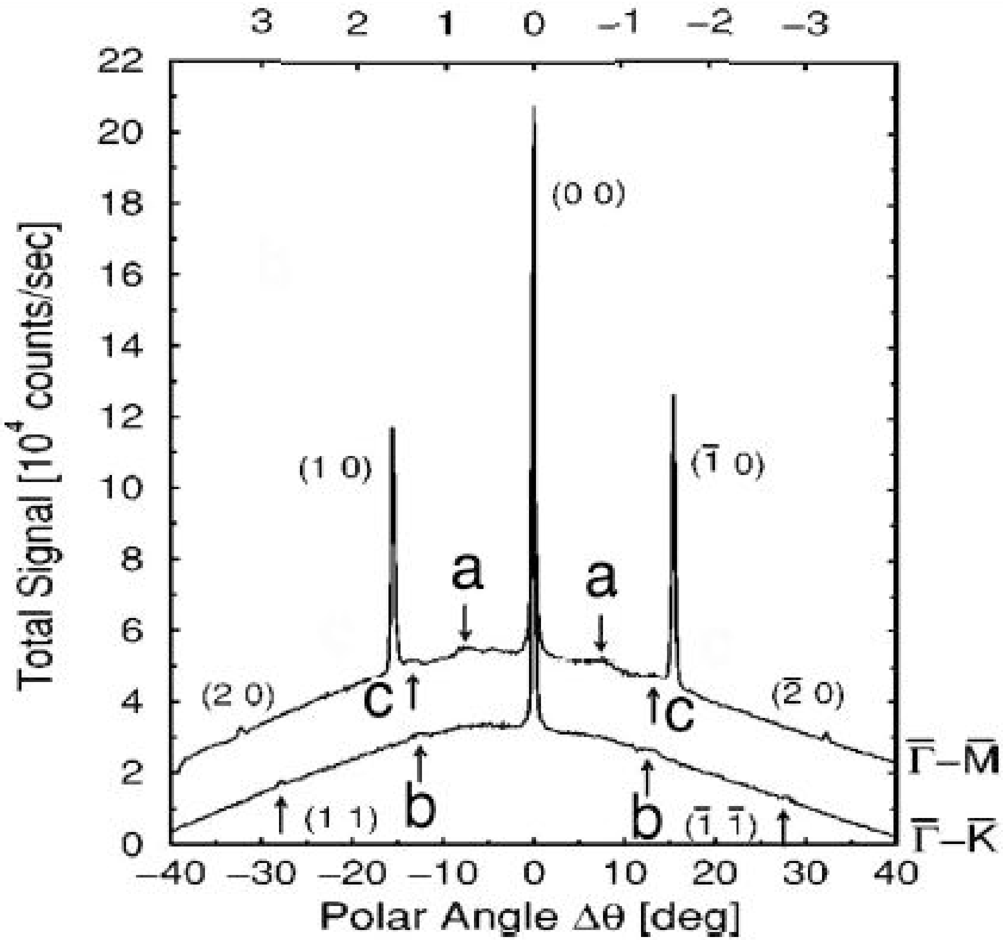


Fig. 2. Distribution of energies for sets of slab structures with a striped surface (a), honeycomb surface (b), and fully proton-disordered surface (c). Energies calculated with TIP4P-ice potential for sets of 200 structures contain-

He-atom scattering
GLEBOV et al JCP (2000)



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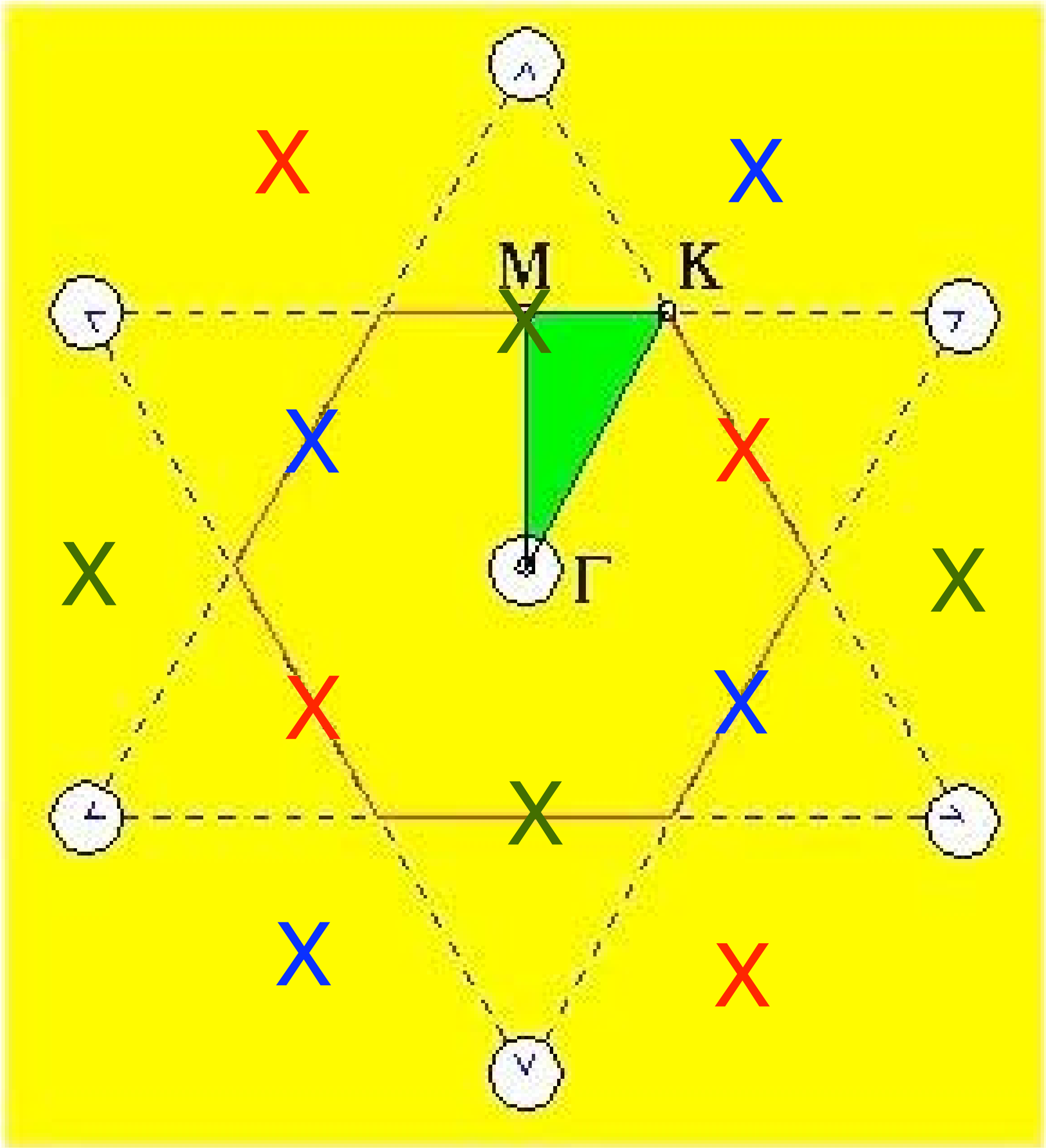
THERE IS 2x1 STRIPED ORDER ON THE LOW-TEMPERATURE ICE SURFACE

CONCLUSION ALSO SUPPORTED BY AB INITIO CALCULATIONS IN MICHAELIDES’s GROUP



THREE 2x1's WERE INDEED MISTAKEN FOR A 2x2

WHAT TEMPERATURE EVOLUTION OF THE 2x1 STRIPED PHASE FROM 0 TO 180 K?

MC WITH REAL POTENTIALS: ONLY OF QUALITATIVE VALUE, # OF STEPS INSUFFICIENT

SIMPLIFIED ISING MODELING : (WAS) UNDER WAY BY V. BUCH

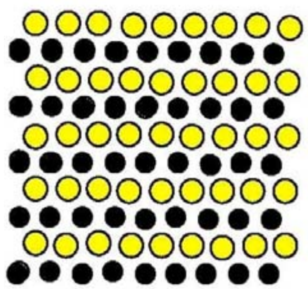
WHAT KIND OF SURFACE PHASE TRANSITION?

Guided by 2D antiferromagnetic Ising model :

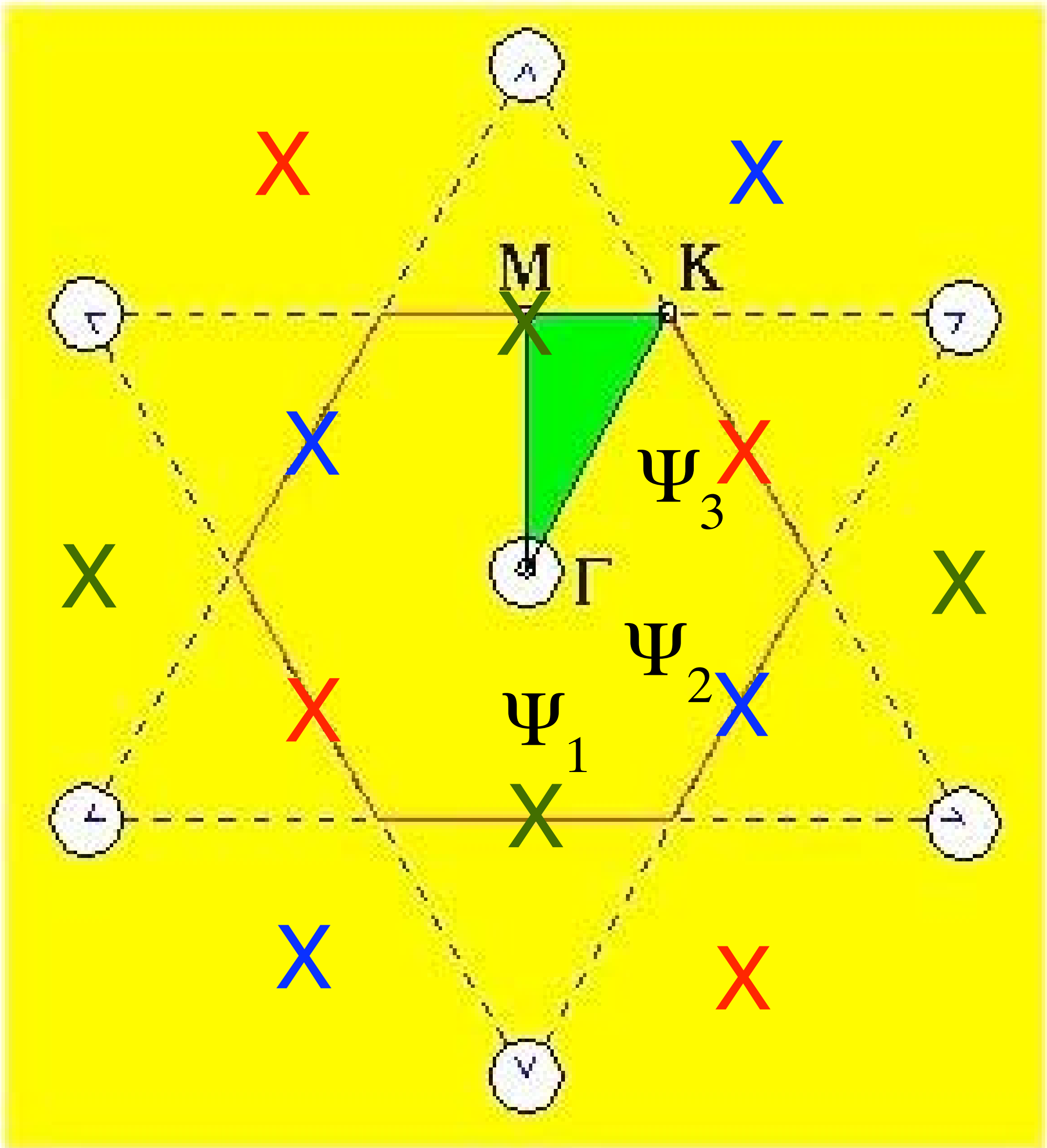
$$H = J_1 \Sigma_{ij} S_i S_j \qquad J_1 > 0 \text{ , } S_i = +1, -1$$

Triangular lattice: frustration, has zero point entropy,
and T_c = 0, disordered at all temperatures.
(G.H. Wannier; P.W. Anderson, (1950)). Striped phase,
honeycomb phase, etc, all degenerate.

If add second neighbor interaction $J_2 > 0$, then T_c > 0
with striped 2x1 order



and first order phase transition between ordered
and disordered phase. (S. Korshunov; A. Rastelli et al (2005))



$$F = -a(\Psi_1^2 + \Psi_2^2 + \Psi_3^2) + b\,\Psi_1\Psi_2\Psi_3 + c(\Psi_1^2\Psi_2^2 + \Psi_2^2\Psi_3^2 + \Psi_3^2\Psi_1^2) + d(\Psi_1^2 + \Psi_2^2 + \Psi_3^2)^2$$

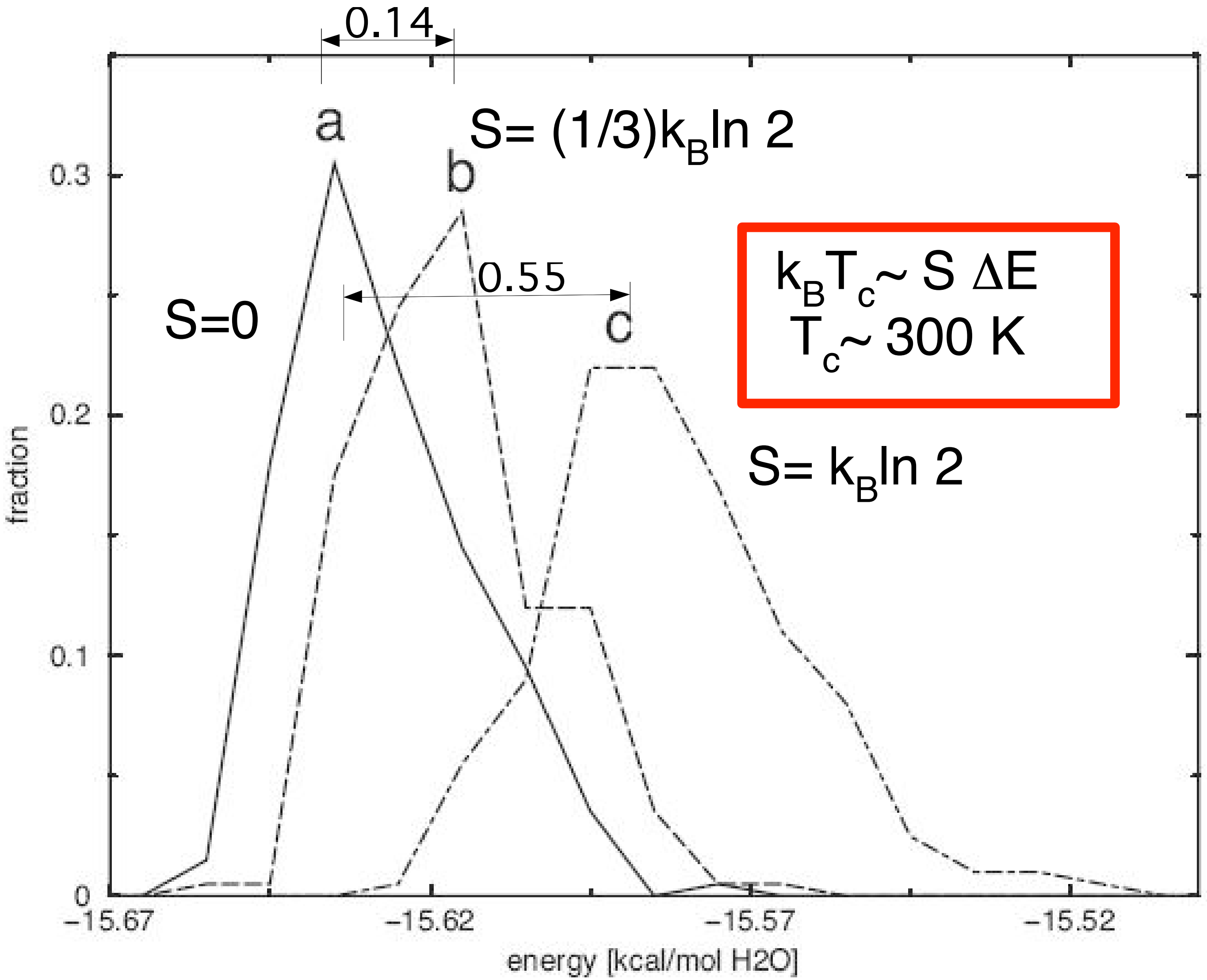
MODIFIED ISING MODEL

First + second neighbor interactions, PLUS 3-body terms

$$H = \sum J_{ij} S_i S_j + \sum_{ijk} t(\theta_{ijk}) S_i S_j S_k$$

The latter discourage honeycomb configurations.

Adjust Js, ts using Monte Carlo energies, including mean energy cost for generating a single defect in striped structure 1.9 kcal/mol ($\sim k_B$1000K), with standard deviation of 0.5 kcal/mol; (note however: at select sites value as low as 0.2 kcal/mol).



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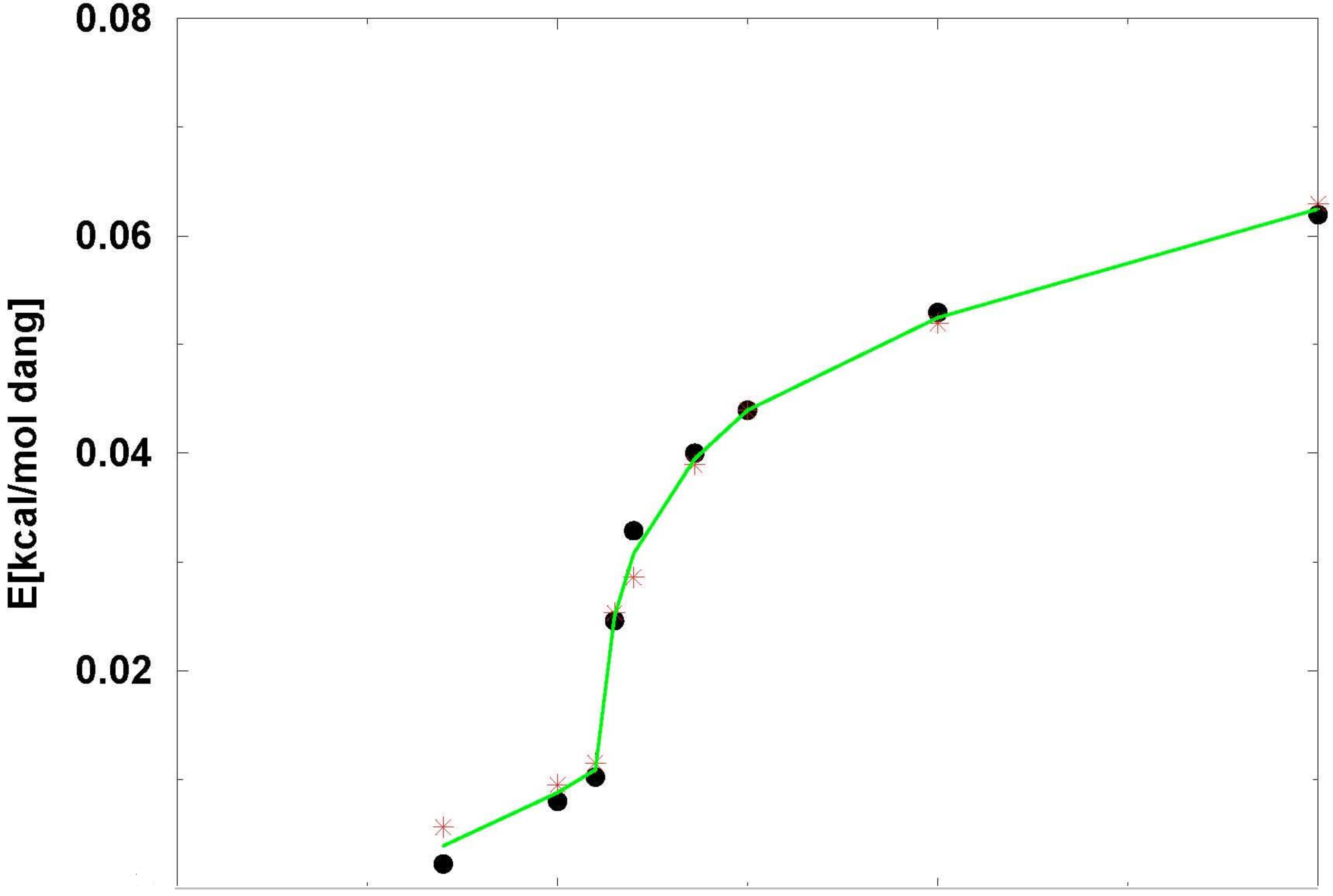
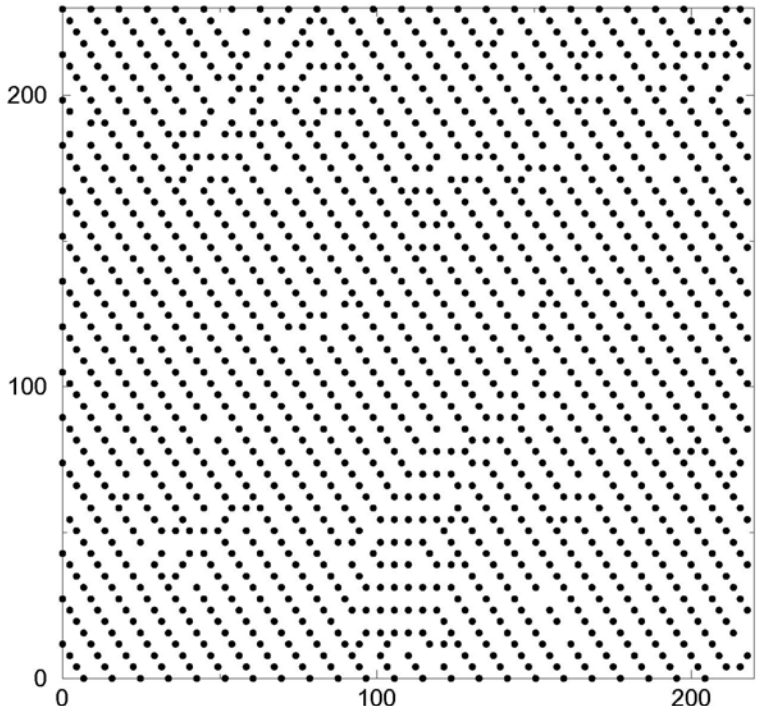
Ising model, 3000 lattice sites, mean energy as a function of T.

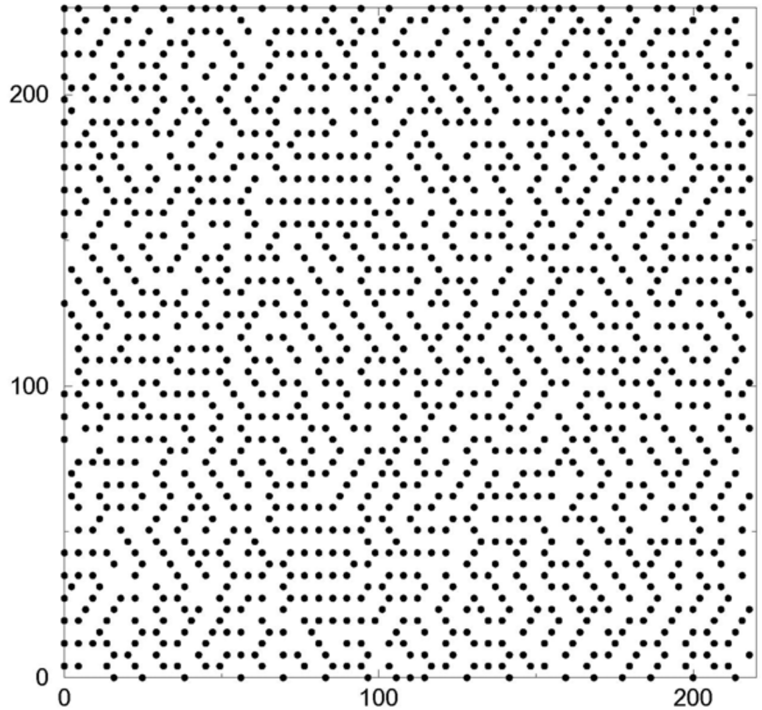
Monte Carlo: First order phase transition around 60 K



Sample dang-H pattern from extended Ising model MC, 50x60 triangular lattice.



order 55K



disorder 75 K

CONSEQUENCES OF STRIPED ORDER?

-- VERY ONE-DIRECTIONAL PROPAGATION OF O-H VERTICAL STRETCH VIBRATION

-- SIMILARLY ONE-DIMENSIONAL DISPERSION OF SURFACE CHARGE-TRANSFER EXCITON

-- IMPLICATIONS FOR SURFACE CHEMISTRY? SUDDEN PROPERTY JUMP AT SOME T_c?

CHEMICAL QUESTIONS (Victoria)

-- influence of d-H , d-O pattern on ice-adsorbate interactions?

-- can adsorbates adjust H-bonding pattern for their own convenience (i.e to improve bonding to the surface)?.

-- possible experimental evidence from SO_2 adsorption on ice.

-- computational support for H_3O+, OH- adsorbate.

CONCLUSIONS PNAS 105, 5947 (2008); and unpublished

-- 2x1 STRIPED PHASE OF PROTONS AT HEXAGONAL ICE SURFACE

-- EXPLAINS MYSTERIOUS He-DIFFRACTION PEAKS BY TOENNIES ET AL., TO A LESSER EXTENT SUM FREQUENCY GENERATION TOO

-- SURFACE ORDER DESPITE BULK DISORDER:

"If I beat you up, you are going to become dangerous. If we talk to each other, that is the only safety from you that I can have"

Victoria Buch

Sum Frequency Generation (SFG) spectra (M.J. SHULTZ et al)

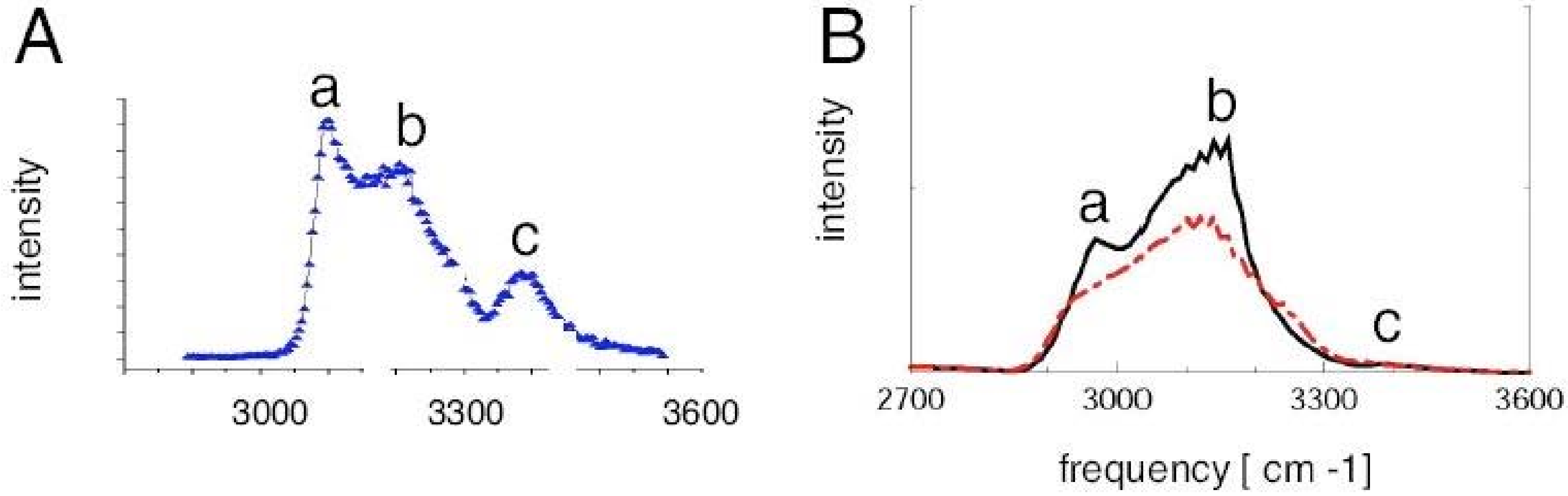
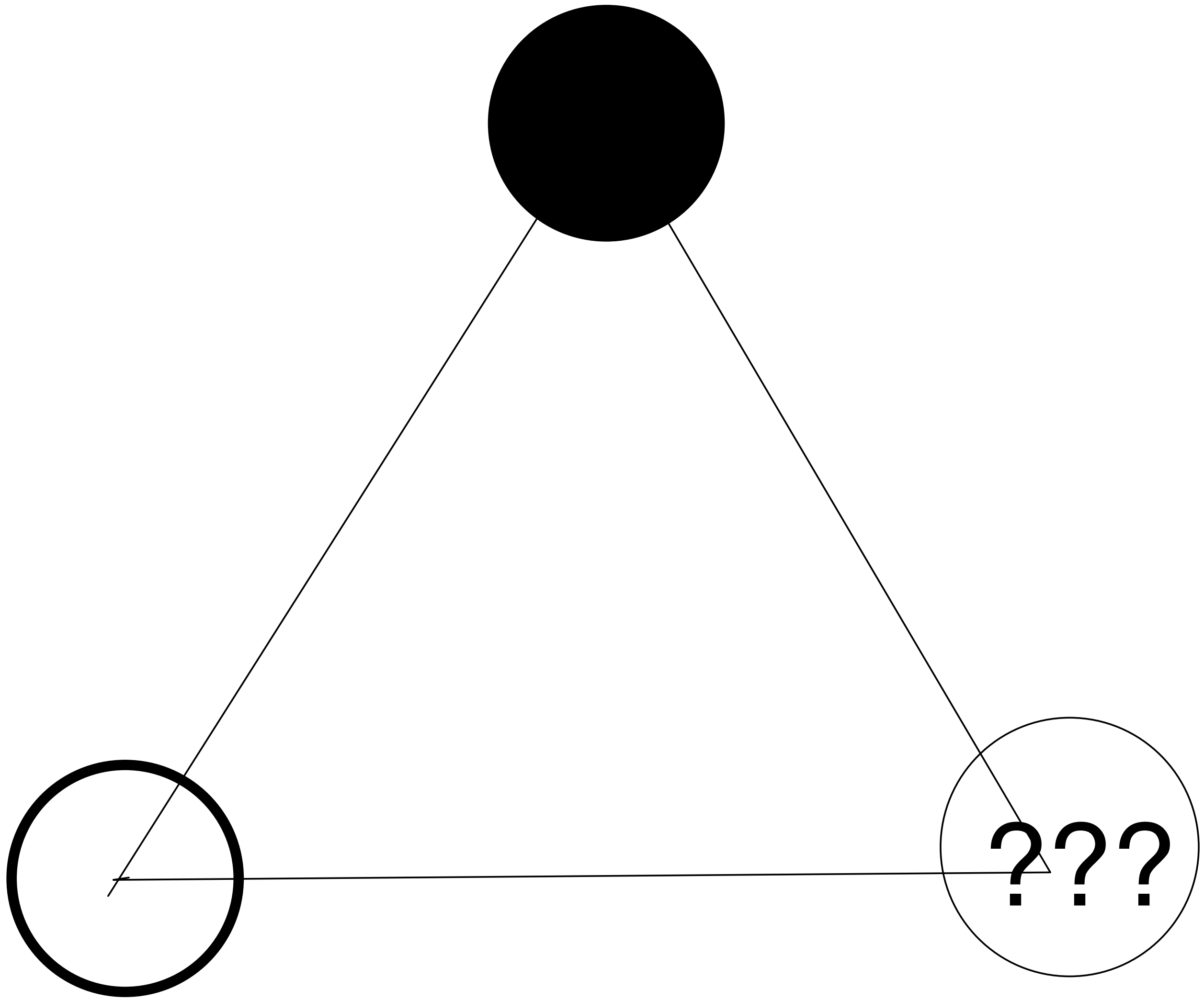


Fig. 5. *ppp* SFG spectrum of the ice basal surface in the H-bonded OH-stretch range at 128 K. (*A*) Experimental spectrum. (*B*) Computed spectra for Fletcher's striped phase (solid line) and for the fully disordered model (dot-dashed line).



FRUSTRATION